CATALYSIS

VOLUME VII

Oxidation, Hydration, Dehydration and Cracking Catalysts

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PREFACE

Volume VII completes the present series of books on "Catalysis." It includes four chapters on catalytic oxidation, one on hydration-dehydration and one on cracking catalysts.

Chapter 1 reviews the work that has been done in attempting to elucidate the nature of silica-alumina cracking catalysts of the type now being used for the production of high-octane gasoline. It complements a chapter on "Catalytic Cracking" that was published in Volume VI of this series.

The study of catalytic hydration and dehydration has not been as extensive as some other fields of catalysis, though it was one of the first to be explored. In recent years the production of butadiene from alcohols, and the possible synthesis of alcohols by the hydration of olefins has led to renewed interest in catalytic hydration and dehydration. This chapter adequately summarizes the factual material as well as current ideas in regard to the mechanisms by which hydration-dehydration catalysts operate.

Seldom has the demand for a good catalyst arisen so quickly as the one which now exists for an effective oxidation catalyst. Hydrocarbons in automobile exhausts must in some way be avoided; their oxidation by a suitable type of catalytic muffler is believed by many to be the most feasible solution to the problem. Hence, an extensive and intensive search is being made for catalysts for oxidizing hydrocarbons. Chapter 3 on hydrocarbon oxidation is therefore very timely.

Certain catalytic oxidation processes have long been a part of our economy; these include the catalytic oxidation of ammonia to nitric oxides and of sulfur dioxide to sulfur trioxide. Chapter 4 includes a discussion of both the theory and practice of these oxidation processes. It also cover the discussion of the catalytic oxidation of carbon monoxide by various solids including Hopcalite. This latter, it may be noted, is one of the early effective oxidation catalysts for carbon monoxide. It was developed jointly by Professor J. C. W. Frazer of The Johns Hopkins University and Professor W. C. Bray of the University of California during World War I.

The use of semiconductor theory in catalysis is especially well illustrated by oxidation catalysts. This is the principal topic of discussion in Chapter 5. Chapter 6 summarizes a few miscellaneous catalytic oxidations.

It is unfortunate that a few catalytic fields have not been as extensively covered as might have been desirable. One of these is the work on halogenation catalysis. Another field that could have taken much more space than was available is the formation of high polymers by relatively new processes such as those developed by Ziegler and Natta. Certain aspects of catalytic hydrogenation could have been expanded with profit. In particular the subject of preferential hydrogenation might well have been treated in more detail. Finally, an up-to-date summary of all that has been learned in regard to the interpretation of electronic structure and catalysis and a detailed discussion of many new tools for studying catalyst surfaces would have been desirable in this final volume. Actually such a chapter was planned but was never completed. However, one of the more important portions of the semiconductor work, that relating to catalytic oxidation, has been covered in detail. The writer accepts full responsibility for these omissions.

It is hoped that this series of books on catalysis has served its purpose of bringing together theory and practice as it exists at the present time. It will be interesting to note in coming years the impact of the extensive application of solid state theory on the trend that is already perceptible toward converting the field of catalysis from what is essentially an art to a level more closely approaching that of a science.

In this, the preface for the last volume of this series, the editor would again like to thank the many experts whose fine cooperation has made these volumes possible. The field of catalysis has long since become so extensive as to make it impossible for any one individual to be acquainted with all of the detailed catalytic "know-how." It is only by the combined and coordinated efforts of a number of experts that treatises such as the present one can be written.

In conclusion, I would like to thank Mr. Hawley of Reinhold Publishing Corporation and his staff for their patient cooperation in all the problems arising in such a series of books. Also, I owe a special vote of thanks to my wife, Leila L. Emmett, for proofreading the series, for her meticulous care in constructing the author indexes and for her patience during the long years in which I have been engaged in editing this series.

March 15, 1960 Paul H. Emmett
Baltimore, Md.

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CHAPTER 1

CRACKING CATALYSTS

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INTRODUCTION

One of the most remarkable technical developments of recent times in the petroleum refining industry is the conversion of natural hydrocarbons of petroleum to motor fuels by catalytic processes. In variety of chemical reactions involved and in scale of application, it surpasses by far any of the other catalytic industrial operations we have witnessed in the past. The catalytic cracking process is carried out in units in each of which several tens of thousands of barrels of oil are treated daily with many hundreds of tons of catalyst. This amount of catalyst may be circulated from reactor to regenerator vessel and back to reactor as much as 40 to 50 times in one day at a temperature of some 500°C in a fluid unit. The petroleum industry consumed in 1956 about 175,000 tons of synthetic alumina-silica cracking catalyst and 100,000 tons of clay catalyst[1].

A large proportion of the gasoline produced in a refinery by distillation, by thermal cracking, and by catalytic cracking, undergoes additional treatment known as "reforming" to enhance its quality by various processes many of which are catalytic, such as dehydrogenation, isomerization, desulfurization, etc. Reforming is at present a second major operation of a refinery, but catalytic reforming may in time surpass catalytic cracking in the tonnage of total oil handled[2].

The oldest method of obtaining fuels from petroleum is separation of volatile fractions by simple distillation. In this way there are obtained gasoline, naphtha, kerosene, gas oil, and lubricating oil fractions, and a heavy residue suitable as fuel oil. Fuels are prepared by treatment of these fractions with chemicals, mostly sulfuric acid and caustic soda, essentially for purification; other products, such as wax, petrolatum and asphalt, are obtained from heavier fractions by crystallization and by precipitation. Until about 50 years ago, the most desired product was kerosene, while gasoline was a most annoying by-product, often presenting a difficult problem of disposal. With the advent of the automobile, gasoline became the main product while the demand for kerosene diminished. From the very beginning it was apparent that gasoline obtained by distillation is far from an ideal fuel for automobiles. It leads to premature detonations and too rapid explosions of fuel in the engine which are obnoxious, harmful to the engine, and are responsible for loss of potential power.

The problem of improving the quality and of increasing the volume of gasoline production was met by introduction of thermal cracking. Gasoline obtained by this process was found to have more desirable burning characteristics than gasoline obtained by distillation. The process consists essentially of the breaking down of heavier oils to products of greater volatility, principally of the gasoline boiling range, by subjecting the oils to heat and pressure (approx. 1000°F (538°C) and *ca.* 500 lb/in^2) in a system of heating coils and cracking chambers. In this process, besides gasoline, gas and a refractory residue are obtained. Much confusion existed for some time as to the methods of judging fuels, and the observed differences were often ascribed to differences in physical properties. Eventually, however, the improvement in gasoline quality obtained by thermal cracking was traced to chemical changes in hydrocarbons of petroleum during cracking, mainly to formation of olefins by cracking of paraffins, and to formation of aromatics by dehydrogenation of naphthenes. In general, it is true that any departure from straight saturated hydrocarbon chains represents an improvement in gasoline performance. For quantitative evaluation, the performance of a gasoline is compared in a standard engine with the performance of reference fuels, which have been calibrated against mixtures of pure *n*-heptane and pure highly branched isooctane. These two hydrocarbons represent the extreme points of the "octane number" scale; zero for *n*-heptane and 100 for isooctane (2, 2, 4 trimethylpentane).

It has been known for some time that further improvement could be accomplished by the use of catalysts in the cracking process. Many types of materials such as metals, metal halides, and metal oxides have been explored as cracking catalysts[3, 4]. However, only aluminum chloride was used industrially for a brief period (McAfee process, used by Gulf Refining Company[5]) but was soon abandoned because of operating difficulties and severe losses of aluminum chloride in the tarry residue[6].

Clays were known to be active for hydrocarbon reactions and their use as cracking catalysts was claimed in various patents issued in Germany as early as 1923. Subsequent patents claimed various treatments of clays. But the clays were readily deactivated during the cracking process by deposition of carbonaceous matter. The French inventor, Eugene Houdry, recognized and demonstrated the superiority of gasoline produced with clays over thermally produced gasoline. Houdry observed furthermore that the activity of clays could be essentially restored by burning off the carbonaceous residue. With the aid of Socony-Mobil Oil Company, Sun Oil Company and the newly organized Houdry Process Corporation, the above discoveries were developed into a commercial process. In 1936, in Paulsboro, New Jersey, the first catalytic cracking unit of the fixed bed type began production using acid treated bentonite in the form of pellets as catalyst. This process was a great success. It was soon followed by development of new, although basically similar processes, and by development of new catalysts by other companies.

The search for new catalysts, undoubtedly inspired by the knowledge of the chemical composition of clays, resulted in the development of various synthetic combinations of alumina and silica. A number of synthetic alumina-silica catalysts, prepared by widely different processes, are in use today. Although more costly than clays, the synthetic materials are preferred by many refiners, the advantages often being enough to justify the difference in cost. Recently, however, substantial improvements in clay catalysts have been reported; catalysts based on clays have appeared which are claimed to be equivalent in performance to synthetics.

Besides alumina-silica, other combinations of oxides have been tested. Of these, the most promising material is magnesia-silica which has undergone extensive tests in commercial units but did not satisfy all the requirements of a commercial catalyst.

The advantages of catalytic cracking over thermal cracking are traceable to specific chemical changes in petroleum hydrocarbons and have been described in detail in Volume VI of this series, by H. H. Voge. Most of the conclusions presented there are based on the exhaustive study of cracking of pure hydrocarbons by Greensfelder, Voge and Good[7]. Briefly, it may be stated that most of the reactions do not take place by an acceleration of thermal cracking reactions by the catalyst, but are brought about by the specific capacity of the cracking catalysts to promote reactions qualitatively different from thermal cracking reactions, most probably because of the difference in the principal intermediates formed—radicals in thermal cracking, and carbonium ions in catalytic cracking.

The presence of a catalyst markedly changes the relative order of stability of several classes of hydrocarbons. Thermally the stability for a given carbon number increases in the order: (1) paraffins and aliphatic olefins, (2) naphthenes, (3) alkyl aromatics, (4) unsubstituted aromatics. In catalytic cracking, stability increases in the order: (1) olefins, (2) aromatics with C_3 or larger substituent groups, (3) naphthenes, (4) polymethyl aromatics, (5) paraffins, (6) unsubstituted aromatics. These two orders represent only a rough segregation. Actual rate ratios depend on conditions as well as on individual structures.

In addition to the rate comparisons, characteristic differences in reaction products have been shown in detail for individual compounds and for the major classes of hydrocarbons. In summary, catalytic cracking gives rise to: (1) more selective cracking and relatively less of the smaller (C_1 and C_2) fragments; (2) more olefin isomerization, both of double bond and carbon skeleton; (3) a more controllable saturation of double bonds, especially in the fractions of higher molecular weight; (4) greater production of aromatics; (5) less diolefin production; and (6) relatively more coke.

Industrial Background

A number of industrial processes are in use for catalytic cracking; the most important have been briefly described by H. H. Voge in Volume VI of this series. These processes have much in common and the essential features of importance to the study of cracking catalysts are outlined below. However, processes for manufacture of synthetic alumina-silica cracking catalysts differ widely and are therefore described in some detail (as far as information is available). Such a description seems appropriate, since many investigators have studied catalysts as received from the manufacturer without inquiry about the method of preparation. However, since manufacturing techniques differ widely there is no reason to expect that all alumina-silica catalysts are comparable in physical, chemical, and catalytic properties. The greatest divergence can be expected between materials prepared in acid and those prepared in alkaline media.

Catalytic Cracking Processes

Oil, of a boiling point range higher than gasoline, is contacted with the catalyst at *ca.* 500°C. During this stage a great number of reactions occur, predominantly cracking of carbon-carbon bonds (hence the name of the process). Cracking is accompanied by a host of reactions which are known to be catalyzed by strong acids: isomerization of paraffins and particularly of olefins formed by cracking of paraffins and naphthenes and by dealkylation of aromatics; transfer of hydrogen (e.g., from naphthenes to olefins, or to olefins from other olefins); transfer of alkyl groups from one aromatic molecule to another; some cyclization and some dehydrogenation. The extent of each reaction depends on the composition of the original oil, particularly the molecular weight and structural characteristics of hydrocarbons present or formed by primary cracking. At this stage, the catalyst is rapidly being covered by a layer of coke, a black, amorphous, organic substance of low hydrogen content (*ca.* 10 per cent H), sometimes erroneously called "carbon." The origin and the mechanism of coke formation have never been conclusively demonstrated. There is some evidence, however, that coke is produced by condensation reactions of polyaromatics with some contribution from polymerization of low boiling olefins and diolefins.

A coke deposit deactivates the catalyst very effectively but the activity is substantially restored when the coke is removed by oxidation. For this purpose the catalyst is first treated with an inert gas, most often steam, to liberate adsorbed heavy hydrocarbons (a procedure called "stripping"). Subsequently coke is burned off the catalyst with air. This procedure, called "regeneration," is carried out at a temperature some 50 to 100°F higher than the "cracking" reaction. Following regeneration the catalyst is ready for the next cycle. It is probable that the surface of the catalyst is exposed to temperatures substantially higher than the measured temperature of the regeneration bed, and that these high surface temperatures contribute to the loss of surface and a progressive loss of activity of the catalyst in the units.

In some of the original cracking units, the catalyst was placed in chambers or tubes filled with catalyst (fixed bed units) and all the above operations were performed in sequence without moving the catalyst. However, it soon was discovered that circulation of the catalyst through a series of vessels has great advantages and today practically all cracking is done in units in which catalyst circulates from the reactor to the stripper, then to the regenerator, and finally returns to the reactor.

The catalyst used is in the form of pellets or beads for one type of unit, or as a ground powder or microspheres for the so-called fluid bed units. The catalyst shapes and particle sizes are selected to suit the various methods used to circulate the catalyst through the unit. Microspheres are manufactured by spray drying of slurries of precipitated gels. The average particle diameter is *ca.* 60 μ with an appreciable spread in particle size (20 to 80 μ). A mass of particles of this size range is readily agitated by the gas or vapor passing through it, and in this state exhibits some of the properties of a fluid.

In commercial operation a catalyst gradually deteriorates in physical properties and loses activity. Many of the reasons for such deterioration are known, but all the factors have not as yet been quantitatively evaluated. The loss of surface area and loss of activity occur by combined influence of heat and steam; contamination with heavy metals contained in oils as organometallic compounds or originating by corrosion of the units leads to an increase in coke production. For these reasons and finally because of the mechanical losses by attrition and loss of fines through stacks, periodic replacement by addition of fresh catalyst (make-up catalyst) is necessary. Thus, the units are operated with a mixture of particles of varying age, of average activity far below that of a fresh catalyst (i.e., 15 to 20 per cent). This mixture is known as the "equilibrium" catalyst.

Methods of Manufacture of Alumina-Silica Catalysts

Principal manufacturers of synthetic cracking catalysts in the United States are the American Cyanamid Co., Davison Chemical Co., Socony-Mobil Co., Houdry Process Corp., and National Aluminate Corp. Catalysts derived from clays are manufactured by Filtrol Corp., Houdry Process Corp., and Minerals and Chemicals Corp., American Cyanamid Co., and National Aluminate Corp. (see later section). Although the exact and detailed methods of catalyst manufacture are not available, a general outline of the methods of various companies can be obtained from patents and from the limited amount of other published information.

Synthetic alumina-silica catalysts manufactured in the early days of catalytic cracking contained 10 to 12 per cent alumina and were relatively dense materials. This composition was considered to be optimum, since it was generally observed that with an increasing alumina content the activity increased only slightly but the coke formation increased substantially. At least two different industrial groups studied alumina-silica catalysts of high alumina content but no advantage was shown[14].

Later improved catalysts with 18 to 30 per cent alumina content (so-called high alumina catalysts) were developed. The first commercial high alumina catalyst was produced by the American Cyanamid Company in cooperation with Shell Development Company[14]. As compared to older type low alumina catalysts, improvement in performance results to a large extent from the improved incorporation of 25 per cent alumina while at the same time increasing the pore volume. In brief, high alumina catalysts have higher activity with the same product distribution and coke formation, a substantially greater activity stability, and are less prone to deterioration leading to stack losses. This subject is discussed in more detail in the section entitled "Changes in Use." High alumina catalysts are preferred by many refiners for these advantages. At the present time they are supplied by most major catalyst manufacturers.

The advantages to be gained by increasing the pore volume (increased pore diameter at constant surface area) are also evident but to a lesser degree in low alumina catalysts. Recently there has been a trend toward increasing the pore volume of low alumina catalysts.

American Cyanamid Catalysts. American Cyanamid Company began manufacturing synthetic alumina-silica cracking catalysts in 1942[8]. This company cooperated with Universal Oil Products Company (U.O.P.) in working out the method for precipitation and washing of the catalyst, which was manufactured originally according to U.O.P. specifications[9]. Although early catalysts were made only in granular form, microspheroidal catalysts have been manufactured since 1946 in increasingly large proportion. In Cyanamid's plant at Michigan City, Indiana, silica hydrogel reportedly is prepared by combination of dilute sodium silicate and sulfuric acid in a series of wooden tanks. The requisite amount of aluminum sulfate solution is then added to the silica hydrogel, and the aluminum salt hydrolyzed by addition of aqueous ammonia. The alumina-silica hydrogel is then washed free of soluble salts on rotary vacuum-type continuous filters. About 15,000 gal. of high purity water are required for each ton of finished catalyst. The washed alumina-silica filter cake is slurried with water and sprayed into an atmosphere of hot combustion gases within a cylindrical chamber. The resulting dehydrated microspheroidal catalyst is separated from the flue gases by banks of conical cyclone separators. The catalyst particles are then classified according to size best suited to the particular fluid cracking units in which the catalyst will be used. The fine grade of catalyst, suited to fluid units with secondary catalyst recovery systems, has an average particle size of 40 μ. The coarse grade of catalyst, best suited to cracking units without secondary recovery units, has an average particle size of about 60 μ.

A number of interrelated variables, such as solids concentration, pH, temperature and time, control the aging or degree of polymerization of the silica hydrogel, and hence the filterability of the alumina-silica hydrogel, and the physical and chemical properties of the final catalyst[10, 11]. In general, the practical range of operation is around silica concentrations of 3.5 to 6 per cent, a pH range of 5.5 to 8.1, and temperatures of 40 to 100°F (4.4 to 38°C). Aluminum is incorporated by hydrolyzing the aluminum sulfate with ammonium hydroxide in presence of the silica hydrogel, with the final pH being adjusted to 5 to 5.5. This operation has been variously referred to as "plating," "coating," or "precipitation" of alumina on the silica carrier. Filtration is carried out with water acidified to pH 4 to 5.5 to aid in sodium removal.

A microspheroidal alumina-silica catalyst manufactured at American Cyanamid's Ft. Worth, Texas, plant in 1951 contained 12.7 per cent alumina, 0.01 per cent Na_2O, 0.05 per cent Fe_2O_3, and 0.3 per cent SO_4. It had a surface area of 649 m^2/g, a pore volume of 0.65 cc/g, a particle density of 0.92 g/cc, and an average pore diameter of 40Å. High alumina catalysts have been produced with a pore volume as high as 0.90 cc/gm, with pore diameters of 65 to 70Å and surface areas of *ca.* 550 m^2/gm.

Davison Catalysts. At Davison Chemical Corporation's plant in Cincinnati, Ohio, microspheroidal alumina-silica catalyst is reportedly prepared by the following procedure[15]. Dilute sodium silicate and sulfuric acid are brought together in a special mixer to form a silica hydrosol which sets in a short time to a hydrogel. The requisite amount of aqueous aluminum sulfate is added to impregnate the hydrogel, then the hydrolysis is carried out by addition of aqueous ammonium hydroxide.

The salt-containing alumina-silica hydrogel slurry is dewatered on a drum filter, and the cake is reslurried and pumped under high pressure through nozzles into a cone shaped spray drier. The fine droplets of alumina-silica hydrogel are dehydrated on passing through a counter current of hot flue gases. The spray-dried catalyst is washed free of soluble salts on a drum filter and then dried.

Socony-Mobil Catalysts. The Socony-Mobil Oil Company's alumina-silica bead catalyst, developed for the Thermofor cracking process, is reportedly prepared in the following general manner[16]. Sodium silicate and acidified aluminum sulfate solutions are rapidly mixed in the proper proportions, by means of eductors, to form a rapid setting alumina-silica sol. Just prior to setting, the sol is passed over a fluted cone and the resulting sol droplets are allowed to descend through a column of hot mineral oil, during which time the droplets assume a spherical shape and then set to rigid hydrogel beads of about 8 mm diameter. The beads then pass into a saline solution of the same concentration as in the beads themselves. The temperature and pH of this solution is adjusted to harden the beads, and to control the density of the ultimate catalyst.

At this point the hydrogel beads are essentially the sodium salt of alumino-silicic acid. Catalytically deleterious sodium is removed by base exchange with aluminum ions, using three equivalent weights of aluminum sulfate for each equivalent weight of sodium removed. Other base exchange agents can also be used: e.g., acids and ammonium salts. Soluble salts are removed from the beads by washing for 18 hr; a sodium scavenger is added to the wash water. Approximately 15,000 gal. of demineralized water are required for each ton of final catalyst. The processed beads are then drained of water and placed on a belt and dried at 280°C for 2 hr. During an additional hour, the beads are "tempered" by drying at 300 to 350°C in steam at one atmosphere pressure. During drying the beads shrink to an average diameter of about 3 mm.

A number of patents disclose details and many variants of this type of process[17]. In 1946 typical catalyst beads contained about 10 per cent alumina, and had a surface area of 420 m^2/g, a particle density of 1.10, and an average pore diameter of 47Å. The principal attributes of the bead catalyst are its great physical ruggedness and the low resistance of the catalyst bed to gas and vapor flow. Its life in commercial operation is about 1 yr[18]. The bead catalyst has been reported to be the cheapest synthetic cracking catalyst available[19].

Plank and Drake[20] have studied the effect of a number of preparative variables on the physical properties of alumina-silicas made by combination of sodium silicate and acidified aluminum salt solutions (7 per cent Al_2O_3– 93 per cent SiO_2). The resulting clear sols were allowed to set to hydrogels, from which the fixed sodium was removed by exchange with various ions. The treated hydrogel chunks were leached free of soluble salts, and dried at 240°C to granular xerogels. The effect of the following range of variables was studied: (1) pH; 5.5 to 9.5, (2) solids concentration;

1.5 to 7.0%, (3) aging time (at pH 7) before base exchanging; 0 to 168 hr, and (4) base exchange medium with gels aged 0 to 168 hr—i.e., NH_4Cl, HCl, $Al_2(SO_4)_3$. Low pH values were found to favor formation of high density and low surface area materials. Increased solids content decreased both density and surface area. Increased aging time moderated changes which could be produced by subsequent base exchange treatment. Thus, by control of these variables it has been possible to vary surface areas from 372 to 751 m^2/g, particle densities from 0.97 to 1.60 g/cc and average pore diameters from 27 to 64Å.

Houdry Catalysts. A number of patents held by Houdry Process Corp. reveal that active cracking catalysts are prepared by interaction of sodium silicate and sodium aluminate, or an aluminum salt, followed by base exchange of sodium with ammonium ions which after drying can be removed by thermal dissociation[21]. Most of these patents are concerned with apparatus and methods of manufacture of such catalysts. Houdry synthetic Type S-45 catalyst (12.5 per cent Al_2O_3) was used by Houdry Process Laboratories' workers in the study of the chemisorption of quinoline. This was prepared according to specification of U. S. Patent 2,433,869 presumably from sodium silicate and aluminate[22].

Other Methods. Numerous other methods for preparing alumina-silica catalysts have been revealed in the literature, and some of the more widely different ones are listed here. Catalysts can be prepared by intimately mixing silica hydrogel and aluminum hydroxide which have been separately prepared and purified[23]; by thermal decomposition of an aluminum salt on the surface of silica xerogel[24]; and by hydrolysis of mixtures of ethyl silicate and aluminum isopropylate[25]. Catalysts can also be prepared by acid dissolution of slags to form colloidal sols, and gelation of the desirable solubilized constituents under controlled conditions[26].

Laboratory Evaluation

Various laboratory methods for evaluation of catalytic activity are the principal basis for predicting the performance of cracking catalysts in commercial operation. Catalysts in granular, pellet, or powder form are usually tested in small fixed-bed reactors, although in some cases the tests are carried out with powdered catalysts in small-scale fluidized fixed-bed reactors. The fixed-bed tests differ in details of apparatus, feed stocks, and in methods of expressing activity and yield data. Table 1 summarizes the conditions of some of the more widely used tests.

Small-scale fixed-bed tests may be divided roughly into two general categories. The first includes tests in which the equal volumes of fresh catalysts are tested at the same conditions using a constant space velocity. The conversions to gasoline, or distillate plus loss (D + L), and gas, and carbon formation[32] are intercompared for varioug catalysts. Among these tests are the widely used "Cat A" test developed by the Catalytic Development Corp., adopted by the Houdry Process Corp. and also used by Socony-Mobil Oil Co., and described by Alexander and Shimp[27], and the Jersey D + L test described by Conn and Connolly[28]. The Atlantic test described by Birkhimer, Macuga, and Leum[29] has been designed for equilibrium rather than fresh catalysts. Direct comparison of the ratios of greatly different activities is not usually made because the space velocity-conversion relation is not linear over the entire conversion range. In addition, since the same volume of each catalyst is tested, differences in catalyst densities are not taken into account.

Table 1. Conditions of Various Test Methods for Catalytic Activity

Test Method	Catalyst Vol. or Wt.	Test Temp. (°F)	Feed Stock	LHSV	Process Period (min.)
"Cat A"	200 cc	800	Lt. East Texas gas oil	1.5	10
Jersey D + L	200 cc	850–60	Lt. East Texas gas oil	0.6	120
Atlantic activity	200 gm	900	East Texas gas oil, medium fraction	0.5 (WHSV)	12
Indiana relative activity	80 ml	930	Mid-continent gas oil	2.7	60
UOP relative activity	25 ml	932	Mid-continent gas oil	4	120

The second category of tests includes those in which relative activities are expressed in terms of ratios of the space velocities required for equal volumes or weights of reference and tested catalysts to produce the same degree of conversion. The relation conversion *vs.* log space velocity is usually linear in the range of 30 to 60 per cent conversion. In determining relative weight activities, catalyst densities are taken into account. Among these methods are the Indiana relative activity method described by Shankland and Schmitkons[30], and the UOP relative activity method described by Ashley and Innes[11] and Sittig[31]. Relative activity data can be obtained also from the Jersey D + L method by variation of the oil space velocity. Measurements of this latter type are very useful as they allow a more direct prediction of catalyst performance in commercial reactors.

Shankland[33] has tabulated the ranges of activity values usually encountered with fresh alumina-silica catalysts with each of the several test methods outlined in Table 1. In general, it is difficult to predict commercial performance accurately and in detail from such tests of a fresh catalyst, because of the aging and contamination which occur during use.

CLAY CATALYSTS

Montmorillonite Clays

Structure and Properties. Naturally occurring crystalline clays of the bentonite type, activated by suitable chemical processing that is essentially a treatment with acids, have been employed in various types of commercial cracking units. The main constituent of bentonite, montmorillonite (*ca.* 90 per cent), is an important component of soils, to which it imparts a substantial fraction of the total cation exchange capacity. This is a factor vital in the nutrition of plants, and has therefore been a subject of intensive study. Montmorillonite clays of various chemical compositions, along with various impurities, are mined in different parts of the United States, but only certain of these clays can be successfully used as a raw material for catalyst manufacture.

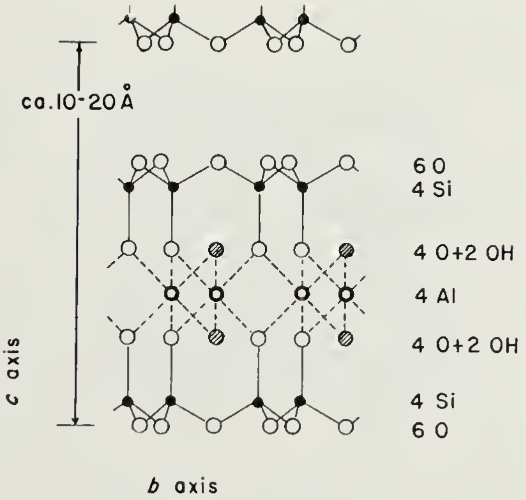


Figure 1. Schematic unsubstituted montmorillonite lattice. (*After* Hofmann, Endell and Wilm[34])

The crystalline structure of montmorillonite was first established by Hofmann, Endell, and Wilm[34], and later elucidated by Marshall[35], Gruner[36], and by Ross and Hendricks[37]. This structure has been arrived at as the result of physical and chemical studies of a wide variety of clays of this general type. The basic structure of montmorillonite is that of a three-sheet lattice which in simplest form consists of a central layer of aluminum atoms surrounded octahedrally by oxygen atoms. This central layer is sandwiched between two layers of silicon atoms, which in turn are surrounded tetrahedrally with oxygen atoms (cf. Figure 1).

In the central layer of the lattice approximately one in every six aluminum atoms has been substituted isomorphously by a magnesium atom.

The aluminum-oxygen octahedra are linked together by sharing oxygens on octahedral edges; in each octahedron four of the six oxygens are also shared with silicon to form silica tetrahedra, and the two remaining shared oxygens also carry a hydrogen atom and thus form hydroxyl groups. The alumina and magnesia octahedra are arranged in a hexagonal close-packed ring. The silicon-oxygen tetrahedra are linked together into planar sheets by shared corner oxygens. These tetrahedra are linked together also into a hexagonal pattern, with the points of the tetrahedra turned inward toward the alumina layer. The oxygens of these points are four of the six oxygens octahedrally surrounding aluminum or magnesium atoms in the central layer. Thus, the hydroxyl groups are generally assumed to be attached to alumina octahedra where they are not linked to the silica tetrahedra in adjacent layers. Shown in true perspective they appear to be located within the opening of the top and bottom oxygens of the two silica layers.

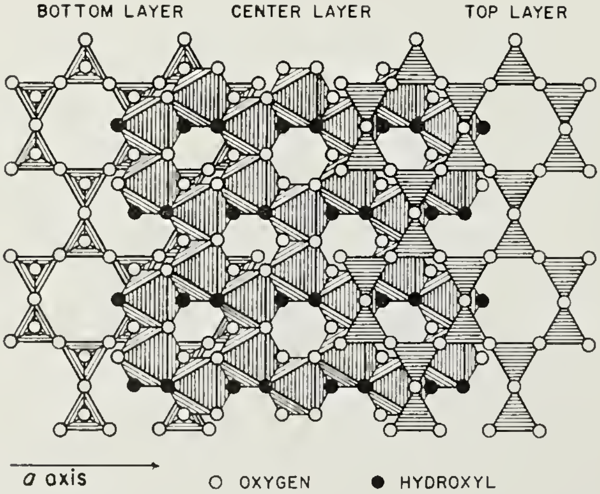


Figure 2. Cut-away model of unsubstituted montmorillonite lattice

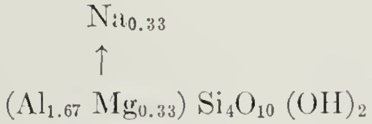
Figure 2 shows a schematic cut-away model of the idealized lattice structure of unsubstituted montmorillonite viewed along the *c* axis. The actual location of the hydroxyl groups cannot be established definitely by x-ray diffraction, however, and is therefore in doubt. Some investigators believe that alternate silica tetrahedra point away from the central lattice layer, and that hydroxyl groups are located on the unshared tips of such tetrahedra, as well as in the octahedral alumina layer. The chief reasons for this alternative postulate are (1) a generally higher hydroxyl content of the clay than expected from the Hofmann, Endell, and Wilm structure, and (2) the liberation of bound water in two temperature regions on differential thermal analysis[38].

In the unit cell, *a* is 5.09Å and *b* is 8.83Å. The central layer of the unit cell normally contains four aluminum atoms. In cases of complete substitution of aluminum by magnesium, as many as six magnesium atoms can be present per unit cell.

The thickness of this rigid three-layer lattice unit is about 6.6Å, and the periodic spacing of stacked lattice units (lamellae) along the *c* axis is *ca.* 10Å or more, depending on the amount and type of liquid present in the interlamellar space.

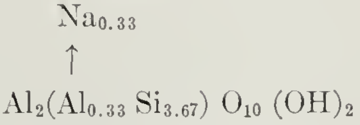
In montmorillonite, natural substitution of substantial amounts of divalent magnesium and smaller amounts of other divalent atoms for trivalent aluminum atoms in the hexacoordinated state results in a negative lattice charge. The studies of Marshall[39] have indicated that partial substitution of trivalent aluminum for tetravalent silicon in the tetracoordinated state can take place, and this also results in inducing part of the total negative lattice charge[40]. This latter configuration predominates in the natural aluminum silicate, beidellite, which often occurs in varying amounts with montmorillonite. To preserve electrostatic neutrality, positively charged alkali cations such as sodium, potassium, and calcium are sequestered naturally, and become fixed external to the silica layers in the interlammelar space. The alkali ions of clays are readily exchangeable with numerous ions of other metals in aqueous solutions. The extent of this property, called "base exchange capacity," is usually in the range of 0.64 to 0.94 meq/g for montmorillonite and 0.38 to 1.08 meq/g for beidellite clays.

Ross and Hendricks[37] have designed ingenious formulas to express the composition of montmorillonite and beidellite, as well as other similar clays in which the group of atoms responsible for the excess negative charge can be readily identified. Typical formulas representing a montmorillonite with some magnesium substitution of aluminum in the central lattice layer, and a beidellite with some aluminum substitution for silicon in the silicate layer, are shown below. The numbers refer to the atom fractions per formula weight.



$$\overset{\displaystyle Na_{0.33}}{\overset{\uparrow}{(Al_{1.67}\,Mg_{0.33})}}\,Si_4O_{10}\,(OH)_2$$

Montmorillonite



$$\overset{\displaystyle Na_{0.33}}{\overset{\uparrow}{Al_2(Al_{0.33}\,Si_{3.67})}}\,O_{10}\,(OH)_2$$

Beidellite

Hofmann, Endell, and Bilke[41] and Hofmann, Endell and Wilm[34] have shown by x-ray diffraction that vapor phase absorption of water between adjacent silica layers of the rigid three-layer lattices of montmorillonite can result in an increase in lattice spacing from *ca* 10 to more than 20Å. Many other polar liquids act in a similar manner.

Hendricks, Nelson and Alexander[42], by means of differential thermal analysis, determined that on absorption of water from the vapor phase, the first step is the hydration of the cations of magnesium, calcium or lithium. Sodium, potassium, hydrogen ions, on the other hand, do not appear to hydrate. As the humidity is increased, the first layer of water adsorption is completed, and additional layers of water molecules are adsorbed. Dyal and Hendricks[43] measured the uptake of ethylene glycol in the vapor phase by montmorillonite, and from the amount of glycol taken up and from the estimated molecular covering power of the glycol, calculated that the total lamellar surface area of montmorillonite corresponds to 810 m^2/g clay. This area is much greater than found by low temperature nitrogen adsorption. Nitrogen apparently does not penetrate to the lamellar surface and measures mostly the external geometric area of the clay particles.

Chemical Activation. Acid treatment has long been a means of activating clays for decolorization of mineral and fatty oils[44] and a similar treatment was applied for preparation of the first clay cracking catalysts. In 1926 Eugene Houdry was the first to obtain a higher grade of gasoline by employing acid-treated bentonite. Since then, various bentonitic clay catalysts activated by sulfuric acid, in powdered, pelleted, and extruded forms, have been used in the industry.

The term "activation" referred originally to an increase in both absorptive and adsorptive properties of clays and was extended gradually to catalytic properties. Treatment with strong mineral acids results in a number of changes in chemical as well as physical properties of clays, some of which are not well understood, and is dependent on the acid concentration, temperature, and time of contact. Various changes have been studied for their effect on the catalytic properties—i.e., (1) replacement of exchangeable cations by hydrogen or other acid ions; (2) dissolution of the clay substance, primarily aluminum, magnesium, and iron as well as dissolution and peptization of silicic acid (which is accompanied by opening of the structure, an increase in pore volume and accessible surface); (3) formation of new phases by reaction of dispersed fragments or dissolved materials or interaction of these with the remaining clay skeleton.

Davidson, Ewing, and Shute[45] showed that hot acid treatment removes magnesium and aluminum from bentonite, thus increasing the catalytic surface, and also replaces exchangeable ions with hydrogen. Thus, they regarded the treated clay as a hydrogen-substituted montmorillonite.

In spite of some divergence of opinions, it is now generally agreed that simple replacement of exchangeable cations by acid ions is not sufficient to produce a highly active cracking catalyst. More severe treatment is required[46, 47], which results in an increase in both surface area and number of acid sites.

Ewing[48] found that as the severity of acid treatment of bentonitic clays is increased, the cracking activity increases to a maximum and then declines. Ewing, Secor and Warner[49] found that maximum activity for cracking is achieved when all but about 15 to 20 per cent aluminum plus ferric oxide is removed from the clay by acid treatment.

Thomas, Hickey, and Stecker[46] extended the work of earlier investigators in studying the effects of acid treatment of montmorillonite obtained from a Western source. Treatment with cold aqueous hydrochloric acid removes substantially all the calcium, potassium, sodium, and magnesium from the interlamellar space. Boiling acid removes, in addition to the above readily exchangeable ions, some of the lattice aluminum and magnesium, in proportion to the concentration and amount of acid used. No silica is removed in this treatment. After complete removal of all the aluminum, and also the magnesium and iron from the clay, it is assumed that there should remain only sheets of amorphous silica.

They observed furthermore that maximum cracking activity occurred with the specimen of montmorillonite when about one-half of the total of the central metal atoms were removed. On the basis of these results Thomas and co-workers postulate then that each aluminum atom removed carries with it two hydroxyl groups from the central layer (formerly shared with two aluminum neighbors), thus forcing the adjacent aluminum atoms to assume the coordination number of four. This induces a negative lattice charge and a hydrogen ion becomes associated with the lattice—a condition which results in catalytic activity. Removal of the newly formed tetrahedral aluminum from the central layer by continued acid treatment is believed to account for the observed decline of activity. The work of Glaeser indicates that the x-ray diffraction pattern of montmorillonite is not destroyed until 80 per cent of the total aluminum and magnesium is removed[50].

Mills, Holmes, and Cornelius[47] suggested that acid attack begins at the edges of montmorillonite platelets and proceeds inward from these edges, rather than by penetrating through the unbroken silicon-oxygen layers of the lamellar surface. This treatment exposes a porous framework of large surface area. The differences between clays that can be activated and those that cannot be activated for cracking by acid treatment are believed to be that in the former some basic constituents (i.e., alumina) remain attached to the silica in the acid leached portion of the structure while in the latter only small amounts of basic constituents remain after treatment.

The influence of severity of hot sulfuric acid treatment on the porous structure of various bentonites has been studied by the same authors[47]. The powdered clays were treated with acid, washed, extruded and calcined at 565°C. With increasing removal of R_2O_3 by acid from a Nevada bentonite, susceptible to activation by acid treatment, both the nitrogen surface area and porosity of the extruded clay pellets increased sharply and then leveled off. On acid activation the several bentonites exhibited substantial differences in cracking activity in spite of great similarity in physical structure (surface, pore size, density, etc.). One of the clays which could not be activated by the usual acid treatment was activated by impregnation with aluminum nitrate, followed by thermal decomposition. This apparently created the internal interaction of alumina and silica necessary for cracking activity.

As a result of his studies of the rate of hydrochloric acid attack on several montmorillonite type clays at constant temperature, Osthaus[51] found that a semilog plot of the undissolved Al, Fe and Mg against time gives either a straight line or two intersecting straight lines of different slopes. From these relations the proportions and amounts of octahedral and tetrahedral metal ions of the same types can be determined, since the tetrahedral metals dissolve at a much slower rate. The dissolution reaction was found to be first order, the rate being proportional to both the amount of undissolved metal ions and the acid concentration. Arrhenius plots of rate *vs.* $1/T$ indicate an activation energy of 17 kcal/mole for octahedral Fe and Al in Polkville montmorillonite.

Milliken, Oblad and Mills[52] found from studies of acid activated bentonite that cracking activity is not associated with any crystalline phase of the catalyst identifiable by x-ray diffraction. They consider that by acid treatment a new, amorphous phase is formed in the presence of the undecomposed clay phase. This phase is formed by the interaction of small fragments of alumina and of silica liberated by acid treatment of small clay crystallites with some oxygen linkages preserved between them. This phase is believed to be essentially identical with synthetic alumina-silica catalyst which according to Milliken *et al.* also consists of a mixture of extremely small alumina and silica particles sharing oxygens.

In bentonite clay the iron is present in the lattice chiefly as an isomorphous substituent for aluminum[53]. Since this iron cannot be completely removed by acid treatment without dissolving out virtually all the aluminum, some iron usually remains in the activated catalyst. Mills found that iron becomes catalytically active after it is first loosened from the lattice by sulfidation followed by oxidation[54]. This activity of the iron causes poorer product selectivity in catalytic cracking: i.e., higher coke and gas formation at constant gasoline yield. A general procedure to loosen and remove lattice iron from bentonite and other clays was developed by

Mills and co-workers. This is capable of decreasing the iron content to about the same level as in synthetic alumina-silica catalysts (e.g., Houdry Type I Catalyst)[55]. In general this procedure consists of vapor phase treatment with various chemical agents to loosen lattice iron, followed by acid treatment to dissolve the iron.

A typical analysis of "Super Filtrol" manufactured from bentonite by the Filtrol Corporation prior to 1947 is shown below. The sulfate content apparently originates from the use of sulfuric acid as activating agent. Presence of anhydrite ($CaSO_4$) in Super Filtrol by x-ray diffraction has been reported[56].

Oxide	Per Cent by Weight
SiO_2	66.6
Al_2O_3	15.4
MgO	4.3
Fe_2O_3	2.3
CaO	2.2
TiO_2	0.4
SO_3	3.0
Volatiles	3.8

Stability of Structure. Webb and Ehrhardt[57] and Davidson[45] found that if Super Filtrol is heated above 600°F (316°C), the clay lattice loses its ability to expand on absorbing moisture. Davidson[58] found, by means of differential thermal analysis, that on increasing the calcination temperature from 800 to 1100°F (427 to 593°C) there is a decrease in bound water content. In the catalytic cracking process a certain amount of dehydration takes place on continued regeneration and use of the catalyst. Davidson suggested that during use part of the oxygen atoms in the remaining hydroxyl groups are gradually replaced by sulfur atoms to form —SH groups, thus accounting for a gradual loss of catalyst activity. This effect can be largely overcome by treatment of the deactivated catalyst with steam at elevated temperature.

A number of investigators have followed, by means of x-ray diffraction, the changes induced in acid activated montmorillonite catalysts by calcination in various ways[46, 56, 57, 59]. These investigators have reported slightly different temperatures of lattice destruction for various batches of acid activated clay catalysts in dry heat. Destruction generally begins in the region of 1475°F (781°C) and is completed in the region of 1560 to 1600°F (849 to 871°C)[46, 56, 59]. With increasing temperature the main products of thermal destruction are first spinel ($MgO \cdot Al_2O_3$), and then mullite ($3Al_2O_3 \cdot 2SiO_2$), and in some cases also sillimanite ($Al_2O_3 \cdot SiO_2$)[56, 59]. In the presence of steam initial destruction of the lattice begins at a lower temperature, *ca.* 1346°F (730°C), and is complete at 1454°F (790°C).

Mills has studied the influence of gases other than steam which at elevated temperature alter the cracking activity and the product selectivity formed over acid activated bentonite catalyst, containing an appreciable amount of iron oxide (2.4 per cent)[54]. Little loss of activity and product selectivity results from precalcination of the catalyst in an atmosphere of air, CO_2, SO_2 and NH_3 at temperatures below 1150°F (621°C). Serious deterioration of product selectivity occurs from precalcination in a H_2S atmosphere above 800°F (427°C), and in an NH_3 or SO_2 atmosphere above 1150°F (621°C). Hydrogen has an adverse influence only if sulfate is present in the catalyst, apparently because hydrogen sulfide formation results. The presence of water vapor tends to lessen the adverse effect of hydrogen sulfide and thus the activity and selectivity of catalysts deactivated by sulfur from cracking sulfur containing feed stocks can be largely restored by mild steam treatment. Resistance to sulfur deactivation and a general improvement in product selectivity, approaching that of iron-free synthetic alumina-silica catalyst, is achieved by removing iron from activated bentonite by the general technique outlined in a previous section.

In the light of these observations, it would appear that sulfur deactivation of clay catalysts is not solely associated with replacement of —OH with —SH groups as postulated by Davidson[58], or with sorption of sulfur compounds as postulated by Conn and Brackin[60], but is connected in large part with the presence of iron. Many clay catalysts, however, free of heavy metals at the outset, eventually acquire metal contaminants from various sources during commercial operation, and it is therefore advantageous to employ steam at various stages of the process to minimize sulfur deactivation[59, 60, 61].

Acidity and Acid Strength. The acid nature of raw and activated clays in aqueous suspension can be demonstrated by pH measurements, by inversion of cane sugar, by evolution of carbon dioxide from alkali carbonates, by color change of indicators, and by titration with alkalis. Characterization of the acid nature of clays in aqueous suspension is complex and difficult to apply quantitatively. Most clays are only partly dissociated and their degree of dissociation depends on the type of base present as well as on the degree of neutralization. In certain cases some clays decompose partly into aluminates and silicates under alkaline conditions.

Paver and Marshall[40] investigated the role of aluminum in well-defined clays of the montmorillonite and beidellite types which had been electrodialyzed. It was found that unlike other trivalent cations, aluminum does not enter appreciably into exchange with the electrodialyzed hydrogen clays. On treatment with neutral salt solutions, such acid clays liberate aluminum as well as hydrogen ions. With increasing salt concentration the amount of aluminum liberated increases to a maximum, until it is approximately equivalent to the base exchange capacity of the clay. Hydrogen ions in varying amount are liberated along with aluminum in all cases. It is striking that more aluminum is liberated by neutral salt than by acid solutions of the same concentration. It has been concluded that hydrogen ion is first liberated by the action of salts and that this hydrogen ion in turn dissolves aluminum from the lattice, by breakage of Al-O-Si linkages.

Grenall[56] developed a method for determination of the acidity of Filtrol clay catalysts, by dispersing the clay samples in aqueous sodium chloride and titrating the liberated acidity with weak potassium hydroxide. The acidity of Filtrol clay decreases approximately linearly with increasing temperature of calcination in air in the range of 900 to 1500°F (482 to 816°C). For several specimens, from the loss of acidity Grenall calculated decomposition temperatures of the clay which were in substantial agreement with those found by x-ray diffraction. At constant concentration of steam, with increasing temperature in the range of 900 to 1400°F (482 to 760°C), the acidity declines rapidly and then levels off.

Thomas, Hickey and Stecker[46] measured the extent of neutralization of aqueous potassium hydroxide by calcined montmorillonite clay which had been treated with hydrochloric acid at different degrees of severity. An appreciable amount of alkali was neutralized by the raw clay itself (0.41 meq/g of clay). With increasing removal of central layer metal atoms, the extent of alkali neutralization by the clay increased, and finally approached a maximum value of 1 meq/g of clay when about one-half of these metal atoms were removed. In case of severe acid treatment, the alkali neutralization method also measures the weak acidity of the exposed siliceous surface of the clay which does not contribute to cracking activity.

The disadvantages of characterizing the acidity of solid catalysts in aqueous media will be discussed in a later section of this chapter that is devoted primarily to synthetic catalysts. In that section also there will be discussed nonaqueous and vapor phase methods of measuring the acidity and acid strength distribution of solid catalysts.

Kaolin Type Clays

Activated kaolinite [$Al_2Si_2O_5(OH)_4$] and halloysite-endellite clays [$(OH)_4Al_2Si_2O_5 \cdot 2H_2O$] are also used for manufacture of cracking catalysts[52, 62]. These two-layer lattice clays consist of alternating sheets of octahedral alumina and tetrahedral silica, with the geometric arrangement for each sheet similar to that of montmorillonite, but with the alignment of the two types of sheets differing considerably. In kaolin the alumina layer is believed to be stretched to fit the silica layer, and to be supported in this position by hydrogen bonding to the next silica layer. Thus the particles that ultimately form have a platyhexagonal shape. In halloysite-endellite structures, interlamellar water layers weaken this support. Thus, there ultimately results formation of tubular particles with a radius of curvature of *ca.* 570Å. Dehydration causes the tubes to split open and flatten out, and a kaolin-like structure results.

These clays have only a small cation exchange capacity that increases linearly with decreasing particle size. Cations are exchanged in the kaolin-type clays only where lattice SiOH groups are exposed. Similarly, anions are exchanged only where lattice AlOH groups are exposed. Kaolinite has no lattice extensibility whereas halloysite-endellite has some extensibility in polar solvents, although far less than montmorillonite. Calcination at *ca.* 550°C destroys the lattice structure of the two clays which then become amorphous.

Kaolinite and halloysite-endellite clays, when treated with acid and then calcined, become catalysts of moderate cracking activity. If they are calcined at 550°C, however, before the acid treatment, much greater activity results, comparable to that of activated montmorillonite[52]. The surface area of activated halloysite is about 160 m^2/g (i.e., Filtrol SR catalyst) compared to about 300 m^2/g for activated montmorillonite.

ALUMINA-SILICA CATALYSTS

Chemistry of Solutions, Hydrosols and Hydrogels

Upon consideration of the several methods for manufacture of satisfactory industrial catalysts (see earlier section) it is apparent that certain basic steps are required:

1. Incorporation of aluminum into a porous silica hydrogel.
2. Purification of the resulting alumina-silica network.
3. Dehydration of the alumina-silica network.

The conditions for preparing the silica hydrogel are chosen to produce a silica gel capable of extensive reaction with the hydrolysis products of an aluminum salt, and at the same time to yield a final catalyst of high cracking activity with the desired physical properties, and with adequate stability for commercial use. An understanding of the fundamental principles of these steps is necessary for proper control of catalyst manufacture and of the chemical and physical properties of the ultimate catalyst. Such an understanding must be based on knowledge of the chemistry of silica and of the silicates, of aluminum salts, and of the alumino-silicates.

Silica Sols and Gels

The usual source of silica for the preparation of cracking catalysts is an aqueous solution of a soluble alkali-metal silicate. The mole ratio of silica to metal oxide in such silicates may range from 0.5 (orthosilicate) through

1.0 (metasilicate) to more than 3 (silicate glasses). The usual commercial source is a sodium "water-glass" with a mole ratio of 3.2 to 3.3; such a material is highly alkaline and contains an equilibrium mixture of silicate anions of varying degrees of polymerization, such as

$$Si_2O(OH)_6 \rightleftharpoons [Si_2O(OH)_{6-n}O_n]^{n-} + nH^+$$

$$Si_3O_2(OH)_8 \rightleftharpoons (Si_3O_2(OH)_{8-n}O_n)^{n-} + nH^+$$

The complicated and strongly pH-dependent equilibria in these systems have been studied extensively but have not been elucidated completely; a modern discussion of the subject has been presented by Iler[63a] together with a comprehensive review of the literature covering polymerization and gelation of silicic acid.

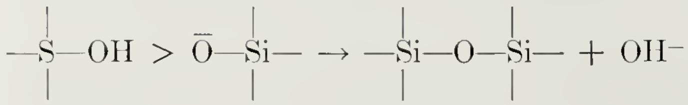
A freshly prepared and carefully filtered dilute solution with molar ratio $SiO_2:Na_2O$ of 3.32 has been shown by light-scattering to have an initial weight-average molecular weight of 325, corresponding to an average degree of polymerization[64] of about 4; aging of such a diluted solution results in considerable further polymerization. If such a solution (fresh)—e.g., 1.0M in SiO_2 with an initial pH about 11—is treated with alkali, it will undergo slow depolymerization; the monomeric form does not predominate at equilibrium until a pH above 13 is attained[63a]. Gradual neutralization of the same solution with acid results in a rapid increase in molecular weight and eventual gelation. If, on the other hand, the silicate solution is added to excess acid solution, a sol of very low molecular weight is formed which undergoes further polymerization relatively slowly. Monomeric silicic acid is a very weak acid with a pKa of about 9.8[63a].

The gelation time in an acidified solution of sodium silicate can vary from a few seconds to several days; it depends in a sensitive way on the pH of the solution, and also depends strongly on the temperature, concentration of silica, and concentration of other electrolytes. Brady, Brown and Huff[65] reported that the rate of polymerization varies as the fourth power of the concentration of a given added electrolyte.

In sols prepared by acidification of alkali silicates, the minimum gelation time occurs in the vicinity of pH 8; the activation energy for the process has a minimum in this region[66-70].

Silica sols that are almost free of electrolyte can be prepared by deionization techniques with ion-exchange resins. The minimum rate of polymerization in such sols occurs at about pH 2 [71]. The minimum gelation time of such sols occurs at pH 5 rather than at pH 8. On the other hand, Goto[72] reports that the rate of disappearance of low-molecular weight silicic acid by polymerization in such sols increases rapidly with increasing pH in the range 7 to 10 in spite of the fact that gelation time increases in this pH range. The apparent discordance between this and earlier findings may perhaps be resolved by the concept that the formation of large aggregates of polysilicic acid is retarded by repulsion between the negative charges on the particles in alkaline solutions. A fairly complete list of references to the recent literature on the kinetics of polymerization in solutions of silicic acid can be obtained from Goto's paper[72] and from a paper by Greenberg and Sinclair[73] on the application of light-scattering techniques to the problem.

The initial reaction in the polymerization of silicic acid is believed to be the condensation of silanol groups with the elimination of water. The increase in the rate of the reaction with decreasing concentration of hydrogen ions above pH 2, with a maximum near pH 8 or 9 suggests that, in this range at least, an important elementary reaction is the interaction of a singly ionized silicic acid with the unionized monomer or the polymer already present, as follows:



$$-\underset{|}{\overset{|}{\mathrm{S}}}-\mathrm{OH} > \bar{\mathrm{O}}-\underset{|}{\overset{|}{\mathrm{Si}}}- \rightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{OH}^- \qquad (1)$$

where the symbol H > O represents hydrogen-bond formation.* It has often been suggested that the branched polymers formed as a result of such reactions may associate by physical interactions into larger aggregates. Definite evidence for such a process has been presented by Brady *et al.*[65], who observed that a silica-sol with a weight-average molecular weight of 600,000 formed by adding acetic acid to potassium silicate (pH 5.7) dissociated almost immediately when potassium hydroxide was added sufficient in amount to neutralize the acetic acid; the dissociated sol had a molecular weight of about 35,000. From intrinsic viscosity measurements, it was observed that the aggregates were highly solvated with an effective density of 0.1 to 0.06; this corresponds to a volume fraction of about 0.045 to 0.03 of silica within the aggregate. As the aggregates grow, two additional processes are believed to occur simultaneously:

(1) Further condensation with the formation of siloxane bonds within the interior of the aggregates, so that the degree of solvation or swelling of the aggregate decreases, and the rigidity of the aggregate increases.

(2) Linking of aggregates to one another, either by chemical reactions such as shown in Eq. (1) or by secondary forces (London forces, hydrogen bonds, etc.).

This will increase the viscosity and turbidity of the system. When the average coordination of an aggregate with other aggregates exceeds two, gelation will occur.

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* Similar suggestions have been made by Plank, by Greenberg and Sinclair and by Ashley and Innes.

The aging of silica sols and gels has been discussed in detail by Iler (*loc. cit.*). During this process, further condensation of silanol groups occurs at a rate that depends on the environment—i.e., pH, temperature, and concentration of electrolyte. The net result is a decrease in the number of free silanol groups and hence in the reactivity of the sol or gel. An additional effect is a decrease in the porosity of the particles constituting the system. When polycondensation proceeds to a sufficient extent, the gel structure contracts as a whole, and bulk liquid exudes from the siliceous network.

Electron microscope studies have shown that the particles isolated from an aged silica sol are essentially spherical in shape[74, 75]. Depending on the preparative conditions, either relatively large isolated spheres may occur or highly solvated clusters of smaller spheres (see Ref. 63, pp. 96–8). The diameters of the particles range from 10Å (mol. wt. *ca.* 1000) to 1000 to 2500Å (mol. wt. *ca.* 10^9). As was pointed out by Carman[76], the surface of each particle will carry silanol groups whose hydroxyl groups complete the tetrahedral coordination of silicon atoms at the surface of the particle. Calculations based on Sears' titration of silica sols and gels with alkali[77] suggest to us that these silanol groups are somewhat stronger than monosilicic acid. Iler and Dalton[78] have presented evidence that dilute sols prepared from deionized silicate at pH 9 consist of dense spherical particles of silica covered with a monolayer of silanol groups together with approximately a monolayer of bound water. In this connection, Holt and King have shown by solubility measurements and by radioactive tracer techniques with Si^{31} that an appreciable fraction of a monolayer of silicic acid is reversibly adsorbed on the surface of quartz at pH 8 to 9 and dissolves at pH 13 [79].

There is little doubt that a dried silica gel (xerogel) consists of a loose packing of essentially spherical particles. A typical gel with a specific surface area of 500 m^2/g would consist on this basis of particles with a surface-average radius of 27Å (mol. wt. 110,000). The physical properties of the xerogel presumably reflect the state of organization of the hydrogel from which it was formed. It has been shown by Sears[77] that silica xerogels have about the same specific surface area as their parent hydrosols or hydrogels. For this purpose the specific surface of the hydrogel was determined by titration with alkali. The pore volume of a xerogel, however, is usually much less than that of its parent hydrogel.

The effects of preparative conditions on the physical properties of the ultimate dried xerogel have been investigated by Plank and Drake[20], among others. Considerable variations result from changes in the temperature, pH and concentration of silica during polymerization, aging time, washing and drying procedures, etc. A high specific surface is favored by low silica concentration at pH 7. At moderate silica concentration it is favored by a low pH; the effects of age depend on the pH and electrolyte present.

A high pore volume (low density) is favored by long aging before drying, by a high concentration of silica and by a high pH during gelation. These effects have been discussed by Plank[70] in terms of a postulated mechanism of gelation and syneresis.

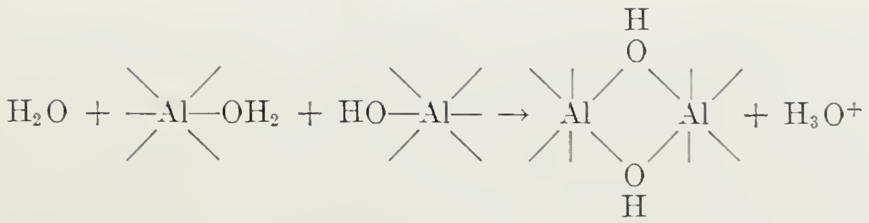
The qualitative principles underlying the polymerization and gelation of silica solutions appear to be fairly well understood. In spite of extensive experimental work, however, a detailed quantitative theory of the phenomena involved is still lacking. In view of the complexity of the system, the lack of a comprehensive theory is scarcely surprising.

Aluminum Salts and Aluminum Hydroxide

The solution chemistry of aluminum hydroxide is analogous in many respects to the solution chemistry of silicic acid. Monomeric species exist below *ca.* pH 3 as $Al(H_2O)_6^{+++}$ and above *ca.* pH 14 as $Al(OH)_4^-$. In the central part of the region between these limits solid phases (sols, gels or crystals) exist. In the transition regions of pH close to these limits, there is evidence for the occurrence of soluble polymeric complexes. The equilibria involving these polymers have been investigated by Brosset and coworkers and by others[80-82].

In strongly acid solutions, aluminum ion is believed to exist as the hexahydrate, $[Al(OH_2)_6]^{3+}$. This species is a moderately strong acid. The species $[Al(OH_2)_5OH]^{2+}$ is unable to exist at appreciable concentrations, however, because rapid polymerization occurs. The data suggest that a number of polymeric cations can exist in the pH range from 3 to 5—i.e., dimers, trimers, etc.—with possibly a cyclic hexamer predominating for which the following structure has been proposed: six aluminum-oxygen octahedra are joined in a ring by the sharing of edges; the bridge positions are occupied by hydroxyl groups, the remaining coordination positions (two for each aluminum ion) are occupied by either water or hydroxyl groups depending on the pH. This structure, with a composition $[Al_6(OH)_{12}(OH_2)_{12-n}(OH)_n]^{6-n}$ is analogous to the ring structures in $Al(OH)_3$ (gibbsite or bayerite). The fact that the position and shape of the titration curves of aluminum salt solutions with alkali depend on the kind of anion that is present suggests that some of the coordination positions of aluminum in these soluble complexes may be occupied by anions (F^-, Cl^-, or $SO_4^=$).

The mid-point of the titration curve of aluminum chloride solution with alkali occurs around pH 3.8 to 4.2. Though it is perhaps unrealistic to attribute a single pK_a to the mixture of acidic species that is present under these conditions, the observation suggests that the source of hydrogen ions in the mixture has an effective pK_a of about 4. A possible source for the acidity is such an interaction as



—i.e., the dissociation of the proton is favored by the formation of hydroxyl bridges between aluminum atoms.

In the strongly alkaline region the stable species is believed to be the ion $[Al(OH)_4]^-$. When acid is added to solutions of this latter species, a solid phase forms either directly or via the intermediate formation of a mixture of polymeric anions. The available data suggest the latter but do not distinguish clearly between the two possibilities[81].

Interaction of Aluminum Salts with Silica Hydrogels

It has long been known that neither silica nor alumina, nor a mixture of the dry oxides, is an active cracking catalyst (see p. 76). It was therefore considered likely that freshly precipitated hydrous oxides may interact in some manner to produce an active solid. In order to elucidate this interaction, Tamele and Ryland studied the precipitation of aluminum hydroxide in absence and in presence of fresh silica gel by potentiometric titration techniques[83, 84]. The observations are summarized in Figures 3 and 4, and Table 2.

The titration curves show rather convincingly that there is an interaction between freshly formed silica sol and the products of hydrolysis of aluminum ions. In Figure 3, Curve 1 represents a titration of 1.48 liters of 2.29*N* hydrochloric acid with 3.08*N* sodium hydroxide. Curve 2 represents a titration at 10°C of the same volume of acid to which a small amount of aluminum chloride had been added to make the solution 0.0606*M* in aluminum chloride. Upon addition of alkali, hydrolysis of the aluminum salt became observable at about pH 3.5; with addition of more alkali, the pH was observed to change slowly with time, presumably because of the slow establishment of equilibrium among the polymeric hydrolysis products. The titration was, therefore, completed rapidly (within a few minutes); the consumption of hydroxyl ion by aluminum at the end of the titration amounted to 3 moles/mole of aluminum. A solid phase of aluminum hydroxide was observed to develop, starting at pH 3.9, and formed a precipitate which settled rapidly at the end of the titration.

Curve 3 represents the titration of the same solution as in Curve 2, but using as a titrant 3.08*N* sodium metasilicate instead of hydroxide. In this silicate, the silica is present largely as the monomer. In this case, formation of clear silica sol occurred from the beginning of the titration, which was again conducted rapidly at *ca.* 10°C. A new plateau was observed about 1.4 pH units below that corresponding to the formation of aluminum hydroxide. No visible precipitate appeared; after completion of the titration the solution remained clear for a short time and then gelled rapidly. The consumption of the silicate base beyond that needed to neutralize the hydrochloric acid present amounted to 4 moles/mole of aluminum. The titration thus corresponds to the neutralization of four equivalents of an

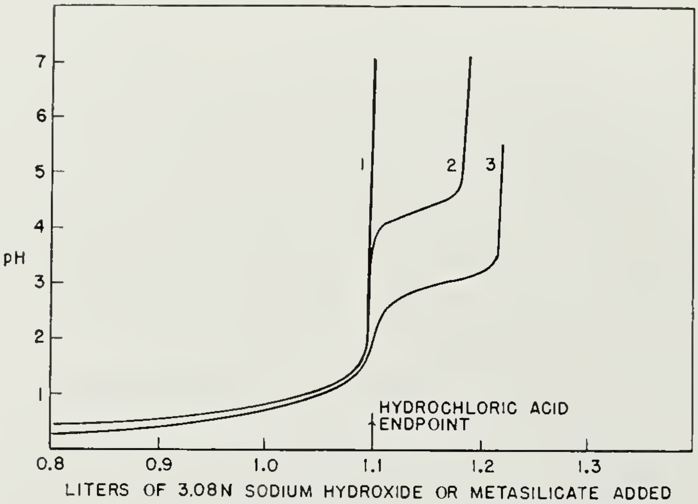


Figure 3. Hydrolysis of aluminum ions in the presence and absence of silica sol. (1) Control: titration of hydrochloric acid with sodium hydroxide. (2) Titration of hydrochloric acid (containing aluminum chloride) with sodium hydroxide. (3) Titration of hydrochloric acid (containing aluminum chloride) with sodium metasilicate. (Republished by permission of E. J. Brill, Publishers, Leiden)

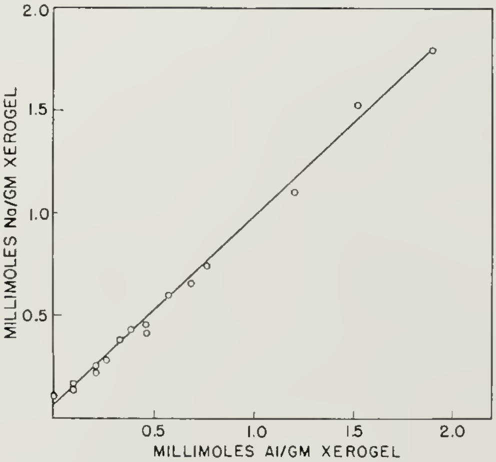


Figure 4. Stoichiometric ratio of sodium to aluminum in alumina-silica complex

acidic substance per mole of aluminum; the effective acid dissociation constant of this substance or mixture of substances is about 20 times greater than that of the intermediate hydrolysis products of aluminum chloride.

A series of gels with progressively increasing amounts of aluminum was prepared by the titration procedure described above. Each was washed free of electrolyte and dried; analysis of the dried gel showed the presence of approximately one millimole of sodium/millimole of aluminum present, in correspondence with the single negative charge indicated per aluminum atom by the titration (Figure 4). This sodium either in the hydrogels, or in the gels dried at 25°C, is readily replaced by exchange with hydrogen,* ammonium, aluminum and other cations. The data of Figure 4, however, show that a small but appreciable amount of sodium is fixed by pure silica gel; this amount is consistent with the acid strength estimated for the silanol groups of polymerized silicic acid.

The conditions employed in these potentiometric studies to demonstrate the formation of base-exchange sites are not normally used in the manufacture of most types of commercial cracking catalyst, though the phenommena observed above undoubtedly play an important role. As described earlier, it is usual in the manufacture of many granular and microspheroidal catalysts to hydrolyze an aluminum salt in the presence of a silica gel that is already well polymerized by aging.

If the silica gel is well aged, the position of the flat part of the titration curve rises and approaches that for the precipitation of aluminum hydroxide, and finally only three equivalents of alkali are required per mole of aluminum to reach neutrality. Part of the range of possibilities is shown in Figure 5[85]. The titration curves shown in this figure were obtained in the following way: a solution $0.77M$ in hydrochloric acid and $0.16M$ in aluminum chloride was neutralized to pH 2.0 by addition of $0.965N$ sodium trisilicate. As discussed earlier the silica is already polymerized to a substantial degree in such silicates. The sol-salt solution was quickly divided into equal aliquots which were aged for various fractions of the gel-setting time (t_s = 143 hr). After the aging of each aliquot, neutralization was rapidly completed in a potentiometric titration with $0.980N$ sodium hydroxide. Curve 1 was obtained after an aging time of 0.0006 t_s; it is similar to Curve 3 of Figure 3. Curves 2, 3, 4, and 5 were obtained after 0.034, 0.162, 0.70 and 1.00 t_s, respectively. Curve 6 is a reference curve for a neutralization carried out with sodium hydroxide with the same amount of aluminum ion with no silica present. Independent observations have demonstrated that very little interaction occurs between $[Al(OH_2)_6]^{3+}$ and silica sol at pH 2; it is evident that prior aging of the silica sol at pH 2

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* In replacement with hydrogen ion, care must be taken to keep the pH of the solution above 2; otherwise dissolution of aluminum may occur.

drastically reduces its rate of reaction with aluminum ion hydrolysis products to form ion-exchange sites during the final neutralization. The analytical data are summarized in Table 2.

As shown by the above data and Curve 1, the highly reactive silica sol (high hydroxyl population) interacted with virtually all the aluminum ion hydrolysis products to form base exchange sites (anionic aluminum). The remaining small amount of unreacted aluminum ions exchanged with a small fraction of the base exchange sites previously created (cationic aluminum). Thus 3.78 instead of 4.0 equivalents of OH were required per mole of original Al^{+++} present, for neutralization.

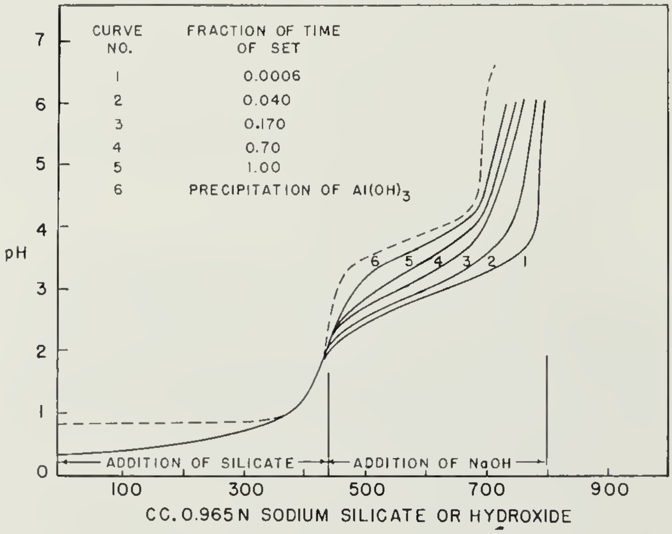

Figure 5. Influence of age of silica sol on nature of titration curve of hydrochloric acid-aluminum chloride solution.

Table 2. Composition of Products of Hydrolysis of Aluminum Chloride in Presence of Silica Sols of Various Ages

Age of Sol (Multiples of 143 hr)	Weight %		Moles Hydroxyl Consumed/Mole of Aluminum to pH 6	Moles of Sodium/Mole of Aluminum in Washed, Dried Gel
	Na_2O	Al_2O_3		
0.0006	5.76	9.97	3.78	0.95
0.034	4.02	9.26	3.64	0.72
0.162	3.72	10.12	3.42	0.61
0.701	3.14	9.98	3.14	0.52
1.00	2.24	10.03	3.07	0.37

In the other extreme (Curve 5) the reactivity of the silica was greatly reduced by prior aging until actual gelation occurred; the silica was able to polymerize with a much smaller portion of the total aluminum hydrolysis products in the short time required to perform the titration. Thus, to a much greater extent the unreacted aluminum ion hydrolysis products entered the cationic base exchange sites already created. This base exchange step involves no additional formation of acidity. The over-all acidity created was only 3.07 equivalents per mole of original Al^{+++}.

Results intermediate between these two extremes are represented by Curves 2 through 4. Some further interaction and rearrangement of the cationic to anionic aluminum during aging and washing of the hydrogels is indicated by the greater Na/Al ratio in the final products in each case than would be expected from the OH/Al ratios obtained from the corresponding titration curves. This is particularly noticeable with the products obtained from the silicas of lowest reactivity. Usually, in actual practice, the silica is aged to a greater extent than corresponds even to Curve 5, and consequently, more fixation of aluminum cations and less fixation of Na^+ and NH_4^+ cations occurs in the final catalyst. In some instances, acidulation during washing replaces some of the alkali ions by H^+, thus fixing additional H^+ as well as Al^{+++} and possibly polymeric basic Al ions on the catalyst surface.

Plank[20, 70] studied the preparation of silica and alumina-silica gels by rapidly mixing together solutions of acid, aluminum salt, and sodium silicate. Even though this latter procedure might be expected to lead to products where aluminum is buried within the framework of silica, Plank found that both the hydrogels as well as the products dried at *ca.* 180°C could be stripped of deposited aluminum (7 to 10 per cent Al_2O_3) with dilute hydrochloric acid (*ca.* 2 to 3 hr at 16°C). After calcination at 700°C, however, only a small percentage of aluminum could be removed by acid. Plank concluded that aluminum forms terminal groups on the silica gel support. Substantially all these terminal groups were accessible to base exchange (NH_4^+, or H^+ for Na^+). In order to explain the negative charge on aluminum, Plank assumed that of the six coordination positions of the aluminum ion, four may be occupied by negative groups such as OH^- or $Si\text{-}O^-$ groups and others by water molecules.

Another approach was made by Milliken and Cornelius* who prepared a series of alumina-silica hydrogels of varying alumina content by co-precipitating silica from sodium silicate with aluminum sulfate in predominantly alkaline media. In these catalysts that were finally adjusted to pH 7, the amount of exchangeable sodium increased in direct proportion to the amount of aluminum present. Up to *ca.* 30 per cent alumina content, one mole of sodium was found for each mole of aluminum in the washed alumina-silica hydrogels. Thus, in this range each mole of aluminum acted as an acid. The ratio of sodium to aluminum decreased linearly to zero as the alumina content was increased from *ca.* 30 to 100 per cent.

These observations were interpreted by the investigators in terms of

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* A summary of this work is to be found in the Chapter by Oblad, A. G., Milliken, T. H., Jr., and Mills, G. A., "Advances in Catalysis," III, New York, Academic Press Inc., 1951.

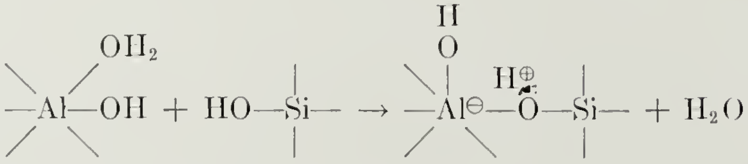
the independent formation of the hydroxides of aluminum and silicon at different rates to form micelles which eventually aggregated to form a gel, rather than in terms of complex formation. Though it is conceivable that the tendency of aluminum hydroxide to precipitate from the aluminate at a rather high pH may favor such a process, the present authors are inclined to believe, because of the similarity between the above observations and ours, that the formation of an acidic complex occurs here also.

Aluminum hydroxide very likely existed in the preparations which had a high alumina content, since soluble cationic aluminum cannot exist under alkaline conditions, and is therefore incapable of entering base exchange positions. Aluminate ion hydrolysis products that do not interact with silica hydrogel have no other recourse than to polymerize with each other to form aluminum hydroxide.

The origin of the additional acidity formed during the interactions described in this section has been considered by many authors. It has often been proposed that under acidic conditions aluminum enters into gel formation with a coordination number of four rather than six. In view of the strong tendency of aluminum ion to maintain sixfold coordination in its aqueous solutions, and in its hydrolysis products, the present authors see no justification for assuming four coordination of aluminum in the hydrous state (see also Ref. 20).

The potentiometric curves shown in Figure 3 indicate that in the presence of excess reactive silica sol the aluminum ion hydrolysis products react preferentially with the hydroxyl groups of the silica sol rather than polymerize to a great extent with each other to form bulk aluminum hydroxide. In other words, under these conditions the tendency to form Al-O-Si bonds is somewhat greater than that to form Al-O-Al bonds at *ca.* pH 3.

The following equation depicts the likely way in which copolymerization of Al-OH and Si-OH groups occurs, with consequent development of a mole of acidity for each aluminum atom fixed in the resulting insoluble copolymer.



$$-\overset{\displaystyle OH_2}{Al}-OH + HO-\overset{|}{\underset{|}{Si}}- \rightarrow -\overset{\overset{\displaystyle H}{\displaystyle O}}{Al^{\ominus}}-\overset{H^{\oplus}}{O}-\overset{|}{\underset{|}{Si}}- + H_2O$$

The unlabeled coordination bonds can be any of the following groups: —OH, —H_2O, —OAl, and —OSi. The number of —OSi groups that can be coordinated with any one aluminum atom probably does not exceed three or four.

Alumina-silica gels have been made by a variety of procedures (see section "Industrial Background"). Though little has been published concerning the details of the chemical reactions that occur during these preparations, it seems likely that the interactions are qualitatively similar to those described above. The completeness of the interaction between aluminum ion hydrolysis products and silica will vary with the preparative details.

Ion-Exchange Properties of Alumina Silica Hydrogels

As a consequence of the phenomena described in the preceding section, appreciable amounts of sodium can be fixed in the structure of catalysts prepared either from the "acid side" or from the "alkaline side." Since the fixed sodium detracts from the thermal stability and activity of the final catalyst, it must be removed: this removal can be accomplished by ion exchange with ammonium ion or aluminum ion by washing with the corresponding salt solutions. The ion exchange properties of the hydrogel are important for these reasons, and also because of the information they can provide about the structure of the gel. The exchange properties observed by Oblad, Milliken and Mills[22] have several important implications:

1. At low concentrations of alumina, one acid site is associated with each aluminum ion combined with silica.
2. The sodium ions combined with the acid sites are readily accessible to other ions in the solution; the acid sites are therefore either on the external surface of the particles constituting the hydrogel, or are accessible by diffusion through the incompletely condensed interior of the particles.
3. The maximum base-exchange capacity at 30 to 32.5 %w Al_2O_3 suggests that the limiting composition of the sodium salt of the acidic species is approximately $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot XH_2O$.

A similar limiting composition for the sodium exchanged alumina-silica complex is indicated by the results of experiments in which materials prepared by the hydrolysis of an aluminum salt in the presence of a large excess of silica gel were extracted with cold 1.0*N* solutions of sodium hydroxide[86]. Silica was dissolved in preference to alumina until a limiting composition approximating $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot XH_2O$ was attained. Materials of the same final stoichiometry have also been obtained by sodium hydroxide treatment of the complex, containing aluminum instead of sodium in the cationic exchange position. This indicates that unlike anionic aluminum that is bonded directly to silica, cationic aluminum dissolves and reacts with the dissolved silica.

Some related information has been presented by Danforth[87] who has measured (by titration to the phenolphthalein end-point) the amount of acidity developed when hydrolyzed aluminum isopropoxide reacted with the various methylethoxysilanes in the presence of water. He found that relatively little acidity was developed with trimethylethoxysilane; one mole of acid was developed per mole of aluminum with dimethyldiethoxysilane as long as the mole ratio of aluminum to silicon did not exceed 1:5; with methyltriethoxysilane about 0.75 mole of acidity was developed per mole of aluminum up to a mole ratio of about 1:3.

Though these experiments present a novel and stimulating approach to the chemistry of alumina-silica, the observations are difficult to interpret unambiguously. The failure of acidity to develop with trimethylethoxysilane can be accounted for by rapid reaction of trimethylsilanols with each other to form $(Me_3Si)_2O$. The observations with dimethyldimethoxysilane have been interpreted by Danforth in terms of the formation of cyclic structures containing one aluminum atom and five silicon atoms linked by oxygen bridges. The precise significance of the observed titer is somewhat uncertain because some ionization of silanol groups is to be expected at the phenolphthalein end-point.

Syneresis and Drying of Hydrogels

The syneresis of alumina-silica gels has been described by Plank and Drake[20]. This is a slow process in which the gel decreases in volume by exuding water. In commercial practice, the gel is usually too dilute to show visible syneresis and is broken up by stirring so that syneresis is difficult to observe; in any case, the gel is usually dried before syneresis has gone very far. In a gel containing 5 to 6 %w solids, the volume not occupied by solids is some 30 times larger than the volume of solid. In the dried gel, on the other hand, the void volume is of the order of 0.4 to 1 cc/g, or from one to 2½ times the volume of solid. Clearly a considerable reorganization of the gross structure of the gel occurs in the drying process. The details of this process are not well understood; it is probable that weak bonds between coherent but deformable aggregates of the dense roughly spherical elementary particles are broken by the forces exerted by surface tension as the meniscus between air and liquid advances through the structure during the drying process. A modern discussion of this phenomenon is given by Iler[63c]. A large pore volume can be retained if the water is displaced by a liquid of low surface tension such as acetone before the gel is dried[89]. If the liquid is evaporated above its critical temperature as in the Kistler process,[90] almost all of the pore volume of the original hydrogel can be retained. The resulting aerogel has a very low density and low mechanical strength.

CHEMISTRY OF THE SOLID XEROGELS

In this section we shall be concerned with the chemistry of xerogels—i.e., gels which have been dried at such temperatures that much of their physically adsorbed and capillary-condensed water has been lost, and with the properties of calcined gels which have lost much of the water of constitution that was originally present as hydroxyl groups or as chemisorbed water. Since cracking catalysts are used at temperatures in the range 500 to 600°C, most studies have been made with catalysts that have been calcined at temperatures in this range.

Physical Structure

It has often been suggested in the past that inorganic gels consist of a loosely packed aggregate of small particles[91, 92, 76]. Direct evidence to support this view has been obtained by electron microscopy of alumina-silica cracking catalysts[11, 93]. Adams and Voge[93] have shown that a fresh calcined American Cyanamid catalyst made by the hydrolysis of aluminum salt in the presence of silica gel was made up of approximately spherical primary particles (average diameter 45Å) packed loosely together to form irregularly shaped primary aggregates ranging in size from 0.05 to more than 3μ diameter. The primary aggregates fit together with only relatively small volumes of void space between them; it may be speculated that some deformation of the aggregates to achieve this fit occurs during the drying operation. In addition, there appears to be aggregation of these primary aggregates into larger secondary aggregates and so on. The bonding among the members of this hierarchy of aggregates is undoubtedly an important determinant of the mechanical strength of the gel.

The spherical shape of the primary particles is consistent with the fact that such gels (provided they have not been heated above 800°C) are amorphous to x-rays[94]. The molecular structure of the ultimate particles can, therefore, be expected to show only short-range order, but not long-range order. In this respect, silica gel and alumina-silica gel differ from alumina gel which usually displays the diffraction patterns of $AlO(OH)$ (boehmite) and of $Al(OH)_3$ (bayerite or gibbsite) after drying at 120°C, and of γ-Al_2O_3 or other anhydrous forms of alumina after calcination above 540°C. Alumina gels may be expected to contain anisometric primary particles. Elkin, Shull and Roess[94] found that alumina-silica gels prepared by hydrolysis of aluminum salts in the presence of silica gel, *or even by the mixing of wet silica gel with wet aluminum hydroxide gel*, were amorphous at all compositions up to 31 %w Al_2O_3. Gels prepared by either method but containing more than 50 %w Al_2O_3 showed the diffraction patterns of crystalline alumina or alumina hydrates.

Surface Area. On the basis of the model described above, the specific surface area will depend on the distribution of the radii of the ultimate particles, and is given by

$$S = \frac{3}{\rho} \sum n_i r_i^2 / \sum n_i r_i^3$$

where ρ is the density of the ultimate particles, and n_i is the number of the ultimate particles of radius r_i . Adams and Voge[93] found by direct measurement of the electron micrographs that the distribution of ultimate particle sizes in the fresh catalyst was relatively narrow. The surface area computed from the distribution agreed closely with that measured by nitrogen adsorption.* In this case, it is possible that the number of very small particles was underestimated because of the limited resolving power of the microscope; the calculated surface area may have been too low.

Elkin *et al.*[94] computed the distribution of particle diameters in similar gels from measurements of the small-angle scattering of x-rays and the assumption that the ultimate particles were spherical. The area computed from the distribution was higher by 15 to 50 per cent than that measured by adsorption of nitrogen. In this case, it is possible that the number of very small particles was overestimated because of the approximations inherent in the interpretation of the scattering data; the calculated surface area may have been too high. The discrepancy between the measured and calculated surface areas was attributed by the investigators to a limited access of nitrogen to the surface of the gel in the regions of contact between elementary particles. If the primary particles are in tangential contact, this effect is important. It is likely, however, that a fillet is present to fill in the contact region between many pairs of particles.

In a structure composed of such very small particles, an appreciable fraction of the solid is contained within the first atomic layer at the surface of the gel. If we assume that the oxygen atoms are approximately close-packed and assign a van der Waals or ionic diameter of 2.80Å to the oxygen atoms, we can calculate that an additional layer of oxygen atoms will increase the radius of a spherical particle by 2.3Å. On this basis the fraction of the oxygen atoms that are on the surface is approximately $2.3\rho S \times 10^{-4}$, where ρ is the density of the ultimate particle and S is the surface area in m^2/g. This fraction ranges from 0.32 at 600 m^2/g to 0.053 at 100 m^2/g for a particle with a density of 2.3 g/cc. Alternative assumptions about the structure will lead to estimates only slightly different from these. The fact that such a high proportion of the material is in or near the surface in a high-area gel is important to the interpretation of some of the chemical properties of such gels.

Pore Volume. For the model under discussion, the pore volume is the sum of the irregularly shaped spaces between the primary particles. The average pore diameter calculated from the ratio of the specific pore volume to the specific surface area has, therefore, only formal significance; so does

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* Low temperature gas adsorption techniques for measuring the surface area of solids, and the theoretical considerations, are thoroughly discussed by P. H. Emmett, in Chapter 2, Volume I, of this series.

the distribution of pore radii computed from physical adsorption or desorption data by means of the Kelvin equation for condensation in cylindrical capillaries. A more significant quantity, perhaps, is the volume fraction of voids, F, given by

$$F = \rho V_p/1 + \rho V_p$$

where V_p is the specific pore volume and ρ is the density of the primary particles. The value of F is related to the mode of packing of the ultimate particles[95]. The types of packing that occur in silica gels have been discussed from this point of view by Iler[63b].

The theory of capillary condensation in an aggregate of spherical particles has been discussed by Haines[96] and by Carman[97]. The former author has shown that hysteresis of the type observed in the adsorption and desorption of nitrogen by silica and alumina-silica gels above $p/p_o = 0.3$ can be accounted for by such a theory.

Quick and convenient methods for the measurement of pore volume by saturation absorption of liquid water, or of carbon tetrachloride vapor have been recently described by Innes[98], and by Benesi, Bonnar and Lee[99].

The technique for obtaining information about the structure of inorganic gels from the low-angle scattering of x-rays has recently been elaborated by Debye[100]. A comprehensive review of the surface areas, pore volumes, and apparent pore-radius distributions of a variety of commercial cracking catalysts has been given by Ries[101, 102].

Chemical Structure

The lack of long-range order in amorphous alumina-silica prevents a determination of the detailed structure by diffraction methods; all of the evidence concerning the structure is indirect. Unanimity of opinion is still lacking about the following matters among others:

1. Distribution of bound water (or hydroxyl groups) between the coordination shells of aluminum and of silicon.
2. Distribution of aluminum on the surface or between the surface and the interior of the primary particles.
3. Distribution of aluminum with respect to coordination number.
4. Structure of the acidic or catalytically active groups on the surface.

Distribution of Bound Water. Calcination of alumina-silica catalysts at elevated temperatures results in the volatilization of large quantities of both bound and sorbed water. Dissociation of any ammonium ions present occurs also. The properties of the small amount of constitutional water remaining after calcination have been studied extensively, because this water is intimately related to the source of protonic acidity. It has been shown that the activity of such catalysts in a number of hydrocarbon reactions is strongly dependent on the water content of the catalyst and on the manner in which it has been added. It is therefore of vital interest to know as much as possible about the state of combination of bound water in alumina-silica catalysts and related materials.

Milliken, Mills, and Oblad[103] found in a series of their experimental alumina-silica catalysts that there was a parallelism between the water content and the alumina content for gels dried at 100°C (containing up to 25 per cent alumina). For gels in the form of the "ammonium salt," each aluminum atom (up to 25 per cent Al_2O_3 content) was accompanied by one additional molecule of dissociable water, and one ammonium ion. Above 30 per cent alumina content, the base exchange capacity declines rapidly and there is no apparent correlation of water content with ammonium ion content. Since each aluminum ion presumably displaced a silicon atom with an average degree of hydration greater than zero this finding may imply that each aluminum atom in the final structure was accompanied by the equivalent of somewhat more than one water molecule, and perhaps as much as 1.5 water molecules in addition to one ammonium ion. When the gels were converted to the hydrogen form before drying, the additional water content increased to 1.44 molecules of water or 2.9 hydroxyl groups per aluminum atom. After drying the gels lost a large part of their exchange capacity.

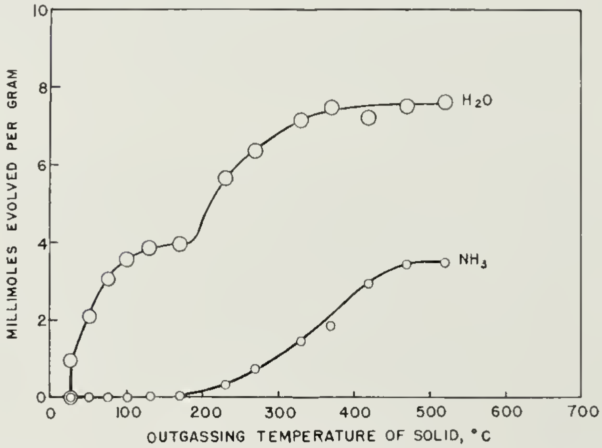


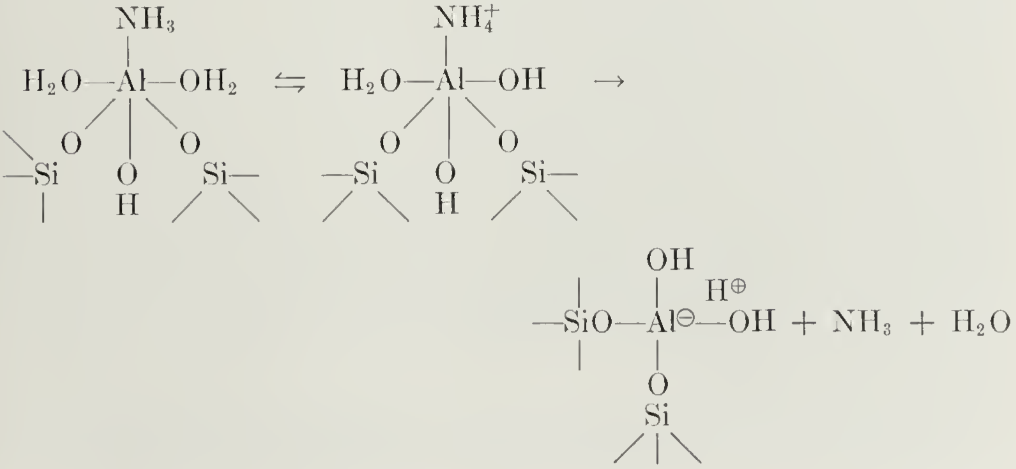
Figure 6. Evolution of water and ammonia from an ammonium salt of alumina-silica complex as a function of temperature. (Republished by permission of The Faraday Society, London)

The thermal decomposition of the ammonium salt of an alumina-silica complex has been studied in detail by Roper[104]. This salt was prepared by addition of sodium silicate to dilute aluminum chloride solution. After exchange with ammonium ion, it contained 3.5 mmole of ammonium ion and 3.6 mmole of aluminum ion per gram of alumina-silica. Figure 6 shows the cumulative loss of water and of ammonia that occurs on increasing the temperature in steps of 20 to 50°C, followed by 2 hr evacuation after each step. The first half of the top curve shows the removal of lightly held water (about 0.9 mmole at 25°C, and 2.9 mmole between 25 and 180°C). At this point dissociation of the ammonium ion begins, accompanied by a renewed loss of water. These processes proceed at different rates as the temperature is increased, but between 180 and 500°C the 3.5 mmole of ammonia is removed together with about 3.6 mmole of water per gram.

Subsequent exposure of the calcined catalyst to dry ammonia (25°C, 13 mm), however, resulted in the adsorption of only 1.4 mmole per gram. A silica gel of similar surface area (175 m^2/g), after evacuation at the same temperature, adsorbed only 0.6 mmole ammonia per gram. Though an appreciable amount of acidity remained after calcination of the catalyst it is clear that most of the original exchange capacity was irreversibly lost. Similar observations have been reported by Mills *et al.* (*loc. cit.*).

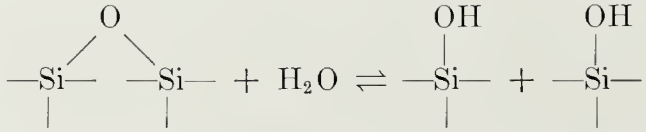
In view of the very high strength of the Al-O bond, it is surprising that the extensive dehydration of the surface aluminum atoms occurs at temperatures as low as 300 to 500°C. The bond energy for the Al-O single bond can be estimated from Pauling's electronegativity scale to be over 100 kcal/mole. The fraction dissociated at 327°C should therefore be of the order of 10^{-35}. The heat of hydration of the aluminum ion has been computed to be 1120 kcal/mole[105].

The energy required for the dissociation shown in Figure 6 must therefore be compensated by some other source of chemical energy. This may be either a change from six to four coordination, with the formation of a smaller number of stronger bonds to the aluminum, or coordination to two oxygen or hydroxyl groups previously uncoordinated to the acidic aluminum atom. The former of these possibilities seems the simpler and the more likely. Though a variety of models can be conceived for the process, a possible model is shown below:

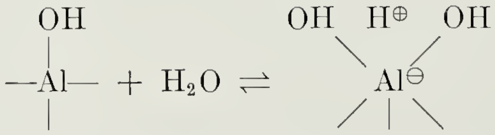


Evidence for the lability of oxygen in the coordination sphere of aluminum and silicon in alumina, silica gel, and Houdry Type S alumina-silica has been obtained by Mills and Hindin[106] from their studies of the exchange reaction with water enriched with O^{18}. It was shown that all or an appreciable fraction of the first molecular layer of oxygen atoms in the surfaces of these solids will exchange with the oxygen of liquid water within 0.25 to 1.0 hr at 100°C. More deep-seated exchange occurs in hundreds of hours with liquid water at 100°C, and occurs very rapidly with steam at 450°C. It is clear from these results that the surface monolayer exchanges much more rapidly than the sub-surface layers of oxygen.

At least two mechanisms can be envisaged for such an exchange. One is the reversible hydrolysis of surface linkages between cations, i.e.,



The second is the temporary enlargement of the coordination sphere of a cation at the surface, i.e.,



From the experimental findings it is evident that the surface oxygen atoms in amorphous silica gel or alumina-silica are highly labile in the presence of water, or other molecules that are capable of strong coordination to aluminum or silicon.

The same authors have made the highly significant observation that bentonite and kaolin clays that had not been acid-treated showed no detectable oxygen exchange even after 720 hrs immersion in liquid water at 100°C. From this it can be concluded that a well ordered siloxane structure is highly resistant, even in its surface layer, to attack by water.

Mills *et al.* have suggested that the bonds to oxygen in the surface of the partially dehydrated silica, and alumina-silica, are in a highly strained state[52]. In the latter case the strain is said to occur at the interfacial contact between silica and alumina micelles.* It seems to us unlikely that a high degree of surface strain actually exists, since, because of the great surface mobility, a more stable structure would be automatically achieved. The observations can equally well be explained by the absence of a high degree of order and the consequent lack of restriction on local variations in structure or coordination number.

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* The dynamics of the solid surfaces of such systems has been discussed by Cook, M. A. and Oblad, A. G., *Ind. Eng. Chem.*, **45**, 1456 (1953).

It is probable that at least a part of the surface of alumina-silica catalyst is similar in its composition and properties to the surface of pure silica. The available information on the hydration of silica surfaces has been reviewed by Iler[63d], who presents convincing arguments to show that the fully hydrated surface of colloidal silica should be characterized by an area of about 12.7Å^2 per silanol or hydroxyl group (either one hydroxyl on every silicon atom or two hydroxyls on every other silicon atom on the surface).

A review of the work of Haldeman and Emmett[107] suggests that their dehydration *vs.* temperature data fall into two categories: samples dried from the hydrogel show a smaller apparent area per hydroxyl group than 12.5Å^2 below 200°C; this suggests the presence of internal silanol groups. This interpretation is supported by the fact that Shapiro and Weiss[108] found a lower apparent water content for silica gel by reaction with diborane than by loss of weight on ignition. The diborane should have little opportunity to react with internal silanol groups.

The second category of samples studied by Haldeman and Emmett includes samples that have been dried for a long time at room temperature or have been heated to 500 to 600°C and then rehydrated at room temperature before dehydration at higher temperatures. These samples show an apparent area per hydroxyl group ranging from 17 to 20Å^2 at 100°C. In both categories, however, the residual water content after dehydration at a given temperature appears to increase with increasing specific surface area.

A comparative study of the surface dehydration of silica gel, alumina, and a Houdry M-46 alumina-silica catalyst has been reported by Haldeman and Emmett (*loc. cit.*). The silica gel was treated with water, calcined at 600°C, rehydrated at 30°C and dried at 110°C. The alumina was calcined at 800°C and similarly rehydrated and dried. The Houdry M-46 alumina-silica catalyst (12.5 per cent Al_2O_3 ; 249 m^2/g) which presumably had been calcined at a high temperature, was rehydrated in the same way. The residual water content of these samples after evacuation at 500°C, rehydration by exposure to saturated water vapor at 30°C for several days, and evacuation at a series of increasing temperatures, is shown in Figure 7, in terms of the apparent number of water molecules per 100Å^2 of surface. The remarkable thing about these data is that the residual water held per unit surface by alumina-silica is about the same as that held by silica itself in the region of 400 to 500°C. Potassium and barium exchange of the alumina-silica catalyst, followed by evacuation at 500°C, does not affect either surface area or residual water content appreciably. Since these metals are known to deactivate such a catalyst, it is reasoned that most of the residual water content is held at sites other than the base exchange sites that are associated with cracking activity.

The same authors have measured the amount of water irreversibly readsorbed ("fixedly held") at a few mm pressure at 150°C, on samples that had been first evacuated at 500°C. Very little water was adsorbed by silica gel under these conditions, but 1.77 molecules of water/100Å^2 were adsorbed by alumina. The alumina-silica sample adsorbed 0.134 molecules of water/100Å^2, or about 7.6 per cent of the amount adsorbed per unit surface area by the alumina. It was pointed out that the water retained by alumina-silica corresponds to much less than one proton per atom of aluminum. It ranges from 1.24 protons per aluminum after evacuation at 100°C to 0.34 at 500°C.

The significance of these observations is by no means clear. It is to be noted that the data cannot be given a thermodynamic interpretation since they do not refer to a specific equilibrium partial pressure of water. In addition, the results of such measurements can be expected to depend on the detailed history of the sample.

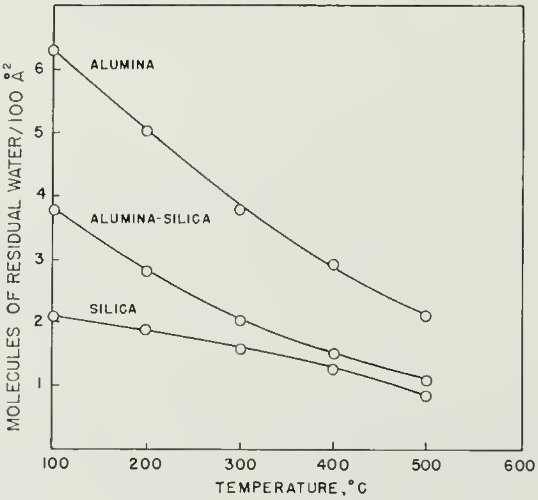
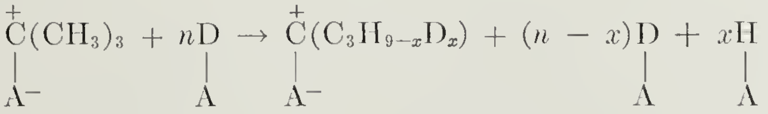


Figure 7. Residual water content of alumina-silica, silica, and alumina at various temperatures. (From the data of Haldeman and Emmett[107])

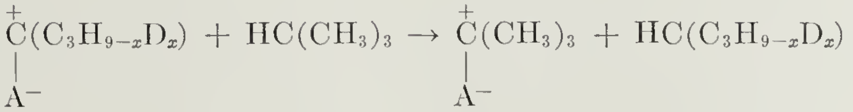
Milliken, Oblad and Mills[52] found the same magnitude of reversible water pickup between 450 and 650°C for various catalytic substances. The catalysts were first dried to constant weight at 650° in flowing air containing 10^{-5} atm partial pressure of water vapor. The gain in weight of the catalysts after exposure to 1 atm of water vapor at 450°C has been expressed as the reversible water pickup. Activated bentonite, activated halloysite, Houdry alumina-silica catalyst, silica gel, and γ-alumina retained 2.4, 1.6, 0.33, 0 and 2.8 molecules of water per 100Å^2, respectively. On the two assumptions that the reversible water in each catalyst was held only on the alumina, and that the alumina present had the same area as the catalyst bulk, *ca.* 1×10^{-4} g reversible water was calculated to be present per m^2 of alumina in each catalyst, as well as for γ-alumina. These assumptions do not appear warranted in view of the foregoing conclusions from the study of Emmett *et al.* and the evidences advanced in a later section showing that much of the aluminum is not on the surface but is actually buried in the interior of the primary particles of cracking catalysts.

Benesi has found a residual water content, after calcination at 550°C, ranging from 1.0 to 1.1 molecules/100Å^2 for three commercial silica gels ranging in surface area from 415 to 745 m^2/g[109]. This is in good agreement with the data in Figure 7. The same investigator has measured the water content of 550°C calcined commercial alumina-silicas with surface areas in the range 506 to 598 m^2/g and found 1.2 molecules of water/100Å^2 for low alumina catalysts (12.5 per cent Al_2O_3) and 1.4 molecules water/100Å^2 for high alumina catalysts (25 per cent Al_2O_3). Again the values are in close agreement with those of Figure 7, and intermediate between the values for the separate oxides.

Exchange Reactions of Bound Water. It has long been known that the bound water in calcined silica, alumina, and alumina-silica is readily replaced by deuterium when the solids are exposed to heavy water. Following the pioneering studies of Hansford[110], a number of authors have studied the exchange reaction between deuterium bound in the catalyst and the hydrogen of hydrocarbons[111-114]. The results of these studies have given some information about the structure of the catalyst surface. They provide considerable insight into the nature of the interaction between the catalyst surface and hydrocarbon molecules. The exchange reactions appear to be typical carbonium-ion reactions in the following respects: (1) isoparaffins react at much lower temperatures than paraffins and the reactions are accelerated by addition of an olefin; (2) extensive polydeuteration occurs; (3) isobutane, in particular, gives a distribution of polydeuterated products that is qualitatively similar to that observed on exchange with deuterosulfuric acid[115], in that all isotopic species occur in the initial products except C_4D_{10}. This observation can be accounted for in both cases by the reaction scheme:



$$\underset{\substack{|\\ A^-}}{\overset{+}{C}}(CH_3)_3 + n\underset{\substack{|\\ A}}{D} \rightarrow \underset{\substack{|\\ A^-}}{\overset{+}{C}}(C_3H_{9-x}D_x) + (n - x)\underset{\substack{|\\ A}}{D} + x\underset{\substack{|\\ A}}{H} \qquad (1)$$



$$\underset{\substack{|\\ A^-}}{\overset{+}{C}}(C_3H_{9-x}D_x) + HC(CH_3)_3 \rightarrow \underset{\substack{|\\ A^-}}{\overset{+}{C}}(CH_3)_3 + HC(C_3H_{9-x}D_x) \qquad (2)$$

where A represents the catalyst surface and A^- a negatively charged site on the catalyst surface.

These exchange reactions occur at temperatures much lower than those required for catalytic cracking; it is remarkable that the activation energy reported for the exchange involving *n*-butane is nearly the same or slightly lower than that for isobutane, though the specific rates for the two hydrocarbons appear to differ by a factor of about 1000 at the same temperature[113]. A similar and even more striking anomaly appears in the comparison of the rates between cyclohexane and methylcyclohexane.

The rate of exchange and the average number of deuterium atoms per molecule of reacted hydrocarbon depend in a very sensitive and complicated way on the water content of the catalyst and on the way in which the water has been added. This point has been studied with isobutane in particular detail by Haldeman and Emmett[114]. They report that the activity for the exchange reaction between isobutane and a deuterated Houdry cracking catalyst (12.5 per cent Al_2O_3) was very small at 150°C when the catalyst had been evacuated at 500°C to a D_2O content of 0.89 %w. Maximum activity (in terms of the rate of formation of isobutane molecules containing at least one atom of D) was obtained by addition of 0.13 per cent D_2O at 150°C. This corresponds also to the amount of water "fixedly adsorbed" at 150°C[107]. Addition of an extra 0.1 per cent D_2O decreased the activity to one-half the maximum. From the same authors' study of water sorption[107] it is known that there is no "fixed adsorption" on dehydrated silica gel at this temperature. Hence the activation by water presumably involves the adsorption of a molecule of water on an aluminum-containing site. Adsorption of additional water on these same sites destroys their exchange activity. On the other hand, rehydration of the surface under other conditions was found to result in considerably more extensive fixation of water with much less activity for hydrogen exchange (cf. Table 3). When exchange does occur in the more extensively hydrated surfaces, however, it results in the formation of deuterobutanes containing a greater number of deuterium atoms per molecule.

It is clear that water (or hydroxyl groups) on the surface of the catalyst exists in a variety of forms. On the catalyst rehydrated by exposure to a low pressure of water vapor at 150°C, at least four forms can be expected: (1) combined water inactive in promoting exchange, possibly for the most part in silanol groups; (2) water involved in the activation of exchange sites; (3) water involved in the deactivation of the active exchange sites; (4) reversibly (probably physically) adsorbed water. For the samples prepared by rehydration after evacuation at 500°C, a tentative assignment of the surface water to these four categories can be made on the basis of the following assumptions:

A. The rate constant for the formation of deuterobutanes (of any degree of deuteration) is proportional to the number of active sites. This is equivalent to assuming that the lifetime of an adsorbed carbonium ion is determined by reaction (2) in the preceding reaction scheme—i.e., by hydride transfer from gas phase isobutane—and all active sites have about the same reactivity for this reaction.

B. An activated site contains one adsorbed water molecule, while a deactivated site contains two.

C. Chemisorption of water to form nonactive sites (as distinct from deactivated active sites) is negligibly slow at 150°C.

D. Evacuation at 150°C converts a deactivated exchange site (presumably containing more than one molecule of water or its equivalent) to an active exchange site, and removes physically adsorbed water.

It is evident that exposure to 20 mm partial pressure of water above 200°C, or protracted exposure to nearly saturated water vapor at 30°C (a treatment that will result in condensation of liquid water in the narrow pores of the catalyst) has at least two effects. It results in the inactivation of active sites and in the fixation of relatively large amounts of chemically combined and catalytically inactive water.

It should be emphasized that the interpretation of the data presented in Table 3 is speculative. Alternative interpretations are certainly possible. The interpretation offered is at least consistent with the observations and thus provides a framework for speculation. The average number of deuterium atoms reacted per molecule of isobutane increases with the surface concentration of both physically adsorbed D_2O and D_2O chemically combined on sites that are incapable of activating isobutane. This is to be expected since the average number of individual exchange events during the lifetime of a given carbonium ion should increase with both the concentration and mobility of surface deuterium.

If the composition of the alumina-silica catalyst near the surface approximates the over-all composition, there should be about 11 atoms of aluminum/1000Å². This is many times greater than the estimated maximum number of sites active for exchange for the same area. It appears that the aluminum atoms involved on the active sites are in a different configuration from the majority of the aluminum atoms near the surface. The cation exchange capacity of the same catalyst was shown to be 0.58 meq of potassium/g or about 14 exchange sites per 1000Å². This is the same order of magnitude as the estimated number of aluminum atoms/1000Å² in the surface and suggests that the surface concentration of aluminum in the catalyst was slightly higher than the over-all concentration (perhaps 15.8 %w rather than the nominal 12.5 per cent Al_2O_3). The catalyst containing this amount of fixed potassium was found to be essentially inactive for isobutane exchange after calcination at 500°C and the standard rehydration procedure. As we have seen, however, there is evidence that the formation of the potassium salt inhibits the structural changes that occur in the hydrogen form of the catalyst when it is calcined. It does appear, however, that the activity for the deuterium exchange reaction is somehow associated with acid sites on the catalyst.

TABLE 3. ESTIMATED DISTRIBUTION AMONG VARIOUS CATEGORIES FOR WATER ADSORBED ON ALUMINA-SILICA CATALYST PREVIOUSLY EVACUATED AT 500°C[a]

Total D_2O (%w)	Added D_2O (%w)	Apparent Molecules $D_2O/1000Å^2$				Exchange Characteristics	
		On Active Sites	On Deactivated Sites	Reversibly Sorbed	Chemisorbed on Inactive Sites	$k_1 \times 10^4$ (b) hr^{-1} min^{-1} g^{-1}	Av. No. D Atoms/ C_4 Reacted
0.89	0.0	0.1			10.6	0.2	2.7
Samples hydrated with D_2O vapor at 150°C							
0.98	0.09	1.18	0	0	10.6	2.6	3.3
1.01	0.12[c]	1.18	0.3	0.0	10.6	2.6	—
1.04	0.15	1.23	0.3	0.2	10.6	2.7	4
1.12	0.23	0.76	1.3	0.7	10.6	1.7	5.7
1.21	0.32	0.45	1.9	1.5	10.6	1.0	6.9
1.34	0.45	0.36	2.1	3.0	10.6	0.8	6.7
Samples cooled in 20 mm D_2O vapor pressure from 500 to 150°C and evacuated at 150°C before addition of D_2O vapor at 150°C							
1.38	0.0	0.77	(0.12)	0.0	15.7	1.7	5.3
1.41	0.028	0.48	0.7	0.05	15.7	1.06	6.0
1.42	0.048	0.32	1.0	0.1	15.7	0.70	
1.50	0.125	0.24	1.2	1.0	15.7	0.52	
1.60	0.224	0.21	1.2	2.2	15.7	0.47	6.5
Sample hydrated by exposure to water vapor at 30°C and relative pressure 0.7 for several days, evacuated at 150°C							
2.17	0.0	0.23		0.0	26.0	0.50	6.8

[a] Calculated from data of Haldeman and Emmett, *J. Am. Chem. Soc.*, **78**, 2922 (1956).

[b] Rate constant for formation of deuterated isobutanes.

[c] Sample evacuated at 150°C after exposure to few mm pressure of D_2O vapor at 150°C.

The authors quoted above have also shown that the deuterated and calcined silica gel is completely inactive for exchange with isobutane. Alumina, on the other hand, showed a slight activity for this reaction. The rate of exchange per unit surface area was about 6 per cent of the maximum activity found for the cracking catalyst.

A variety of models can be postulated for the active sites in these reactions. One attractive possibility is that a particular form of four coordinated aluminum accepts a molecule of water and expands its coordination shell to five. This species can become six-coordinated by accepting a carbonium ion; on the other hand, addition of another molecule of water would create a stable and catalytically inactive six-coordinated structure.

A similar critical effect of the hydration of calcined cracking catalyst on its activity for other hydrocarbons has been demonstrated by Hindin, Oblad, and Mills[113]. It was shown that the addition of 0.05 %w of water to a Houdry catalyst that had been calcined at 525°C (12.5 per cent Al_2O_3, approximately 250 m^2/g) resulted in high activity for both the isomerization and the cracking of 2-methylpentane at 100°C. Addition of 0.09 %w of water resulted in an appreciably lower activity. The added 0.05 %w of water corresponds to about 0.67 molecules of water/1000$Å^2$. This is the same order of magnitude as the water required to activate a catalyst calcined at 500°C for hydrogen exchange with isobutane.

An additional reaction that has been used to study the surface characteristics is the exchange reaction between hydrogen and deuterium to form hydrogen deuteride. Though this reaction is very effectively catalyzed by alumina-silica cracking catalyst in the temperature range from 150 to 300°C, and is accelerated only slightly if at all by pure silica, it has been shown by Holm and Blue[116] that pure alumina after suitable dehydration is a much more effective catalyst for this reaction than is alumina-silica containing 10 to 25 per cent Al_2O_3. In general, the catalytic activity of alumina-silica for this reaction shows a very different dependence on the composition of the catalyst from that shown by the cracking, isomerization, and hydrogen-exchange reactions of hydrocarbons. It must be concluded that this reaction is sensitive primarily to factors other than those that accelerate the hydrocarbon reactions promoted by cracking catalysts.

Distribution of Aluminum. *Aluminous Aggregates.* In view of the occurrence of polymeric species in solutions of partially hydrolyzed aluminum salts, it is conceivable that a given aluminum atom in an alumina-silica catalyst may have other aluminum atoms, as well as silicon atoms, as immediate neighbors (connected by oxygen or hydroxyl bridges). The extent to which aluminous aggregates occur on a catalyst surface is not known.

Some authors[22, 52, 103] have contended that calcined alumina-silica catalysts consist of an intimate mixture of small aluminous and siliceous aggregates with the silicon and aluminum atoms sharing oxygen atoms at the interfaces between the aggregates. The catalytically active sites are assumed to occur at these shared interfaces.

This model appears to be based on the following lines of evidence:

1. Ammonium salts of alumina-silica catalysts lose virtually all of their ion-exchange capacity on calcination; only a small part of the original am-

monia content can be restored by treatment of the calcined catalyst with ammonia vapor. A possible explanation for this behavior is the formation of aluminous aggregates on calcination, but an alternative explanation is possible as discussed later.

2. The densities of calcined alumina-silica gels are approximately equal to the densities of mixtures of gamma alumina and silica of the same average composition.

In connection with the second point, it has been called to our attention by Adams[117] that the same thing is true of crystalline sillimanite, $Al_2O_3 \cdot SiO_2$.

We do not feel that there is any necessity to postulate the existence of alumina aggregates of appreciable size in a suitably prepared alumina-silica catalyst containing less than 30 per cent alumina. Small aggregates involving bonds of the type Al-O-Al may exist, however, in certain cases.

Plank[118] has observed that phosphate ions are adsorbed from diammonium hydrogen phosphate solutions by an alumina-silica containing 9 per cent alumina, as well as by a calcined alumina gel. He has suggested that this finding indicates the presence of Al-O-Al groupings in the catalyst. Danforth[119] has interpreted his studies of alkali "metal deactivation" of various alumina-silica catalysts to indicate that chains of polymeric aluminum are present in the acidic groups.

At higher concentrations of alumina or in incompletely reacted systems, aluminous aggregates of appreciable size probably do occur. As was mentioned earlier, Elkin[94] *et al.* have shown that crystalline alumina or alumina trihydroxide is detectable by x-ray diffraction in catalysts containing 50 per cent alumina.

Tamele *et al.*[83] have shown that in catalysts made by interaction of aluminum hydroxide sol with moderately aged silica hydrogel at pH 3.2 to 3.8, a considerable fraction of the aluminum in the range of 0 to 5 per cent was catalytically inactive (see last section). More recently, Barrett, Sanchez, and Smith[120] have shown that gamma-alumina can be detected in alumina-silica catalysts containing 25 per cent alumina that have been heated above 850°C. This effect is not observed, however, except in catalysts that have been made by hydrolyzing aluminum salts in the presence of well-aged silica sols of large particle size and low reactivity. It is not observed in low alumina catalysts prepared from reactive silica.

Surface and Interior of Primary Particles. The distribution of aluminum atoms or ions between the surface and the interior of the primary particles is also not known with certainty. It is important to resolve this question, however, since presumably only those aluminum ions that are in or near the surface of the calcined catalyst will contribute to its catalytic activity. The outer surface of the elementary particles is covered by oxygen atoms, hydroxyl groups, or strongly bound water molecules. By surface aluminum ions we shall mean those aluminum ions that occupy interstices between the first and second outer oxygen layers.

The available data appear to be consistent with the following postulates:

1. The distribution of aluminum within the primary particles of a hydrogel may be relatively uniform or the aluminum may be concentrated near the exterior of the primary particles, depending on the method of preparation. It is even conceivable that the aluminum might be concentrated near the center of the primary particles under some preparative conditions, or as the result of chemical treatments of the gel after it is formed.
2. Again, depending on the preparative conditions, a variable fraction of the aluminum will form ion-exchange sites neutralized by the ions of either alkali metal, ammonium or hydrogen. The remainder of the aluminum is utilized either in the neutralization of exchange sites (cationic aluminum) or in the formation of small aluminous aggregates.
3. In the hydrogel or in partially dried xerogels, dehydration of the interior of the primary particles is incomplete and ionic mobility is great enough to permit ion-exchange between an external solution and an appreciable fraction of the internal exchange sites. In view of the very small size of the primary particles the mobility required is very small.
4. If the aluminum ions are concentrated near the surface of the primary particles, conversion of the exchange sites to the ammonium salt before drying of the hydrogel will tend to prevent migration of the aluminum ions into the interior of the primary particles during the drying operation.
5. After calcination of the hydrogen or ammonium form of the xerogel, internal dehydration of the primary particles is essentially complete and mobility of the aluminum ions within the primary particles is negligibly small in dry atmospheres at temperatures below 550°C. The concentration of aluminum in the surface layers can be altered, however, by subsequent protracted treatment with aqueous solutions and especially by treatment with strong acids or bases. Redistribution of aluminum between the surface and the interior of the primary particles can also be effected by exposure to sufficiently high temperatures, especially in the presence of steam.

The experimental evidence supporting these postulates will be discussed in the next and subsequent sections.

In catalysts made from the "acid side" by hydrolysis of an aluminum salt in the presence of silica gel, it might be expected that most of the aluminum would occur on the external surface of the primary particles. If these particles have an incompletely condensed internal structure, however, some aluminum ions would be expected to diffuse into the interior, there to react with residual internal silanol groups. On the other hand, gels made from the "alkaline side" by acidification of mixtures of sodium silicate and sodium aluminate, or an aluminum salt, might be expected to have a more nearly uniform distribution of aluminum.

Plank and Drake[20] have shown that the aluminum can be extracted nearly completely with dilute hydrochloric acid in 2 to 3 hr at 16°C from hydrogels containing 7 to 10 per cent alumina, prepared by instantaneous mixing of solutions of an acidified aluminum salt with solutions of sodium silicate. A similar extraction after the gels had been dried at 177°C also gave nearly complete removal of aluminum, but only a small fraction of the aluminum was extracted after the gels had been calcined at 700°C. From this finding he concluded that the aluminum is concentrated near the surface of the primary particles in hydrogels or in partially dehydrated xerogels. An alternative explanation, however, is that the very small primary particles constituting the gel are appreciably permeable to hydrogen ion and aluminum ions until internal dehydration is nearly complete.

The present authors have made similar studies of the rate of extraction of aluminum at room temperature with a large excess of $1.0N$ hydrochloric acid from two commercial catalysts that had been calcined at 565°C in dry air. One sample was an American Cyanamid microspheroidal catalyst containing 11.8 %w Al_2O_3 ; its specific surface area after calcination was 620 m^2/g. The second sample was a Houdry porous bead catalyst containing 10.2 %w Al_2O_3 ; its specific surface after calcination was 466 m^2/g.

Before extraction with acid, the large particles were ground to pass through a 100-mesh screen. With such a finely divided material the rate of extraction of aluminum should not be limited by diffusion of ions within the pores of the gross particles of catalyst. The average time required for an ion to diffuse from the center of the particle to the external solution is computed to be only a small fraction of a minute. The results of the extraction experiments are shown in Figure 8. The logarithm of the per cent of the original aluminum content retained by the catalyst is plotted versus the time of extraction. The results show that the major part of the aluminum is extracted rapidly from the American Cyanamid catalyst (*ca.* 68 per cent in 1 hr), and therefore was in or close to the surface layer of the primary particles. On the other hand, only about 30 per cent of the aluminum in the Houdry catalyst was similarly accessible to the acid, even after 9 hr contact time. If the aluminum atoms were uniformly dispersed in the primary particles, it would be expected on the basis of the observed surface areas that 32 and 25 per cent, respectively, in these catalysts would be associated with the surface layer of oxygen atoms on the hydroxyl groups. The observations are, therefore, consistent with a relatively uniform distribution of aluminum throughout the elementary particles of the Houdry catalyst, and an appreciable concentration of aluminum near the surface of the elementary particles of the Cyanamid catalyst. This demonstration of the difference in chemical behavior of the two cracking catalysts of similar over-all composition emphasizes the necessity for consideration of the method of preparation in interpreting the results of any study of the chemical behavior of cracking catalysts.

It was pointed out in the previous section that both cationic and anionic aluminum exist in cracking catalysts prepared from the "acid side." Cationic aluminum exists in such a catalyst that contains 25 per cent alumina, even after calcination at 565°C. Sodium hydroxide has been found to alter the catalyst composition from $Al_2O_3 \cdot 5SiO_2$ to $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$, after water washing. This results from an extensive structural attack as shown by the decline of surface area from 550 to 88 m^2/g.

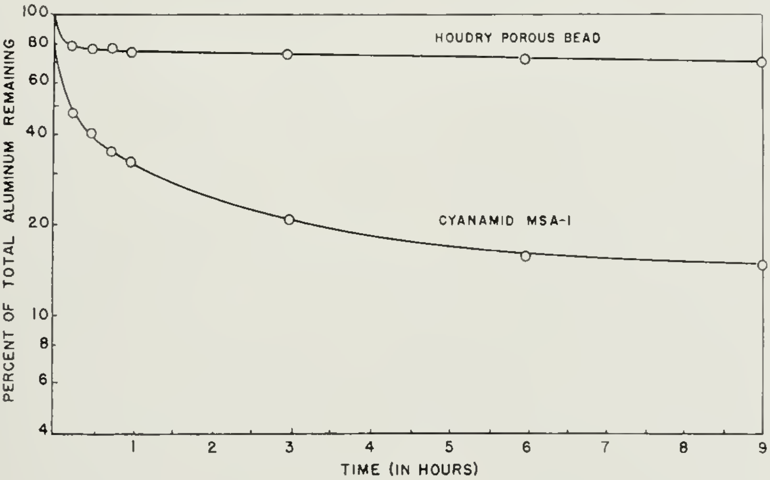


Figure 8. Comparative rates of removal of aluminum from alumina-silica catalysts by 1*N* aqueous hydrochloric acid.

At some elevated temperature, the rate of diffusion of aluminum ions within the structure of the primary particles will become high enough to produce a relatively uniform distribution of aluminum throughout the interior of the primary particles in a relatively short time. The results quoted above imply that this temperature is higher than 565°C, in the absence of steam.

Coordination of Aluminum and Silicon. The question of the distribution of aluminum atoms or ions among the coordination numbers 4, 5, and 6 is important because it can be expected that the proton acidity is somehow related to the aluminum coordination number.

Coordination numbers are likely to be more variable in a liquid or an amorphous solid (which can be regarded as a supercooled liquid) than in crystalline solids. It has been emphasized also by Weyl[121] that coordination number and symmetry are less restricted at the surface of solids than in the interior of crystals. For example, a coordination number of 5 for surface aluminum is conceivable. The more general rules[122] concerning the stability of ionic solids, however, can still be expected to apply. Among these are the electrostatic valence rule and the generalization that structures involving shared edges or faces between coordination polyhedra are less stable than those in which only corners of coordination polyhedra are shared.

In many crystalline oxides of small cations, the arrangement of the oxygen atoms approximates a close-packing of spheres (e.g., alumina, and the spinels). In such structures the volume per gram atom of oxygen ranges between 8.5 and 10.5 cc; the theoretical value is about 9 cc for oxide ions with a crystal radius of 1.40Å. In the cristobalite form of crystalline silica the structure is more open and one-third of the oxygen atoms are missing from the close-packed structure. The expected volume per gram atom of oxygen is therefore $\frac{3}{2} \times 9$ or 13.5 cc; the observed value is about 13 cc. In this structure the oxygen vacancies occur in a regular pattern. In vitreous silica, with a volume of 13.6 cc/gram atom of oxygen, it appears likely that oxygen vacancies from the close-packed structure occur in the same proportion, but the vacancies must occur in an irregular arrangement. For a calcined alumina-silica containing 12.4 %w Al_2O_3 the particle density of 2.308[123] yields a calculated volume for oxygen of 13.2 cc. This high value suggests that the cracking catalyst has an open structure similar to that of vitreous silica. The argument is not altogether convincing, however, since a mixture of two phases with the same average composition, one an alumina phase with a molar volume of 9 cc for oxygen and the other a vitreous silica phase with a corresponding volume of 13.6 cc, would have an average molar volume for oxygen of 12.9 cc.

The structure of cristobalite consists of silicon tetrahedra linked together by the sharing of corners; octahedral holes are essentially absent from this structure and probably occur much less frequently in the structure of vitreous silica than in the close-packed structures. The composition of commercially useful alumina-silica catalysts ranges from $Al_{0.238}Si_{1.82}O_4$ (10 %w Al_2O_3) to $Al_{0.605}Si_{1.54}O_4$ (25 %w Al_2O_3). If the structure is similar to that of silica, it should be possible to accomodate most of the cations in tetrahedral holes. The silicon can be expected to occupy tetrahedral holes for several reasons: from the electrovalent or ionic point of view the small radius of the silicon ion should lead to tetrahedral coordination; from the covalent point of view silicon should form tetrahedral sp^3 bonds. A high degree of covalency (at least 50 per cent) is predicted for the silicon-oxygen bond on the basis of the difference in electronegativity. The fact that the dielectric constant of crystalline or glassy silica at audiofrequencies is only slightly greater than the square of the refractive index implies a high degree of covalency. Tetrahedral coordination of silicon with oxygen is almost universal among the crystalline silicates.

The coordination number of aluminum with oxygen is much more variable; coordination numbers of 4, 6 and in one case 5 have been observed in crystals. Octahedral coordination ($z = 6$) is observed in the hydrous oxides and in the spinels of divalent metals; it is believed to occur also in aqueous solutions of aluminum salts. In the crystalline alumino-silicates, octahedrally coordinated aluminum occurs frequently in chains and in cyclic structures in which the octahedra are joined together by the sharing of edges. Tetrahedral coordination is observed in the aluminates of alkali metals and in the zeolitic alumino-silicates, the structures of which are stabilized by large alkali cations. In the sillimanite form of Al_2SiO_5 half of the aluminum is 6-coordinated and half is 4-coordinated.

From this recital, it appears that the energetic difference between tetrahedral and octahedral coordination of aluminum by oxygen is relatively small; the choice depends on the details of the structural environment. In crystalline substances, the octahedral bond distance between aluminum and oxygen is about 1.90Å; this leads to a distance of 2.68Å between the centers of adjacent oxygen atoms in the coordination shell. Tetrahedral coordination involves a smaller number of bonds between aluminum and oxygen but the bonds are stronger than in the octahedral case. The bond distance ranges between 1.66 and 1.76Å, corresponding again to a distance of 2.72 to 2.88Å between the centers of the nonbonded oxygens in the coordination shell. The structure is thus destabilized to a lesser extent than is the octahedral one by a smaller number of weaker repulsions between oxygen atoms. The tetrahedral configuration of aluminum is remarkably close to that of silicon, which has a silicon-oxygen distance of 1.60 to 1.64Å and an oxygen-oxygen distance of 2.62 to 2.68Å. It is apparent that tetrahedrally coordinated aluminum should fit very well into a silica network. Iler stated that the influence of silica on the crystal habit is great because cristobalite has the same structure as potassium aluminate without the potassium. Thus, silica could enforce a tetrahedral discipline on aluminum without a large stabilizing alkali cation being necessary.

It has frequently been pointed out that in alumino-silicates the structure is made up of coordination tetrahedra linked by the sharing of corners. Those tetrahedra containing aluminum and linked at all corners to silica tetrahedra require a positive charge nearby to provide local electroneutrality. This is an example of the electrostatic valence rule; each of the oxygen atoms bounding a tetrahedrally coordinated aluminum ion receives from the aluminum an electrostatic bond of strength $3/4$. If the same oxygen atom is a corner of a silicon tetrahedron, it receives a total bonding of $1\,3/4$ which is insufficient to neutralize a formal charge of -2. A proton coordinated to the aluminum-oxygen tetrahedron will neutralize this charge deficiency. This is presumably the reason why alumina-silica retains "water of constitution" more tenaciously than does silica, and also the reason why complete dehydration of alumina-silica or of kaolinite ultimately leads to the formation of sillimanite, mullite, or alumina. In these latter structures the arrangement of coordination polyhedra is such that local electroneutrality can be achieved without the requirement of protons or other ions of small radius and small charge.

It was predicted by Pauling[122] that the proton coordinated to and providing charge neutralization for an aluminum-oxygen tetrahedron surrounded by four silicon-oxygen tetrahedra should be strongly acidic. Indeed, tetrahedrally coordinated aluminum was early proposed by Thomas[25] as the source of the strong acid properties of alumina-silica cracking catalysts.

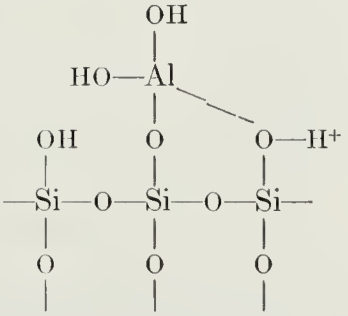
Evidence for the occurrence of tetrahedrally coordinated aluminum in samples of naturally occurring quartz crystals containing a few per cent of alumina impurity has been obtained by Griffiths, Owen and Ward,[124] who have observed that such crystals develop an electron-spin resonance after irradiation with x-rays. A theoretical analysis of these and related spectroscopic observations by O'Brien[125] leads to the conclusion that the resonance is caused by the excitation of a negatively charged tetrahedral AlO_4 group which in its ground state has its charge compensated by an adjacent proton or lithium ion. The significance of this observation for the structure of alumina-silica catalysts has been pointed out by Gray[126].

It has been shown by Oblad, Milliken and Mills[22] that the transformation of silica gel to cristobalite (not to the thermodynamically more stable tridymite) by heating to 1160°C is facilitated by the presence of small amounts of coprecipitated alumina (less than 6 %w Al_2O_3). This observation may perhaps be taken as indirect evidence for the occurrence of tetrahedrally coordinated alumina.

Attempts have been made to deduce the structure of amorphous alumina-silica gels from the structure of the crystalline compounds that are formed on heating to high temperatures. It is known that such gels form either sillimanite ($Al_8Si_4O_{20}$), or the structurally related mullite (possibly $HAl_9Si_3O_{20}$), at high temperatures; the available evidence appears to us to favor the former compound as the product from gels containing less than 25 %w Al_2O_3. From differential thermal analysis, it is known that the formation of the crystalline product from the amorphous gel is exothermic and occurs rapidly around 980 to 1000°C[126-128]. The same product is formed, however, when crystalline kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ is heated to this temperature. In view of the relatively high mobility of the atoms in this temperature range, it is clear that no definite conclusions can be drawn about the relation between the final and initial structures.

The usual parameters for describing a crystalline material, such as symmetry, coordination number, and uniform bond length, are not necessarily all valid for the surface of a crystal[121]. Thus, surface ions or groups are defect structures and differ somewhat from those in bulk crystals, because they are exposed to an unsymmetrical attraction[129]. Therefore, at the surface some of the rules discussed above may be violated—i.e., the uniformity of coordination number or bond length. This situation probably holds true for both amorphous and crystalline cracking catalysts in which the ratio of surface ions to bulk phase ions is much higher than in nonporous crystalline materials.

Hansford[110] in 1947 considered the possible arrangement of various surface end-groups and their interaction as the source of surface acidity. He considered that the aluminum hydroxide deposited on the surface of silica gel is first attached by a condensation reaction. Subsequently, aluminum of the hydroxide interacts with the oxygen of an adjacent silanol group, resulting in the dissociation of a proton (see below).



Milliken, Oblad and Mills[52] have reasoned that at the point of interfacial contact between discrete aluminous and siliceous particles in a cracking catalyst, bond sharing at the contact of the two dissimilar oxides results in interfacial six coordinated aluminum being under "strain." In the presence of both the silica and a basic ion a reversible shift of coordination from six to four occurs. Even very weak bases, such as olefins and paraffins, are believed capable of causing this coordination shift. The demonstrated thermal mobility of the catalyst structure and the ease and extent of deuterium exchange studies described earlier in this section, are cited as supporting evidence for this postulate. Water vapor is believed to create additional surface acid sites by increasing the number of low energy sites available. Aluminum ions in the acid state are believed to be unstable.

An alternative suggestion of the origin of surface acidity which is independent of the consideration of the coordination number of aluminum has been advanced by Tamele[104].

It is well known that Si-OH and Si-O-Si groups on the surface of silica as well as AlOH and Al-O-Al groups on the surface of alumina are not strongly acidic. It has been shown, however, that aluminum atoms embedded in a silica gel surface display very strong acidity.

It is reasonable to assume (and it has been discussed in an earlier section) that in the preparation of catalysts by hydrolysis of aluminum salts in the presence of silica gel, the hydrolyzing aluminum ions interact with the silanol groups of the silica gel and are thus immobilized in the form of Si-O-Al groups on or near the surface. Such aluminum atoms on the surface of silica can be attached to one, two and at most to three silicon atoms in this fashion and thus become a part of the silica network (see Figure 9).

The electrophilic property of the aluminum ions thus placed onto the surface may be traceable to the electrical asymmetry of the $Al^{3+}:O:Si^{4+}$ groups. It is probable that the electron pair in the Al:O bond is shifted toward the more highly charged silicon ion (as indicated by arrows). The aluminum-oxygen bond becomes more ionic, and the aluminum ion more positive, and thus it is able to split the hydrogen ion from a water molecule by acquiring the hydroxyl ion. It is also possible for additional water of hydration to become attached to the group to satisfy whatever coordination number the geometry of the surface group requires.

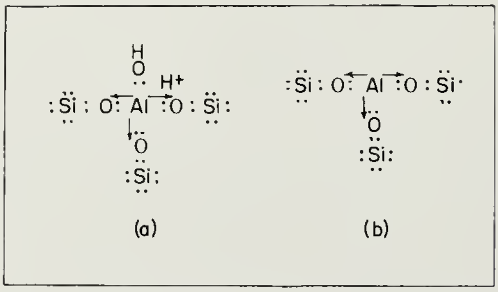
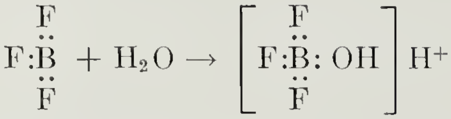


Figure 9. Active sites on alumina-silica cracking catalyst.[83] (a) Hydrous: hydrogen acid. (b) Anhydrous: Lewis acid. (Republished by permission of E. J. Brill, Publisher, Leiden)

It is easy to speculate on the possible relation of such a group to the corresponding anhydrous Lewis acid. In reality, however, undoubtedly much more extensive structural changes occur in the solid on dehydration after calcination than the idealized diagrams of Figure 9 would indicate.

This concept of hydrogen acid formation on the surface finds some support in the behavior of boron trifluoride with water. Meerwein and Pannwitz[130] observed formation of a well defined strong acid by interaction of BF_3 with one molecule of water:



$$\overset{\displaystyle F}{\underset{\displaystyle F}{F:\ddot{\underset{..}{B}}}} + H_2O \rightarrow \left[\overset{\displaystyle F}{\underset{\displaystyle F}{F:\ddot{\underset{..}{B}}:OH}}\right]H^+$$

Interestingly, a different but still strong acid was formed with two molecules of water. The third molecule of water decomposed the mixture to boric and hydrofluoric acid.

Evans and Polanyi[131] found that the role of traces of water in promoting the activity of boron fluoride for polymerization of isobutene was traceable to the formation of the above hydrogen acid.

It may be in place to point out that the above consideration and observations all deal with simplified concepts of groups on a cracking catalyst surface rather than with the real surface structure of laboratory or plant preparations. Such models may thus be misleading and should be used with care; for example, the ratio of ionic radii between oxygen and aluminum would probably preclude tri-coordinated aluminum.

The groups that exist on the surface of freshly prepared cracking catalysts are undoubtedly much more complicated, and these are further altered structurally by calcination, steaming, etc. Thus, hydrolyzing aluminum ions are mostly in various stages of polymerization, the equilibrium depending on experimental conditions. Substantial variations of the acidity of a single surface aluminum atom can occur as a result of the distribution of its surrounding groups or atoms. Thus, the strength of the resulting acid should be related to the number of Si-O groups combined with a single aluminum ion. The strongest acid should result when the maximum of three Si-O groups are combined with an aluminum atom.

It should be also considered that aluminum ions and their polymeric hydrolysis products may occupy the "base exchange" positions. This is the type of aluminum that we have called "cationic aluminum" in the section on catalyst preparation.

Changes in Use

As the catalyst circulates in a commercial fluid unit from reactor, to stripper, to regenerator, and back to the reactor, it is subject to more or less severe deactivation from the combined influences of high temperature, steam, and mechanical and thermal shock. As a result, the catalyst undergoes changes in both physical and chemical structure. The surface area and pore volume decrease, and so does the catalytic activity. The nominal temperature to which the catalyst is exposed ranges from 460 to 550°C in the reactor and stripper to as high as 650°C in the regenerator; there is evidence (see below) that the temperature actually obtained on the surface of the catalyst in the regenerator may be much higher than the nominal temperature in that vessel. The partial pressure of steam ranges from a little over one atmosphere in the stripper to a few tenths of an atmosphere in the reactor and regenerator.

In order to maintain the desired level of activity in the cracking unit, it is necessary to make periodic or continuous additions of fresh catalyst; the amount added may range from a few per cent to one or two tenths of one per cent of the total catalyst inventory per day. Some catalyst is unavoidably lost from the unit either as stack fines or as slurry in the heavy fractions of the product; deliberate withdrawals of catalyst may be made, in addition, to control the inventory.

As a result of the more or less continuous addition of fresh catalyst, and withdrawal or loss of used catalyst, a steady-state distribution of catalyst age is eventually attained in the catalyst inventory; the nature of this distribution can be calculated from the addition rate if complete mixing of the added catalyst with the rest of the inventory is assumed. The steady-state mixture of catalyst particles of various ages is commonly called "equilibrium catalyst." It differs from fresh catalyst not only in physical structure and catalytic activity, but also in chemical composition. The catalysts in use acquire contaminants such as sodium, iron, nickel, copper, and vanadium from metallo-organic compounds in the feed to the reactor and from abrasion of the material of the catalytic cracking unit itself. The amount of this contamination is in general very small, but it can be sufficient to cause appreciable changes in the selectivity and activity of the catalyst (see later discussion).

Laboratory Studies of the Aging Process

In an effort to duplicate the aging effects which occur in commercial units, a number of studies have been made in which silica gel or cracking catalysts were exposed for various lengths of time to high temperatures both in the presence and in the absence of steam.

Low temperature nitrogen adsorption-desorption isotherms have been used by Tamele and co-workers[132] to describe the influence of calcination on the pore structure of silica gel in presence of water vapor and under anhydrous conditions.

It was found that with increasing temperature up to 850°C, anhydrous calcination causes a small reduction in pore volume and a similar small decrease in surface area, which are, however, proportionate. Thus, the average pore radius calculated from the ratio of pore volume to surface area remains essentially constant. Calcination under these conditions at 900°C results in complete collapse of the gel structure.

Calcination over the same range of temperatures in the presence of water vapor at a pressure of 1 atm caused a much larger reduction in both pore volume and surface area—which, however, were no longer proportionate—with the result that the average pore radius became progressively and rapidly larger with increasing temperature at constant time of steaming. In the presence of water vapor, the structure of the silica gel was found to collapse completely at 800°C.

Ries and his associates[133, 134] have made very extensive studies of the effects of such treatments on the surface area and pore structure of a variety of commercial cracking catalysts and other microporous materials.

A review and discussion of the results of many such studies has been given by Ries[101]; his findings can be summarized as follows: from measurements of the physical adsorption of nitrogen, the effective diameters of the pores in fresh magnesia-silica catalysts occur in a smaller range (20 to 30Å) than in fresh synthetic alumina-silicas (30 to 50Å). Clay catalysts have smaller surface areas and usually a considerably wider range in their pore-size distribution than do synthetic catalysts. Sintering in vacuo brings about essentially complete loss of surface area within a short time at 1000°C with alumina-silica catalysts, 850 to 900°C with clay catalysts, and about 800°C with magnesia-silica catalysts. At substantially lower temperatures—i.e., 600–700°C—the rate of loss of surface area is very small in vacuo, but is considerably increased by the presence of steam. Acceleration of the sintering process by steam is more pronounced for alumina-silica than for magnesia-silica catalysts. The physical changes produced by this so-called steam deactivation differ from those produced by vacuum deactivation at higher temperatures in the following important respects:

1. During aging at high temperatures (800 to 1000°C) in high vacuum the distribution of pore radii (as defined by the Kelvin equation for the relative vapor pressure of liquids in cylindrical capillaries) remains almost unchanged, and the average pore radius (defined by the ratio of specific pore volume to specific surface area) remains approximately constant.
2. During aging at lower temperatures (500 to 600°C) in the presence of steam the average pore radius increases considerably; the distribution of pore radii broadens and the median pore radius increases.

Recent studies of the aging process by means of electron microscopy have shown that these last two observations are consistent with the model presented earlier in this chapter for the structure of synthetic alumina-silica catalysts. Ashley and Innes[11] have shown that the ultimate particles in an alumina-silica catalyst increase substantially in size when the catalyst is steamed for 120 hr at a steam pressure of 15 psig. In a study of the structural changes produced in a commercial alumina-silica catalyst (12.5%w Al_2O_3) under various conditions, Adams and Voge[93] established the following facts:

1. Deactivation by steam at relatively low temperatures (450 to 650°C) results primarily in a growth of the larger elementary particles at the expense of the smaller ones. The distribution of the diameters of the elementary particles broadens, and the mean diameter increases. The decrease in the specific surface area can be quantitatively accounted for by the change in the measured distribution of elementary particle radii.

2. Deactivation at high temperatures (850 to 950°C) results in local fusion or collapse of small regions within the structure of the catalyst so that pore volume and surface area locally are simultaneously destroyed. The radius distribution of the elementary particles in the unfused regions remains essentially identical with that in the fresh catalyst.

A systematic study of the kinetics of deactivation of the same sample of commercial cracking catalyst over a wide range of conditions was presented in a companion paper by Schlaffer, Morgan and Wilson[135]. These authors showed that the following empirical equations accurately describe the rate of change in specific surface area S over a wide range of conditions:

$$\text{either } -\frac{dS}{dt} = kS^n$$

$$\text{or } -\frac{d}{dt}(S/S_0) = k'(S/S_0)^n$$

where S_0 is a constant with the dimensions of specific surface area. The constants k and n were found to vary smoothly with temperature and with the partial pressure of steam over the range of conditions investigated (0 to 7 atm steam, 478 to 950°C). The rate of change of surface area was accelerated by the presence of steam at all temperatures; at the lower temperatures the rate is negligible in the absence of steam.

The form of the empirical equations given above is consistent with a theory of sintering that has been presented by Herring[136]. According to this theory, the value of n in such an equation is sensitive to the transport mechanism (vaporization, surface diffusion, volume diffusion or plastic flow) whereby matter is transferred to the more stable, larger particles which grow at the expense of the less stable smaller ones in an aggregate of small particles. The empirical values of n observed by Schlaffer *et al.* however, are in many cases larger than the values expected from Herring's theory; these larger values presumably reflect the influence of factors which were not explicitly considered in the theory. Exceptionally large values of n (20 to 35) were observed during the early stages of the deactivation of the catalyst in a stream of "dry air" at high temperatures; the occurrence of these anomalously high values is believed to reflect the occurrence of "self-steaming," whereby the aging process is accelerated by water vapor released by reaction between hydroxyl groups in the catalyst. As deactivation proceeds, less and less water vapor is emitted, and the deactivation process slows down markedly. Indeed it is found that the late stages of the deactivation process under these conditions can be described by a much more reasonable value of n (approximately 4).

Figure 10 shows the linear relation obtained by plotting log S *vs.* log $(t + B)$ for deactivation conducted in 1 atm of steam at several temperatures.

Plots of this kind have been used in the petroleum industry for many years to describe the stability of cracking catalysts. The constant B is adjusted to obtain linearity; its significance has been discussed in terms of the integrated form of the empirical rate equation for deactivation.

During the deactivation of synthetic alumina-silica catalyst at temperatures above 900°C the fractional decrease in pore volume is very nearly equal to the fractional decrease in surface area; hence the apparent average pore radius remains approximately constant as Ries has shown. As the temperature is decreased, the rate of change of the pore volume decreases relative to the rate of change of the surface area. At 478°C, a 50 per cent loss in surface area is accompanied by only an 11 per cent loss in pore volume. The slope of a plot of relative surface area versus relative pore volume during deactivation can therefore be used as a rough index of the temperature at which deactivation occurred.

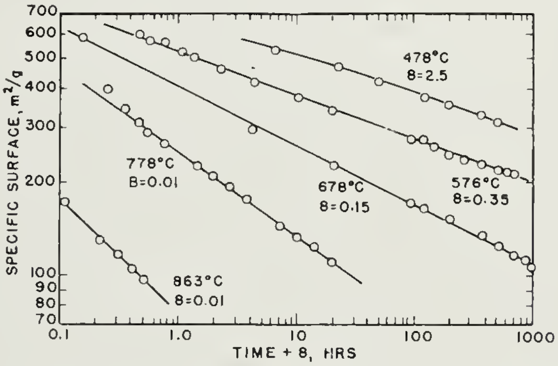


Figure 10. Aging of alumina-silica catalyst in 1 atm steam at various temperatures. (Schlaffer, Morgan and Wilson.[135] Republished by permission of the American Chemical Society, Washington)

These various observations can be accounted for by the following model for the mechanism of deactivation of synthetic alumina-silica catalyst: at low temperatures in the presence of steam, the catalyst loses surface area by an increase in the average diameter of the elementary particles; material is transported from the smaller particles to the larger ones primarily by "surface processes" (surface migration and vapor-phase transport), whereby the specific surface area S decreases appreciably but the specific pore volume V_p is changed only slightly. As a consequence, the average pore radius, formally proportional to the ratio V_p/S, increases monotonically. As the temperature increases, on the other hand, "volume processes" (volume diffusion or plastic flow) which have a higher activation energy become increasingly important. This type of process results in the loss of both surface area and pore volume. At the highest temperatures, above 900°C, surface area and pore volume are destroyed in the same proportion, so that the average pore radius remains approximately constant. The vapor-phase transport process which predominates at low temperatures in the presence of steam may involve the formation of volatile species such as $Si(OH)_4$.*

Crystallographic changes in cracking catalysts were observed by Oblad and co-workers[22] who studied by x-ray diffraction the products obtained on heating their synthetic alumina-silicas of varying alumina content, at 1160°C in dry air. Silica alone gave the cristobalite pattern, as was also found by Krejci and Ott[137]. With increasing alumina content the cristobalite pattern was first strengthened (at 2.6 per cent alumina), and then weakened (at 15 per cent alumina). In the range of 13 to 36 per cent alumina, mullite predominated, and above 50 per cent alumina, corundum predominated. This is in keeping with the earlier observations of Webb and Ehrhardt[57] who found that catalysts containing *ca.* 10 per cent alumina and deactivated at 1093°C show the x-ray pattern of quartz and of sillimanite or mullite.

Barrett *et al.*[120] studied the transformations induced by high temperatures in a series of four catalysts containing 25 per cent alumina. These catalysts were prepared by addition of ammonium hydroxide to aluminum sulfate in presence of silica sols of progressively decreasing reactivity (i.e., increasing average particle diameter). X-ray studies show that in the region of 700 to 1250°C, catalysts prepared from the less reactive silicas had a greater tendency to form γ-alumina preceding the ultimate formation of mullite that occurred in all instances. The γ-alumina is believed to form from crystallization of amorphous alumina and the mullite from an amorphous alumina-silica phase.

Although the catalysts prepared from the less reactive silicas have lower initial surface areas and cracking activity, they have relatively greater stability of surface area and of activity than those prepared from more reactive silica sols.

The circumstances under which deactivation occurs in a commercial cracking unit are complicated not only by cyclic exposure to the conditions in the reactor, stripper and regenerator, but also by the possibility that the surface of the catalyst during regeneration attains much higher local temperatures than the nominal temperature in the regenerator. This possibility, which had been considered by earlier workers in the field, received very strong support from the data published by Small, Kirkaldy and Newton[138]. These investigators showed that only a high-temperature treatment (e.g., 200 hr at 850°C) would reduce a fresh fluid cracking catalyst to the combination of properties (surface area, pore volume and weight activity) characteristic of the "equilibrium" catalyst in a fluid unit.

Even more convincing evidence for the occurrence of high local temperatures on the catalyst was presented by a group of investigators at Shell De-

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* Adams and Voge, *loc. cit.* Schlaffer, Morgan and Wilson, *loc. cit.*

velopment Company who traced the course of deactivation in a commercial fluid unit by a combination of radioactive tracer and catalyst fractionation methods[139]. A small charge of fresh catalyst tagged with radioactive Sc^{46} was added to the equilibrium inventory of a commercial unit, from which samples were drawn after 1, 17 and 35 days of further operation. These samples were fractionated by a combination of "sink-float" sedimentation methods which segregate the particles of catalyst in accordance with their skeletal density, specific pore volume, or average pore radius. By measuring the radioactivity of the fractions into which the catalyst sample is separated by these methods, the distribution of physical properties in the deactivated tagged catalyst can be determined.

In the skeletal density method[139], dried portions of a catalyst are immersed in a graduated series of binary mixtures of carbon tetrachloride and either ethylene dibromide or acetylene tetrabromide. Those particles float which are lighter than the liquid mixture, the rest sink. This method is useful for isolating those particles which are effectively less dense than the rest because a portion of their internal pore volume has been sealed off to form trapped voids. In the pore volume method, the pore volume is completely filled with water before immersion in the sedimentation media. For a given medium with density greater than unity, the buoyancy will be greater for those particles which have higher specific pore volume. In the pore radius method,[139] about 50 per cent of the pore volume is filled with water before immersion in the sedimentation fluid. Those particles which have a small average pore radius will take up a larger share of the added water than those which have a large average pore radius and will therefore be more buoyant. After fractionation, the catalyst particles are dried for measurement of their specific surface area and pore volume.

The results of this study showed that under commercial conditions about 75 per cent of the surface area and 50 per cent of the pore volume of the fresh catalyst were lost in one day. Both the rate of deactivation and the loss in pore volume relative to the loss in surface area indicate that this initial deactivation occurs at a high effective temperature. The subsequent deactivation rate was much slower and more nearly consistent with the nominal temperatures in the unit, and surface area declined more rapidly than pore volume. The formation of trapped voids continued slowly during the later stages of deactivation.

Under most commercial cracking conditions, the early alumina-silica catalysts that contained 10 to 14 per cent alumina left much to be desired in regard to stability of both physical structure and activity. Extensive laboratory study by Tamele, Ryland and co-workers showed that greater stability of these properties can be obtained by preparing catalysts with a large average pore diameter, a high surface area, and a substantially greater alumina content than formerly employed[12]. It is important that the alumina be combined efficiently with the silica to avoid higher coke and lower gasoline formation on cracking various feed stocks at the same conversion level. Table 4 shows typical laboratory data obtained with both high and low alumina catalysts. The stability of surface area and of activity was determined after steaming the catalysts for 24 hr at 1 or 2 atm pressure, at 565°C. The activity tests were conducted with 6 to 14 mesh granules in a fixed bed reactor, using West Texas gas oil, at LHSV 4, 500°C, and a 60-min process period. Activities are expressed as the ratio of space velocities required to produce the same conversion of gas oil at constant catalyst weight as compared to a reference catalyst arbitrarily assigned an activity of 100.

Table 4. Relative Stability of High and Low Alumina Cracking Catalysts

Test Conditions: West Texas gas oil
LHSV 4
500°C
60-min process period

Stream Treatment 565°C-24 Hr	Catalyst No. 1		Catalyst No. 2		Catalyst No. 3	
	% Al_2O_3 24.2 Pore Dia. 56.3Å		14.3 23.2Å		11 32.0Å	
	Weight Activity	Surface Area	Weight Activity	Surface Area	Weight Activity	Surface Area
None	116	493	100	520	96	594
1 atm	83	346	48	219	45	291
2 atm	68	272	34	157	—	—

Later a practical preparative procedure was developed for high alumina catalyst of the above specification[13]. Subsequently a joint process development program was entered into by Shell Development Company and American Cyanamid Company[14]. The latter company now manufactures microspheroidal high alumina catalyst of high pore volume, designated "Aerocat Triple A."

In a large scale test, Cyanamid high alumina catalyst was gradually charged to the Shell Oil Houston refinery fluid cracking unit that contained Cyanamid low alumina catalyst. This unit operated on this catalyst for 360 days. At the end of this test, with 90 per cent inventory replacement, the surface area of the equilibrium catalyst had risen from 87 to 106 m^2/g. During this time it was possible to reduce the severity of cracking by about 30 per cent (at the same conversion). The cracking selectivity was unaffected. Catalyst stack losses were much less than for low alumina catalyst[14].

Similar observations were made during a test of another high alumina catalyst at the Baytown refinery of the Humble Oil and Refining Company[140]. An increase in the C_5-430°F naphtha occurred at the expense of butane and lighter products. Yield structures have been compared for high and low alumina catalysts, at both constant catalyst activity, and at constant catalyst cost.

A test at the Buffalo refinery of the Frontier Oil and Refining Company has also verified that a high alumina catalyst has greater structural and activity stability than a low alumina catalyst[141]. In addition, this catalyst "has reduced susceptibility to poisoning by oil-borne metals and thus results in lower cost operation." These desirable features allow adjustment of the unit operating conditions so that at the same conversion level there is a reduction in coke, light gases and C_3 hydrocarbons, with an increase in C_4 hydrocarbons, with the same gasoline yield.

Contaminants

Metal contaminants originate both from the feed stocks and from the metal process equipment. For laboratory studies, catalysts artificially contaminated with various metals have been employed to reproduce the observed poorer selectivity of equilibrium catalysts that become contaminated during refinery use.

Mills[142] has shown that certain metals such as iron, nickel, copper and vanadium, when impregnated on Houdry synthetic type M, TCC Filtrol and Houdry type I catalysts (derived from clay) cause increasing coke and gas yields at the expense of gasoline, with increasing metal content. Nickel and copper are about ten times more potent than iron, at the same metal concentration. Similar effects were produced by exposing fresh catalysts to metal-contaminated feedstocks. Wide variation in the amount and types of metals can occur, depending on the source and type of the feedstock.

McEvoy, Milliken, and Mills[143] devised a method for removing outer surface fractions of varying depth from contaminated particulate catalysts by rubbing attrition. On cracking metal-containing feedstocks in the vapor phase over bead and pelleted catalysts, the concentration of deposited metals has a sharp negative gradient between the outer surface and the center of an individual catalyst particle. The radial distribution pattern is fairly independent of the total metal concentration. The distribution of metals was found to be similar for clay cracking catalysts used in both commercial moving bed ("Houdresid") and pilot plant mixed phase processing of various residues. In one instance about 44 per cent of the final nickel and 48 per cent of the total vanadium were found within the first 35 μ of the outer surface of a catalyst particle that was 4 mm in diameter. Rubbing attrition occurs in most commercial cracking operations and is important in removing a large portion of the metals picked up by the exterior surface of the catalyst. This material is eventually eliminated as stack "fines."

Duffy and Hart found[144] that in a typical refinery fluid cracking unit only a part of the metals present in the feed processed actually remain on the catalyst. To maintain the same carbon production in a commercial unit with two blends of marginal heavy gas oil and clean gas oil, it was necessary to charge an average of 2.4 tons of catalyst/lb of nickel plus vanadium in the feed. The metal content of a contaminated cracking catalyst is not a direct indication of the carbon production since the metals are usually present in both active and inactive state.* The rates of metal activation and deactivation, as well as the rates of decomposition, are believed to be factors determining the instantaneous catalyst selectivity.

Rockroth *et al.*[145, 146] studied a Davison alumina-silica catalyst that was contaminated by fluidizing the powdered catalysts in contact with various metal-containing feeds, at temperatures where vaporization of the feed occurred but cracking was at a minimum. Contaminant levels equal to those of equilibrium catalysts were built up by use either of plant feeds or of light gas oils containing various metal naphthenates. The Atlantic D + L test was used for evaluation of catalyst activity and product distribution. Carbon producing factor (CPF) was defined as the ratio of carbon formed over a contaminated catalyst compared to that of an uncontaminated reference catalyst, at the same conversion.

The CPF for an individual metal was found to vary with the molecular weight of the oil depositing the metal on the catalyst, the metal concentration, the nature and amounts of other metals on the catalyst surface, the catalyst activity level, and the extent of steam deactivation of the catalyst after metal contamination. The degree of dispersion or surface coverage by a given metal appears to have an important effect on catalyst CPF. The CPF of the various metals increases in approximately the same order as expected from their hydrogenation-dehydrogenation activity: i.e., $Ca < Na < Cu < V < Fe < Cr, Zn < Ni$.

Numerous investigators have observed that sodium decreases the cracking activity of alumina-silica catalysts. Small *et al.*[138] pointed out that, unlike heavy metals, sodium does not affect catalyst selectivity and apparently decreases only catalyst surface acidity. Further effects of sodium on the crackability of various types of hydrocarbons will be discussed in a later section of this chapter.

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* Small *et al.* (*loc. cit.*) made similar observations on equilibrium catalyst and concluded that metals laid down rapidly on fresh catalyst surface are gradually sealed off during the catalyst deactivation.

Acidity and Acid Strength

Evidence for the development of acidity during the various stages of catalyst preparation has already been described in previous sections. It was pointed out that drying and calcination results in removal of much of the bound water and brings about a substantial decrease in the base exchange capacity of the catalyst. Nevertheless, it has been shown by a number of investigators that the catalyst is still acidic after calcination. Qualitative observation of the acidity of alumina-silica catalyst was reported first in 1933 by Gayer* who prepared a catalyst containing *ca.* 1 per cent Al_2O_3 that was active for polymerization and cracking. The surface of this catalyst was acid to methyl orange.

The methods that have been used to measure the acidity of cracking catalysts include treatments with basic substances in aqueous solution, in organic solvents and in the vapor phase. The aqueous methods have been criticized by several authors[22, 88, 147]. Their principal disadvantages are:

(1) Water reacts with the catalyst surface and alters its structure; mobility of the surface structure is especially pronounced in the presence of liquid water. In particular, water is likely to react with any Lewis acids or anhydride structures that may be present in the surface. Some of the water thus reacted may form proton acids.

(2) Water is a relatively strong base and will accept protons from a strong proton acid to form hydronium ions; hence, no acids stronger than the hydronium ion can be studied in a dilute aqueous system.

Nevertheless, a number of studies of catalyst acidity in aqueous systems have been made. The methods used have included titration with alkali hydroxide[25, 56, 147-150], the liberation of acid from catalysts by means of ion-exchange and its subsequent determination[22, 151-153], measurement of the amount of carbon dioxide liberated from a bicarbonate solution, and studies of the rate of inversion of sucrose[22, 103]. Though these methods, especially in their early applications, provided valuable evidence concerning the chemical behavior and acidic nature of cracking catalysts, they are not recommended for the measurement of the acidity available at the substantially dehydrated surfaces of calcined cracking catalysts[22, 88, 147]. Hansford[88] has suggested that the adsorption of alkali hydroxides is a measure of surface area rather than of the acidity of the catalyst. This may well be true if the adsorption is measured at a high pH; titration with a very weak hydroxide solution to a nearly neutral pH on the other hand, should provide useful information comparable to that obtainable from ion-exchange measurements.

We have already seen that ion-exchange measurements can provide some information about the acidity of the surface of a calcined catalyst. A meas-

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* Gayer, F. H., *Ind. Eng. Chem.*, **25**, 1122 (1933).

urement of ion-exchange capacity based on the use of ammonium acetate has been shown by Plank[152], to give results which correlate very well with cracking activity. Holm *et al.*[154] have shown an excellent correlation between the catalytic activity for the polymerization of propylene and the ion-exchange capacity with ammonium acetate. The latter investigators have also proposed an acid-strength index which is based on the equilibrium constant for the exchange reaction. The significance of this equilibrium constant has also been considered by Plank[118] who shows that its value is consistent with a pK_a of between 3.2 and 3.6 for the hydrated aluminosilicic acid in water.

Vapor Phase Methods

Measurements of the amount of a basic substance that is adsorbed by a catalyst from the vapor phase can in principle provide a great deal of detailed information about the acidity of the surface. If the measurements are made at equilibrium over a sufficiently wide range of temperature and pressure, the energy and entropy of adsorption can be determined as a function of the surface coverage by standard thermodynamic methods. The presently available published data obtained by these methods, however, are not sufficiently extensive to permit such an analysis. The principal experimental difficulties are associated with the extremely low equilibrium pressures at low surface coverages and low temperatures, and with catalytic decomposition of many of the basic substances at high temperatures.

The tenacity with which ammonia is retained by a calcined alumina-silica cracking catalyst at elevated temperatures is a manifestation of its high acid strength. Roper[155] has shown that at any given temperature the uptake of ammonia at 7.5 mm pressure is substantially greater per unit of surface for a cracking catalyst than for silica gel, and persists to higher temperatures. The data shown in Figure 11 were obtained with a "high-alumina" catalyst (25 per cent Al_2O_3) outgassed in a high vacuum at temperatures ranging from 800 to 965°C, to vary the surface area. The silica was similarly outgassed in the temperature range of 980 to 1134°C. The difference between the amounts of ammonia adsorbed by alumina-silica and by silica per unit of surface at 200°C is about 2 μmoles/m^2.

Stone and Rase[156] have used the method of differential thermal analysis to measure the heat evolved during the chemisorption of the vapors of water, ammonia, and piperidine at 330°C on various alumina-silica catalysts which had been equilibrated with dry nitrogen at that temperature. The rapid chemisorption resulted in the development of an exothermic peak which was complete in 4 or 5 sec; replacement of the base-containing gas flowing over the sample with dry nitrogen gave an endothermic peak which developed more slowly and was associated with desorption. The authors defined the difference between the exothermic and endothermic peak heights as the net peak height and showed a correlation between the net peak height for either water or piperidine and the Jersey D + L cracking activity for a number of fresh and deactivated alumina-silica catalysts.

Richardson and Benson[157] have reported gravimetric studies of the adsorption of pyridine and of trimethylamine on a Davison cracking catalyst that had been calcined at 850°C. Samples were outgassed at either 20° or 300°C to a final pressure of 10^{-5} mm. The catalyst contained 2.6 %w volatile matter after outgassing at 20°C. These studies are similar to those of Mills *et al.*[158] in that adsorption was not measured at accurately known equilibrium pressures; consequently, the results cannot be given a precise thermodynamic interpretation. Nevertheless, a number of significant observations were made. The sample outgassed at 300°C contained 0.3 %w volatile matter, equivalent to 0.16 mmole of water/g; it adsorbed 0.14 mmole of pyridine/g at 300°C and 200°C, and only slightly more—0.18 mmole/g—at 24°C. The sample outgassed at 20°C contained volatile matter equivalent to 1.4 mmole of water/g and adsorbed 0.89 mmole of pyridine/g. The amount of measured acidity clearly increases with the increasing content of combined water.

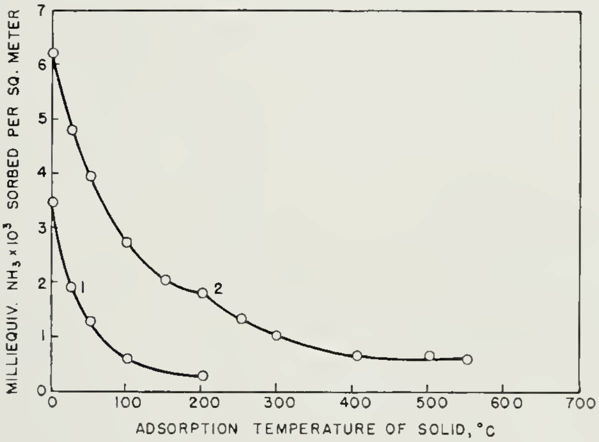

Figure 11. Surface concentration of ammonia on pure silica gel (1) and on an alumina-silica catalyst (2) as a function of temperature; NH_3 pressure, 7.5 cm Hg. (Republished by permission of The Faraday Society, London)

By rough calorimetric measurements the authors found a heat of 33 to 38 kcal/mole for the adsorption of an unspecified amount of trimethylamine on the catalyst after outgassing at 300°C. Since the heat of adsorption very probably decreases with increasing amounts of sorbed base, the value obtained for the heat of adsorption is an average over a distribution of unspecified width; nevertheless, as the authors pointed out, the observed heat is comparable in magnitude to the heat of formation of solid ammonium chloride from gaseous hydrogen chloride and ammonia, and to the energy of the nitrogen-aluminum bond in the complex formed between aluminum chloride and amines[159].

Richardson and Benson also report measurements of the adsorption of trimethylamine and of pyridine on samples prepared by pelleting a fluid cracking catalyst; these measurements were complicated, however, by a very slow desorption which may have resulted from the formation of extremely narrow pores during the pelleting operation.

It is worthy of remark that strong adsorption of ammonia has been reported by Webb[147] to occur on the surface of dehydrated gamma-alumina at 175°C (at a pressure of about 10^{-3} mm) to the extent of about 0.2 μmole/m^2. The total adsorption per unit surface at 175°C and 10^{-3} mm was changed very little, if at all, by treatment of the alumina with HF, though the tenacity with which the ammonia was retained at higher temperatures was increased appreciably by this treatment. Since pure alumina is not useful as a cracking catalyst, this observation raises serious questions for future research to explore.

Mapes and Eischens[160, 161] have used infrared absorption spectroscopy to study the nature of ammonia chemisorbed on alumina-silica catalyst at 175°C; an American Cyanamid catalyst was used that had been calcined at 500°C. Under the conditions used in this work, ammonia was not appreciably adsorbed by pure silica gel. Calcined catalyst treated with dry ammonia showed relatively strong absorption bands similar to those of NH_3 and relatively weak bands similar to those of NH_4^+ in ammonium salts. The apparent amount of NH_4^+ was increased by addition of water to the catalyst. These very important observations provided the first direct evidence about the nature of the binding between nitrogen bases and acidic sites on the surface of a dehydrated cracking catalyst. The results indicate that Lewis acid sites exist in the catalyst and may be more numerous than the Bronsted acid sites, at least for this type of catalyst. As discussed in a later section, however, the preponderance of evidence indicates that Bronsted acid sites are much more important than Lewis acid sites for cracking activity.

Solution Methods

The number and strength of the acidic groups on the surface of a solid can in principle be characterized just as well by the equilibrium adsorption of basic substances from solution as from the vapor. The interpretation of adsorption from solution is complicated by two factors: the finite heat of solution of the base in the solvent, and the competition between the solvent and the basic solute for the surface of the solid. The second of these factors can be minimized by the use of an inert solvent or one that is only weakly basic. Solution measurements suffer a disadvantage in the relatively narrow range of temperatures over which they can conveniently be made. They are readily adapted, however, to the use of a variety of basic solutes.

It was observed by Lewis[162] that acids such as aluminum halides can be titrated in a nonaqueous solvent with an indicator dye to show the end-point. Johnson and Tamele[104, 163] greatly extended the scope and convenience of the solution methods by using this principle to titrate the acid group on the surface of calcined cracking catalyst; the titrant was *n*-butylamine in dried benzene. Butter yellow (*p*-dimethylaminoazobenzene) was used as indicator; this dye ($pK_a = +3.3$) gives an acid color with solid $KHSO_4$ but not with either pure silica or alumina dried in air at 500°C. The indicator was added to a suspension of the catalyst in benzene; titrant was added in small increments, with agitation after each addition, until the red color of the acidic form of the adsorbed indicator was discharged.

TABLE 5. ACIDITY OF SYNTHETIC ALUMINA-SILICA CATALYSTS

Al_2O_3 %w	0.001	0.12	0.32	1.04	2.05	3.56	10.3	25.1
mg atoms of Al/g	2×10^{-4}	0.024	0.063	0.204	0.402	0.700	2.02	4.92
Acidity, meq/g								
Catalyst dried at 200°C	0.0	0.09	0.21	0.30	0.41	0.47	0.58	0.45
Catalyst dried at 500°C	0.0	0.05	0.10	0.22	0.26	0.31	0.35	0.32
Specific surface, m^2/g	788	722	699	695	622	622	545	450

The results obtained by this technique with a series of experimental alumina-silica catalysts are shown in Table 5. These catalysts were made by the interaction of a pure silica gel which was prepared and aged at pH 3, with increasingly larger amounts of a freshly peptized aluminum hydroxide sol. From the method of preparation, the alumina in these catalysts should have been concentrated near the surface of the elementary particles of the silica but interaction was not complete in all cases. The occurrence of aluminous aggregates appears likely at the higher alumina contents. For the catalysts calcined at either 200 or 500°C, the acidity increased rapidly with increasing alumina content up to 10 %w Al_2O_3, after which the acidity declined. Thus maximum values of 1.07 and 0.64 μ-moles of acidity/m^2 were found for the catalyst containing 10 per cent alumina, dried at 200 and 500°C, respectively. This is comparable to values of 0.7 and 0.85 μ-mole/m^2 obtained with American Cyanamid low alumina catalyst dried at 200 and 500°C, respectively. A value of 0.74 μ-mole/m^2 was found for Davison magnesia-silica catalyst dried at 500°C.

In the above series, the acidity values obtained for the catalysts containing small amounts of alumina and dried at 200°C are much higher than one equivalent per gram-atom of aluminum; the reason for this is not understood, particularly since the silica employed was itself nonacidic. There may be some adsorption of amine by the incompletely dehydrated siliceous portion of the surface. At the highest alumina content, less acidity was measured than expected, probably because of the incompleteness of the interaction between the two oxides.

Measurement of the acid strength of catalyst surfaces by means of dyes has been studied by several investigators. Weil-Malherbe and Weiss[164] observed that certain basic dyes that give deep colors with strong acids in nonpolar solvents also give similar colors with both raw and acid-activated clays. It was suggested that the alkylation and cracking activities of clays are related to the proton-donating properties of the clay surfaces, as shown by the color reaction of the basic dyes.

A quantitative interpretation of the significance of the color changes shown by indicator dyes adsorbed on acidic solids was proposed by Walling[165]. He defined the acid strength of a solid surface as "the ability of the surface to convert an adsorbed neutral base to its conjugate acid" and proposed that a useful measure of acid strength of a surface is the H_0 function of Hammett and Deyrup. The significance of this function is discussed below.

In case the indicator dye assumes its acid form by accepting a proton from the surface, the color of the dye is governed by the following equilibrium equation:

$$a_{\mathrm{H}^+}a_{\mathrm{B}}/a_{\mathrm{BH}^+} = K_a = a_{\mathrm{H}^+}C_{\mathrm{B}}f_{\mathrm{B}}/C_{\mathrm{BH}^+}f_{\mathrm{BH}^+}$$

where a_{H^+} is the thermodynamic activity of protons in the system, a_{B} is the activity and C_{B} is the concentration of the neutral form of the dye; a_{BH^+}, C_{BH^+} are the corresponding quantities for the conjugate acid, and f_{B}, f_{BH^+} are activity coefficients. K_a is the dissociation constant of the conjugate acid of the indicator.

In this formulation, the concentration C_{BH^+} of the conjugate acid of the indicator is given by

$$\log C_{\mathrm{BH}^+}/C_{\mathrm{B}} = -\log K_a + \log a_{\mathrm{H}^+}f_{\mathrm{B}}/f_{\mathrm{BH}^+} = -\log K_a - H_0 = \mathrm{pK_a} - H_0$$

where H_0 is the generalized acidity function of Hammett and Deyrup[166, 167].

Thus, the color change of the indicator (determined by $C_{\mathrm{BH}^+}/C_{\mathrm{B}}$) is primarily a measure of the thermodynamic activity a_{H^+} of the protons on the surface of the catalyst; this concept provides a quantitative definition of acid strength at the solid surface. It has been suggested that the ratio $f_{\mathrm{B}}/f_{\mathrm{BH}^+}$ in a given solvent should be relatively independent of the structure of the base.

An alternative definition of H_0 can be formulated for the case in which the indicator dye takes on its acid color by forming a complex with a Lewis acid site in the surface of the solid.* The stability of such coordination complexes may be modified by steric effects as well as by the basicity of the indicator itself.

Walling tested several acidic solids with a series of indicators whose conjugate acids are more strongly colored than their basic forms, and whose pK_a values spanned the range from +3.3 to +0.43. He showed that basic solvents—e.g., acetone—decrease the apparent acid strength of the solid surface, as does bound or adsorbed water. With isooctane as a solvent he showed that alumina-silica, magnesia-silica and activated clay cracking catalysts have high acid strengths, corresponding to between $0.1N$ and $1N$ HCl. Pure silica and alumina were found to be nonacidic.

Recently Benesi[168] has extended this technique by using a series of Hammett indicators covering a range of pK_a from +6.8 to −8.2, corresponding to proton activities differing by a factor of the order of 10^{15}. The indicators are listed in Table 6, together with the concentrations of sulfuric acid required to convert half of the indicator to its conjugate acid.

TABLE 6. INDICATORS USED FOR ACID STRENGTH MEASUREMENTS (Benesi,[168])

Indicator	Basic Color	Acid Color	pK_a	H_2SO_4 (%w)
Neutral Red	Yellow	Red	+6.8	8×10^{-8}
Phenylazonaphthylamine	Yellow	Red	+4.0	5×10^{-5}
Butter yellow	Yellow	Red	+3.3	3×10^{-4}
Benzeneazodiphenylamine	Yellow	Purple	+1.5	0.02
Dicinnamalacetone	Yellow	Red	−3.0	48
Benzalacetophenone	Colorless	Yellow	−5.6	71
Anthraquinone	Colorless	Yellow	−8.2	90

Alumina-silica and alumina-boria catalysts, as well as activated clay catalysts, after calcination at 550°C, were found to have very high acid strengths, higher even than that which corresponds to the values of H_0 in 90%w sulfuric acid. The high acid strengths found in this study appear to result from the use of a high temperature of calcination (550°C) and the resulting extensive dehydration of the catalyst surface. A similar high acid strength ($H_0 < -8.2$) was found for an alumina-silica catalyst that had been heated to 880°C *in vacuo*; a slightly lower acid strength was observed in a catalyst that had been exposed to 1 atm of steam at 576°C. Magnesia-silica catalysts, on the other hand, were observed to have much lower acid strengths ($H_0 \simeq +1.5$ to -3.0) even after calcination at 550°C.

Benesi[169] has also developed a successive approximation technique for measuring the amount of an organic base (e.g., *n*-butylamine) required per

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* Walling, Hammett, *loc. cit.*

gram of catalyst to just prevent a given indicator dye from developing its acid color on the catalyst surface. The important features of the technique are: (1) the equilibration of the catalyst with the amine solution is carried out in closed containers so that water vapor is excluded; (2) an indicator solution is added to aliquots of the system after equilibration with the amine. This not only permits more rapid equilibration but also permits a simultaneous determination of the titers with respect to several indicators. The solvent used in this procedure must be rigorously purified and dried.

By means of this procedure, it has been found that 90 per cent of the acid centers on fresh synthetic alumina-silica catalyst (calcined at 500 to 550°C) are very strong, with $H_0 < -8.2$. Assumption of an area of 20Å^2 for an acid site leads to the conclusion that only 7 per cent of the surface of low alumina catalyst is covered by acid sites. The number of acid sites was found to be of the order of 0.6 μ-mole/m^2, comparable in magnitude to the amount of residual water on the surface (*ca.* 2 μ-moles/m^2). On the other hand, though the population of acid centers on the surface of an experimental magnesia-silica catalyst was found to be larger, the strength of the centers was much lower, as shown in Figure 12.

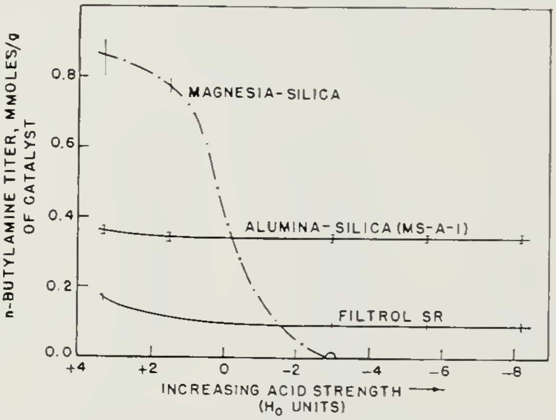

Figure 12. Butylamine titers *vs.* acid strength for cracking catalysts calcined at 550°C. Vertical lines denote titer uncertainties. (After Benesi.[169] Republished by permission of the American Chemical Society, Washington)

Clays differ somewhat from synthetic alumina-silica in their distribution of acid strengths. Kaolinite and "Filtrol" SR catalyst have a relatively low population of surface acid sites but all the sites are very strong acids (Figures 12 and 13).

The acid strength of the surface acids of attapulgite covers a broad range and the population of acids is moderate. The acid strength range and acid population of montmorillonite depends greatly on the nature of its exchange ions (cf. Table 7). The hydronium ion-exchanged clay has strong surface acids (pK_a, −3.0) and a moderate acid population (0.55 mmole/g). The raw clay has a lower acid strength (+1.5 to −3.0) and total acid population (0.09 mmole/g) (cf. Figure 13). The sodium form of the clay has the lowest acid strength (+3.3 to +1.5) and acid population (0.04 mmoles/g).

It should be pointed out that no proof is available that this titration measures only the number of proton acids on the surface of the catalyst. All that can be said with certainty is that the titration measures the amount of base required to raise H_0 to a certain critical value characteristic of the color change for a given indicator. The base that reacts with the catalyst surface before the end-point is reached may be bound by either Lewis or Bronsted sites; the titration itself provides no way of distinguishing the two possibilities, even if the indicator used is primarily responsive to protons.

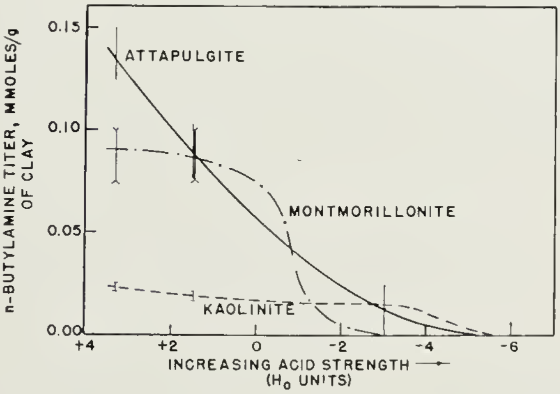

Figure 13. Butylamine titers *vs.* acid strength for clays dried at 120°C. Vertical lines denote titer uncertainties. (After Benesi.[169] Republished by permission of the American Chemical Society, Washington)

TABLE 7. ACIDITY OF MONTMORILLONITE IN RELATION TO TYPE OF EXCHANGEABLE CATION

	Surface Area (m^2/g)	Butylamine Titer (mmole/g) in the H_0 Range			
		+3.3 to +1.5	+1.5 to −3.0	to <3.0	Total
Naturally occurring form	44	0.00	0.09	0.00	0.09[a]
Sodium form	41	.03	.01	.00	0.04[a]
Hydrogen form	52	.10	.00	.55	0.65[b]

[a] Titer uncertainty is ±0.01 mmole/g.

[b] Titer uncertainty is ±0.05 mmole/g.

An alternative procedure for characterizing acidic solid surfaces has been explored and developed by Trambouze and his associates[153, 170-4]. This procedure employs a thermometric titration of a suspension of the solid in dry benzene with a benzene solution of a relatively weak base such as dioxane or ethyl acetate. The end-point is determined by a change in the slope of a plot of temperature rise *vs.* volume of titrant. The titer determined in this way is postulated to be a measure of the number of Lewis acid sites on the surface of the sample. It has been shown that the thermometric titer (mmole dioxane/g) increases regularly for alumina-silica catalysts with the temperature of calcination in the range 300 to 750°C. This result implies that at least a major part of the heat liberated in the titration results from the interaction of dioxane with nonhydroxylic groups. At the same time the base-exchange capacity with aqueous ammonium acetate was found to decrease in such a way that the sum of the base-exchange capacity and the thermometric titer was approximately constant for a given catalyst. This behavior is illustrated in Table 8 which shows data obtained for two alumina-silica gels dried at various temperatures.

TABLE 8. ION EXCHANGE AND THERMOMETRIC TITERS FOR ALUMINA-SILICA GELS CALCINED AT VARIOUS TEMPERATURES

5.1%w Al_2O_3[174]

Drying Temperature, °C	25	180	300	400	500	600	750	900
Ion-exchange titer, meq/g	1.2	0.90	0.65	0.55	0.50	0.50	0.20	0
Thermometric titer, meq/g	—	0.1	0.5	0.7	0.7	0.7	1.0	—
Sum	1.2	1.0	1.15	1.25	1.2	1.2	1.2	

15%w Al_2O_3[153]

Drying Temperature, °C	20	100	300	500	600	700
Ion exchange titer, meq/g	2.0	1.8	0.9	0.7	0.3	0.1
Thermometric titer, meq/g	—	—	1.0	1.2	1.7	1.9
Sum	(2.0)	—	1.9	1.9	2.0	2.0

The interpretation of these results offered by Trambouze *et al.* is that heating of an alumina-silica gel results in the decomposition of a protonic acid group involving tetracoordinated aluminum to form water and a Lewis acid which is represented as tricoordinate aluminum.

It is interesting that rehydration of the calcined catalyst during the ion-exchange step does not lead to regeneration of all of the protonic acids destroyed during calcination. However, since water is a stronger base and a smaller molecule than dioxane, it is hard to believe that the calcined catalyst would not combine with at least as many moles of water as of dioxane. If such a rehydration occurs when the calcined catalyst is exposed to ammonium acetate solution during the ion-exchange measurement, it is clear from the results reported by Trambouze that this rehydration does not lead to the reconstitution of the ion-exchange sites that were destroyed during calcination.

It has also been reported by Trambouze *et al.*[171] that the thermal stability of the proton acid centers in alumina-silica decreases smoothly with increasing alumina content, goes through a minimum at moderate alumina contents, and thereafter increases to a level which remains roughly constant at higher alumina contents. Here the stability is expressed by the ratio of the ion exchange titers after calcination at 500°C to those measured after calcination at 110°C. This observation suggests that one mechanism for the destruction of proton acid sites may involve an interaction between two alumina-silica complex sites to form an oxide or hydroxyl bridge between two adjacent aluminum atoms.

Progressively dehydrated aluminum trihydroxides have also been studied by the thermometric methods[172, 175]. The titrant consumption increases with increasing dehydration of the aluminas, accompanied by increasing surface area, with values as high as 1.6 meq/g being measured (7 μ-moles/m^2). Extensive dehydration of the aluminas resulted in greatly reduced titers notwithstanding the fact that the surface areas were still substantial. Except in cases of extreme dehydration of the aluminas, the amounts of bound water (in meq/g) greatly exceeded the uptake of titrant.

In view of the interesting results obtained by Trambouze and his collaborators, the technique of thermometric titration would appear to merit further study. For example, it would be useful to know more about the detailed nature of the interaction of dioxane or of ethyl acetate with the surface of a dehydrated alumina or alumina-silica. In addition, it would be desirable to know whether an interaction between proton acid or hydroxyl groups and dioxane makes any significant contribution to the thermometric titer and to the heat liberated during the titration.

Acidity and Activity

The discovery of the acidity of cracking catalysts led naturally to speculations that the acidity is responsible for their cracking activity. It was noted that the catalysts do not merely accelerate the rate of the thermal cracking reactions of petroleum, but direct the cracking process along the route of an entirely different series of reactions. Thus, with the catalyst, olefins crack more readily than paraffins; the products from both olefins and paraffins are more highly isomerized and contain a higher proportion of C_3 and C_4 hydrocarbons than the products from thermal cracking. This was followed by observations that at temperatures below those of cracking, the catalysts bring about certain reactions already known to be promoted in varying degree by strong acids, and by many acidic salts such as aluminum chloride and zinc chloride.

It is now generally accepted that the cracking of various species of hydrocarbons proceeds primarily by a cationic or carbonium ion mechanism that is induced by acidic groups on the catalyst surface[7, 25, 110]. The formation of the carbonium ion is presumed to involve exchangeable protons associated with the aluminum on the catalyst surface. The rates and mechanisms of cracking of the various types of hydrocarbons are discussed in detail in the chapter by H. Voge, in Vol. VI of this series. Brief mention of the many kinds of reactions that in the aggregate are loosely called "cracking" has been made in the introduction to this chapter.

In a study of the relation between catalyst acid strength and acidity, and catalyst activity and product distribution, it is desirable to express activity by a parameter that is directly related to the reaction rate of a well defined reaction; ideally to the reaction rate constant. Much of the published work has been carried out, however, with complex mixtures of hydrocarbons, such as gas oils, and the activity has been expressed as "conversion to lower boiling products," or "amount of gasoline produced." Neither is related to reaction rates in a simple manner. Conversion thus defined does not include changes in hydrocarbon structure within the boiling range of the gas oil. The amount of gasoline produced is even less suited to be taken as the sole measure of activity. The definition of "gasoline" is vague. It usually represents the fraction from C_4 to C_{12} hydrocarbons; in industrial practice, it may or may not include all the C_4 hydrocarbons, depending on the customer's requirements. Again it is not the only product of reaction, and no account is thus taken of the substantially large gaseous fraction, and of its composition. It is well known that different types of catalysts vary substantially in the relative amounts of products obtained by cracking a given petroleum fraction, even at the same conversion.

It has been demonstrated by Tamele, Ryland and co-workers that neither silica nor alumina free of impurities is an active catalyst for the cracking of hydrocarbons. The influence of the common impurities of silica and alumina on activity has also been studied[83]. Traces of aluminum were found to be present in nearly all available commercial as well as most "chemically pure" sodium silicates, and consequently are found in the gels precipitated from these materials. Aluminum can be completely removed from the silica by twice repeated dissolution of the gel in alkali and reprecipitation in acid medium. A series of silica gels were found to have progressively lower activity for the sensitive reaction of cracking (dealkylation) of isopropyl benzene with progressive removal of aluminum; at 0.001 per cent Al the activity was negligible.

Aluminas were found to be contaminated and activated by ions adsorbed from the solutions from which they were prepared, such as chloride or sulfate, which are difficult to remove by washing. The activity for cracking of isopropyl benzene was found to decrease with progressive removal of chloride ions and was substantially negligible with relatively small amounts of chloride ions.

As described in the previous sections, numerous techniques have been devised to measure surface acidity. Only comparatively recently, however, have techniques been developed for measuring acid strength. In a few cases correlation has been made of acidity with activity for cracking or polymerization of certain types of hydrocarbons. Several investigators have followed the effect on activity of progressive neutralization of a catalyst surface with inorganic and organic cations, a technique that decreases the acid population of the catalyst surface. Relatively little has been deduced about the influence of acid strength on cracking reactions, although some information has been gained by comparison of the extent of cracking of several types of hydrocarbons, and of the nature of the resulting products.

Topchieva and co-workers[176] found for a series of synthetic alumina-silicas of similar surface areas that about 30 per cent alumina content gave maximum gasoline yield, on cracking decahydronaphthalene, cetane, and gas oil at constant LHSV. They related the observed activity to the calculated concentration in the catalyst of the alumino-silicic acid, $Al_2O_3 \cdot 4SiO_2 \cdot XH_2O$.

Thomas[25] observed maximum weight activity with Pennsylvania gas oil at 500°C, with catalysts of 44 to 63 per cent alumina content. A series of catalysts were prepared by cohydrolysis of aluminum isopropylate and ethyl orthosilicate. Maximum sodium hydroxide adsorption of 2.43 meq/g catalyst was measured at *ca.* 44 per cent alumina content. This was much less than the 8.33 meq/g that would be expected if all the aluminum were in the form of the $(HAlSiO_4)_x$, proposed by Thomas as the formula for the solid acid. This difference was attributed to incomplete copolymerization of the alumina and the silica.

Fischer and Brandes[177] found that at constant space velocity of a standard gas oil at 427°C, the cracking activity of synthetic alumina-silica catalysts increases with increasing surface area. At the same surface area, activity increases with increasing acidity, as determined by *n*-butylamine titration. Introduction of foreign metal oxides changes neither the acidity nor the activity. Deterioration of the product selectivity increases with increasing nobility of the metals.

Plank and co-workers studied the mechanism and kinetics of cracking of methylcyclohexane and of *n*-decane at 495°C over alumina-silica, hydrofluoric acid-treated alumina-silica, and magnesia-silica catalysts[178]. The first two catalysts differed primarily in their rates of reaction with methylcyclohexane and *n*-decane. The fluorided catalyst had both a higher reaction rate constant as well as poisoning constant. This was attributed to a greater concentration of Lewis acid sites. The lower rate of carbon splitting, hydrogen transfer, and isomerization of methylcyclohexane over magnesia-silica catalyst, as compared to the other two catalysts, has been postulated to be the result of its very low concentration of Lewis acid sites of the necessary acid strength.

Gladrow and co-workers[179] found that in the cracking of cetane, at 20 per cent conversion, pelleted alumina-silica catalyst gives a greater proportion of C_3-C_4 hydrocarbons, at the expense of C_5 hydrocarbons, than does pelleted magnesia-silica catalyst. This was considered to be a result of the more intense action of the alumina-silica catalyst. Thus, this catalyst gives a higher conversion than magnesia-silica catalyst at 510°C at LHSV 4 with *n*-heptane, which is more refractory than cetane. The higher conversion obtained with magnesia-silica catalyst with cetane at LHSV 2, appears to result from its more extensive action—i.e., greater density of active centers. In order to obtain the same conversion with magnesia-silica catalyst it required 60 per cent more acidity titratable with *n*-butylamine. Alumina-boria and activated clay catalysts gave results intermediate between those of alumina-silica and magnesia-silica catalysts.

The studies of surface acid sites by Benesi[169] discussed in the previous section support the above deductions of Gladrow *et al.* It has been shown that while the acid strength of the sites on alumina-silica catalysts is indeed much greater than on magnesia-silica catalysts, the population of acid sites is definitely much lower.

Johnson[163] has found a correlation of the acidity of a series of alumina-silica catalysts with their rate of propylene polymerization in a static system at 200°C. The catalysts were calcined at 200°C and their acidities were determined with *n*-butylamine in benzene solution using *p*-dimethylaminobenzene as indicator. The rate data indicate a first order reaction retarded by products, thus

$$dx/dt = k(a - x)/(1 + bx)$$

in which a is the initial pressure of propylene, and x the pressure drop in time t. For this series of catalysts the polymerization activity was a linear function of acidity (cf. Figure 14). This correlation was possible because of the similar distribution of acid strengths on the catalyst surfaces. A magnesia-silica catalyst that had about the same acid site population (0.4 meq/g) as a commercial alumina-silica catalyst was about ten times less active at 200°C for polymerization.

Schlaffer[83] used the same series of alumina-silica catalysts, calcined however at 500°C, to study the relation of activity for isopropylbenzene cracking (at 500°C) and catalyst acidity. The activity (k') was derived from the conversion-space velocity relationship and is believed to be proportional to the reaction rate. The activity was a nonlinear function of catalyst acidity; rising rapidly at first and then leveling off with increasing catalyst acidity (cf. Figure 15). The reaction rate appeared to be directly proportional to the square root of the number of acid sites.

Prater and Lago[180] made a detailed study of the kinetics of isopropylbenzene cracking. Using a Socony bead catalyst (10 per cent Al_2O_3) in a differential reactor, they have estimated that this catalyst contains 0.87 × 10^{17} acid sites/m^2. In good agreement with the above value, these authors calculated an average value of 1.27 × 10^{17} sites/m^2 of surface from the amounts of chemisorbed quinoline required to deactivate Houdry catalysts (12 per cent Al_2O_3) of various surface areas, as reported by Mills and co-workers[158]. This is additional supporting evidence that only a small

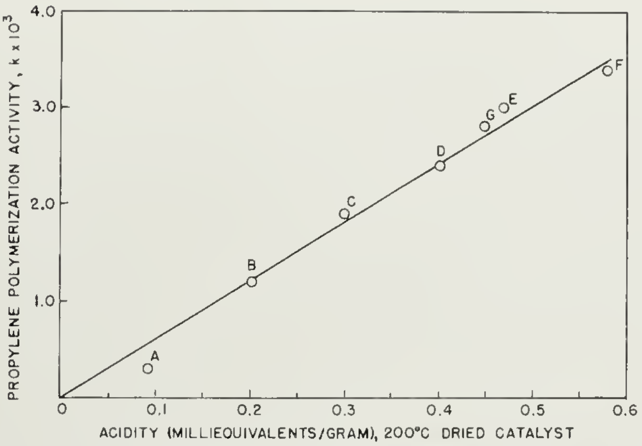

Figure 14. Dependence of propylene polymerization activity at 200°C on acidity for a series of alumina-silica catalysts.

Catalyst	A	B	C	D	E	F	G
Al_2O_3, %	0.12	0.32	1.04	2.05	3.56	10.3	25.1

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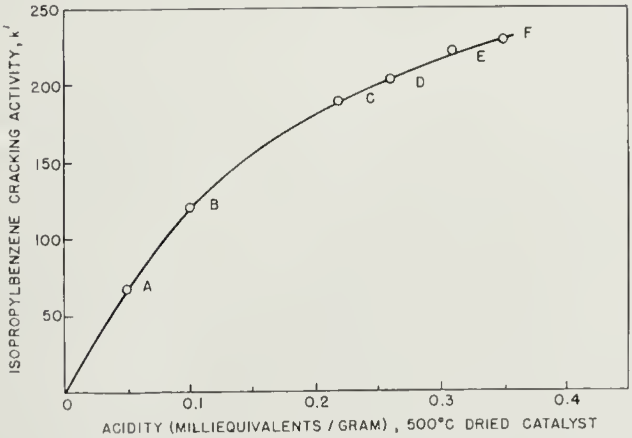

Figure 15. Dependence of isopropylbenzene cracking activity at 500°C on acidity for a series for of alumina-silica catalysts.

Catalyst	A	B	C	D	E	F
Al_2O_3	0.12	0.32	1.04	2.05	3.56	10.3

(Republished by permission of The Faraday Society, London) fraction (3 per cent) of the total aluminum in these catalysts acts as a solid acid.

Bitepazh[151] demonstrated that as Na^+ is progressively removed from a dried synthetic zeolite by treatment with dilute hydrochloric acid, followed by calcination, the activity for cracking of a 210 to 300°C boiling range oil increased rapidly. The activity for cracking of butylbenzenes was high for catalysts that had been calcined after exchange with the ions Al^{+++}, Th^{++++}, or NH_4^+. The catalysts that had been exchanged with Zn^{++} and Mg^{++} were much less active, and the exchange with Ba^{++} ion gave an inactive catalyst. The extent of exchange of all of these ions, except Na^+, was not specified. It was postulated that monovalent alkali cations block the catalyst surface, thus rendering it inactive, whereas multivalent cations occupy only a portion of the surface sites, leaving the other sites free to promote cracking reactions. Each ion supposedly has its own specificity.

Mills and co-workers[158] showed that 1.14 meq K^+/g exchanged on an uncalcined Houdry synthetic catalyst destroyed virtually all of its catalytic activity for the Cat A test, and for cumene cracking. Since this treatment resulted in no loss of surface area, and the activity could be completely restored by exchange of the K^+ with H^+ or NH_4^+, this effect could not be attributed to a "fluxing action" of the alkali on the catalyst during calcination. A similar effect for the calcined catalyst was produced by much less K^+: i.e., a severe loss of activity occurred with as little as 0.04 meq K^+/g catalyst.

Topchieva and co-workers[181] found that the adsorption of Na^+ on synthetic alumina-silicas reduces the extent of the simultaneous reactions of hydrogen redistribution and isomerization of cyclohexene at 350°C. At this temperature cracking does not occur.

Stright and Danforth[150] found that addition of progressively larger amounts of Li^+ to several cracking catalysts reduced their activity for cumene cracking at 500°C in proportion to the amount of Li^+ added. The activities finally leveled off at about 10 per cent conversion. This was observed with Socony bead alumina-silica, UOP alumina-zirconia-silica, Davison magnesia-silica, and Shell alumina-boria catalysts. The amount of Li^+ required for complete deactivation was about one-fifth that needed if the entire amounts of aluminum or magnesium ion were actually functioning as acids, in each case. Similar results were obtained for the bead catalyst with isopropyl benzene at *ca.* 480°C where the leveling off occurred at *ca.* 40 per cent cracked. Diisobutylene cracking at LHSV 2 at *ca.* 400°C was little influenced by Li^+ addition. In this case, the effect of Li^+ was probably obscured by the very low LHSV employed, since at this temperature the same conversion of *ca.* 86 per cent would be expected from an LHSV as high as 63.

Further studies by Danforth[119] showed that the effectiveness for inactivating Socony bead catalyst and UOP catalyst for cracking cetane, increased with increasing atomic radius of the alkali metal ion. Thus, the order found was $Ca^+ > K^+ > Na^+ > Li^+$, on an equivalent basis; Ba^{++} acted similarly to K^+. The greater effectiveness of the larger alkali ions was attributed to their power to cover simultaneously several aluminum atoms believed to be bound together in polymeric chains on the catalyst surfaces. It was also suggested[182] that for cetane cracking, the loss in conversion per meq of each alkali was a fundamental characteristic of each catalyst for the four different types studied. Since this effect was little changed by "destructive calcination," it was deduced that large sections of the active sites become buried by this calcination, without changing the spacing of sites available for the cracking reaction.

Rijnders and Schuit[183] believe that two types of sites exist on alumina-silica catalysts. Type "A" contains protons; these promote cracking reactions. Type "B" sites consist of aluminum ions. Type A sites crack *n*-heptane (I) at 525°C, and 2,2,4-trimethylpentane (II) at 525°C, both without hydrogen formation. They also crack heptene-1 (III) at 380 to 440°C, and isopropylbenzene (IV) at 380 to 440°C, as well as polymerize propylene (V) at 150 to 200°C. Type A sites are deactivated by K^+ adsorbed from the alcoholate solution. Type B sites are inactive for cracking reactions (I) and (II) but have some activity for reaction (IV) and (V).

The above authors studied also γ-alumina treated with hydrofluoric acid. They believe that substantially similar acid sites are present on the surface. In this case the OH^- groups of γ-alumina are presumably replaced by F^- ions which have the same size and charge, but are more electronegative and will enhance the electrophilic properties of the Al^{3+} ions.

Mills and co-workers[158] found an exponential relation for isopropylbenzene cracking *vs.* meq of various organic bases preadsorbed on Houdry alumina-silica catalyst. The effectiveness for deactivation was a function not only of the basicity of the nitrogen compounds but also of their thermal stability. The strong deactivating effect of quinaldine appeared to be a result of its polymerization on the catalyst surface. The order of effectiveness decreased as follows: quinaldine > quinoline > pyrrole > piperidine > decylamine > aniline. A linear relation was found on plotting the log of the amount of quinoline that could be chemisorbed at 315°C on alumina-silica, magnesia-silica, zirconia-silica, and Filtrol catalysts *vs.* the per cent gasoline yielded by the "Cat A" test.

Using a molecular area of $36 Å^2$ for the flat-lying quinoline molecule, it was calculated by Mills *et al.* that the active sites of an alumina-silica catalyst occupied only 4 per cent of its total surface area. At 425°C, LHSV 8, and a 30-min. process period, a similar catalyst cracked 10.1 mmoles of isopropylbenzene/g of catalyst. From the number of millimoles cracked and the number of active centers per gram of catalyst, measured by quinoline chemisorption (0.03), it was calculated that the catalyst catalyzed 340 scissions per active center, during the 30-min. process period.

CONCLUSION

In the past 20 years considerable advances have been made in the understanding of the properties and the behavior of solid acid catalysts. Most of the effort has been devoted to alumina-silica catalyst and to clays because of their industrial importance and very little study has been given to other acidic solids. Unfortunately, very little attention has been paid by many investigators to the influence the methods of preparation have on final catalyst properties. For this reason it is difficult to compare the results of various investigations of different alumina-silica catalysts. Nevertheless, many observations made have been of sufficient generality to constitute substantial progress in this field.

Thanks to electron microscopy we are well informed regarding the shape and the size of particles and the nature of porosity of alumina-silica cracking catalyst. The work reported was done with alumina-silica gels prepared by hydrolysis of an aluminum salt in the presence of silica gel. It appears that the ultimate particles of the fresh gel are small spheres of *ca.* 45Å diameter with narrow distribution of sizes. These small spheres pack readily into aggregates of *ca.* 0.5 to 3μ in diameter during aging and these in turn aggregate further on setting of the gel. The pore structure is then the interconnected maze of interstices and void spaces between the ultimate particles. The spherical shape of the ultimate gel particles and packing of these into larger aggregates was not altogether unexpected in view of the previous knowledge of silica gel structure. Since all industrial alumina-silica catalysts are predominantly composed of silica gel it seems highly probable that other industrially prepared alumina-silica catalysts have similar physical structure to that reported above, with the possible exception of those prepared in very alkaline environment. Unfortunately, data on this subject are lacking.

There is no such clarity with regard to the chemical nature and the architecture of the surface of these gels, and yet even in this difficult field certain far-reaching steps in understanding have been made. It has been demonstrated beyond doubt that the major factor responsible for the activity of alumina-silica is the high acidity of the catalyst surface. Neither silica nor alumina gel alone under normal conditions is appreciably acid or active for acid catalyzed reactions. Much progress has been made in characterization of acidity of cracking catalysts. The measurement of acidity of completely insoluble solids called for very novel and interesting methods of approach; at present, both the number of acid sites as well as the acid strength can be measured with a relatively high degree of confidence.

The acidity of alumina-silica is traceable to the presence of aluminum ions in or near the surface of the silica gel in some specific spacial arrangement which gives rise to very high acid strength of such sites, far beyond any observed either on silica gel or alumina gel alone. There are widely differing opinions regarding the structure and the origin of these sites. This subject is still in the stage of intriguing speculation. Most models of the acid sites are based on crystallographic considerations; it is argued that upon introduction into a gel network composed predominantly of silica tetrahedra, aluminum and oxygen will assume the same arrangement as silica (tetrahedral) with the result that a site deficient in positive charge will be created.

Believing that the extension of crystallographic concepts to surfaces may be misleading, one of the authors earlier proposed a model based on electrical properties (polarization) of the chemical bonds in the group Al^{3+}: O:Si^{4+}, and polarization of water to form a hydrogen ion at the site. It is believed that, on the surface, at most only three silicon atoms will combine with trivalent aluminum atoms in this manner. The degree of polarization of these bonds is independent of the coordination number of aluminum with oxygen. The coordination number may be variable and not constant on a relatively mobile surface, particularly in presence of sorbed water.

On the other hand, another group of workers believes that there are no permanent acid sites on the alumina-silica catalyst surface at all and that the gel is a simple mechanical mixture of extremely small silica gel and alumina gel particles. Acidity of the surface is believed to be generated in the solid only in response to the approach of a base which causes a reversible crystallographic change at the points of contact of the silica gel and alumina gel particles. In the presence of a base, certain aluminum and oxygen ions closely adjacent to silica tetrahedra assume tetrahedral form with the consequent appearance of acidity and revert to the former nonacid state when the base is removed. (This change is often referred to as the "flip-flop" mechanism.)

It seems to us, however, that the evidence for a permanent chemical attachment of aluminum via oxygen to silica in an acid site is very convincing. Alkali silicates and aluminates have been known for a long time to interact with formation of mixed gels having base exchange properties. It also has been found that silica gel reacts readily with hydrolyzed aluminum ions in acid media with formation of similar materials. In view of this it is believed that copolymerization (condensation reaction) takes place between the hydroxyl groups of silica with hydroxyl groups of hydrolyzed aluminum ions. The resulting materials have base-exchange properties and behave as acids. The acidity is traceable to the incorporation of aluminum ions in the silica gel framework. Such gels undergo substantial structural changes upon dehydration and calcination; it has been observed, however, that although the number of acid sites is substantially reduced, the acid strength of the remaining sites is greatly increased. It seems therefore reasonable to postulate that strong acidity has developed by further interaction of aluminum chemically bound to the surface of the silica network.

Only a small part of the aluminum in a calcined catalyst is involved in formation of acid sites on the catalyst surface. Aluminum atoms are embedded not only in the catalyst surface but also in the interior of the primary particles composing the catalyst mass. The distribution of aluminum on the surface and in the interior of the primary particles of an individual catalyst depends heavily on the procedural conditions used in its preparation, as well as on the conditions of thermal activation. Some evidence has been presented for the existence of aluminum ions located at some of the acid sites in form of compensating cations (presumably hydrolyzed), in catalysts prepared on the "acid side." The presence and role of these cations in acid catalysis remains to be clarified by further work.

A calcined alumina-silica catalyst contains a small amount of structurally bound water (*ca.* 1 per cent) which is mostly in form of catalytically inactive hydroxyl groups (such as terminal SiOH groups). A small portion of the total bound water is essential for activity since, presumably, it provides protons for the acidic surface alumina-silica sites. These acidic sites are inactivated by uptake of inorganic or organic bases. The dehydrated acid sites have been often termed Lewis acids; they could also be considered acid anhydrides. A dehydrated aluminum cation attached to an acid site may also be considered a Lewis acid. Following drastic water removal, protons are eventually removed as water by simultaneous abstraction of a hydroxyl group from silica gel or from the anion part of the acid site. This may result in progressive destruction of the surface and a loss of activity. Further clarification of the chemistry of dehydration and calcination is most desirable. Unfortunately these materials are amorphous and are therefore not accessible to study by diffraction methods.

After normal calcination there are undoubtedly two kinds of sites, some occupied by protons and some dehydrated sites without protons. This is indicated by the results of the infrared studies of the surface of a calcined catalyst ammoniated at 175°C, which show the presence of NH_4^+ ion and adsorbed NH_3 on the surface. Catalytic cracking is, however, believed to be promoted primarily by protonated acid sites. The contribution of the anhydrous sites to the over-all reaction has not as yet been made clear.

It has been reported that some dehydrated gels could be handled in aqueous media (e.g., for acidity determination) without rehydration of the Lewis acid sites, but in the majority of cases, rehydration of the sites was reported to be very rapid. The ease of water removal and rehydration of acid sites may conceivably vary on various gels, and depend on the temperature and other conditions. It would be greatly desirable to resolve the apparent inconsistencies of observations in this field. Attention by the investigators to the origin of the catalyst and details of the methods of preparation may be of help in this respect.

As far as other acidic solids are concerned, only acid-treated clays have been successfully used on a scale comparable with alumina-silica as cracking catalysts and consequently have been studied to an appreciable extent. Their study proceeded simultaneously with that of alumina-silica system. It has been shown that simple base exchange with an acid does not activate a bentonite clay; a deep acid treatment with partial dissolution of a good deal of alumina and magnesia is necessary. Thus, a suggestion has been made that acid treatment removes from the crystalline structure certain aluminum atoms and hydroxyl groups which leaves only 4-coordinated groups in the clay. On the other hand certain observations have been reported recently which make it appear likely that the activation is traceable to the formation of an amorphous active phase during and following acid treatment—by interaction of dissolved alumina with finely dispersed silica particles. Thus acid sites are created that are similar to those in amorphous alumina-silica catalysts. Little has been published about the structure and source of activity of activated kaolin or halloysite type catalysts. It is known, however, that they contain strong surface acids and therefore the active portions of such catalysts are probably similar in structure to those of amorphous alumina-silica catalysts.

Alumina-boria and magnesia-silica catalysts have been considered as possible substitutes for alumina-silica catalysts. Alumina-boria (activated alumina impregnated with boric acid) is very similar in its catalytic behavior with hydrocarbons to alumina-silica catalyst but is substantially more active below the temperature of volatilization of boric acid. Magnesia-silica (prepared in various ways: e.g., by mechanical mixing of the two oxides followed by calcination) is interesting because of its somewhat different distribution of activity for cracking of various types of hydrocarbons. It has been found also to be substantially less acidic than alumina-silica catalyst and to have its acidity distributed over a broad range. Very little has been published regarding the behavior and the chemical nature of the above catalysts, although magnesia-silica was tested at one time on a rather large scale. Interesting information regarding acid catalysis would no doubt also be obtained by study of materials which are acidic but which for various reasons are unsuitable for industrial use: e.g., aluminum salts such as fluorides, or phosphates, or alkali or alkaline earth metal acid salts such as phosphates, sulfates, etc. The choice, however, is limited because many solid materials that are acidic either have a low specific surface or have strong dehydrogenating properties.

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CHAPTER 2

CATALYTIC DEHYDRATION AND HYDRATION

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INTRODUCTION

In the early development of the science of catalysis, many of the laboratory studies were concerned with dehydration. Oxide catalysts such as Al_2O_3 were easily prepared and did not readily poison, alcohols were convenient reactants, and the products were easily analyzed. The results were disappointing in that our knowledge of the nature of catalysis in general was not greatly advanced. In more recent times we have learned that the structure of a typical dehydration catalyst such as alumina is far from simple. The nature of the surface and the kinds of bonds which it can make to the adsorbate molecules are still not clearly understood.

Much of the incentive to study dehydration catalysis came from the need to prepare olefins from alcohols. Once large quantities of C_2H_4 and other unsaturated hydrocarbons became available from petroleum, the interest in dehydration declined. There remained a need for laboratory-scale preparation of unsaturated compounds for teaching and research purposes, and a comparatively few large-scale industrial processes such as the Lebedev synthesis of butadiene.

To what extent a determined and searching study of dehydration reactions would pay dividends is controversial. For many dehydration reactions there is no difficulty in finding an effective catalyst. The difficulties, and the dividends, come from the study of compounds which can be dehydrated in more than one way, and in preparing selective catalysts for each of the possible mechanisms. The production of butadiene, both from ethanol and from butanediols, are the well-known examples.

We cannot be certain who first observed a catalytic dehydration, possibly it was Priestly. In 1797 Bondt, Deiman, van Troostwyk and Lauwerenburg[25] were reported to have formed ethylene by passing ethanol or ether over heated alumina or silica. Jahn (1880) obtained appreciable ethylene from ethanol over a zinc-zinc oxide catalyst at 300 to 350°C while at about 500°C he obtained acetaldehyde and hydrogen[137]. Much the same result was noted by Berthelot and Jungfleisch[20] when they passed ethanol through a heated glass tube. Squibb[248] in 1895 carried out a combined dehydration and decarboxylation of acetic acid over $BaCO_3$. At the turn of the century Nef[191] decomposed ethanol into a mixture of olefin, aldehyde and other gases, in the presence of pumice. Grigorieff[101] dehydrated ethanol and also ether to ethylene using alumina at 300°C.

Possibly the first realization of the economic significance and potential of catalytic dehydration came with a series of papers by Ipatieff,[125b-136], commencing in 1902 when he proposed the use of alumina as a general method of obtaining olefins from alcohols.[125b] Ipatieff and his collaborators carried out a rapid survey of the dehydration possibilities of a large number of alcohols (both cyclic and aliphatic) as well as of ether and glycol. In many of the early experiments the equipment was necessarily far from ideal, the temperature too high, and to our present way of thinking the catalysts were too impure to permit reliable generalizations to be reached.

The expansion of the field to include a large variety of reactants and catalysts[78] was carried out by a steadily increasing number of workers of whom the best known are Sabatier and Senderens. The early work is described in a book by Sabatier and Reid[234], much of which is still valuable reading. Some of the information offered, for example on the relative activity and specificity of different catalysts, is no longer acceptable. We now know that variation in method of preparation of a given catalyst can lead to differences in behavior as great as the differences between catalysts of obviously different chemical composition.

EXAMPLES OF DEHYDRATION REACTIONS

Some of the better known examples will be used to illustrate the nature of dehydration reactions in general. With this as background the mechanism of dehydration catalysis will then be discussed.

Ethanol Dehydration to Ethylene

A large part of our knowledge of catalytic dehydration comes from studies of the dehydration of ethanol in the presence of alumina. At sufficiently high temperatures (>300°C) the products are almost entirely C_2H_4 and water (Grigorieff[101])

$$C_2H_5OH \rightleftharpoons C_2H_4 + H_2O \qquad (1)$$

The role of the catalyst is to hasten the approach to the equilibrium described by Eq. (1) and to favor reaction (1) rather than alternative reactions such as dehydrogenation. As shown in Figure 1, the equilibrium constant for the dehydration of ethanol increases with an increase of temperature. Thus choice of temperature as well as catalyst and flow rate determines the percentage of ethanol which can be converted to ethylene. In addition, the relative concentration of reactant and products in the reaction zone are a function of equipment design and of pressure. It is sometimes possible therefore to displace the equilibrium a little to the right. In practice, conversions of 90 to 98 per cent (Martello and Ceccotti[180]) are readily obtained.

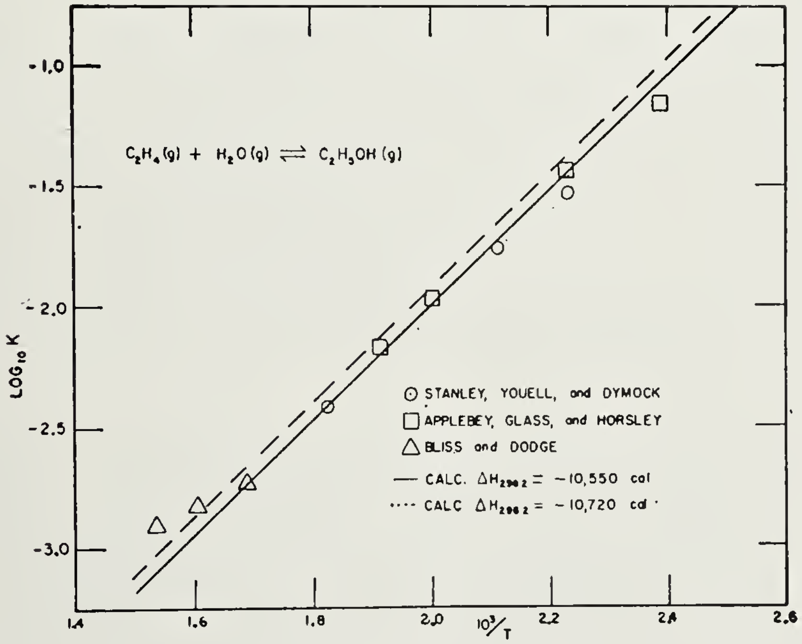


Figure 1. Experimental versus calculated values of K_p for the equilibrium: $C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$. (From Barrow[14])

At progressively lower temperatures than those used for ethylene production, more and more diethyl ether appears in the reaction products, and below 260°C the dehydration follows almost entirely the course[241]

$$2C_2H_5OH \rightleftharpoons C_2H_5OC_2H_5 + H_2O \qquad (2)$$

Since the ether can in turn be dehydrated to ethylene, it will be evident that ethylene production (1) is the result either of direct dehydration of ethanol to olefin, or consecutive dehydration of ethanol to ether and then to ethylene, or a combination of both. Much of the work on dehydration mechanism has concerned itself with a decision among the three alternatives.

As may be expected from Eq. (1), ethylene production can be diminished by increasing the pressure (Feilchenfeld[84]):

Pressure	Conversion to ether	To ethylene	
20 atm	70%	4.4%	355°C on Al_2O_3
40 atm	50%	<1%	

However, increase of pressure accentuates the difficulty of desorption of the products. Feilchenfeld[84] found that under his conditions of high pressure the conversion to ether corresponded to less than 1/10 of the equilibrium value (for values of the equilibrium constant see Table 27).

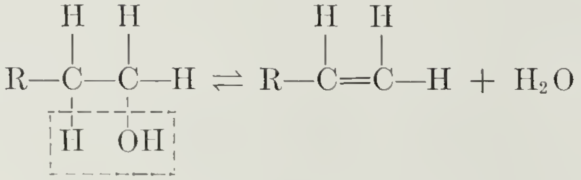
Even at temperatures from 20 to 100°C some compounds are observed to lose the elements of water to the catalyst. Usually however it is not until the temperature is raised to 200°C or more that the water can, in turn, be removed from the catalyst at a convenient rate, thus making the dehydration of the reactant a continuous rather than a batch process. We shall therefore expect to find in many studies of dehydration catalysis that the over-all rate is limited by the rate of desorption of water. In practice this limitation cannot always be overcome by raising the temperature, since the result may be side reactions such as dehydrogenation, polymerization or decomposition of the product. Diminished pressure is therefore resorted to in some laboratory preparations. In commercial practice there is a natural tendency to avoid the use of low pressures.

Higher Alcohols

The higher homologs of ethanol behave in essentially the same way as ethanol on dehydration, giving an ether at the lower temperatures and an olefin at the higher. Some isomerization of the olefin may occur. The first section of Table 1 contains a list of products of dehydration of simple alcohols, and others will be found in Table 3.

Secondary and tertiary alcohols, of the general formulas $(C_nH_{2n+1})_2 \cdot CHOH$ and $(C_nH_{2n+1})_3COH$, respectively, yield the olefin (or a mixture resulting from isomerization) but usually no ether. The failure to produce ether is presumably a result of the ease of dehydration to olefin, which is considerably greater than for primary alcohols (Sabatier and Reid[234]).

It will be clear that dehydration of monohydric alcohols to olefins consists essentially in removing the elements of water (H and OH) from two adjacent carbon atoms



$$R-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \rightleftharpoons R-\overset{H}{C}=\overset{H}{C}-H + H_2O \qquad (3)$$

As might be anticipated, the ease of removal of the H atom from the β-carbon atom increases as R is varied from H to CH_3 to large alkyl groups.

Table 1. Types of Dehydration Reactions and Corresponding Catalysts

Reactants	Catalysts	Products	Authors
Alcohols			
Methanol	Al_2O_3. Also SiO_2 or Cr_2O_3 or Al_2O_3 activated with oxides of groups 1, 6, 7 & 8	dimethyl ether	128
2(Alcohol)	synthetic methanol catalyst	higher primary or secondary alcohols	97
Ethanol	Al_2O_3. Also Al_2O_3-SiO_2; TiO_2; Cr_2O_3; W_2O_5; SiO_2; ZrO_2	ether	128
Ethanol	Al_2O_3; SiO_2. Also P_2O_5; ZrO_2; W_2O_5; TiO_2; K_2CO_3; Al_2O_3 with CuO, NiO or Cr_2O_3; ThO_2; $Mg_3(PO_4)_2$ on coke; H_3PO_4; molybdites	ethylene	25
1-Propanol (propyl alcohol)	Al_2O_3	dipropyl ether	128
1-Propanol	Al_2O_3	propylene	126
2-Propanol (isopropyl alcohol)	Al_2O_3. Also ZnO; $Ca_3(PO_4)_2$; ascanite clay	isopropyl ether + propylene	128, 126
2-Methyl-1-propanol (isobutyl alcohol)	pumice. Also Al_2O_3	2-methyl-propene (isobutylene) + 1-butene	191
2-Methyl-2-propanol (tert-butyl alcohol)	pumice. Also $AlPO_4$; Al silicate; $Al_2(SO_4)_3$	2-methyl-propene	191
1-Butanol	Al_2O_3. Also Fe_2O_3 + Al_2O_3; SiO_2 + TiO_2; Na_2PO_3 + bauxite	1-butene (α-butylene)	129, 204
1-Butanol	H_3PO_4 + Al_2O_3	2-methylpropene	158
1-Butanol	Al_2O_3	1-butene + *cis*-2-butene + *trans*-2-butene (pseudobutylenes)	190
2-Butanol (sec-butyl alcohol)	Al_2O_3	1-butene + *cis*-2-butene	136
Methyl butanols	Al_2O_3	methyl butenes	129
2-Methyl-2-butanol (tert-amyl alcohol)	Al_2O_3	3-methyl-2-butene (β-isoamylene)	242
3-Methyl-1-butanol (isoamyl alcohol)	Al_2O_3. Also Al_2O_3 + additives	isoamyl ether + amylene	128
1-Pentanol (amyl alcohol)	Al_2O_3. Also $AlPO_4$	dipentyl ether + pentene	151

TABLE 1—*Continued*

Reactants	Catalysts	Products	Authors
Alcohols—continued			
3-Pentanol (diethyl carbinol)	$H_3PO_4 + SiO_2$	olefins (both normal and rearranged)	146
1-Octanol	Al_2O_3	1-octene	242
2-Octanol	Al_2O_3	2-octene	242
1-Dodecanol	Al_2O_3	didodecyl ether or dodecene	276
1-Hexadecanol	Al_2O_3	hexadecylene	236
Tertiary alcohols	finely divided metals	unsaturated hydrocarbons	234
Unsaturated Alcohols			
2-Propene-1-ol (allyl alcohol)	W_2O_5	propene + propenal (acrolein) together with some propane, propanal (propionaldehyde) and ethylene	221
(For other examples see under "Diene Formation")			
Cyclic Alcohols			
1-Cyclopropyl ethanol in toluene	Al_2O_3	vinylcyclopropane	245
Cyclohexanol	Al_2O_3. Also SiO_2	cyclohexene	129
o-Methylcyclohexanol	Al_2O_3	methylcyclohexenes	129
Phenylcyclohexanol	ThO_2	phenylcyclohexene	233
1,2-Diethylcyclohexanol	Al_2O_3	1-ethyl-2-ethylidene cyclohexane	145
Cyclohexylcyclohexanol	ThO_2	cyclohexylcyclohexene	233
Phenol	ThO_2	diphenyl ether	218
Phenol + CH_3OH	ThO_2	methylphenyl ether	226
o-Aminophenylethyl alcohol	bauxite; bauxite + $CuCO_3$; TiO_2; ZrO_2; ZnO etc. Also K_2CO_3; SiO_2	*o*-aminostyrene + indole + indolin	125
Diphenyl carbinol (benzohydrol)	ThO_2	dibenzohydryl ether	233, 38
Phenyl benzyl carbinol	ThO_2	stilbene	233
Methyldiphenyl carbinol	ThO_2	1,1-diphenyl ethylene	233
Decahydronaphthol	Al_2O_3	octahydronaphthalene	234
Borneol	Al_2O_3 + CuO	camphene	132
1-Menthol	Al_2O_3; Al salts	menthenes	242
Cholesterol	floridin; bentonite; bauxite; kieselguhr; etc.	dicholesteryl ether	21

Table 1—*Continued*

Reactants	Catalysts	Products	Authors
Diols			
Glycol	Al_2O_3	acetaldehyde	129
Glycols	MgO (or ZnO) with ZrO_2, CeO_2 or ThO_2. Also $CaHPO_4$; $CaSO_4$; Al_2O_3; SiO_2; BeO; B_2O_3; $CaCO_3$	unsaturated carbonyls	11
1,2-Propanediol	SiO_2; NaH_2PO_4	propanal (propionaldehyde)	91
1,4-Butanediol	H_3PO_4 with NaH_2PO_4 on C	tetrahydrofuran	117
2,3-Butanediol	most dehydration catalysts	methylethyl ketone	62, 282
2-Methyl-1,3-butanediol	kaolin	2-methyl-1,3-butadiene (isoprene)	165
2,3-Dimethyl-2,3-butanediol (pinacol)	Cu. Also Al_2O_3; Al phosphate	2,3-dimethyl-1,3-butadiene	165
1-2-Pentanediol	kaolin; Al_2O_3; P	pentanal (valeraldehyde)	15
1,4-Pentanediol	kaolin; Al_2O_3	tetrahydromethylfuran	15
1,4-Pentanediol	P	1,3-pentadiene	15
1,5-Pentanediol	kaolin; Al_2O_3	tetrahydropyran	15
1,5-Hexadeine-3,4-diol	Al_2O_3	1-cyclopentene-1-carbonal (1-cyclopentene aldehyde)	271
2,4-Pentanediol	kaolin; Al phosphate	3-pentene-2-ol or 1,3-pentadiene (piperylene)	165, 205
2,5-Dimethyl-2,5-hexanediol	$Al_2O_3 + H_3PO_4$	2,5-dimethyl-2,4-hexadiene	103
$[RCH(OH)C\equiv]_2$	$CoMoO_4$	alkyl furans	50
1,2-Ethylbenzenediol	H_3PO_4 on pumice	phenylacetaldehyde	75
Heterocyclic Compounds			
Tetrahydrofuran	H_3PO_4 with NaH_2PO_4 on C	1,3-butadiene	117
Methylbutylene oxides	kaolin	isoprene	164
2,3-Dihydropyran	Al silicate on SiO_2	acrolein + ethylene	36
2,2,5,5-Tetramethylfuranidine	Al_2O_3	2,5-dimethyl-2,4-hexadiene + 2,5-dimethyl-1,5-hexadiene	289
Methyltetrahydrofuran	BPO_4. Also BeO; La_2O_3; Al_2O_3; ThO_2; TiO_2	1-methyl-1,3-butadiene	272
Tetrahydrofurfuryl alcohol	Al_2O_3	1,2-dihydropyran	154

TABLE 1—*Continued*

Reactants	Catalysts	Products	Authors
Ethers			
Dimethyl ether	Al_2O_3	C_2H_4	266
Diethyl ether	Al_2O_3 ; SiO_2	C_2H_4	25
Glycol monoethyl ether	Al_2O_3 ; ThO_2	1,3-butadiene	43
Didodecyl ether	Al_2O_3	dodecene	276
Ketones and Aldehydes			
2(Acetone)	ThO_2	4-methyl-3-penten-2-one (mesityl oxide)	176
3(Acetone)	Al_2O_3	2,6-dimethyl-2,5-heptadien-4-one (phorone)	135 244
3(Acetone)	Al_2O_3 . Also bauxite	1,3,5-trimethylbenzene (mesitylene)	134, 65 155
Methanol + acetone	Al_2O_3	hexamethyl benzene	209
Methylethyl ketone	ThO_2	heptenones	283
3-Hydroxy-2-butanone (acetoin)	Al + SiO_2 + W_2O_5	methyl vinyl ketone	102
2(Acetaldehyde)	UO_2 or ThO_2 or TiO_2 on C	2-butenal (crotonaldehyde)	219
Acids and Esters			
Formic acid	TiO_2 ; W_2O_5 . Also glass; SiO_2 , or ThO_2 + SiO_2 , or P_2O_5 + SiO_2 , or TiO_2 + SiO_2 , with Al phosphate	carbon monoxide	228
Acetic acid	H_3PO_4 on C	acetic anhydride (also propionic anhydride from propionic acid)	68
Acetic anhydride or acetone	sulfates of Al; Cr; Mn; Ca; Ba; Sr; Mg; Ag	ketene	152
2(Acetic acid)	$BaCO_3$; $CaCO_3$. Also ThO_2 ; UO_2 ; ZnO; MnO; Na metaphosphate	acetone, carbon dioxide	248
Alcohols + acids (aliphatic or aromatic)	TiO_2 ; ThO_2 . Also ZrO_2 ; SiO_2	esters or ketones or olefins	227
2(Organic acid)	MnO	ketone	230, 231
Ethyl chloride	Al_2O_3 ; Al salts	vinyl chloride	242
Propyl chloride	Al_2O_3 ; Al salts	propene	242
Amides			
Amides	Al_2O_3 . Also SiO_2 ; chromites of Fe or Ni or Mn	nitriles	24
Propionamide	H_3PO_4 on Al	propionitrile	116

TABLE 1—*Continued*

Reactants	Catalysts	Products	Authors
Amides—continued			
Ethylene cyanhydrin	SiO_2 ; C	propenenitrile (acrylonitrile)	124
Condensation with Ammonia or Amides			
Carbon monoxide + ammonia	CeO_2 ; Al_2O_3	hydrocyanic acid	34
Aliphatic or aromatic or cyclic aliphatic alcohols + ammonia or aniline	Al_2O_3 ; ThO_2 . Also W_2O_5 ; CeO; NiO	alkyl and aryl amines	229
Ethanol + ammonia + hydrogen	CdO; ZnO; Al_2O_3 ; SiO_2 ; ThO_2	pyridine, picoline, butadiene, collidine, parvoline	63
Aldehydes + ammonia	ThO_2	nitriles	178
2(Acetaldehyde) + ammonia	Al_2O_3	pyrrole + picolines + collidines	47
2(Acetaldehyde) + aniline	Al_2O_3	quinoline bases	48
Ketones + ammonia	ThO_2	ketimines	183
Dipropyl ether + ammonia	Al_2O_3 ; ThO_2	dipropylamine	44
Acetic acid + ammonia	Al_2O_3 + ThO_2	acetonitrile	117
Vinyl acetate + amines	bauxite	unsaturated bases	122
Diene Formation			
Ethanol	Al powder	1,3-butadiene + acetaldehyde + ethylene	90
Ethanol	ZnO + Al_2O_3 . Also SiO_2 + MgO + TaO_2 ; SiO_2 + MgO + Cr_2O_3 ; etc.	1,3-butadiene	167
Ether	Al powder	1,3-butadiene	84a
Ethanol + acetaldehyde	Al_2O_3	1,3-butadiene + 1,2-butadiene	198
1-Propanol, or 2-propanol, + acetaldehyde	Al_2O_3	1,3-pentadiene (piperylene)	199
1,3-Butanediol	kaolin. Also monophosphates + C; red P; NaH_2PO_4 ; BPO_4	1,3-butadiene	165
1,4-Butanediol	H_3PO_4 + NaH_2PO_4 on C	1,3-butadiene	117
2,3-Butanediol	ThO_2	1,3-butadiene	282
2,3-Butanediol + methylethyl ketone + amine + water	Al + SiO_2 + W_2O_5	1,3-butadiene	102

Table 1—*Continued*

Reactants	Catalysts	Products	Authors
Diene Formation—continued			
2-Butene-1-ol	Al_2O_3 ; Al silicate	1,3-butadiene	165
3-Butene-2-ol	Al_2O_3 . Also ThO_2 ; Al + SiO_2 + W_2O_5	1,3-butadiene	206
2-Methyl-1,3-butanediol	Al phosphate	isoprene	165
1-Methyl-1-butanal	kaolin	isoprene	164
2,3-Epoxy-2-methylbutane (2-methyl-2-butylene oxide)	kaolin. Also red P; NaH_2PO_4	isoprene	164
1-Pentene-3-ol	Al_2O_3	1,3-pentadiene	205
2-Pentene-4-ol	kaolin	1,3-pentadiene	165
2-Hexene-4-ol	kaolin	2,4-hexadiene	165
1-Heptene-3-ol	Al_2O_3	1,3-heptadiene	69
Miscellaneous			
Glycerol	Al_2O_3	propenal	220
Alcohols + hydrogen sulfide	ThO_2 . Also CdS; Al_2O_3 ; bauxite; charcoal; bleaching earth	thiols and thioethers	224
Phenols + hydrogen sulfide	ThO_2	small yield of thiols and thioethers	224, 225
Butyric acid	ThO_2 or MnO	dipropyl ketone (dehydration accompanied by decarboxylation)	233
Benzoic acid + phenylacetic acid	Fe_2O_3	phenylbenzyl ketone (dehydration accompanied by decarboxylation)	174
Phenylcarbinol (benzyl alcohol)	ThO_2	resin (dehydration accompanied by polymerization)	233
1,3-Butanediol	ZrO_2 + SiO_2 ; MgO (or ZnO) stabilized by addition of ZrO_2 , CeO_2 or ThO_2	1-butene-3-one + 2-butenal (dehydration accompanied by dehydrogenation)	11
Diphenylcarbinol (benzhydrol) + methanol	ThO_2	diphenylmethane (dehydration accompanied by hydrogenation-dehydrogenation)	232
3(Diphenylcarbinol)	Cu	benzophenone + 1,1,2,2-tetraphenylethane (dehydration accompanied by disproportionation)	233

Apparently the rule does not hold rigidly. Freidlin and Levit[88] found the following sequence for ease of dehydration: isopropyl > isobutyl > *n*-butyl > *n*-propyl > ethanol.

Up to this point we have assumed that the catalyst is alumina or something similar. Early in the study of catalysis it was suggested that oxide catalysts fall into two main classes, dehydrating and dehydrogenating. Although no longer considered entirely reliable, the well-known table of Sabatier and Mailhe[223] (Table 2) illustrates the distinction. Less well known, but of considerable interest in a discussion of reaction mechanism, is that on certain oxides such as thoria ether formation is difficult to demonstrate, while dehydration to olefin occurs readily (Sabatier and Mailhe[223]; Pearce and Rice[200]; Balaceanu and Jungers[12]).

TABLE 2. RELATIVE DEHYDRATION AND DEHYDROGENATION CAPACITIES OF VARIOUS CATALYSTS, ACCORDING TO SABATIER AND MAILHE[223]

Catalyst	Vol. Gas Liberated/min.	C_2H_4 Content of Gas (%)	H_2 Content of Gas (%)
ThO_2	31	100	traces
Al_2O_3	21	98.5	1.5
W_2O_3 (blue)	57	98.5	1.5
Cr_2O_3	4.2	91	9
SiO_2	0.9	84	16
TiO_2	7.0	63	37
BeO	1.0	45	55
ZrO_2	1.0	45	55
UO_2	14	24	76
Mo_2O_5 (blue)	5	23	77
Fe_2O_3	32	14	86
V_2O_3	14	9	91
ZnO	6	5	95
MnO	3.5	0	100
SnO	45	0	100
CdO	11.2	0	100
Mn_3O_4	12	0	100
MgO	traces	0	100
Cu (lightly reduced)	110	0	100

Reaction temperature 340 to 350°C. Oxides prepared below 350°C.

Ether

Dehydration of diethyl ether to ethylene over alumina occurs rapidly at about 300°C as we should expect.

$$C_2H_5OC_2H_5 \rightleftharpoons 2C_2H_4 + H_2O \tag{4}$$

However, the reaction is not necessarily straightforward. At least to some small extent there is hydration of ether to ethanol, and at high space velocities or low temperatures the reaction may be represented approximately by (Balaceanu and Jungers[12])

$$C_2H_5OC_2H_5 \rightleftharpoons C_2H_4 + C_2H_5OH \tag{5}$$

Exchange Reactions

By making use of the heavy isotope of oxygen, the following exchange reaction can be demonstrated on alumina (Karpacheva and Rozen[149])

$$C_2H_5O^{16}H + H_2O^{18} \rightleftharpoons C_2H_5O^{18}H + H_2O^{16} \tag{6}$$

It is of considerable importance to discussions of mechanism of catalytic dehydration that reaction (6) proceeds readily at 200°C, well below the temperature required for ethylene production.

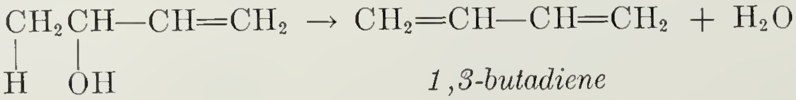
Much earlier, Sabatier and Mailhe[225] carried out the analogous exchange

$$C_2H_5OH + H_2S \rightleftharpoons C_2H_5SH + H_2O$$

Thoria was used as catalyst in order to avoid poisoning by the sulfide. The high temperature employed, 300 to 380°C, was presumably required by H_2S adsorption, or desorption of the thioalcohol, since ethanol can be chemisorbed on thoria at much lower temperatures.

Unsaturated Alcohols

Methyl vinyl carbinol can be dehydrated over thoria[283] at temperatures as low as 90°C. The double bond labilizes the hydrogen of the methyl group:



$$\underset{\displaystyle|\atop\displaystyle H}{CH_2}\underset{\displaystyle|\atop\displaystyle OH}{CH}{-}CH{=}CH_2 \rightarrow \underset{\textit{1,3-butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + H_2O$$

Methanol

Methanol, the first in the series of primary alcohols, is atypical since intramolecular dehydration would lead to the highly reactive methylene radical rather than an olefin. Thus, although the low temperature condensation (250 to 300°) follows the usual pattern, yielding dimethyl ether (Sabatier and Mailhe[223]), the catalysis at high temperatures does not proceed cleanly. Grigorieff[101] obtained mainly formaldehyde and hydrogen in the presence of broken glass at red heat. According to Sabatier and Reid[234] and Topchieva and Ballod[261] the variety of products include C_2H_4, C_2H_6, H_2, CO and CO_2. Thus alumina, although one of the better and more popular dehydration catalysts, is so unspecific as to catalyze dehydration, hydrogenation, polymerization, dehydrogenation and oxidation, providing the temperature is high (400°C in this instance).

Condensation (Intermolecular Dehydration)

Perhaps the most striking feature of intermolecular dehydration[2], relative to the more common intramolecular dehydration, is that the temperature required is substantially lower; for ethanol, about 100°C lower, and there are occasional more remarkable examples. Methylethyl ketone for example undergoes condensation on thoria at room temperature[283]. Considerable significance may be attached to these observations. If the elements of water are to be drawn from two hydroxyl groups (rather than from a hydroxyl group and a methyl group) much less activation is required. This was the primary evidence to show that in the dehydration of primary alcohol to olefins the most difficult step energetically is the removal of hydrogen from a carbon atom. Subsequent confirmation by exchange studies has already been mentioned.

In practice the temperature employed in condensation reactions is raised as high as possible, compatible with little production of olefin or other undesired products, in order to accelerate the desorption of water from the catalyst. Condensation at 100°C for example would be too slow to be attractive commercially.

In connection with the dehydration of ethanol we have already mentioned condensation to yield an ether. Closely related is the esterification of alcohol with acetic acid (Sabatier and Mailhe[227]):

$$CH_3COOH + HOC_2H_5 \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Other simple condensations can be used in the preparation of amines (Sabatier and Mailhe[222]), e.g.:

$$C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O$$

In a more elaborate type of condensation two molecules of alcohol combine with one of aldehyde or ketone to yield an acetal:

$$2C_2H_5OH + OCHCH_3 \rightarrow (C_2H_5O)_2CHCH_3 + H_2O$$

Geuther[92] (in 1863) used as catalyst glacial acetic acid or HCl while for the same reaction Sabatier and Mailhe[234] found alumina to be satisfactory. Later it was shown by Heinemann, Wert and McCarter[107a] that an acetal was formed in 52 per cent yield by percolating ethanol and propionaldehyde through a bed of bauxite at 25°C, while at 50°C no acetal could be detected.

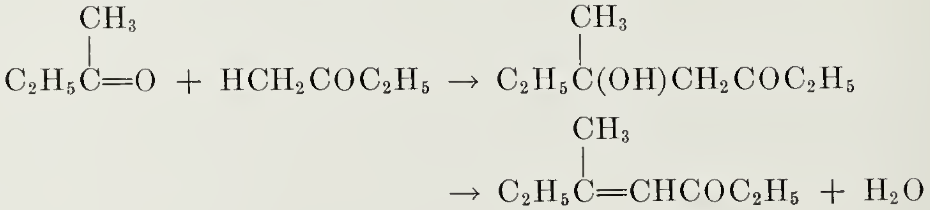
An important, if less typical, condensation occurs in the process of crotonization, in which the participants are two molecules of aldehyde or ketone (Sabatier and Mailhe[234]).

$$CH_3CHO + CH_3CHO \rightarrow \underset{(\textit{crotonaldehyde})}{CH_3CH{=}CHCHO} + H_2O$$

Here one of the methyl groups must be activated and the reaction is correspondingly slow. It is generally supposed that the reaction proceeds by way of an aldol condensation (see for example Gorin[93a]):

$$CH_3CHO + HCH_2CHO \rightleftharpoons CH_3CH(OH)CH_2CHO$$

In spite of the need to activate hydrogen of a methyl group, the apparently analogous condensation of methylethyl ketone will proceed on thoria even at low temperatures[283], presumably as follows:



$$C_2H_5\overset{CH_3}{\overset{|}{C}}{=}O + HCH_2COC_2H_5 \rightarrow C_2H_5\overset{CH_3}{\overset{|}{C}}(OH)CH_2COC_2H_5$$

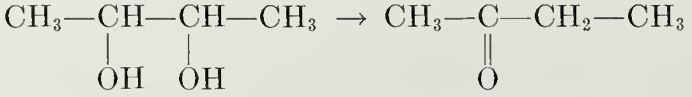
$$\rightarrow C_2H_5\overset{CH_3}{\overset{|}{C}}{=}CHCOC_2H_5 + H_2O$$

*3-methyl-3-heptenone-5**

Further investigation is desirable to determine whether, because of its basicity, suitably prepared thoria[282] is exceptionally active in catalyzing aldol condensations; also, whether it is unusually effective in activating the methyl group during intramolecular dehydration, e.g., of ethanol to ethylene.

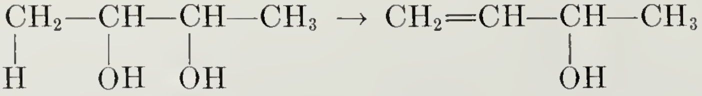
2,3-Butanediol

Here, within the one molecule, elimination of water may occur either between two hydroxyl groups—Eq. (7)—or between a hydroxyl and a methyl group—Eq. (8):



$$CH_3{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 \rightarrow CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}CH_3 \tag{7}$$

methylethyl ketone



$$\underset{H}{\underset{|}{CH_2}}{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 \rightarrow CH_2{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 \tag{8}$$

methyl vinyl carbinol

Unlike the situation in ethanol dehydration, the reactions cannot be consecutive—the more readily formed methylethyl ketone cannot be converted to methyl vinyl carbinol or to butadiene. If either of the latter products are required it is therefore necessary to select a catalyst which is specific for their formation, with virtually complete suppression of reaction (7). That such a degree of specificity can be attained in dehydration catalysis, and in

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* It is not known with certainty whether the double bond is in the 2- or the 3-position.

spite of a much more favorable[282] free energy change for (7), demonstrates that theories for the mechanism of dehydration which confine themselves to the dehydration characteristics of a single catalyst are of limited value. The high degree of specificity also suggests that the two types of catalysts differ markedly in their structure.

Butadiene Production

Special attention will be given to dehydration reactions which lead to butadiene, both because of their economic importance and because they illustrate very well that some of the severe problems in specificity and multiple catalysis can be solved when the need is great. In one respect we cannot be proud of the solutions which were obtained—many of the answers were found empirically. We still do not understand fully the nature of the processes which were evolved. Without that understanding, the experience gained in their development is not readily applied to the development of new ones.

Butadiene is easily prepared by dehydration of methyl vinyl carbinol[206, 283]. Large-scale production of the latter however has not eventuated. During World War II attempts* were made to base butadiene production on 2,3-butanediol, which can be produced economically by a fermentation process. The diol can be dehydrated to butadiene[282]. Pilot-plant operation of the fermentation was interrupted by bacteriophage. Meanwhile improvements in the yield of diene from ethanol led to large-scale operation of the Lebedev and related processes, which inhibited further work with 2,3-butanediol.

A considerable amount of butadiene has been produced, especially in Germany, by dehydration of the 1,3 and 1,4-diols, whose conversion to diene requires a lesser degree of specificity than that of the 2,3-isomer.

Butadiene From 1,3-Butanediol. 1,3-Butanediol is readily dehydrated to 1,3-butadiene by a variety of catalysts described in the patent literature dating back to 1914 or earlier. Kyriakides[165] obtained butadiene by passing the diol over kaolin at 380 to 400°C and suggested the mechanism

$$\begin{tikzcd} CH_3CHOHCH_2CH_2OH \arrow[r] & CH_3CH{=}CHCH_2OH + H_2O \arrow[d, "\textit{crotyl alcohol}"] \\ & CH_2{=}CHCH{=}CH_2 + H_2O \end{tikzcd} \tag{9}$$

Later the I. G. Farbenindustrie A.-G.[120] used red phosphorus on pumice to increase the yield to a claimed 99 per cent at 300°C, or phosphates such as

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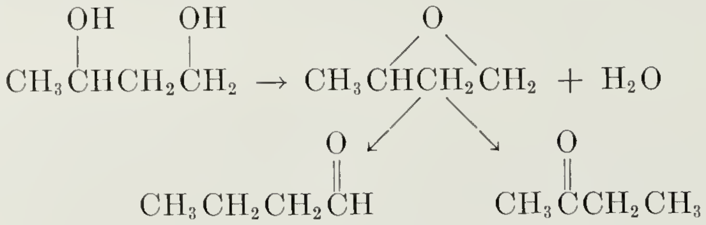
* Much of the work was described in confidential wartime reports. A brief description including bibliography and a list of U.S. and Canadian agencies which collaborated in the investigations is given by Fisher.[84b]

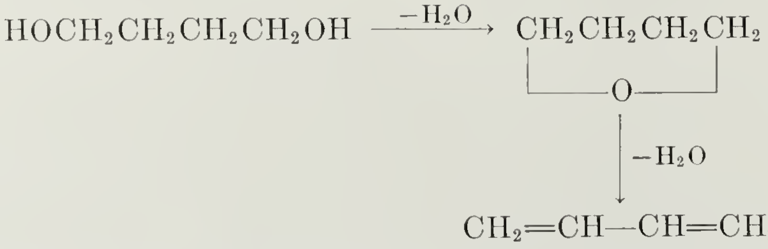
NaH_2PO_4, giving a yield of 85 to 90 per cent at 220°C[123]. During World War II the German production from 1,3-butanediol* was based on a catalyst consisting of H_3PO_4 and NaH_2PO_4 on coke, and an operating temperature of 275 to 280°C, with a diene yield of 81 per cent[117]. Some of the more interesting recent catalysts are boron phosphate, and solid synthetic resin-type acids [formed for example by condensing HCHO, C_6H_5OH and $HOC_6H_4SO_3H$] which lower the temperature required to 170°C.

If the 1,3-diol is dehydrated by 50 per cent sulfuric acid in the cold, the products are *n*-butyraldehyde and methylethyl ketone (Kadiera[141]). The reaction possibly proceeds by way of an oxide (Lieben[170]; Kyriakides[165]). A similar view is expressed by Beati and Mattei[15] for the pentanediols. We may therefore suppose that the heterogeneous gas phase dehydration of 1,3-butanediol on a catalyst such as alumina will tend to follow the course



from which it is seen that in choosing a catalyst for dehydration of the diol to crotyl alcohol, the object is to prevent interaction of the two hydroxyl groups and to activate hydrogen on the second carbon atom. Presumably the successful phosphate catalysts adsorb 1,3-butanediol by way of the hydroxyl on the 3-carbon atom, and with the other hydroxyl group sufficiently remote from the surface to prevent chemical interaction. The crotyl alcohol which desorbs may then be readsorbed at the remaining hydroxyl for dehydration to butadiene, a reaction for which no great specificity is required.

Butadiene From 1,4-Butanediol†. The mechanism here is particularly interesting in that the dehydration definitely proceeds via an oxide (tetrahydrofurane), which becomes the principal product at sufficiently high space velocities.



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* The product of hydrogenating aldol produced by condensation of acetaldehyde.

† The product of hydrogenating 1,4-butynediol produced by condensation of acetylene with formaldehyde.

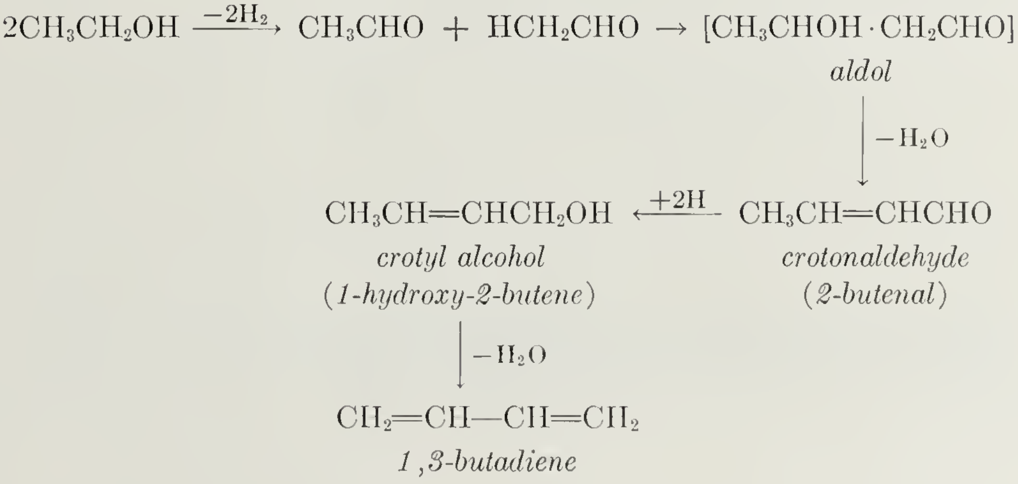
As operated at Ludwigshafen[117] the conversion to diene was deliberately limited to about 20 per cent per pass, the tetrahydrofurane being recycled. Essentially the same phosphate-on-carbon catalyst was used as for the 1,3-diol, at 285 to 295°C and with a yield of 89 per cent.

The Lebedev Process. Because of its strategic and economic importance before and during World War II, the production of butadiene from ethanol has been the subject of detailed investigation. Although it is not a straightforward dehydration process, a mixed dehydration-dehydrogenation catalyst usually being employed, some of the experimental studies have made valuable contributions to our knowledge of dehydration.

In 1904, Gdanovich[90] passed ethanol over aluminum powder at 600°C and observed that a little butadiene was produced along with acetaldehyde and ethylene. Filippov[84a] later showed that ether gave better yields than ethanol.

World War I saw various efforts being made to synthesize rubber. Kyriakides (1914) showed that isoprene, the basic unit of natural rubber, could be prepared by passing 1,2-epoxy-2-methylbutane over kaolin at 440 to 460°C at reduced pressure[164]. Alternatively, 2-methyl-1,3-butanediol could be dehydrated over aluminum phosphate at 450°C and 15 to 20 mm Hg pressure[165]. Shortly afterward Ostromislenski and Kelbasinski[198] obtained 1,3-butadiene by condensing ethanol and acetaldehyde over impure alumina (with pure alumina some $CH_2{=}C{=}CHCH_3$ was formed). Butadiene proved to be the most convenient monomer for preparation of rubber-like materials and from this time on was the subject of intensive research.

The principal credit for the development of the Ostromislenski reaction into an industrial process for butadiene production goes to Lebedev. According to an early patent[167], ethanol was passed over a single catalyst ($ZnO + Al_2O_3$) at 400°C and preferably under reduced pressure. As described by Gorin[94] and by Kagan *et al.*[142], the Lebedev process is made up of the steps



$$2CH_3CH_2OH \xrightarrow{-2H_2} CH_3CHO + HCH_2CHO \rightarrow [\underset{\textit{aldol}}{CH_3CHOH\cdot CH_2CHO}]$$

$$[CH_3CHOH\cdot CH_2CHO] \xrightarrow{-H_2O} \underset{\substack{\textit{crotonaldehyde}\\ \textit{(2-butenal)}}}{CH_3CH{=}CHCHO}$$

$$\underset{\substack{\textit{crotonaldehyde}\\ \textit{(2-butenal)}}}{CH_3CH{=}CHCHO} \xrightarrow{+2H} \underset{\substack{\textit{crotyl alcohol}\\ \textit{(1-hydroxy-2-butene)}}}{CH_3CH{=}CHCH_2OH}$$

$$CH_3CH{=}CHCH_2OH \xrightarrow{-H_2O} \underset{\textit{1,3-butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

a big part of the evidence being that addition of acetaldehyde, aldol or crotonaldehyde into the feed ethanol increases the yield of butadiene. There is also some evidence that the alcohol acts as a donor of atoms which hydrogenate crotonaldehyde. In turn, a dehydrogenation, a condensation, a hydrogenation and a dehydration take place on the one catalyst. In spite of the difficulties in preparing an appropriate mixed catalyst, yields of 50 to 70 per cent have been claimed. A simpler mechanism was put forward by Quattlebaum, Toussaint and Dunn[207]:

$$2CH_3CHO \xrightarrow{-H_2O} CH_3CH{=}CHCHO$$

$$\Big\downarrow +C_2H_5OH$$

$$CH_2{=}CHCH{=}CH_2 + CH_3CHO + H_2O$$

In the United States, attempts were made to improve the yield by using two successive catalysts (see Corson *et al.*[51]). If, however, the Gorin[94] mechanism is correct in showing the two dehydration steps as separated by steps requiring a hydrogenation-dehydrogenation catalyst, a two-stage process does not remove the need for a mixed catalyst.

As might be expected, some of the ethanol is dehydrated to ethylene and ether. In addition, the reaction products contain acetaldehyde, 2-butene, propylene, acetic acid, ethyl acetate and 1,1-diethoxyethane along with smaller amounts of methylethyl ether, crotyl alcohol, butanol, butyraldehyde, methylethyl ketone, pentadienes, pentenes, hexaldehyde, hexadienes and hexenes. Crotonaldehyde is presumably too reactive to escape in significant quantity from the reaction zone.

Possibly a little of the butadiene obtained in the Lebedev process results from a mechanism different from the one shown above, and applicable to Ostromislenski's conditions[198]. It will be remembered that the latter obtained butadiene by condensing ethanol with acetaldehyde over alumina. One of the conceivable reaction sequences is

$$CH_2{=}CHOH_a + HCH_2CH_2OH_a \rightarrow CH_2{=}CHCH_2CH_2OH$$

adsorbed acetaldehyde and ethanol — *1-hydroxy-3-butene*

$$\Big\downarrow -H_2O$$

$$CH_2{=}CH{-}CH{=}CH_2$$

However, the presence of 1,2-butadiene, which he observed as a by-product when pure alumina was used as catalyst[198], and his claim that 1,3-butanediol and crotyl alcohol are intermediates[197], suggest as the main reactions

$$2CH_3CHO \rightarrow CH_3CHOHCH_2CHO \xrightarrow{2H}$$

$$\underset{\textit{1,3-diol}}{CH_3CH(OH)CH_2CH_2OH} \xrightarrow{-H_2O} \underset{\textit{crotyl alcohol}}{CH_3CH{=}CHCH_2OH} \xrightarrow{-H_2O}$$

$$CH_3CH{=}C{=}CH_2 \rightarrow CH_2{=}CHCH{=}CH_2$$

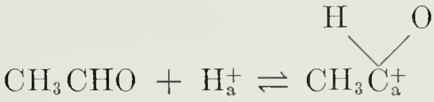
and possibly to some extent

$$CH_3CHO + HCH_2CH_2OH \rightarrow \underset{\textit{1,3-diol}}{CH_3CHOHCH_2CH_2OH} \rightarrow$$

$$\underset{\textit{crotyl alcohol}}{CH_3CH{=}CHCH_2OH} \rightarrow CH_3CH{=}C{=}CH_2 \rightarrow CH_2{=}CHCH{=}CH_2$$

Also a little dehydration of diol to methyl vinyl carbinol, and thence to 1,3-butadiene, probably occurs.

The failure to detect 1-hydroxy-3-butene as an intermediate suggests that acetaldehyde is adsorbed by the process



$$CH_3CHO + H_a^+ \rightleftharpoons CH_3\overset{H\ \ OH}{C_a^+}$$

rather than

$$CH_3CHO \rightleftharpoons CH_2{=}CHOH \rightleftharpoons CH_2{=}\overset{+}{C}H_a + \overset{-}{O}H_a$$

There is clearly a need for more emphasis on the investigation of catalytic condensation (as opposed to intramolecular dehydration).

Since pure alumina is a weak hydrogenation-dehydrogenation catalyst, crotonaldehyde is an unlikely intermediate under Ostromislenski's conditions. It should also be noticed that adding methyl vinyl carbinol to the ethanol feed in the Lebedev process would undoubtedly increase the yield of diene as does crotonaldehyde and acetaldehyde. Although Gorin, Charskaya and Bochkareva[94a] appear to have shown that 1,3-butanediol is not an important intermediate in the Lebedev process, the proof does not apply necessarily to the diene synthesis carried out by Ostromislenski.

If the crotonaldehyde mechanism can be bypassed, for example by inhibiting aldol formation, a two-stage process becomes more attractive, the first stage employing a purely dehydrogenation and the second a purely dehydrating catalyst.

Condensation may also be a significant step in another multiple catalysis, the Fischer-Tropsch process for synthesis of higher hydrocarbons from CO and H_2[284].

Practical Details. Descriptions of catalyst preparation, and details of the commercial production of butadiene from ethanol in the United States, can be found in papers by Toussaint, Dunn and Jackson[269]; Kampmeyer and Stahly[144]; and Corson *et al.*[51]. The best yield mentioned by the latter is 56 per cent at 400 to 425°C for the 1-stage process, and the best catalysts are silica-magnesia-tantala or silica-magnesia-chromia. They believe that the silica component is responsible for acetaldehyde condensation while the tantala catalyzes the removal of an oxygen atom from crotonaldehyde.

For the 2-step process the best yield of butadiene was 64 per cent at 350°C, and approximately this figure seems to have been attained in commercial production.

For a more detailed review of butadiene production from alcohol the reader is referred to Toussaint and Marsh[270].

MECHANISM OF DEHYDRATION

From the examples given in the previous section, the reader will have gathered that the general pattern of dehydration catalysis consists in the removal from a reactant molecule of a hydroxyl group, and the removal of a proton from the same or a second molecule. Exchange studies as well as low-temperature condensation reactions indicate that removal of the hydroxyl group requires little activation when the catalyst is appropriate. Removal of the proton is usually, if not always, more difficult. How difficult is determined by the nature of the group from which it is abstracted (e.g., $—CH_3$, $—CH_2—$, $—NH_2$, etc.) and by the nature of the groups in close proximity (e.g., presence of a double bond).

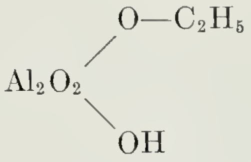
In discussing the mechanism of dehydration, there has been a tendency to take as evidence the results obtained with a single reactant, and a single catalyst. Almost all deductions regarding mechanism have hinged on the relationship between ether and ethylene production from ethanol on alumina, and to a lesser extent the tendency of some oxide catalysts to dehydrogenate rather than dehydrate alcohols. With such a narrow view there is little likelihood of reaching an explanation of dehydration reactions in general. On the other hand, not all of the evidence required for a broad approach is yet available. A notable example of the deficiencies is the lack of kinetic results of sufficient detail to indicate whether ether formation results from the collision of two adsorbed molecules of alcohol or one adsorbed and one gaseous. Another obvious need is for kinetic studies with oxide catalysts as compared with phosphate, sulfate, etc.

In 1904 Ipatieff[128] showed that both ether and ethylene occurred as products of ethanol dehydration, possibly as consecutive reactions, and that an increase in pressure favored ether formation. He demonstrated the reversibility of the dehydration to ether and also showed that alumina must contain a certain minimum amount of water if it is to be an effective dehydration catalyst. The latter concept was also put forward in 1903 by Sabatier[234].

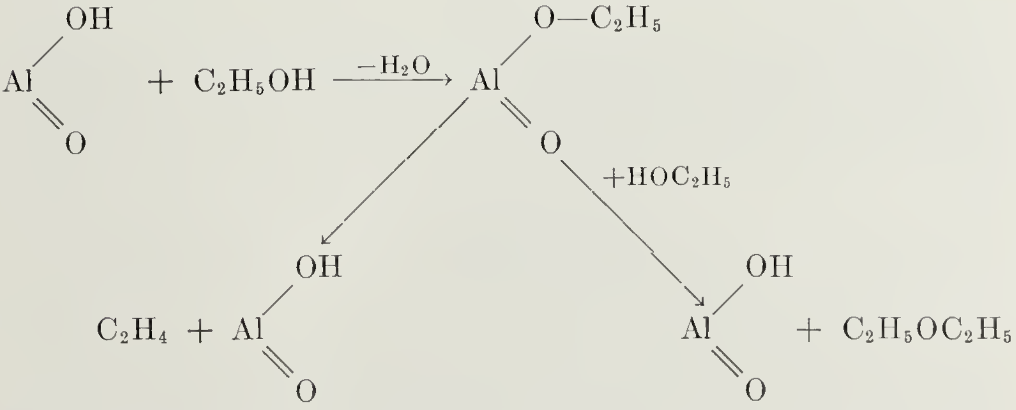
There have been many suggestions that ethanol reacts first with the catalyst to form an alcoholate or related complex and that this decomposes to yield ether or olefin. Possibly the origin of these ideas lies in the work of Tishchenko (1899)[259] on the decomposition of aluminum alcoholates, but the fundamental concept was made clear in 1851 by Williamson[281]. He showed that potassium ethylate reacts with ethyl iodide to yield diethyl ether, then went on to propose that when ethanol is dehydrated in the presence of sulfuric acid there are two distinct steps, the first giving ethyl hydrogen sulfate and the second giving ether, with regeneration of the catalyst:

$$C_2H_5OH + H_2SO_4 \xrightarrow{-H_2O} C_2H_5HSO_4 \xrightarrow{+C_2H_5OH} C_2H_5OC_2H_5 + H_2SO_4$$

For the reaction on alumina, Senderens[239a] suggested as intermediate a surface complex which he wrote



later criticized by Ipatieff[129]. The latter author proposed



It will be clear that there are three alternatives for the dehydration of ethanol to ether and ethylene, which may be described as "consecutive," "parallel" and "simultaneous" and are indicated respectively by the following schemes:

$$\text{ethanol} \rightleftharpoons \text{ether} \rightleftharpoons \text{ethylene} \qquad (10)$$

$$\text{ethanol}\begin{cases}\rightleftharpoons \text{ether}\\ \\ \rightleftharpoons \text{ethylene}\end{cases}\qquad (11)$$

$$\begin{tikzcd}
 & \text{ether} \arrow[dr, shift left] \arrow[dl, shift left] & \\
\text{ethanol} \arrow[ur, shift left] \arrow[rr, shift left] & & \text{ethylene} \arrow[ll, shift left] \arrow[ul, shift left]
\end{tikzcd}\qquad (12)$$

For 50 years from the time when Ipatieff[128] discovered that ether as well as ethylene could result from ethanol dehydration, there have been sporadic attempts to prove by simple kinetic studies the correctness or otherwise of the "consecutive" mechanism, favored by most of the early workers.

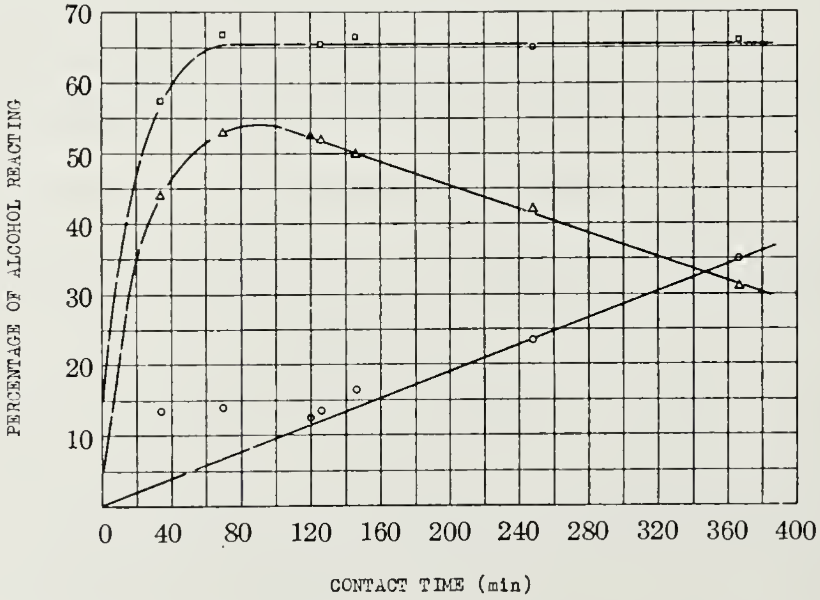


Figure 2. Dehydration of ethanol at 300°C as a function of contact time (expressed as length of run in minutes). Top curve, total percentage of alcohol decomposed. Middle curve, percentage of alcohol converted to ether. Bottom curve, percentage of alcohol converted to ethylene. (From Pease and Yung[201])

It was shown by Pease and Yung[201] that as the contact time is increased, during dehydration of ethanol, the conversion to ether increases to a maximum and then declines (Figure 2). They concluded that although the consecutive scheme applies to their results, direct dehydration of ethanol and ethylene is possible. They showed that dehydration of alcohol to ether is reversible. In a later paper[202] they described quantitative work, on the equilibrium

$$\underset{\textit{ethanol}}{\mathrm{ROH}} \rightleftharpoons \underset{\textit{ether}}{\mathrm{ROR}} + \mathrm{H_2O} \qquad (13)$$

which set the limit of conversion in the direction left to right at about 62 per cent at 275°C (estimated subsequently by Clark, Graham and Winter[49] to be about 85 per cent at 250°C; experimentally they obtained 80.8 per cent). From Pease and Yung's work it is evident that if ROR is passed over a catalyst to give $C_2H_4 + H_2O$, there will be a tendency toward establishment of the equilibrium (13); i.e., some of the water formed along with C_2H_4 will react with ROR to give ROH.

The inadequacy of the consecutive scheme was made clear by Adkins and Perkins[3]. Working with butanol dehydration they found that the ether could not be an intermediate in the formation of any considerable amount of the butene obtained. Shortly afterward, Adkins, with Bischoff[22], confirmed his previous finding by showing that whereas ethanol and ether have about the same stability on Al_2O_3, the ether is much the more stable on TiO_2 and is therefore not a necessary intermediate in olefin formation.

A significant step toward the understanding of dehydration catalysis in general was made by Dohse[64] when he was able to show that the decomposition of isopropanol over alumina was retarded by a product (water). When the retarding effect of water was eliminated, the dehydration of the alcohol to the olefin was zero order.

Resolution of the problem of which of the 3 alternatives (10), (11), and (12) is correct, and at the same time a realization of why a clear-cut decision between them was not readily obtained, originated in the concept of carbonium ion formation at the catalyst surface (discussed in detail later). The gas phase dehydration of an alcohol by a solid catalyst by way of a carbonium ion was clearly described by Whitmore[279] in 1932. Further experimental evidence to support the hypothesis was provided by Henne and Matuszak[108] in a study of the dehydration of 10 secondary and 2 tertiary alcohols. The nature of the olefin produced and the double bond shifts were in accord with Whitmore's concept.

Whitmore's hypothesis implied that the dehydration equilibria should be written (as given later by Brey and Krieger[37]):

$$\begin{tikzcd}
& C_2H_5OC_2H_5 \arrow[d, shift right] & \\
C_2H_5OH \arrow[r, shift left, "-\bar{O}H"] & C_2H_5^+ \arrow[l, shift left] \arrow[u, shift right, swap, "+ C_2H_5\bar{O}H - H^+"] \arrow[r, shift left, "+H^+"] & C_2H_4 \arrow[l, shift left]
\end{tikzcd}$$

in which the carbonium ion $C_2H_5^+$ may be formed when either ethanol or ether is chemisorbed on the catalyst. The "simultaneous" mechanism is no more than a reflection of the identity of adsorbed ethanol and ether (or identity of one of several adsorbed forms of each) and the reversibility of all of the reactions concerned in the over-all catalysis. Brey and Krieger make the point which we shall discuss in detail later that the rate-determining step in dehydration of ethanol on alumina is removal of a proton from the methyl group of adsorbed alcohol.

Theoretical considerations in favor of an ionic activated complex at the surface were brought forward by Eyring, Hulburt and Harman[81] in 1943.

When interpreting his results on 1-dodecanol dehydration Walker (1949) was unable to determine which of the three alternative schemes was applicable, but he clearly recognized that the "simultaneous" mechanism might prove to be correct[276]. In 1951 Balaceanu and Jungers[12] reinvestigated the kinetics of ethanol and ether dehydration over alumina, from which they deduced the following sequence of reactions:

$$\begin{tikzcd}
2C_2H_5OH \arrow[r, "-H_2O"] & C_2H_5OC_2H_5 \arrow[r] & C_2H_5OH + C_2H_4 \arrow[d, "-\frac{1}{2}H_2O"] \\
 & & \frac{1}{2}C_2H_5OC_2H_5
\end{tikzcd}$$

At temperatures of 260 to 400°C the direct dehydration of ethanol to C_2H_4 was claimed to play a secondary role.

A further investigation was carried out by Topchieva and Yun Pin[262, 263]. Summarizing their results up to 1955, they concluded that they were best described by the "simultaneous" mechanism. They went on to propose a reaction scheme almost identical with that given by Ipatieff[129]. This differs from the Whitmore hypothesis, as written by Brey and Krieger[37], in showing adsorbed alcohol as covalently rather than ionically bonded to the catalyst.

Topchieva and Yun Pin claimed to have shown that the kinetics of dehydration of ethanol on Al_2O_3 are largely independent of the presence of SiO_2 and Na^+, and that the "acid" centers on an alumino-silicate catalyst are inactive or nearly so for dehydration catalysis[264, 265]. They reiterated earlier suggestions (e.g., Eucken and Wicke[80]) that the active sites for dehydration are OH groups at the surface of the catalysts and that only one such site is involved per molecule dehydrated.

Bremner[35] reviewed the carbonium ion hypothesis in 1948, supporting Whitmore's conclusions and adding further examples of reactions (e.g., self-saturation) which follow the predictions of the hypothesis. Bremner also suggested that the adsorbed carbonium ion is formed by way of an oxonium ion (conjugate acid) which results from donation of a proton by the catalyst to the alcohol molecule:

$$ROH + H_a^+ \rightarrow R\overset{+}{O}H_{2_a} \rightarrow R_a^+ + H_2O_{a\ \mathrm{or}\ g}$$

Subscripts a and g refer to the adsorbed and the gaseous state, respectively. Some support for adsorption processes of this type can be gleaned from Eischens and Pliskin's[72a] review of infrared spectra of adsorbates.

Bremner's views were expanded by Dowden[67], with the suggestion that insulator catalysts depend for their activity on the presence at the surface of cation vacancies, and to a lesser extent, anion vacancies. Hauffe[107] has recently discussed dehydration in terms of the reaction of isopropanol on zinc oxide. He does not believe that the positions of the zinc and the oxygen ions at the surface have any appreciable influence upon the selectivity of the catalysts for dehydration of the alcohol. Instead, he prefers to think that the selectivity is determined by the Fermi potential of the electrons of the semiconducting catalyst and the height of the potential barrier which the electrons have to overcome in the exchange process.

An important rôle has also been attributed by Schwab *et al.*[237] to the Fermi potential in the dehydration of formic acid on $Ni—Al_2O_3$.

Carbonium Ion Mechanisms

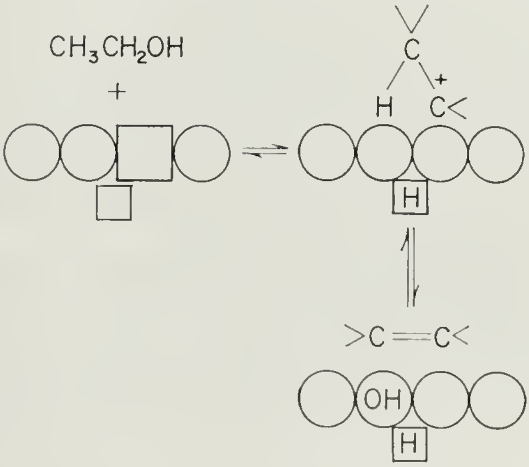
Olefin Formation. In its present form Whitmore's hypothesis, after modifications by Bremner and Dowden, may be described as follows, using ethanol as type-reactant:

$$\begin{array}{ccc} C_2H_5OH_g + H_a^+ & \rightleftharpoons & C_2H_5\overset{+}{O}H_{2_a} \\ & & \big\updownarrow\ -H_2O_a \\ H_2C{=}CH_{2_g} & \xrightleftharpoons{-H_a^+} & \overset{+}{C}H_3CH_{2_a} \end{array}$$

The adsorbed proton forms part of an OH group of the catalyst surface. With the subscripts removed, the scheme is applicable to liquid phase catalysis by strong acids. On Taft's view the final step in the acid-catalyzed process takes place via an unstable π complex[253]; if true also for the gas phase catalysis, we may rewrite the desorption of ethylene as

$$H_2C{=}CH_{2_g} \xrightleftharpoons{-H_a^+} [H_2C \xrightleftharpoons{H^+} CH_2]_a \rightleftharpoons H_3C{—}\overset{+}{C}H_{2_a}$$

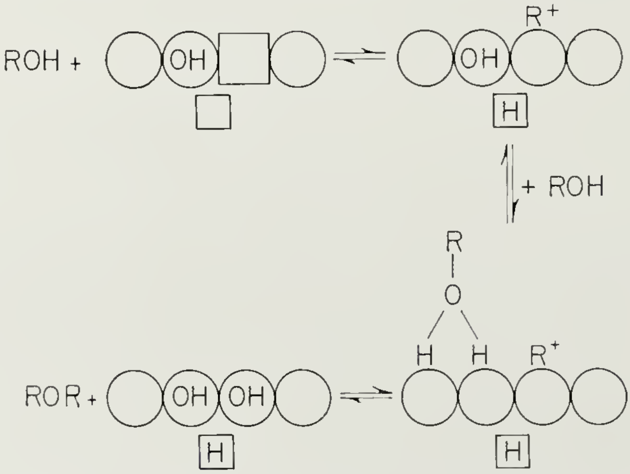
At high temperatures the formation of the oxonium compound by proton addition to the alcohol is possibly bypassed. Above the temperature at which ether ceases to be an appreciable fraction of the products, we may regard the alcohol as dissociating directly into the adsorbed carbonium ion and a hydroxyl ion which occupies an anion vacancy at the surface:



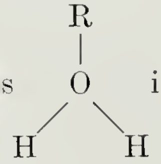
(14)

The circles represent filled lattice sites while the squares represent vacancies, the smaller squares being cation vacancies. The carbonium ion is regarded as attracted by the cation vacancy, and its migration across the surface depends upon migration of the vacancy. In the case of ethanol dehydration to ethylene it is not clear whether the migration of cation vacancies plays an important role in the catalytic process. It is possible, however, that desorption of ethylene and of water is thereby facilitated.

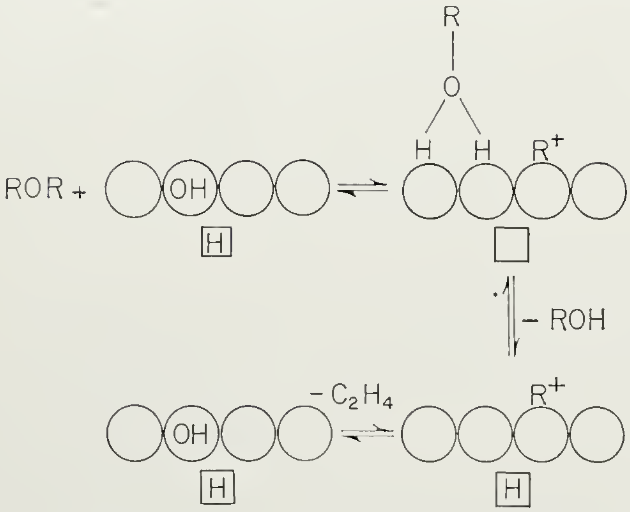
Ether Formation. Whether the ether molecule results from collision of adsorbed alcohol with gaseous alcohol, or whether from collision of two adsorbed molecules, has not been definitely established. The essential features of the reaction are probably contained in the scheme:



(15)

Two kinds of adsorbed ethanol are shown—the carbonium ion R^+ and the oxonium ion, which is written here as  in order to suggest that the RO group is held by two hydrogen bonds to oxygen ions of the catalyst surface. It is not essentially different from Bremner's[35] $\overset{+}{\mathrm{ROH_2}}$ or de Boer's $\mathrm{R{-}\overset{\delta-}{O}{-}\overset{\delta+}{H}}$ (dipole adsorption). In deference to Bremner[35] and Dowden[67], the first step in the above process may be considered to take place by way of the oxonium ion rather than directly to R^+.

Ether Dehydration. At high temperatures (above 350°) the concentration of OH groups at the catalyst surface will be too low to permit much desorption of alcohol. But at lower temperatures there will be a tendency to follow the course:



(16)

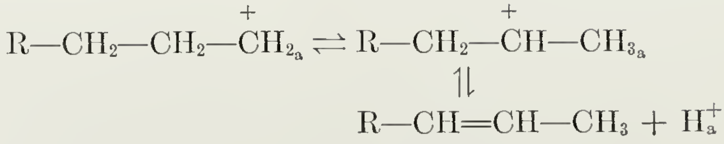
In other words since desorption of alcohol held as $R\overset{+}{O}H_2$ requires less activation than dehydration of adsorbed ethanol, and since at moderate temperatures the catalyst still retains a high concentration of OH groups, a molecule of ethanol is rapidly desorbed following upon the adsorption of ether. At long contact times some ethanol will, of course be readsorbed and dehydrated.

In order to represent adequately the large variety of experimental results which have been described, it is necessary to write all of the reactions as reversible, including the desorption of ethylene. During the catalytic hydration of ethylene to ethanol, ethylene can reasonably be assumed to be chemisorbed by reacting with an OH group of the catalyst to yield an adsorbed carbonium ion. All of the reactants and products in alcohol dehydration have in common an identical adsorbed species.

Isomerization. During the lifetime of the carbonium ion which results from adsorption of one of the more complex alcohols, there is a tendency for it to isomerize[83] to the form which has the greatest resonance energy, particularly if the catalyst is acidic (Smith[247]). Dehydration of an alcohol may therefore lead to a mixture of olefins. Henne and Matuszak[108] have shown that their nature is largely predictable. The first-formed olefin results from proton elimination from a carbon atom adjacent to the carbonium carbon, with double bond formation between the two:

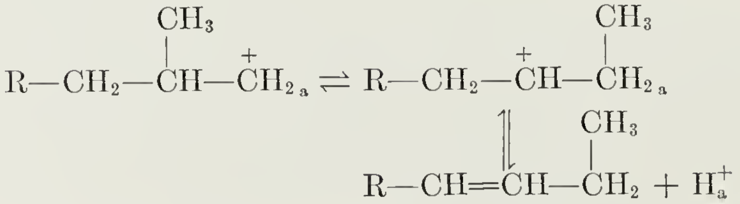
$$R—CH_2—CH_2—\overset{+}{C}H_{2_a} \rightleftharpoons R—CH_2—CH{=}CH_2 + H_a^+$$

Isomerization occurs by addition of H_a^+ or $\overset{+}{C}H_{3_a}$ in a new position subsequent to formation of the first olefin. Whitmore[279] and later Dowden[67] assumed a prior isomerization, for example:



$$\begin{array}{l} R{-}CH_2{-}CH_2{-}\overset{+}{C}H_{2_a} \rightleftharpoons R{-}CH_2{-}\overset{+}{C}H{-}CH_{3_a} \\ \qquad\qquad\qquad\qquad\qquad\qquad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\qquad\qquad\qquad R{-}CH{=}CH{-}CH_3 + H_a^+ \end{array}$$

or



$$\begin{array}{l} R{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}H{-}\overset{+}{C}H_{2_a} \rightleftharpoons R{-}CH_2{-}\overset{+}{C}H{-}\overset{CH_3}{\overset{|}{C}}H_{2_a} \\ \qquad\qquad\qquad\qquad\qquad\qquad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\qquad\qquad R{-}CH{=}CH{-}\overset{CH_3}{\overset{|}{C}}H_2 + H_a^+ \end{array}$$

Table 3 is taken from Henne and Matuszak; other examples of isomerization will be found in Tables 1 and 4.

As expected, the extent of isomerization increases with temperature. Musaev and Zizin[190] analyzed the gases obtained by dehydration of 1-butanol and 2-butanol over Al_2O_3 with the result shown in Table 4.

Homogeneous Catalysis and Exchange. Dostrovsky and Klein[66] have studied oxygen exchange between water and either 1-butanol or 2,2-dimethyl-1-propanol in the presence of sulfuric acid at 125°C. Some of the results are summarized in Table 5.

From this work, and from work on the hydration of 1-butene, Dostrovsky and Klein concluded that the exchange takes place during a bimolecular reaction between the solvent and the conjugate acid of the alcohol

$$H_2O^{18} + R\overset{+}{O}H_2 \rightleftharpoons H_2O + R\overset{18}{O}H_2{}^+ \tag{17}$$

This is in preference to the reactions

$$R\overset{+}{O}H_2 \rightarrow R^+ + H_2O$$

$$R^+ + H_2O^{18} \rightarrow R\overset{18}{O}H_2{}^+$$

which are not in accord with the experimental evidence.

A reaction analogous to (17) was suggested for the formation of *n*-alkyl ethers:

$$ROH + R\overset{+}{O}H_2 \rightarrow H_2O + R(\overset{+}{O}H)R$$

presumably followed by

$$R(\overset{+}{O}H)R + H_2O \rightleftharpoons ROR + H_3\overset{+}{O}$$

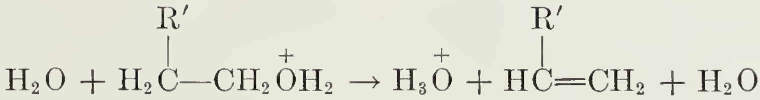
For olefin formation the suggested sequence was

$$ROH + H_3\overset{+}{O} \rightarrow H_2O + R\overset{+}{O}H_2$$

$$R\overset{+}{O}H_2 \rightarrow H_2O + R^+$$

$$R^+ \rightarrow \text{olefin} + H^+$$

or alternatively



$$H_2O + H_2\overset{\overset{R'}{|}}{C}\text{—}CH_2\overset{+}{O}H_2 \rightarrow H_3\overset{+}{O} + H\overset{\overset{R'}{|}}{C}{=}CH_2 + H_2O$$

It is likely that some of the above conclusions can be extended to heterogeneous gas phase catalysis.

Proof. Specific proof of the carbonium ion mechanism is difficult to provide. It will be seen, however, that it is capable of explaining many of the phenomena of dehydration catalysis and to be in reasonable accord with the properties of the catalysts (described below). For reaction in acid solution the carbonium ion hypothesis is widely accepted.

An interesting observation that appears to be in harmony with Whitmore's hypothesis as applied to heterogeneous catalysis is that made by Krylov, Roginskii and Fokina[162] after examining a number of oxide catalysts. Those oxides which form the most stable adsorption bonds with phenol act as dehydrogenation catalysts (as tested with isopropanol) while those which adsorb pyridine act as dehydration catalysts. It is a reasonable assumption that adsorption of pyridine occurs by proton addition to the N atom to give the analog of an oxonium ion.

Chemisorption

Usually the over-all rate of catalytic dehydration depends upon some or all of the factors: rate of conversion reaction on the surface; rate of adsorption of a reactant; and equilibrium concentration of a reactant or product. Both adsorption equilibrium and adsorption rate measurements may be required for a full analysis of the kinetics of the catalysis.

A large number of adsorption isotherms, isobars and heats of adsorption of water, alcohols, ethers and olefins has been published. No attempt to survey will be made since the measurements seldom relate to the conditions of temperature and surface coverage operative during steady-state catalysis. Rather less is known about rates of adsorption and desorption at high temperatures and at surface coverages appropriate to practical catalysis. A suitable though difficult experimental technique based on pressure change has been described[285] but few results are available. The complementary and

TABLE 3. DEHYDRATION ACCOMPANIED BY IZOMERIZATION

(From Henne and Matuszak)[108]

Alcohol	Reagent[a] and Temp. (°C)	Olefin Yields (moles/mole of alcohol)								Residue,[b] (g/mole)
		Total	No Shift		Double-Bond Shift		Carbon Shift			
CCCCCC | O H			CCC=CCC	CC=CCCC	C=CCCCC					
	A 385	0.92	0.71	0.14	0.07					6.1
	AS300	.92	.58	.23	.12					5.1
	Ph250	.86	.62	.19	.06					8.7
	Ph L	.88	.62	.25	.02					8.3
	S L	.81	.61	.20	—					12.3
CCCCCCC | O H			C=CCCCCC	CC=CCCCC	CCC=CCCC					
	A 385	1.00	0.28	0.70	0.02					2.0
	AS300	.94	.11	.52	.31					4.3
	Ph300	.84	.14	.28	.42					2.3
	F 385	.89	.13	.51	.26					5.6
	Ph L	.92	.08	.72	.12					7.0
	S L	.94	.08	.71	.15					1.5
CCCCCCCC | O H			CCC=CCCCC	CCCC=CCCC						
	A 380	0.92	0.46	0.46						8.1
PhCCCC | O H			PhC=CCC	PhC=CCC						
	A 390	0.96	0.36^{b}	0.60^{c}						3.0
	AS300	.91	.68	.23						9.0
CCCCCCC C | O H			CCCCC=CC C	CCCC=CCC C	CCC=CCCC C		(CC=CCCCC C + CCC=CCCC C			

							+ CCC=CCCC C mixed)			
	A 385	0.91	0.46	0.26	0.20		—			8.1
	AS300	.92	.50	.20	.15		0.07			8.5
	Ph250	.82	.14	.20	—		.48			15.0
	Ph L	.87	.58	.16	.11		.03			4.7
	S L	.86	.43	.28	.16		—			10.0
CCCCCCC C | O H			CCCCCC=C C	CCCCC=CC C						
	A 385	0.97	0.36	0.61						3.4
CCCCC C | O H			CCCC=C C	CCC=CC C	CC=CCC C	C=CCCC C	CC=CCC C	CC=CC C C		
	A 380	.87	.44	.44	—	—	—	—		4.7
	AS300	.94	.02	.14	.55	.11	.11	.02		5.0
	Ph250	.87	.06	.12	.46	.12	.12	—		9.3
CCCCC C | O H			CCC=CC C	CC=CCC C	C=CCCC C		CC=CCC C	CC=CC C C		
	A 385	0.93	0.47	0.39	0.08		—	—		3.9
	AS300	.93	.19	.50	.12		0.12	—		4.4
	Ph250	.89	.12	.46	.06		.15	0.09		9.1
	Ph L	.93	.23	.70	—		—	—		10.0
	S L	.86	.14	.70	.02		—	—		8.0
CCCCC C |C O H			CC=CCC C C				CC=CCC CC			
	A 375	0.84	0.72				.12			10.0
	A 350	.89	.76				.13			8.0

TABLE 3—*Continued*

Alcohol	Reagent[a] and Temp. (°C)	Olefin Yields (moles/mole of alcohol)								Residue[d], (g/mole)
		Total	No Shift		Double-Bond Shift		Carbon Shift			
C CCCCCC C | O H			C CCC=CCC C	C CCC=CCC C			C=CCCCC CC	CC=CCCC C C	CCC=CCC CC	
	A 350	0.32	0.09[b]	0.06[c]			0.17	—	—	81.4
	A 375	.90	.36	.09			.40	0.05	—	14.0
	A 385	.79	.33	.14			.19	.14	—	15.6
	A 400	.89	.40	.04			.40	.04	—	16.0
	AS300	.64	.12	—			.12	.24	0.10	39.4
	Ph250	.89	—	—			.22	.22	.30	9.4
	Ph L	.38	—	—			.08	.25	.02	67.2
	S L	.67	.10	—			.10	.39	.10	24.6
C CCCC | O H			C=CCC C	CC=CC C	CCC=C C					
	A 150	0.73	0.29	0.44	—					15.3
	A 200	.86	.18	.64	0.04					3.4
	A 250	.88	.27	.53	.08					2.6
	A 300	.93	.30	.55	.09					1.3
	A 350	.93	.35	.47	.11					2.2
	A 400	.92	.22	.56	.14					2.6
CC CCCCC C | O H			CC CCC=CC C				CC C=CCCC C			
	A 260	0.51	0.21				0.31			27.0

[a] A = alumina; AS = aluminum sulfate; F = fluoridin; Ph = phosphoric acid; S = sulfuric acid; L = liquid phase.

[b] Low boiling isomer.

[c] High boiling isomer.

[d] Residue: in most cases, it was mainly unreacted carbinol. On phosphoric acid at 250° or higher, it was mostly polymerized olefins.

less troublesome method[277] based on change in electrical conductivity of the catalyst has been applied less to dehydration than to dehydrogenation catalysts.

It has been known for many years that in a flow-system, conversion of ethanol to ether is detectable at temperatures down to about 180°C. We may reasonably assume that the ether formation is preceded by chemisorption of the ethanol. With the more reactive alcohols chemisorption is detectable at much lower temperatures. 2-Propanol is noticeably dehydrated to the ether at 100°C (Nekrasov and Krentsel[192]) and to propene at 82°C if low pressures are employed (Balandin and Vasserberg[13]). The unsaturated alcohol methyl vinyl carbinol is slowly dehydrated on thoria to 1,3-butadiene at 90°C (Winfield[283]), and there is no reason to doubt that chemisorption is involved. In the same paper it was concluded that methylethyl ketone can be slowly chemisorbed on thoria at 25°C.

TABLE 4. EFFECT OF TEMPERATURE ON IZOMERIZATION DURING DEHYDRATION
(From Musaev and Zizin[190])

Reactants	Temp. (°C)	Products		
		$CH_3CH_2CH{=}CH_2$	*cis*-$CH_3CH{=}CHCH_3$	*trans*-$CH_3CH{=}CHCH_3$
$CH_3CH_2CH_2CH_2OH$	340	78%	15%	7%
	400	72	16	12
	450	50	30	20
$CH_3CH_2CH(OH)CH_3$	340	34	44	22
	400	35	42	23
	450	34	40	26

TABLE 5. RATES OF EXCHANGE AND DECOMPOSITION OF ALCOHOLS IN AQUEOUS ACID AT 125°C
(From Dostrovsky and Klein[66])

Alcohol	Normality of Sulfuric Acid	$k \cdot 10^8$*	
		Exchange	Decomposition†
1-Butanol	0.917	56	16.4
1-Butanol	0.092	7	—
2,2-Dimethyl-1-propanol	0.960	1.4	51

* k is the rate constant in $sec.^{-1}$

† By decomposition is meant conversion to another alcohol, to an ether or an olefin.

Good confirmatory evidence for low-temperature chemisorption is provided by exchange studies. Oxygen exchanges at an appreciable rate between alcohol and the OH groups of an alumina catalyst at 200°C (Karpacheva and Rozen[149]). Even at room temperature the oxygen exchange between water and alumina is readily detectable (Whalley and Winter[278]). More recently there has appeared evidence for a slow but definite irreversible adsorption of water and several alcohols on silica, alumina etc. at room temperature (Kipling and Peakall[153]). The authors calculated that their γ-alumina had sufficient surface oxide ions to chemisorb 3.37 mmoles of water/g. The amount found by experiment was 3.43 mmoles/g (i.e., close to 1 molecule of water per surface oxide ion). On the basis of molecular size it can be shown that at most one methanol molecule can be adsorbed for every two surface oxide ions, or one molecule of higher alcohols for every three surface oxide ions. Experiment bears out these expectations reasonably well (Table 6).

TABLE 6. IRREVERSIBLE ADSORPTION BY γ-ALUMINA AT ROOM TEMPERATURE (From Kipling and Peakall[153])

Adsorbate	Chemisorption (mmoles/g)	
	Calculated	Observed
Water	3.37	3.42
Methanol	1.68	1.47
Ethanol	1.12	0.88
1-Butanol	1.12	0.71

Probably there are two kinds of adsorbed reactant important to dehydration catalysis[35, 58]. In the present review the more strongly held is regarded for convenience as a carbonium ion, while the weaker form is considered to be held by hydrogen bonds*. Both types are discussed in the section on "Structure."

It is well known that the last traces of water are not removed from metal oxides until the temperature is raised to a very high level, usually in the range 600 to 1000°C. Clearly there will be some relation between the temperature required to remove a molecule of water from the solid at a given pressure and the energy released when the molecule is readsorbed. When water is removed from thoria at 270° and about 10^{-4} to 10^{-5} mm Hg pressure, the heat of readsorption at $\theta = 0$ is about 24 kcal/mole (Winfield[283]). (By heat of adsorption at $\theta = 0$ is meant the heat obtained by extrapolating from the heats at higher values of θ.) It has to be remembered that θ is taken to be zero after thorough degassing at a specified temperature and

---

* It should be noted that although a hydrogen bond is generally regarded as a chemical bond, certain authors[61] prefer not to regard molecules held at surfaces by hydrogen bonds as chemisorbed.

pressure, and that in fact the surface coverage has then a small but finite value; heating to the sintering temperature would remove more water.

To what surprisingly large values the heat of adsorption can reach is well illustrated in the work of Oblad, Weller and Mills[196], who have observed heats of adsorption of water on γ-alumina as high as 95 kcal/mole at a pressure of 0.13 mm Hg. The degassing conditions appear to have been 704°C and 10^{-3} mm pressure.

Summing up our present knowledge of chemisorption in relation to dehydration catalysis, it may be said that alcohols, ketones and other hydroxylic compounds can be chemisorbed slowly at room temperature, and that in the adsorbed entity the OH group is labile or detached. Certain adsorbates (e.g., unsaturated alcohols) require little activation for loss of a proton from a carbon atom, and in these cases the low temperature chemisorption is followed by a slow dehydration. In order to lift the rate of proton removal (and the rate of desorption of water) to a level convenient for catalysis in a flow-system, it is usually necessary to increase the temperature to 200°C or more. When the adsorbate is a saturated alcohol we may reasonably expect that proton removal is much slower than chemisorption.

The recent work of Kipling and Peakall[153] leads to a somewhat different picture of adsorbed water or alcohol to that of Dowden[67], de Boer[58] and others. It is too early to judge which is the more correct. The main points to be clarified concern the number of layers of OH ions at the surface under conditions of steady-state catalysis, and the importance or otherwise of cation defects in determining the rate or the specificity of the catalysis. It now seems possible that when a catalytic reaction is taking place at 200 to 400°C there are between one and two complete layers of OH ions at the surface.

Adsorption Coefficients. The impracticability of measuring adsorption isotherms at high temperatures (at which alcohols undergo rapid dehydration) has led to indirect estimates of the equilibrium amount adsorbed. Bork[31] and others have obtained from the kinetics of their catalyses "relative adsorption coefficients," which usually consist of the adsorption coefficient of a given molecular species present relative to that of water.

More recently Antipina and Frost[7, 8] have described a method which they claim permits determination of the absolute adsorption coefficients of the products of dehydration of ethanol from kinetic data for the over-all catalysis in the presence of diluent gases. They have shown that a number of catalytic reactions, in a flow system, obey the equation

$$v_0 \ln [1/(1 - y)] = \alpha_i + \beta_i v_0 y \tag{18}$$

whose derivation assumes a unimolecular reaction at a uniform surface on which the adsorption of reactants and products follows the Langmuir adsorption isotherm

$$\theta = \frac{bp}{1 + bp}$$

The constant b atm^{-1} is the Langmuir adsorption coefficient while θ is the fraction of surface covered by the gas whose pressure is p atm; v_0 is the reactant feed rate in mmoles min^{-1} (cc of catalyst)$^{-1}$ and y is the fraction decomposed. α_i and β_i are independent of v_0 or y and are defined by

$$\alpha_i = \frac{k_1 S b_1}{1 + \delta_i + n + \sum_{q=2}^{i} b_q + \frac{b_i}{\nu_i} \cdot \delta_i} \tag{19}$$

$$\beta_i = \frac{n - b_1 + \sum_{q=2}^{i} b_q}{1 + \delta_i + n + \sum_{q=2}^{i} b_q + \frac{b_2}{\nu_2} \cdot \delta_i}$$

in which k_1 is the surface rate constant; S the active surface area; $n + 1$ the number of product molecules resulting from decomposition of one molecule of reactant; b_1, $b_2 \cdots b_i$ are the adsorption coefficients* for the several molecular species present (e.g., b_1 for ethanol, b_2 for water); ν is the stoichiometric coefficient†; δ_i is the number of moles of diluent per mole of reactant in the feed gas (e.g., moles of argon per mole of ethanol).

If we let α_0 be the value of α_i in the absence of diluent gas, and introduce a quantity D_i given by

$$D_i = \left[1 + \frac{b_i}{\nu_i}\right] / k_1 S b_1 \tag{20}$$

we then have from Eq. (19)

$$1/\alpha_0 = (1 + n + b_2 + \cdots b_i)/k_1 S b_1$$

and

$$1/\alpha_i = 1/\alpha_0 + \delta_i D_i \tag{21}$$

from which it is clear that $1/\alpha_i$ is a linear function of δ_i.

If instead of using one of the reaction products (e.g., water or ethylene) as diluent we add an inert gas such as argon, to the extent δ_u, its adsorption on the catalyst can be considered to be negligible and we have

$$1/\alpha_u = \left(1 + \delta_u + n + \sum_{q=2}^{i} b_q\right) / k_1 S b_1$$

---

* Antipina and Frost's coefficient b_1 (etc.) is the Langmuir adsorption coefficient b multiplied by the total pressure and the stoichiometric coefficient.

† Presumably defined in an earlier paper (not available).

while

$$D_u = 1/k_1Sb_1 \tag{22}$$

Thus

$$1/\alpha_u = 1/\alpha_0 + \delta_u D_u \tag{23}$$

Finally by combining experimental determinations of D_i with those of D_u obtained under corresponding conditions, Eqs. (20) and (22) are combined to give

$$D_i = D_u(1 + b_i/\nu_i)$$

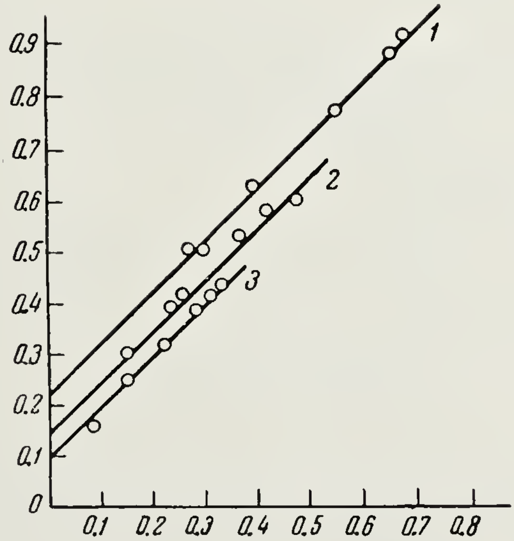


Figure 3. Determination of α_i in Eq. (18). (From Antipina and Frost[7])

For water or for ethylene the stoichiometric coefficient is unity,

$$\therefore\ D_i = D_u(1 + b_i)$$

or

$$b_i = \frac{D_i - D_u}{D_u} \tag{24}$$

By plotting experimental values of $v_0 \ln [1/(1 - y)]$ against v_0y (for a series of values of v_0) Antipina and Frost obtain a straight line whose intercept on the ordinate gives the value of α_i for a given value of δ_i (Figure 3 and Eq. 18). The slope gives β_i which proves to be unity for ethanol dehydration. Varying δ_i while keeping the temperature constant provides a series of values of α_i (Figure 3). Their reciprocals are now plotted against δ_i and the slope of the resulting straight line gives D_i (Figure 4 and Eq. 21).

Using argon as diluent, corresponding values of D_u are likewise obtained. The coefficients b_i for water or for ethylene are then provided by Eq. (24). Table 7 shows some of the values of b_i determined by Antipina and Frost for ethanol dehydration to ethylene, on alumina claimed to be free from acid or alkali.

If soundly based, Antipina and Frost's method for determining adsorption coefficients is of considerable value, and has therefore been treated in detail. Since their paper contains errors in derivation, further work is desirable to confirm the applicability of the equations. The coefficients in Table 7 suggest that, under the conditions of steady-state catalysis of ethanol dehydration, ethylene is adsorbed about as strongly as water.

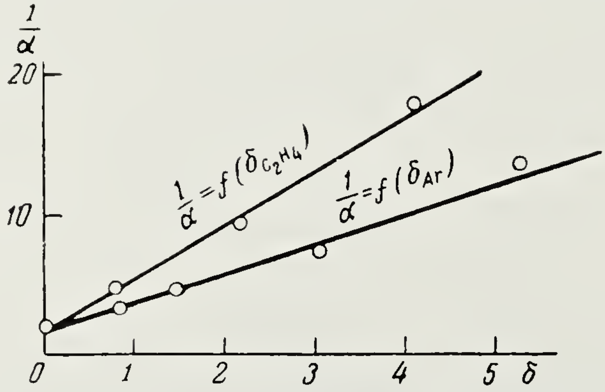


Figure 4. Determination of D_i in Eq. (21). (From Antipina and Frost[7])

Table 7. Adsorption Coefficients for Ethylene and Water (From Antipina and Frost[7])

Temp. (°C)	D_u	D_i		b_i	
		H_2O	C_2H_4	H_2O	C_2H_4
380	0.400	7.35	6.44	17.4	15.1
415	0.366	5.23	4.43	13.3	11.1
450	0.195	2.45	2.10	11.5	9.8

Note: When the pressure is 1 atm, and the stoichiometric coefficient is unity, the dimensionless values of b_i in Table 7 should have the same numerical value as the Langmuir adsorption coefficient b, whose dimensions are atm^{-1}. In the table in their paper Antipina and Frost appear to give values of b in atm^{-1}, presumably obtained by dividing b_i by the pressure in atm (close to 1) without explanation in the text.

As regards relative adsorption coefficients, Bork and Markova[30] were able to determine the ratio of the adsorption coefficient of water to that of ethanol by following the dehydration of water-ethanol mixtures. Surprisingly enough the value was close to 0.65 for both alumina and thoria catalysts, at 330 to 398°C. The consistency of the ratio invites a more searching interpretation of its significance.

For the dehydration of HCOOH on SiO_2 at 245 to 300°C Freidlin and Levit[86] calculated the relative adsorption coefficients (H_2O:HCOOH) given in Table 8. It will be seen that the preferential adsorbability of water increased as the temperature was lowered, and that ignition of the catalyst lowered the adsorption of the reactant more than that of the product. The promoting effect of K_2O could well be due to an increase in adsorbability of formic acid. From kinetic measurements of the dehydration of methanol and ethanol to ethers at 280° Balaceanu and Jungers[12] found the following adsorption coefficients relative to that of ether:

Water	Methanol	Ethanol
5	2	2

TABLE 8. RELATIVE ADSORPTION COEFFICIENTS (H_2O:HCOOH) AS A FUNCTION OF TEMPERATURE, IN THE DEHYDRATION OF FORMIC ACID ON SiO_2

(From Freidlin and Levit[86])

Temp. (°C)	204	245	285	300
Untreated SiO_2		2.5	1.1	1.1
SiO_2 promoted with H_2O	1.4	0.7	0.6	
Ignited* SiO_2		3.1	1.8	

* 4 hr at 800°C.

Kinetics

Ethanol Dehydration to Ethylene. The experimental results of Brey and Krieger[37] for the catalysis on Al_2O_3 at 350 to 400°C fit the equation

$$22400R = \frac{kLK_aP_a}{K_aP_a + K_wP_w}$$

which is based on the assumptions that the surface reaction (conversion of adsorbed ethanol to adsorbed product) is rate-determining, that ethanol and water are strongly adsorbed while ethylene and ether are not, that only one active site is involved per molecule of ethanol reacting, and that the reverse reaction can be neglected because of the magnitude of the equilibrium constant.

R is the rate in moles C_2H_4/cc of catalyst bed/sec; k is the rate constant; L is the number of active sites per cc of catalyst bed; K_a and P_a are the equilibrium adsorption constants and the partial pressure, respectively, of alcohol; K_w and P_w are the analogous quantities for water adsorption.

Since K_a and K_w are of the same order of magnitude, the equation shows that when the partial pressure of water is kept small by one device or another, the over-all reaction is zero order. From this and other investigations of the dehydration of simple alcohols to olefins it was concluded that the alcohol is adsorbed strongly (about as strongly as water) and rapidly compared with the rate of the subsequent step in which the adsorbed species (suggested elsewhere to be a carbonium ion) loses a proton to yield olefin. Desorption of the latter is considered to be rapid compared with the surface reaction. Unless precautions are taken to accelerate the net rate of desorption of water it significantly retards the over-all rate of catalysis.

TABLE 9. APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR DEHYDRATION OF ETHANOL AND ETHER

Reactant	Product	Catalyst	E_{exp} (kcal/mole)	a*	Authors
Ethanol	diethyl ether	Al_2O_3	14		12
"	" "	"	22.6		264
"	" "	$Ca_3(PO_4)_2$	38.3	2×10^{15}	88
Ethanol	ethylene	ThO	30		110
"	"	ThO_2 + pumice	64.5		1
"	"	Al_2O_3	20.2	3.5×10^{8}	29
"	"	"	24		30
"	"	"	12.1		7
"	"	"	38		12
"	"	"	14.5		264
"	"	Al_2O_3 + additive	8.9-18		274
"	"	$Ca_3(PO_4)_2$	40.6	4×10^{15}	88
"	"	W_2O_5	18.9		1
Diethyl ether	ethylene	$Ca_3(PO_4)_2$	34.5	5×10^{13}	88
" "	"	Al_2O_3	24		12
" "	"	"	14.5		264

* a is best expressed as molecules/sec/sq cm of surface, but many authors have failed to state the units employed. Values of a quoted in this and later tables are therefore useful only for comparison with others determined by the same authors.

For the same reaction, and again with alumina as catalyst in a flow system, Antipina and Frost[7] obtained experimental results which conformed to Eq. (18), which may be written in the form

$$k_1 = (\text{const.})\, v_0[-\beta y - \ln (1 - y)] \qquad (25)$$

where k_1 is the surface rate constant; v_0 is the ethanol feed rate; y is the fraction decomposed; β is a constant found experimentally to be unity.

By mixing the reactant with diluents such as argon, C_2H_4 or H_2O it was shown that the activation energy for the catalysis is nearly independent of the degree of dilution[7].

Tables 9 and 10 present values which have been obtained with a variety of catalysts for the apparent activation energy E_{exp} (kcal/mole of reactant) and the frequency factor a in the simple Arrhenius equation

$$\text{Rate} = a.e^{-E\text{exp}/RT}$$

Ethanol Dehydration to Ether. Essentially the same equation as (18), but containing an arbitrary factor x_p, was used by Topchieva and Yun-Pin[264] to describe the conversion of ethanol to ether on alumina:

$$k = N_0x_p[-x - \ln(1 - x)] \tag{26}$$

where k is the apparent velocity constant, N_0 is the number of moles of reactant introduced per hour and x is presumably the fraction reacted. The equation is based on the assumption of a bimolecular reversible reaction in a gas stream from which one of the reaction products is rapidly adsorbed.

TABLE 10. APPARENT ACTIVATION ENERGIES FOR DECOMPOSITION OF ETHANOL ON A VARIETY OF CATALYSTS

(Taken from Schwab and Schwab-Agallidis[238])

Catalyst	Heat Treatment (°C)	E_{exp} for H_2 Production (kcal/mole)	E_{exp} for C_2H_4 Production (kcal/mole)
α-Al_2O_3*		28.5–30	28.5–41.5
γ-Al_2O_3		—	31
$BaSO_4$		27	—
C (activated)		28	48
CaF_2*		22.5–26	26–45
$Ca_3(PO_4)_2$		—	35
$Ca_3(PO_4)_2$	1000	27.5	43.5
CeO_2	1050	32	49
Ce_2O_3	300	26	38
Cr_2O_3		22	22
Cr_2O_3	glowed	28	68
ThO_2	300	34	34
ThO_2	600	25	33
ThO_2	1000	32	41
TiO_2		32	34
ZnO*		17–25	37–56

* Various methods of preparation.

Dehydration of Ether to Ethylene. According to Topchieva and Yun-Pin,[264] Eq. (26), after removal of the factor x_p, describes their results obtained for the conversion of diethyl ether to ethylene over alumina. Activation energies and frequency factors will be found in Table 9.

Dehydration of Methanol to Dimethyl Ether. There do not appear to be many catalysts on which the dehydration to ether goes cleanly. Balaceanu and Jungers[12] believed that their kinetic results with alumina supported the assumption of a second-order reaction between molecules of adsorbed methanol.

Dehydration of Other Aliphatic Monohydric Alcohols. In his book Ipatieff[129] stated that the maximum decomposition rates for primary, secondary and tertiary alcohols are in the ratio 1:4:8. Adkins and Perkins[3] put the ease of dehydration as follows: 2-butanol > 2-propanol > ethanol > 2-methyl-1-propanol > 1-propanol > 1-butanol. Bork[29] found for dehydration on alumina the order 2-propanol > 2-butanol > 1-propanol > 2-methyl-1-propanol > 1-butanol > ethanol (Table 11). Later however, Bork and Tolstopyatowa[32] amended the order to 2-propanol > 2-methyl-1-propanol > 1-butanol > 1-propanol > ethanol and the same sequence was obtained by Freidlin and Levit[88] (Table 12) using as catalyst tricalcium phosphate (which requires higher activation energies).

TABLE 11. APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR DEHYDRATION OF ALCOHOLS TO OLEFINS ON ALUMINA AT 350°C
(Taken from Bork[29])

Reactant	E_{exp} (kcal/mole)	a*
Ethanol	20.2	35.4×10^7
1-Butanol	18.0	8.3×10^7
2-Methyl-1-propanol (isobutyl alcohol)	16.4	3.2×10^7
1-Propanol	18.3	15.1×10^7
2-Butanol	14.9	4.1×10^7
2-Propanol	16.0	10.3×10^7

* Dimensions not given by author.

Note: In both Table 11 and Table 12 the reactants are arranged in the order of increasing rate constant, as determined by the respective authors. This differs considerably from the order of decreasing activation energy.

TABLE 12. APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR DEHYDRATION OF ALCOHOLS AND ETHER ON TRICALCIUM PHOSPHATE
(From Freidlin and Levit[88])

Reactant	Temp. Range (°C)	E_{exp} (kcal/mole)	a*
Ethanol	333–387	40.6	4×10^{15}
1-Propanol	322–356	38.6	5×10^{15}
1-Butanol	319–353	55.0	3×10^{21}
2-Methyl-1-propanol (isobutyl alcohol)	312–334	68.0	5×10^{24}
2-Propanol	262–297	37.8	4×10^{16}
Diethyl ether	333–395	34.5	5×10^{13}
Ethanol on glowed $Ca_3(PO_4)_2$	388–434	36	5×10^{13}
Ethanol on SiO_2	352–391	22.5	1.3×10^9

* Dimensions not given by authors.

Note: Catalyst is $Ca_3(PO_4)_2$ except where otherwise indicated.

Working with 2-propanol as reactant and alumina as catalyst, Dohse[64] showed that the water formed during the reaction was slow to desorb and therefore retarded the over-all reaction by diminishing the surface area available to the reactant.

Like the short-chain alcohols, 1-dodecanol can be dehydrated to either an ether or an olefin; the reaction on alumina is zero order (Walker[276]).

TABLE 13. APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR DEHYDRATION OF ANALOGS OF ETHANOL

Reactant	Product	Catalyst	E_{exp} (kcal/mole)	a*	Author
Methanol	dimethyl ether	Al_2O_3	18		12
1-Propanol	propene	W_2O_5	16.4		1
1-Propanol	propene	$Ca_3(PO_4)_2$	38.6	5×10^{15}	88
2-Propanol	propene	$Ca_3(PO_4)_2$	37.8	4×10^{16}	88
2-Methyl-1-propanol	butenes	W_2O_5	13.9		1
2-Methyl-1-propanol	butenes	ThO_2 + pumice	59.5		1
2-Methyl-1-propanol	butenes	$Ca_3(PO_4)_2$	68	5×10^{24}	88
2-Methyl-2-propanol	butenes	W_2O_5	~7.9		1
1-Butanol	butenes	$Ca_3(PO_4)_2$	55	3×10^{21}	88
1-Butanol	1-butene	Al_2O_3	28		12

* Dimensions not given by authors.

TABLE 14. APPARENT ACTIVATION ENERGIES FOR DEHYDRATION OF FORMIC ACID (From Freidlin and Levit[87])

Catalyst	E_{exp} (kcal/mole)	a*
SiO_2 (uncalcined)	14.5	9.5×10^7
SiO_2 (thermally deactivated)	15.4	7×10^7

* Dimensions not given by authors.

Table 13 gives the apparent activation energies and frequency factors for the dehydration of a variety of alcohols other than ethanol.

It is of interest to compare with these values, and the ones for ethanol, the activation energies for the exchange reactions

$$H_2O^{18} + MO^{16} \rightleftharpoons H_2O^{16} + MO^{18}$$

$$RO^{16}H + MO^{18} \rightleftharpoons RO^{18}H + MO^{16}$$

which are no more than a few kcals per mole (Karpacheva and Rozen[147, 149]). MO^{16} represents an alumina surface.

Dehydration of Formic Acid. In Table 14 are given Freidlin and

Levit's[87] values for the apparent activation energy and the frequency factor at 200 to 300°C for the silica-catalyzed reaction

$$HCOOH \rightarrow H_2O + CO$$

Addition of K_2CO_3 to the catalyst diminished E_{exp}.

Some of the earliest kinetic studies were concerned with the dehydration of formic acid to CO on glass, in competition with the dehydrogenation to CO_2 (Hinshelwood, Hartley and Topley[109]). The observed values of E_{exp} were 16 and 28 kcal/mole respectively. It was noted that in spite of the considerable difference in E_{exp} the reaction rates were of the same order of magnitude.

Dehydration of Diols. On thoria at 300 to 400°C, 2,3-butanediol is dehydrated to methyl vinyl carbinol with an activation energy of 25 kcal/mole and a frequency factor $a = 3 \times 10^3$ moles/l/sec (Winfield[282]). Due to retardation by water, the percentage conversion at a given space velocity is inversely proportional to the total pressure. In the alternative dehydration of diol to methylethyl ketone, E_{exp} is approximately 16 kcal/mole. Little or none of the surface of a properly prepared thoria catalyst is capable of catalyzing the reaction to methylethyl ketone. As a result, a is very small (.03). Possibly both E_{exp} and a refer here to reaction on the walls of the vessel rather than on the thoria.

At 350°C and ordinary pressures, the surface which is potentially active is almost entirely covered with adsorbed water while catalysis proceeds. It is not until the total pressure is reduced to about 20 mm Hg that one-half of the potentially active surface becomes available for adsorption of the diol. If the surface is in equilibrium with the product water in the gas phase, less than 0.2 per cent of the total surface would be covered with water. Yet the percentage of the total surface which is potentially active for diol dehydration is high, as indicated by the large reduction in available surface observed when measuring diol adsorption isotherms[283]. It is concluded that during the catalysis the surface concentration of water is of the order of 100 times greater than the equilibrium concentration.

Under the conditions described it can be assumed that the rate of adsorption of water is negligible compared with the rate of desorption. Also, that on the fraction of the surface accessible to reaction the latter attains equilibrium or nearly so. We then have

$$k_{exp} = k_7 e^{-E_{exp}/RT} \quad \text{(over-all catalysis)}$$

$$k_{exp} = k_{12}(1 - \theta)e^{(E-E_0)/RT} \quad \text{(surface reaction)}$$

$$k_{exp} = k_9 \theta e^{-E_p/RT} \quad \text{(desorption of water)}$$

(taken from Winfield[283]) where k_{exp} is the observed rate constant while k_7, k_{12} and k_9 are constants assumed to be independent of temperature (this however is a crude approximation). E_0 is the activation energy for the surface reaction, E the heat of adsorption of reactant and E_p of product; $(1 - \theta)$ is the fraction of potentially active surface that is available for adsorption of reactant.

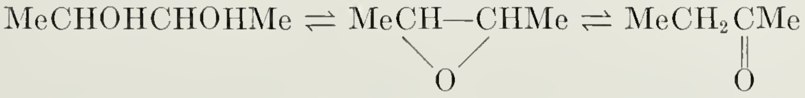
From the above equation is obtained the approximate expression

$$E_{\mathrm{exp}} = (1 - \theta)(E_0 - E) + \theta E_p$$

Because of difficulties in obtaining a reliable estimate of θ, the interesting quantity E_0 cannot be determined except by working at such low pressures that θ is close to zero.

At high surface coverage (of potentially active sites), E_{exp} will be low. Since however the surface accessible to reactant is then small, the observed frequency factor is small and so also the over-all rate of catalysis.

Some methylethyl ketone is always formed when 2,3-butanediol is dehydrated. Hale and Miller[102] have suggested (following Beati and Mattei[15]) that the ketone results from tautomerization of *s*-dimethylethylene oxide



$$\mathrm{MeCHOHCHOHMe} \rightleftharpoons \underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{MeCH{-}CHMe}} \rightleftharpoons \underset{\overset{\|}{\mathrm{O}}}{\mathrm{MeCH_2CMe}}$$

By adding methylethyl ketone to the butanediol feed Hale and Miller have been able to suppress dehydration to ketone and thus increase the yield of diene (presumably via methyl vinyl carbinol). Addition of water and of an amine were also claimed to be beneficial.

Concluding Remarks on Mechanism

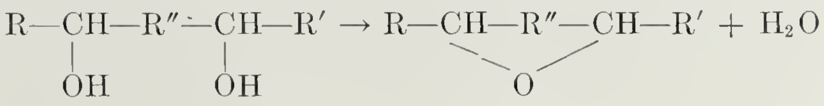
While we remain largely in ignorance of the surface structure of dehydration catalysts it is difficult to probe deeper into the mechanism of the catalysis, beyond the superficial ideas described in the previous section. Their inadequacy is apparent if we attempt to use them to explain why thoria catalyzes the dehydration of ethanol to ethylene, but has little activity for dehydration to ether[12, 200], or why almost all dehydration catalysts convert 2,3-butanediol to methylethyl ketone while thoria leads to the formation of methyl vinyl carbinol in spite of a less favorable free energy change[282].

Irrespective of whether dehydration reactions are intramolecular or intermolecular, we may classify them into two main categories:

(1) *Ether mechanism.* The elements of water are removed from two hydroxyl groups[79], which may be either in the same or in two different molecules:

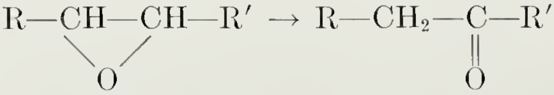
$$\mathrm{ROH + HOR' \rightarrow ROR' + H_2O}$$

or



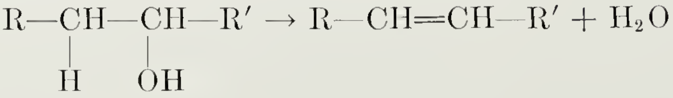
$$\mathrm{R{-}\underset{|\atop OH}{CH}{-}R''{-}\underset{|\atop OH}{CH}{-}R' \rightarrow R{-}CH{-}R''{-}CH{-}R' + H_2O}$$ with O bridging the two CH groups of the product: $$\mathrm{R{-}\underset{\diagdown}{CH}{-}R''{-}\underset{\diagup}{CH}{-}R'}\ (\mathrm{O})$$

(R″ may be either absent or contain one or more carbon atoms, while R and R′ may be H or alternatively contain one or more carbon atoms). If the oxide ring is small the molecule isomerizes readily to an aldehyde or ketone[15, 131],



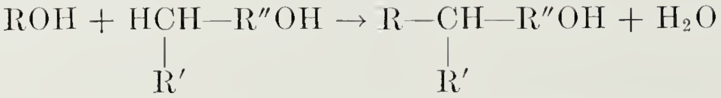
$$R\text{—}\underset{\diagdown\; O \;\diagup}{CH\text{—}CH}\text{—}R' \rightarrow R\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}R'$$

(2) *Olefin mechanism.* The water molecule that is removed is made up of one hydroxyl group together with a hydrogen atom withdrawn from either a CH_3 or CH_2 group, rarely* a CH group (Graves[97]):



$$R\text{—}\underset{H}{\underset{|}{CH}}\text{—}\underset{OH}{\underset{|}{CH}}\text{—}R' \rightarrow R\text{—}CH{=}CH\text{—}R' + H_2O$$

or



$$ROH + H\underset{R'}{\underset{|}{C}}H\text{—}R''OH \rightarrow R\text{—}\underset{R'}{\underset{|}{C}}H\text{—}R''OH + H_2O$$

From scattered remarks in the published literature it appears that alumina and most other dehydration catalysts favor the ether, while thoria and perhaps tungsten oxide favor the olefin mechanism. While alumina can in many cases be made to catalyze the olefin mechanism by raising the temperature, thoria is markedly slow to catalyze the ether mechanism at any temperature, although a good catalyst for the olefin mechanism. Additions of water to the feed can favor the olefin mechanism for the dehydration of 2,3-butanediol as remarked earlier.

We have seen that there is no satisfactory theory to account for the specificity displayed by thoria, and the considerable difference sometimes found between the products obtained by homogeneous as compared with heterogeneous dehydration catalysis. On the whole the result on alumina is the same as that obtained in a solution of a strong acid.

Some of the facts are fitted by a hypothesis which assumes that the mobility or otherwise of cation defects in the catalyst determines the course of reaction, and that considerably higher temperatures are required for cation mobility in thoria than in alumina. The Tammann[210] temperature is 1580°C for thoria compared with 930°C for alumina, and the temperature for complete water removal is probably about 300°C higher than for alumina. A second hypothesis could be devised on the basis of the lack of acidic properties of thoria, and its tendency to be basic. A third could perhaps be founded on the supposition that at a given temperature there are many

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* Note however that according to Sabatier and Murat[233] the loss of a hydrogen atom from a CH group sometimes occurs readily, e.g., in the reaction

$$\phi_2COH\text{—}CHMe_2 \rightarrow \phi_2C{=}CMe_2 + H_2O$$

more anion vacancies at the surface of alumina than thoria. Possibly the truth lies in a combination of factors.

It will be clear that there is room for much more experimentation. It would be a useful contribution to reinvestigate the dehydration of ethanol over thoria, using preparations which are known to be highly specific—e.g., for the dehydration of 2,3-butanediol to methyl vinyl carbinol—and to determine the effect of water concentration on the mechanism. Also it would be helpful to investigate systematically the dehydration properties of a series of oxides, graded according to their acidity, or affinity for water, or the mobility of their cation defects, each pair of adjacent oxides in the series being prepared by nearly identical means.

Elsewhere, the views of Taft *et al.*[253] on the mechanism of the homogeneous hydration of ethylene have been mentioned. Their conclusions refer to solutions which contain appreciable water. In the absence of water the mechanism cannot be the same. Useful information could be obtained by a modern investigation of the mechanism of ethanol dehydration in a solution which contains alcohol, sulfuric acid and virtually no water. According to the work of Williamson[281], and some but not all of those who have reported since on the same question, the compound $C_2H_5HSO_4$ occurs as a definite stage in ether or ethylene formation. In such a simple system all of the possible reaction steps can readily be written down for ether formation, and also for ethylene formation. If this is done we obtain the expected result that high concentrations of alcohol favor ether production, but the unexpected result that increasing the water concentration favors ethylene production (provided that the temperature is high enough) by providing a proton-acceptor to facilitate removal of a proton from the methyl group.

CATALYST STRUCTURE

By a combination of x-ray[74] and electron diffraction, spin-resonance, infrared and contact-potential measurements of the catalyst, its surface and the adsorbate, together with new developments in coordination chemistry, it is possible that a useful picture of the surface of an operating catalyst will finally be provided. To do so by calculations based on the bulk structure of the crystal and the fundamental properties of matter has proved impractical (see for example de Boer[58]). At present our picture of the surface is highly conjectural and a matter of controversy. A description here of some of the concepts which have been put forward may be of assistance to some readers, but will be restricted to aspects of structure which have a particular significance for dehydration catalysis. For a more detailed discussion of the environment which surrounds an adsorbate molecule at the surface of a catalyst[76], reviews by de Boer[58, 59], Eischens and Pliskin[72a], Griffith and Marsh[100], Hulburt[115], Selwood[239] and Taylor[256] should be consulted.

Alumina

While it is difficult to determine the surface structure of a pure compound, the task is greatly enlarged if the solid is a mixture. Most of the information which we have refers to solids which are "pure" compounds except that they contain water, whose presence is inevitable at the temperatures ordinarily used in catalyst preparation and operation (Table 15).

As the commonest dehydration catalyst, alumina has received considerable attention in structure studies. It occurs in a number of forms (usually designated α, γ, δ, etc.) some or all of which exist in several modifications. While the consensus of opinion is that the catalytically active form is γ-alumina (see for example Rubinshtein *et al.*[214]), its nature cannot be regarded as settled beyond dispute.

By x-ray diffraction Verwey[275] detected two different modifications of γ-alumina. Seven patterns (all formerly considered to be from γ-alumina) were later detected by Stumpf *et al.*[251] when they followed the phase transformation which occur during thermal decomposition of the four alumina hydrates.

TABLE 15. WATER CONTENT OF ALUMINA AS A FUNCTION OF TEMPERATURE OF ACTIVATION

(From Munro and Horn[189])

Activation Temp. (°C)	300	320	410	450	500	550	580
Residual water (%)	13.8	12.7	8.5	5.5	4.3	2.3	1.4

Probably all samples of alumina can be considered crystalline, as regards the surface. Glassy specimens exhibit electron-diffraction rings even when no rings can be obtained with x-rays (Cowley[53]). Aluminum atoms are situated between each layer of oxygen and the oxygen atoms are close-packed. While some of the metal atoms are in tetrahedral holes, others are in octahedral. For a detailed description see de Boer[60], and Cowley[52].

It is generally believed that the surface of the crystallites consists of a close-packed layer of oxygen atoms. For this to be so, even after grinding, there must be regions in which either the metal atoms have receded from the surface or oxygen (from water) has been overlaid. Consider for illustrative purposes an imaginary cleavage of a crystallite along one of the oxygen layer-planes, in the presence of water vapor. The instantaneous result would be two new surfaces of which one is made up of oxygen ions, the other aluminum ions. If now water is adsorbed so that OH ions completely cover the aluminum surface, while an equal number of hydrogen ions are added to the complementary oxygen surface, the result on both is a close-packed layer of oxygen. Minor readjustments in the position of the cations will follow, with the effects tapering off toward the interior of the crystallite. Examination of a solid model suggests that no more than half of the protons will remain above the outermost oxygen layer. The others will migrate to oxygen atoms and cation vacancies below the surface.

It will be clear from the foregoing description that some of the water present in alumina will be held by strong forces, related to the energy required to move aluminum and hydrogen ions from the subsurface region to a position above the anions. This water, and the water held at faults, can be removed by resort to very high temperatures, but the process will be accompanied by a contraction of surface and a healing of faults, neither of which is readily reversible. There appears to be a high temperature range in which the contraction and the healing are not as complete as the removal of water, and the result is the creation of defects which confer on alumina activity for dehydrogenation catalysis (Boreskov *et al.*[28], Oblad *et al.*[196], and early observations by Senderens[240]).

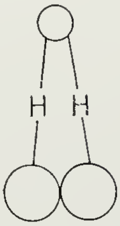
At low temperatures cation vacancies and the accompanying anion vacancies in the alumina crystallites are occupied by protons and OH ions, as a result of adsorption or solution of water. As the temperature is raised, more and more of the adsorbed and occluded water will be desorbed. It is likely that the resulting vacancies, where they are at or near the surface, are the sites on which during catalytic dehydration the alcohol or other reactant is chemisorbed most strongly.

de Boer's Picture. According to de Boer[60] the composition of the crystallite, over a distance of about two atomic diameters from the surface, is approximately AlOOH when the water content of the crystallite is 4 per cent (which is in the range likely to apply during catalysis). The surface may be imagined to consist almost entirely of oxygen atoms, one-half of which have a hydrogen atom attached. If the structure were entirely ionic, the surface would be made up of $\overset{-}{O}H$ and $O^{=}$ ions. But whereas the interior of the crystallite is known from x-ray studies to be best described in terms of Al^{3+} and $O^{=}$ ions, the surface atoms are supposed to be held by bonds which have appreciable covalent character. The degree of covalency is unknown.

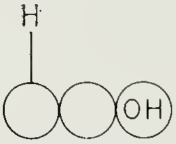
In order to account for the higher than theoretical concentration of OH groups at the surface (1.455 of theoretical), de Boer supposes that aluminum ions have receded towards the interior. Throughout the bulk of the crystallite the composition corresponds to the spinel $Al_8(Al_{12}H_4)O_{32}$. (These remarks relate still to an alumina which contains, over-all, 4 per cent water.)

When the water content is allowed to increase beyond 4 per cent, further water taken up is held as adsorbed molecules, until finally a closed unimolecular layer is present. Any further adsorption is by van der Waals forces.

A convenient representation of the chemisorbed molecules is to show them as held by two hydrogen bonds:



which is essentially the same as de Boer's[58] dipole adsorption. Strongly held protons, other than those within the crystallite, are probably best shown vertically above the surface oxygen atoms or as part of a surface group:



Need for Water. There are many claims that the presence of water in the catalyst is essential: e.g., Sabatier[234], Ipatieff[128], Eucken and Wicke[80], Munro and Horn[189], Brey and Krieger[37], and Hansford[104]. For the dehydration of ethanol to ether, Munro and Horn[189] obtained the greatest catalytic activity when the alumina contained 5.5 per cent water (Figure 5). There was no activity above 13.8 per cent water.

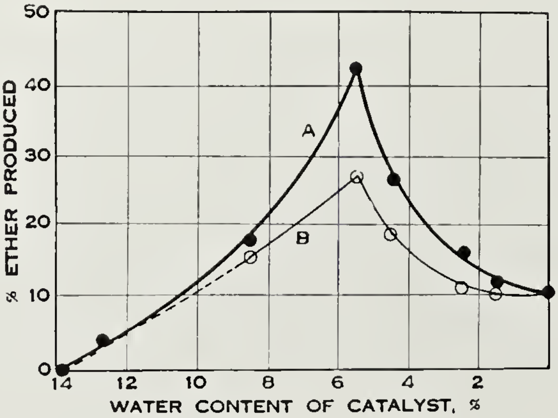
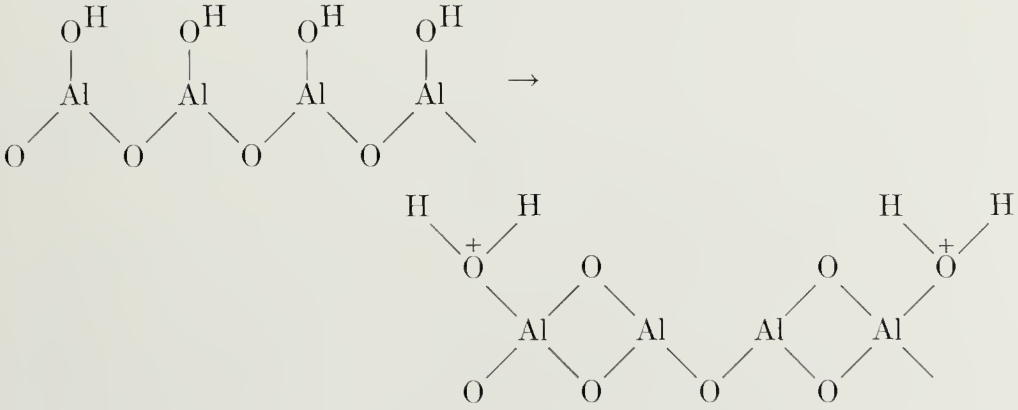


Figure 5. Optimum water content of alumina catalyst, in dehydration of ethanol to ether at 250°C (negligible ethylene formation). (A) Results with fresh catalyst. (B) Results after passage of 50 cc of ethanol (3-hrs use) over 13 g of alumina. (From Munro and Horn[189])

It does not seem to have been proved that the presence of water is essential for dehydration of ethanol to ethylene. Although removal of the water diminishes the catalytic activity, the effect could be due to loss of surface area and healing of faults at the high temperature required. In the dehydration of ethanol to ether, the occurrence of an optimum water content of the catalyst can be explained in part by water displacing the equilibrium in favor of ether rather than ethylene production. Nevertheless the belief that water is necessary is widely held. Since water is inevitably present during dehydration catalysis, it is difficult to see how the concept of its necessity may be severely tested.

One of the ways in which we may regard the need for water is described by de Boer[57]. Like Bremner[35], he supposes that the conditions and the mode of catalysis at the surface of a solid dehydration catalyst are related to those which are thought to prevail in homogeneous acid-catalyzed dehydration. Even "perfectly neutral" alumina can function as a proton-active catalyst, if water is present. Just as the aluminum atom in $H^+[AlBr_4]^-$ assumes a coordination number of four and the resulting negatively charged complex ion attracts a proton, so at the catalyst surface some aluminum atoms are supposed to be part of a negatively charged complex. The resulting structure, according to de Boer, can be represented as lying between the two limiting structures:



In other words, the partial transfer of charge from a water molecule to an aluminum atom confers acidic properties on the adsorbed water molecules. They then act as proton donors, which can transfer H^+ to an alcohol molecule at the surface, forming Bremner's oxonium ion $\overset{+}{ROH_2}$, which can undergo exchange reactions with either water or a second alcohol molecule just as in acid solution.

Pore Structure. A description is given by de Boer[59] of the drying of boehmite and diaspore (alumina monohydrates) and of gibbsite and bayerite (trihydrates). With the latter two, the mechanism of water removal is complex and depends upon granule size and method and rate of drying. "Various sorts of capillaries, having different orientations, shapes and sizes, develop during the progress of the dehydration of the trihydrates. All accessible pores widen at higher temperatures, while the surface area decreases."

Up to 600°C ignition has little effect on the dehydrating activity, according to Boreskov *et al.*[28]. At higher temperatures the surface shrinkage (disappearance of the narrow pores) causes the total dehydration activity to decline, but the specific activity is actually increased by ignition temperatures up to 1000°C. Pore size and total surface are changed little if at all by the presence of NaOH (Boreskov *et al.*[26]). The heaviest and largest particles of $Al(OH)_3$ provide on drying the most active γ-alumina, but apparently the reason is that the coarse grain permits rapid diffusion of reactants to the particles (Rubinshtein *et al.*[214]).

TABLE 16. SURFACE CHARACTERISTICS AND ACTIVITY OF ALUMINA AS A FUNCTION OF METHOD OF PREPARATION

(From Boreskov *et al.*[26])

Catalyst	Dry Weight (g/cc)	Micropore Volume (cc/g)	Surface Area (m^2/g)	Specific Rate of Catalysis for Ethanol Dehydration
I	0.34	0.62	245	1.05
II	0.36	0.6	245	0.8
III	0.40	0.57	235	0.97
IV	0.36	—	127	1.15

Preparation: Catalyst I, by precipitation of $Al(OH)_3$ from aqueous $Al(NO_3)_2$ using NH_4OH under conditions favorable to production of large pores. Washed, dried, ground to a particle size of 0.5 mm, heated at 450°C for 5 hr, then given an additional wash with aqueous NH_4Cl.

Catalyst II, as for I but the final wash was omitted.

Catalyst III, as for I but pelleted rather than ground, before heating.

Catalyst IV, as for III but there was no final wash; the material was heated in water vapor for 4 hr.

Some of Boreskov's results are summarized in Table 16. The catalytic activity of the various alumina preparations was determined by measuring the rate of ethanol dehydration to ethylene at 420°C. Although heating in water vapor (temperature not given) greatly diminished the surface area of catalyst IV, it will be noticed that the activity of the remaining surface was if anything increased. Possibly this can be explained in terms of inaccessibility of the small pores which are lost during the heat treatment. It would be useful to determine whether the catalytic specificity of catalyst IV was also enhanced.

Thorium Oxide

Compared with alumina, thoria has no acidic properties and is slightly basic, as witnessed by the existence of a carbonate (Beckett and Winfield[16]). Since in general a tendency toward basicity runs in the reverse direction to the tendency to coordinate, the bonds in thoria can be expected to have less covalency than in alumina.

The oxide prepared by heating thorium oxalate to moderate temperatures is not identical with that obtained from salts such as the nitrate or sulfate (see for example Kohlschütter and Frey[156]). In order to prepare a thoria which was highly active for the dehydration of 2,3-butanediol to methyl vinyl carbinol and butadiene it was found necessary[282] to heat thorium oxalate, rather than other salts, to about 350°C. In the presence of traces of nitrate or sulfate the oxalate decomposition followed a different course and the resulting thoria tended to yield methylethyl ketone rather than methyl vinyl carbinol.

From chemical examination it was concluded that the active thoria consisted of about 98 per cent ThO_2 together with small amounts of water and thorium carbonate, the latter being an intermediate in thorium oxalate decomposition at moderate temperatures[16]. X-ray diffraction showed the presence of not only the thoria lattice but also an unidentified lattice with a parameter 2.3 times as large.

Although pure thoria (M.P. 3300°C)[166] is unlikely to sinter much below 1200°C, the x-ray diffraction powder patterns become sharper after heating the active thoria at 500°C. Presumably the small amount of water present at 500°C greatly increased the mobility of the surface atoms. There was also a decline in catalytic activity. It was not established whether the loss of activity was due to decline in surface area or fading of the larger of the two observed crystal lattices.

Thoria prepared at high temperatures has a density of 10 g/cc but the density of the active material was 5.5. The surface area was 56 sq m/g as determined by water adsorption at 50°C compared with 24 sq m/g by N_2 adsorption (B.E.T. method). It is therefore possible that the "sponginess" was due to holes which could be filled by hydroxyl ions but not by N_2. At a higher level of organization a large surface area[96] was provided by a splitting of the crystal into plates, while the plates themselves appeared to consist of a stack of very thin laminae whose ends, nearly transparent to electrons of the electron-microscope, could be observed projecting into the central aperture of the relic crystals.

Thoria prepared from the oxalate at temperatures below 700°C, but not thoria from the nitrate or the hydroxide, is easily peptized by HCl to form a solution. The difference does not appear to be explainable in terms of different surface areas, but is in harmony with the view expressed above that the lattice of the active material is expanded. The thoria prepared from the oxalate at 350°C was not white but cream to gray in color. Under ultraviolet light there was a fluorescence which varied with different samples from brown to purple or violet, and which could possibly be developed into a test for catalytic activity of preparations containing thoria. Whether the color (both in the ultraviolet and visible regions) was due to carbon, carbonate or an excess of thorium was not determined.

Recently it has been found that when thoria is prepared from thorium and water at 200 to 600°C, three types may be distinguished—black, gray or white, and metallic (Deal and Svec[55]). It is now fairly definite that the compound ThO can be prepared, but it is not definite whether it contains Th^{II} or a mixture of Th^{IV} and Th^{O} (Katzin[150]).

It has long been known that thoria has the curious property of increasing the density of water allowed to stand above it (see for example Peel, Robinson and Smith[203]). From this it could have been deduced that an exchange reaction between water and thoria can proceed at room temperature. In recent years, the exchange with H_2O^{18} has been briefly studied (Whalley and Winter[278]). As with alumina, there is a rapid exchange of oxygen atoms of water with oxygen of the surface and part of the interior of the adsorbent, followed by a very slow exchange involving a large proportion of the oxide oxygen. At 120°C, 3.5×10^{20} atoms of oxygen/g of thoria are rapidly exchangeable, corresponding to a "surface" of 27 sq m/g in a thoria whose surface area as determined by N_2 adsorption is 3.8 sq m/g.

Enough has been written to make it clear that there are at least three classes of thoria catalyst (nonspecific dehydration, specific dehydration and dehydrogenation), that much of the early work on dehydration over thoria should be repeated with better-defined and reproducible preparations, and that from an economics point of view thoria would repay systematic study.

Silica

In the past two years some papers have appeared on the surface structure and hydration of silica. Using as indicator the fluorescence of rhodamine adsorbed from aqueous solution, Stöber[250] has demonstrated the presence of OH groups at the surface. The firmly held water is removed by heating over the temperature range 200 to 800°C. The amount of water held seems to be small compared with alumina, the surface being only 13 to 25 per cent covered at 25°C at the break-point of water adsorption isotherms measured by Young[288]. The fraction of surface found by Gregg[98] to be covered with water at 200 to 900°C appears in a table in the next section.

In Table 17 are given some surface properties determined by Kohlschütter and Kämpf[157].

Oxides in General

Mobility of Sorbed Water. By measuring oxygen exchange between H_2O^{18} and oxides or their hydrates it has been demonstrated in several laboratories that there are varying degrees of mobility of oxygen within the lattice and at the surface. Table 18 taken from Mills and Hindin[184] refers to alumina and silica gels dried at the temperature indicated, and to

TABLE 17. SURFACE PROPERTIES OF SILICA AS A FUNCTION OF IGNITION TEMPERATURE
(From Kohlschütter and Kämpf[157])

Ignition Temp. (°C)	Specific Surface (m^2/g)	Saturation Volume† (mm^3/g)	Ignition Loss** (mm^3/g)	Ignition Loss per Unit Surface (mm^3/m^2)	Kelvin Pore Radius (Å)
100	618	371	61.5	0.10	11.4
400	609	373	31.6	0.05	11.1
700	586	342	16.3	0.03	10.9
1000	341	216	3.01	0.01	11.1

* Determined by the BET method using N_2 as adsorbate.

† Amount of water adsorbed at the saturation pressure p_0 of the BET equation.

** Loss after heating to constant weight at 1100°C. Values given are in mm^3 of water vapor (at NTP) per gram of completely water-free SiO_2. Note that the effective pore radius is about 2.8Å greater than the Kelvin radius given in the table. Porosities were found to be 44.9 per cent after ignition at 100°C and 37.8 per cent after ignition at 1000°C.

TABLE 18. OXYGEN EXCHANGE BETWEEN WATER AND OXIDE CATALYSTS
(From Mills and Hindin[184])

Adsorbent	Max. Drying Temp. (°C)	Exchange[a] in 15 Mins.	Oxygen[b] Present as OH		Oxygen[c] on Surface	Exchange[d] in 1 Month
			From Surface Area	From Ignition Loss		
SiO_2	100	20	6	23	24	71
	450	8	6	9	24	41
	760	7	8	3	30	41
Al_2O_3	100	26				
	450	24				
SiO_2-Al_2O_3	730	15				

[a] Percentage of total oxygen of the adsorbent which is in equilibrium with H_2O^{18} at 100 to 105°C.

[b] Percentage of total oxygen of the adsorbent which is calculated to be present as OH.

[c] Percentage of total oxygen of the adsorbent which is calculated to be on the surface.

[d] Percentage of total oxygen of the adsorbent which exchanges with H_2O^{18} in 1 month.

an activated silica-alumina catalyst. There appears to be a rapid exchange which can be accounted for by oxygen atoms at the surface of the catalyst, and a slow process which in the course of a month may involve a large percentage of the oxygen atoms of the interior of the adsorbent.

Karpacheva and Rozen[148] express their results in terms of the percentage, A, of the oxygen of the adsorbent which will exchange with water in a given time (Table 19). They also give the activation energy per mole, E, required to achieve certain specified percentages of exchange A'. The increase of E with A' is said to be nearly linear, as with activated adsorption on a uniformly heterogeneous surface.

In conjunction with the above results it is useful to note the water content of alumina as a function of temperature (Table 20) determined while the temperature was raised during 12 hr from 100 to 1200°C (Boreskov *et al.*[27]).

More recent results of a similar nature are presented in Table 21 taken from Gregg[98], who has also provided some interesting figures for the fraction of surface covered by OH groups after ignition at specified temperatures.

Active Sites. About 1 per cent of the surface of their thoria catalyst was estimated by Hoover and Rideal[110] to be active for the decomposition of ethanol. Poisoning experiments indicated that the processes of dehydration and dehydrogenation did not take place on the same sites.

Table 19

Temp.	200°C	400	600
A	20%	30	50
E	1.75 kcal	5.1	7.5
A'	5%	20	30

Table 20

Temp. (°C)	20	200	450	600	800	1000	1200
% H_2O	17	4.5		1.1			0
Surface area (m^2/g)			245		235	127	10.5

Dohse[64] estimated the number of active sites on his bauxite catalyst as 2–3 × 10^{19}/g. Vasserberg[274] determined the distribution of catalytically active centers on the surface of a mixed alumina catalyst used in dehydration of alcohols. The number of active centers was 1.7 × 10^{19}/g of catalyst. 5 to 10 per cent of the total surface of an alumina catalyst used by Boreskov[26] for ethanol dehydration was estimated to be active.

From studies with a considerable number of catalysts, Schwab *et al.*[238] concluded that the same centers are used for the dehydration of formic acid as for ethanol, but a different type of center for dehydrogenation of either reactant. A silica gel investigated by Freidlin and Levit[87] had ten times as many sites for formic acid as for ethanol decomposition, and the activity depended on the purity rather than the mode of preparation. They concluded that the active centers for formic acid dehydration were homogeneous. After heating the silica to 1100°C, the nature of the sites had altered, so that formic acid was decomposed to CO_2 instead of CO.

Topchieva and Yun-Pin[265] claimed that the "acid" sites in a silica-alumina catalyst were not effective in dehydration. Adsorption of Na^+ reduced the velocity of cumene cracking by a factor of 10 but had little or no effect on the rate of dehydration of ethanol (per unit surface area[260]). By addition of acid or an acid salt such as $NaHSO_4$, Zhabrova *et al.*[290] were able to make zinc oxide function as a dehydration catalyst.

TABLE 21. WATER CONTENT OF "OXIDES"
(From Gregg[98])

				Silica			
T°C	200°	400°	600°	800°	900°		
S'	715	639	546	397	237		
w	65	40	17.5	5.5	2		
θ	0.46	0.32	0.16	0.07	0.04		
				Alumina			
T°C	400°	500°	600°	700°	800°	900°	1000°
S'	300	243	224	166	148	118	99
w	69	35	19	14	12	8	6
θ	1.15	0.7	0.4	0.4	0.4	0.3	0.3
				Titania			
T°C	110°	205°	306°	406°	505°		
S'	308	161	122	80	72		
w	91.0	22.2	9.6	2.4	1.4		
θ	1.5	0.7	0.4	0.15	0.1		

T = Temperature of calcination; S' = specific surface, m^2/g of anhydrous solid; w = water content, mg/g of anhydrous solid; θ = fraction of surface covered with OH.

Preparation: silica from silicon ethoxide + pure water; alumina from aluminum ethoxide + pure water; titania from titanium sulfate in aqueous sulfuric acid, + water.

Time of calcination, usually 2 hr.

Variations in Particle Size and Lattice Parameter. Rubinshtein *et al.*[213a] have studied the effects of changes in degree of dispersion* of oxides and in lattice parameter on their catalytic activity. At 400 to 460°C the dehydration of 1-butanol over magnesia was favored by an expanded lattice when the parameter was varied within the range $a = 4.16$ to $a = 4.24$Å. With the lattice parameter held constant at $a = 4.2$Å the dehydration activity was greatest with a dispersion of 25 to 30Å. By contrast, dehydrogenation was favored by a smaller lattice parameter and lower temperature.

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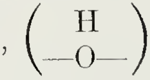
* Rubinshtein *et al.*[213a] determined by x-ray methods the lattice constants and the size of what he refers to as "the primary crystals," which were 22 to 63Å in diameter. By examining a large number of magnesias prepared by different means they were able to select a range of samples suitable for their catalytic experiments.

A similar study has been made by Balandin and Kukina[12a] on the dehydration and dehydrogenation of isopropanol over chromia. Extension of this approach to the more efficient dehydration catalysts should provide valuable results.

Coordination Chemistry in Dehydration Catalysis

Within recent years there have been advances in coordination chemistry which are contributing to our understanding of catalysis. The emphasis has been on complexes of the transition metals, with a reluctance to work on the complexes of silicon, aluminum etc., partly because of their lack of visible light absorption. There has however been some development of ideas on the structure of hydrous metal oxides (see review by Rollinson[213]). Whatever may be learned from the latter about the bridging of metal atoms by hydroxo-,  $\left(\overset{\text{H}}{\text{—O—}}\right)$, and ol-, (—O—), groups has a bearing on the question of surface structure of dehydration catalysts.

The bonds from metal to ligand which occur in solutions of the metal complexes cannot be described fully in terms of either covalency or ionic bonding, but moderately well by a combination of both (using crystal field theory as well as the descriptive approach of Pauling). Regarding the bonds at the surface of a dehydration catalyst (containing water, as it inevitably must during use) we know practically nothing concerning the degree of covalency, the occurrence of inner orbital bonding, or of π bonding. Attention to the properties of ions such as Al^{III}, Ti^{IV}, Zn^{II} etc. in solution may well provide us with a scale by which to judge the strength of binding and the nature of the binding at the surface of dehydration catalysts.

If we wish to classify oxides there are two rather obvious criteria: (1) whether the metal ion is one which may readily change its valency state, and (2) whether there is appreciable π bonding of oxygen to metal. If the answer to (1) is yes, usually the oxide will catalyze dehydrogenation. If on the other hand we write down all of the oxides in which the metal ion may have a filled set of orbitals as the outermost orbitals (Table 22) we find that the list includes all of the accepted dehydrating oxides and very few which are predominantly dehydrogenating. The table contains a few oxides in which the metal is in fact not too difficult to reduce, and in these instances the stoichiometry of the oxide, while it is acting as a catalyst, is not definitely known (e.g., oxides of vanadium, molybdenum, wolfram).

Magnesia is anomalous in having a much greater tendency to catalyze dehydrogenation than could be anticipated. A reverse effect is illustrated by the case of chromia, at least some preparations of which are good dehydration catalysts.

In general, π bonding is expected to be a prominent tendency of those transition metal ions in which few of the *d* orbitals are occupied.[152a]. For example in vanadium and chromium the tendency is stronger than in iron. It is possible that unexpected catalytic properties displayed by oxides of vanadium, chromium, zirconium, molybdenum, tantalum and wolfram are related to the presence of π bonds. An observation of Hunt and Taube[116a] is perhaps pertinent. The water in hydrated forms of Al^{III} and Th^{IV} exchanges with the solvent water in about 3 min., indicating a considerable degree of ionic character in the metal-oxygen bonds. Hydrated Cr^{III}, on the contrary, exchanges very slowly (half time about 40 hr).

The much greater tendency toward π bonding in silica than in alumina is no doubt responsible in part for the considerable differences in their catalytic activity.

TABLE 22. OXIDES WHICH ARE EXPECTED TO BE PREDOMINANTLY DEHYDRATING RATHER THAN DEHYDROGENATING

	Na_2O		K_2O		Rb_2O		Cs_2O	
	MgO		CaO		SrO		BaO	
Al_2O_3		Sc_2O_3		Y_2O_3		La_2O_3	R.E.*	
SiO_2		TiO_2		ZrO_2		HfO_2		ThO_2
P_2O_5		V_2O_5		Cb_2O_5		Ta_2O_5		
				MoO_3		WO_3		UO_3

* R.E. = Rare earths from Ce_2O_3 to Lu_2O_3.

CATALYST PREPARATION

Most of the dehydration catalysts in common use are metal oxides, and they are therefore frequently prepared by dehydration of the hydroxide. Hydroxide gels are difficult to wash free from alkali and foreign ions, which may prove to have a deleterious effect either directly as catalyst poisons or by influencing the mode of decomposition during the drying process.

It is sometimes found that a larger surface, a different disposition of the surface and somewhat different catalytic properties can be obtained by decomposition of an organic salt of the metal, e.g., an oxalate. Sometimes it is possible to select for the decomposition a salt or a coordination complex which is amenable to purification by repeated crystallization or distillation.

For an account of catalyst preparation in general, see "Catalysis," Vol. I, and also the very helpful review by Griffith and Marsh[100]; for the preparation of oxides in general, see Fricke and Hüttig[89].

Alumina

Senderens[242] at first prepared his alumina catalysts by decomposing the sulfate at red heat. Later he achieved a higher activity and less dehydrogenation with an alumina prepared via $Al(OH)_3$. The latter was precipitated in easily washable form from a solution of sodium aluminate treated with dilute sulfuric acid. It was washed a number of times with cold and then with boiling water, and finally dried at a low temperature. When he carried out the precipitation with aluminum sulfate and ammonia or sodium carbonate, the product was voluminous and difficult to wash. It was shown that increasing thoroughness of washing increased the catalytic activity of the final product. Low activity and low specificity (with respect to dehydration *vs.* dehydrogenation) observed by some of the earlier investigators may well have been due to insufficient washing of precipitates.

A procedure similar to that of Senderens was recommended by Clark, Graham and Winter[49]. A 10 per cent solution of sodium aluminate was allowed to stand until hydrolyzed. After a number of washes with cold and then hot water, the product was dried by gradual heating to 350°C. It was then washed with water and the cycle of heating and washing continued until the product was neutral to phenolphthalein. The final drying was carried out at 400°C, which appeared to be the optimum temperature for activation. Absolute purity of the catalyst was claimed to be essential for good yields of ether from ethanol.

Bentley and Feachem[18] later confirmed the beneficial effect of alternate hydration and dehydration of the catalyst. In addition to the washing action they believed that there was a breaking up of the crystal surface, which increased its area. To avoid introducing sodium ions, Alvarado[4], and later Feachem and Swallow[82], used ammonia as precipitant.

It is interesting that Alvarado's catalyst, which gave a high yield of ether from ethanol, was dried at 250 and used at 269°C. At these temperatures little conversion to γ-alumina would be expected.

The transition of α-alumina hydrates to γ-alumina at 400°C has been followed by weight-loss and surface area determinations (Russell and Cochran[217]); the highest surface area resulted from heating the trihydrate.

As a laboratory procedure, considerable interest attaches to de Boer's[57] preparation of alumina via aluminum propoxide as a means of avoiding contamination with foreign ions and of obtaining what he describes as "perfectly neutral alumina." By carrying out the hydrolysis at a benzene-water interface a very stable hydrous alumina of area 400 to 500 m^2/g can be obtained (Harris and Sing[105]).

Activation Temperature. It is well known that even the metal oxides, which are among the most refractory of materials, can suffer loss of their catalytic properties at the higher temperatures used in catalytic reactions. There are two processes to be distinguished here, which are interrelated: (a) loss of water from the lattice; (b) migration of metal and oxygen ions, resulting in reorganizations such as decrease in surface area, loss of defects or even change of crystal habit. Whereas the temperature required for (b) is in the absence of water approximately the Tammann[210] temperature (0.52 × M.P. in °K), process (a) occurs at a much lower but less definable temperature. Moreover, work with a number of alumina catalysts indicates that process (b) is so facilitated by the presence of water vapor (and therefore a high proportion of OH ions in the catalyst) that it can become troublesome at 300 to 400°C. Some experimenters have not clearly distinguished between the loss of activity by overheating which is due to loss of surface area, and the temporary loss of activity which occurs when the water content is reduced below the optimum value (discussed elsewhere).

In 1904 Ipatieff[128] recommended that the activation temperature should not exceed 400°C. Both lower and higher temperatures were used by many subsequent investigators although 400°C was perhaps the most favored. We may suspect that in some instances the activation took place or continued during use of the material as a catalyst. Although not strictly comparable, since the starting material was a commercial alumina which had already been activated, the following results from Brey and Krieger[37] are of interest: Heating at 600 to 900°C (for periods of 3 to 20 hr) resulted in an approximately linear decrease in area with increasing temperature. There was a greater loss of area in the presence of water vapor. The decrease in area was accompanied by a sharpening of the x-ray diffraction pattern, indicating crystallite growth. As the drying temperature was increased above 600°C there was a decrease in specific activity. Whether the decrease in specific activity was due to a reversible removal of water (i.e., the water content temporarily fell below the optimum value for catalysis) or to a decrease in the concentration of defects is not clear. The latter interpretation is the more probable since the specific activity was claimed to be independent of whether water was present during drying.

Closely related to the thermal history of the oxide is the ease of solution in acids. Ipatieff[128] claimed that an alumina catalyst should be readily soluble in warm HCl, H_2SO_4 or concentrated NaOH solutions. Although this relation between solubility and activity generally holds, it should be noted that Clark, Graham and Winter[49] found their most active alumina to be less readily soluble in acids than other preparations which they tested.

Thoria

From a remark by Sabatier[234] that the mode of preparation of thoria had little effect on its activity we may judge that his preparations were all equally poisoned or were overheated. Kramer and Reid[160] observed loss of activity if their thoria was heated much above 400°C, while Winfield[282] noted a slow loss at 450°C.

When studying ethanol decomposition over thoria at about 330°C, Hoover and Rideal[110] observed both dehydrogenation and dehydration if the catalyst was prepared by adding ammonia to a solution of thorium nitrate and drying the resulting gel at 120°C. A catalyst prepared by heating thorium nitrate, supported on pumice, at 300 or 400°C until no more acid was liberated yielded practically no aldehyde when used to decompose ethanol.

For the dehydration of 2,3-butanediol to methyl vinyl carbinol it was found that preparation of thoria from the nitrate or hydroxide was unsatisfactory[282]. The highest activity and specificity was attained by preparation via the oxalate, with ashing at 350 to 400°C. Carriers such as pumice or silica gel favored the competitive dehydration to methylethyl ketone.

Table 23. Influence of Method of Preparation of Titania on its Catalytic Properties at 350°C

(From Rudisill and Engelder[215])

Method of Prep.	Temp. of Ignition (°C)	Gas Evolved/cc Alcohol (ml)		% Composition of Gas Mixture				
		1st hr	2nd hr	C_2H_4	H_2	C_2H_6	CO	CO_2
Sulfate, washed	300	150	140	67.8	7.7	22.8	1.2	1.4
Sulfate, not washed	300	155	84	69.7	4.8	23.8	0.9	1.1
Oxalate	300	84	27	40.9	20.6	35.7	1.4	1.1
Chloride	300	104	85	46.4	38.7	14.6	0.9	0.5
Hydrolysis of chloride	300	117	103	76.0	4.6	18.0	0.4	1.5
Sulfate, washed	350	112	99	73.3	8.5	17.1	0.8	0.7
Sulfate, not washed	350	150	81	66.0	3.1	29.1	0.9	1.0
Oxalate	350	89	25	31.0	27.9	36.9	0.9	3.0
Chloride	350	111	92	48.9	29.8	18.3	0.7	1.1
Hydrolysis of chloride	350	139	128	70.8	4.7	22.9	1.0	1.1

The catalysts were prepared by precipitating $Ti(OH)_4$ from a solution of the sulfate, chloride or oxalate by adding NH_3, or by boiling. The latter method is referred to in the table as "hydrolysis of chloride."

Titania

A large number of titania catalysts was prepared by Rudisill and Engelder[215] and tested for activity in the dehydration of ethanol to ethylene at 350°C (Table 23). The best results were obtained by precipitating the oxide from a solution of the sulfate or by hydrolysis of the chloride. Preparation via the oxalate was unsatisfactory, leading to a product which tended to catalyze dehydrogenation of ethanol and hydrogenation of ethylene. In general, increase of ignition temperature above 350°C diminished the activity for catalytic dehydration. Grinding before ignition was distinctly beneficial.

It should be noted that none of Rudisill and Engelder's preparations can be regarded as acceptable dehydration catalysts for ethanol—all permit appreciable dehydrogenation.

Methods of titania preparation were also discussed by Bischoff and Adkins[22], with the following main conclusions: The surface conditions that determine relative catalytic activity are apparently determined not only by the size and shape of the radical attached to the titanium when the compound goes into the solid state, but also by the mechanism of hydrolysis and dehydration of the catalyst source.

Table 24 presents their experimental results relating activity and specificity with preparative method. In additional experiments they showed that differences in activity shown by the various preparations are not accompanied by corresponding differences in adsorption of the products of the catalytic dehydration.

TABLE 24. THE INFLUENCE OF MODE OF PREPARATION OF A SERIES OF TITANIA CATALYSTS ON DEHYDRATION ACTIVITY AND SPECIFICITY

(From Bischoff and Adkins[22])

Source of TiO_2 Catalyst	Liters of Gas Produced (NTP)/hr/2.0 g of TiO_2								
	Butanol at 430°C			Ethanol at 400°C			Diethyl Ether at 430°C		
	C_4H_8	C_4H_{10}	H_2	C_2H_4	C_2H_6	H_2	C_2H_4	C_2H_6	H_2
Butyl titanate*	5.6	0.25	0.0	3.2	1.2	0.0	—	—	—
Titanic acid	5.0	0.4	0.0	3.4	1.6	0.0	3.4	1.2	0.0
Ethyl titanate*	4.9	0.45	0.0	3.4	1.5	0.0	—	—	—
Methyl titanate*	3.8	0.7	0.1	2.3	1.4	0.0	3.1	1.3	0.0
Titanous chloride†	3.2	0.4	0.25	2.6	1.6	0.1	3.2	1.4	0.1
Sodium titanate**	1.3	1.1	0.95	1.3	1.6	0.7	1.0	0.8	0.3

* Exposed to air until hydrolyzed to a solid. Ground, then exposed until no odor of alcohol remained. Treated with liquid water, then dried at 120°C.

† Hydrolyzed with ammonia to give the hydrated oxide. Exposed to air until oxidized to titanic acid. Washed free from chlorides and dried below 150°C.

** Treated with large excess of water, giving titania. Dried at 120°C.

Promoters

A number of authors have mentioned the conspicuous lack of information relating to the promotion of dehydration catalysts. Where promotor action has been studied, almost invariably it has concerned a reaction which is not a pure dehydration. One may suspect that most dehydrations are best catalyzed by a pure oxide, and that, when properly prepared, the best oxide available cannot be further enhanced in activity. When, on the other hand, the principal constituent of the catalyst is a compound which is known to permit appreciable dehydrogenation (e.g., ZnO), there is no doubt that its usefulness as a dehydration catalyst can be increased, by addition of alumina for example (Balandin and Vasserberg[13]), but this can scarcely be regarded as promoter action. In much the same category is the considerable number of studies of so-called promoters for the Lebedev synthesis of butadiene from ethanol. The function of the additives is largely or entirely to catalyze additional reactions (dehydrogenation and hydrogenation) rather than to accelerate dehydration.

In general, the addition of an acid or acid salt enhances dehydration activity, as demonstrated for example by Zhabrova, Kutseva and Roginskii[290] who tested the effect of additions to ZnO of $NaHSO_4$, H_2SO_4, H_3PO_4, H_3BO_3, $Al_2(SO_4)_3$ etc. Commencing with a "neutral" alumina catalyst, de Boer[61a] showed that addition of acid (HCl) increased its activity for alcohol dehydration. It is not known whether the promoter effect here is attributable to hydrogen ions taken into the lattice or to HCl forming $AlCl_3$ which volatilizes, leaving aluminum vacancies, which become filled by protons.

The earliest recorded promoter effect is that of water, in small concentration, which has already been discussed. A temporary stimulation by chloroform (in certain concentrations) of ethanol dehydration to ethylene was noted by Hoover and Rideal[110].

Formic acid is atypical in its dehydration behavior. Bischoff and Adkins[22] for example noticed that its dehydration was independent of whether they ignited their titania catalyst. While mineral impurities poison an SiO_2 catalyst for ethanol dehydration, they enhance its activity for the dehydration

$$HCOOH \rightarrow CO + H_2O$$

as does also the addition of the alkali K_2O[87]. Although we may guess that the unique properties of CO are in some way responsible for the anomalies, no adequate explanation of the latter seems to have been offered.

Poisons

The study of inhibitors has also been neglected, or so it appears. Except for fouling by polymerization products and carbon deposits, the common dehydration catalysts such as Al_2O_3 are not prone to poisoning. Thoria is even resistant to sulfides[225].

A few isolated reports of inhibition studies come to mind. For example, Hoover and Rideal[110] found that ethanol dehydration to ethylene on thoria was retarded by acetaldehyde. Kline and Turkevich[154] noticed that the use of Al_2O_3 for dehydration of tetrahydrofurfuryl alcohol poisoned it for the dehydration of ethanol.

The one inhibitor mentioned repeatedly in the early literature is alkali. Some comments on the necessity for its removal during catalyst preparation have already been made. Bischoff and Adkins[22] found that ammonia was much more effective than water in favoring dehydrogenation (at the expense of dehydration) of butanol in the presence of TiO_2. Among the recent work is a more detailed investigation by Boreskov *et al.*[26], of the inhibitory effect of alkali[246a] on the dehydration activity of alumina. Some of their results are presented in Figure 6.

Perhaps the most stimulating remarks on poisoning phenomena are the following, taken from Dowden[67] and Bremner[35]: Poisons include those compounds, such as benzene, which have a large affinity for carbonium ions, and all substances which compete with the substrate for protons, yielding strongly adsorbed positive ions. In general ions which take up network-modifying positions in glasses* can be expected to act as poisons while those which take up network-forming positions can be either mild promoters or inhibitors, depending upon the reaction to be catalyzed.

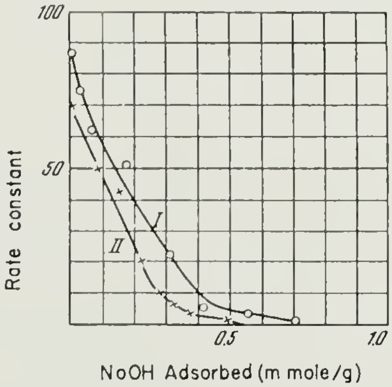


Figure 6. Influence of NaOH additions to an alumina catalyst on the rate of dehydration of ethanol to ethylene at 420°C. I and II are described in Table 16. (From Boreskov *et al.*[26])

CATALOG OF DEHYDRATION REACTIONS

In Table 1 are listed many of the gas phase dehydration reactions which have been studied in the past 160 years. Rather than attempt to achieve a complete list, the object is to show the range of usefulness of heterogeneous dehydration catalysis, and the kinds of catalyst which have been favored by both the early and the recent workers in the field. The author mentioned in each example is usually the first to have reported the reaction, and the catalyst first referred to is the one used by this same author, followed in many instances by a selection used by later investigators. Where

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* All oxides in which the ratio cation radius:anion radius is less than 0.414 are considered to be potential glass-formers. The network-formers include Al_2O_3, TiO_2, ZrO_2, ThO_2, SnO_2 and ZnO.

additional references are required they may be found in the tables prepared by Berkman, Morrell and Egloff[19], and by Innes[125a].

The most striking impressions gained on sifting the material available for Table 1 are:

(1) Almost any dehydration reaction can be carried out in the gas phase if required, and for convenience and speed this is the preferred method. There are a few reactions which are still best carried out slowly at low temperatures in the presence of sulfuric acid, either through lack of systematic search for suitable conditions for heterogeneous gas phase catalysis or because of the high boiling point of the reactant. Sometimes the latter can be conveniently handled by passing the liquid reactant through a bed of ion-exchange resin.

(2) Where specificity is not necessary (except to exclude nondehydrating reactions) alumina is usually as good or better than other catalysts which have been tried, and has the virtue of cheapness. Yet the literature abounds with descriptions of the use of more expensive or more elaborate catalysts which give smaller yields. There appear to be a few dehydrations for which a mixed catalyst is superior but well-authenticated cases are rare.

(3) Where it is necessary to discriminate between alternative dehydration paths, alumina is often unsuitable. Some of the rarer oxides may have the required specificity, when properly prepared, but there is a tendency to support them on materials which are themselves nonspecific dehydration catalysts, and which therefore detract from the specificity of the supported oxide.

(4) Attempts are frequently made to discover, without the aid of a guiding hypothesis, a mixed catalyst which is superior to a single compound. A little consideration shows that the chances of success are very small indeed. About 30 metal oxides are essentially dehydrating in their action. A thorough empirical search for the best combination of 2 oxides therefore requires the testing of 435 mixtures. Since at least 2 different preparative methods should be tried for each oxide, the number becomes 1740 or more. The situation is even worse when the investigator wants a combined dehydration-dehydrogenation catalyst, but has no theory to help narrow the selection to a few combinations. Since there are available about 30 oxides which may be classified as largely dehydrogenating, and again supposing on the average 2 methods of preparation of each oxide, there are at least 3600 mixtures to be examined. In searching for an improved Lebedev process, a number of workers have tested 3 component catalysts. A complete empirical survey would involve over 100,000 combinations.

CATALYTIC HYDRATION

In common with dehydration, the early history of hydration is far from clear. The hydration of pinene to terpin hydrate using alcoholic nitric acid as catalyst was described by Wiggers[280a] in 1846. Goriainoff and Butleroff (1873)[93] were able to show that ethanol could be obtained by passing ethylene into strong sulfuric acid at 160 to 175°C. Later Butleroff[42] found that at ordinary temperatures, 2-methyl-1-propene (isobutylene) reacted slowly with 10 per cent aqueous nitric acid or 50 per cent aqueous sulfuric acid to yield trimethyl carbinol. At 100°C there was some polymerization of the olefin. By a similar technique, 2-butene (pseudobutylene) was converted to 2-butanol (sec-butyl alcohol). At about the same time Wischnegradsky[286] hydrated 1-pentene (amylene) to dimethyl ethyl carbinol in nearly theoretical yield using 66 volume-per cent aqueous sulfuric acid cooled in ice. In another experiment the pentene was hydrated to a mixture of dimethyl ethyl carbinol and methyl isopropyl carbinol. Essentially these same processes have persisted up to the present time for the hydration of olefin by-products of the petroleum industry.

Also dating well back into the 19th century is the current process for hydrating acetylene to acetaldehyde by passing it into an aqueous solution containing mercury salts and an acid. The method seems to have originated with Kutscheroff.[163a]

Early in the present century Ipatieff[128] noted a hydration of ether to ethanol over alumina and later carried out a few experiments on the hydration of ethylene and amylene by aqueous acids. Sabatier showed little interest in hydration reactions, but he remarked in a paper with Espil[218] that diphenyl ether could be hydrated on thoria with 50 per cent conversion to phenol. Addition of sulfuric acid to a variety of olefins was described by Michael and Brunel[182], and a more comprehensive work was published by Brooks and Humphrey[39] in 1918. They hydrated a large number of olefins in sulfuric acid of various concentrations at 0 to 15°C, and in many instances obtained high yields of the corresponding secondary or tertiary alcohols.

One of the earliest I.G. patents[121] on hydration described the conversion of propylene and higher homologs to 2-propanol etc. at 100 to 250°C and pressures of 10 atm or more using aqueous solutions of acidic catalysts containing bismuth, copper or silver compounds.

With a few exceptions, such as that described in the first Lonza patent[73] for acetone from acetylene, little serious effort was made to employ heterogeneous gas phase catalysis until 1928–30, when several major companies took out patents. Slade[246], with I.C.I. Ltd., described the hydration of ethylene over thoria, or H_3PO_4 on charcoal, at 400 to 500°C and 25 to 200 atm pressure. McKee and Burke[173] claimed the use of a long series of conventional dehydration catalysts for the hydration of butenes and higher homologs at 300°C or more. Probably the most active ethylene hydration catalyst, cadmium metaphosphate, was covered by Horsley[111] and I.C.I. Ltd. in a patent issued in 1930.

Of the gas phase processes for hydration of unsaturated hydrocarbons, the first to go into large-scale production seems to have been the synthesis of acetone from acetylene (Shawinigan Chemicals Ltd.)[71, 243]. Shortly afterward (1947), the Shell Company in Houston put into operation their first plant for heterogeneous hydration of ethylene to ethanol[139].

To an increasing extent the early liquid-phase catalyses, which could be operated at relatively low temperatures, are now being replaced by heterogeneous processes. As against the high reaction temperatures and correspondingly low conversions per pass, the latter offer the advantages of convenience and lower maintenance costs.

It is not difficult to see why the heterogeneous processes have been slow to develop. For olefins the equilibrium is in favor of dehydration, even at ordinary temperatures. To induce rapid reaction an elevated temperature is desirable, but it swings the equilibrium so far in favor of the olefin that the maximum attainable conversion may be much less than 1 per cent. High pressures are therefore necessary to lift the conversion to an economic level.

The best catalyst is not necessarily the one which has proved most satisfactory for the reverse reaction. Indeed some of the more successful hydration catalysts are not typical dehydration catalysts. Among the more obvious reasons are:

1. A different set of adsorption characteristics is desirable: e.g., a stronger adsorption of unsaturated molecules relative to alcohols.
2. Ether formation cannot be suppressed as readily as in dehydration.
3. At high pressures unsaturated molecules tend to polymerize. A contact agent which catalyzes the polymerization is therefore to be avoided. The problem is far less acute in dehydration, for which pressures of 1 atm or less are the rule.

Examples of Hydration Reactions

The most important industrial chemicals produced by catalytic hydration are ethanol, 2-propanol, acetaldehyde, acetone, butanol and acetic acid. The reactions involved in their manufacture are discussed briefly below. Information available on gas phase hydration in general is summarized in Table 25. Reviews by Berkman, Morrell and Egloff[19]; Emmett[77]; Aries[10]; Tapp[255]; Randall[208]; Krentsel[161] and Moiseev and Syrkin[186] should also be consulted.

Ethylene to Ethanol. Acid phosphates or phosphoric acid appear to be the most successful catalysts. Although additives such as oxides of manganese and boron have been recommended (Stanley, Youell and Dymock[249]), it is doubtful whether they are in common use. According to Appleby, Glass and Horsley[9], cadmium metaphosphate is so active that it permits equilibrium to be approached from both sides at temperatures as low as 175°C, provided that their instructions for its preparation are ad-

Table 25. Hydration Reactions and Corresponding Catalysts

Reactant	Catalyst	Product	Conditions	Author
Olefins				
Ethylene	Al_2O_3 ; $Al_2(SO_4)_3$	acetaldehyde, presumably via ethanol	300–400°, 1 atm 0.2–0.4% conv.	280
"	ThO_2 ; H_3PO_4 on C	ethanol	400–500°C, 25–200 atm	246
"	$Cd_2(PO_3)_4$	ethanol		111
"	acid phosphates + $MnO + B_2O_3$	ethanol		249
"	Al_2O_3 ; W_2O_5 etc.	ethanol	360–380°, 70–135 atm	235
Ethylene and olefins	$Cd(PO_3)_2$ + metaphosphates of Ba, Sr, Ti, Cr and (or) Te	alcohols	100–300° 1–100 atm	112
Olefins	$Al(PO_3)_3$ + a metaphosphate of Ca, Cd, Zn, or bivalent Cu, Ni, Sn or Pb	alcohols	250–300°, > 100 atm	113
Ethylene	$Cd_2(PO_3)_4$	ethanol	200°, 1 atm, 1% conv.	9
"	Al_2O_3 ; W_2O_5 etc.	ethanol	320–378°, 7–11 atm	23
"	phosphates* of Mg, Al, Ca, Fe, Ni, Sr, Ba, W, Th or oxides of Al, W or Th	ethanol		10
"	W_2O_5	ethanol	300°, 300 atm, 23% conv.	258
"	H_3PO_4 on "Celite"	ethanol	300°, 70 atm, 4.2% conv.	139
"	$W_2O_5 + SiO_2$	ethanol	300°, 130 atm, 4% conv.	172
"	Al_2O_3	ethanol	350°, 1 atm	185
Propene	acid phosphates + $MnO + B_2O_3$	2-propanol		249
"	$WO_2 + ZnO$ on SiO_2	2-propanol	225°, 100–200 atm, 94% yield	143
"	W_2O_5	2-propanol	230°, 250 atm, 6.5% conv.	211
"	H_3PO_4 on SiO_2 , diatomaceous earth or kieselguhr	2-propanol	180°, 17 atm, 4% conv.	56
"	W_2O_5	2-propanol	270°, 250 atm, 16% conv.	169

TABLE 25—*Continued*

Reactant	Catalyst	Product	Conditions	Author
Olefins—continued				
Propene—*continued*	SiO_2 on Al_2O_3	2-propanol	250°, 100 atm, 15% yield	171
"	W_2O_5 (promoted)	2-propanol (+ 1-propanol + di-isopropyl ether + polymers)	260°–320°, 80–200 atm, 8% conv.	216
"	$SiO_2 + W_2O_5$	2-propanol	180°, 14.5 atm, 13% conv.; 200°, 37 atm, 17% conv.	188
2-Methylpropene (isobutene)	$W_2O_5 + C$	2-methyl-2-propanol (tertbutanol)	201°, 250 atm, 14.3% conv.	173
Butene, pentene, hexene etc.	Al_2O_3; $AlPO_4$; ThO_2; ZrO_2; TiO_2; V_2O_5; kaolin etc.	alcohols	>300°	179
2-Butene	Cu_2Cl_2 on pumice; H_3PO_4; ThO_2; $Cu_3(PO_4)_2$	2-butanol	427°, 330 atm, up to 7.6% conv.	249
Butenes	acid phosphates + $MnO + B_2O_3$	alcohols		168
Butene and pentene	SiO_2 on Al_2O_3	alcohols	250°, 100 atm	171
Butenes	$W_2O_5 + C$	butanols	100–500 atm	168
2-Butene	BPO_4	2-butanol	385°, up to 615 atm, 8.5% conv.	54
Acetylenes				
Acetylene	Al_2O_3	acetaldehyde detected	160–250°, 1 atm	33
"	ThO_2; $Th(CO_3)_2$; $Th(OH)_4$; double salts of Th with alkalis or alkaline earths	acetone	350–450°, 1 atm	73
"	alkaline earths; ZnO; SnO; Al_2O_3; MgO; V_2O_5; MnO_2; Cr_2O_3; TlO_2; etc.; Pb; Fe	acetone	400–450°, 1 atm	119
"	Bi molybdate	acetaldehyde + acetic acid		194

TABLE 25—*Continued*

Reactant	Catalyst	Product	Conditions	Author
Acetylenes—continued				
Acetylene—*continued*	$Fe(OH)_3 + ZnO$	acetone	400–500°, 1 atm	243
"	$Cd(H_2PO_4)_2$	acetaldehyde	>250°, 1 atm	101a
"	$ZnO + V_2O_5$; Cd vanadate + Fe_2O_3	acetaldehyde + acetic acid	400–425°, 1 atm	153a
"	$2ZnO \cdot V_2O_5$	acetone	450°, 1 atm, 60–70% yield	40
"	silicophosphoric acid	acetaldehyde		135a
"	Cd + Ca compounds	acetaldehyde	300°, 1 atm, 95% yield	195
"	oxides†, phosphates, borates, sulfides, selenides, chlorides, silicates, vanadates, chromates or molybdates of some or all of the metals Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Sn, Ce, W, Hg, Pb, Bi and the alkaline earths	acetone	250–450°, usually 3–10 atm	194
"	$Fe_2O_3 + ZnO$	acetone + H_2 + CO_2	420°	71
"	$Fe_2O_3 + ZnO$	acetone + H_2 + CO_2	470°	140
"	$H_3PO_4 + ZnHPO_4 + CuHPO_4$ on C	acetaldehyde	250°, 1 atm, 48.5% conv.	287
"	$Al_2O_3 + ZnO + W_2O_5$	acetaldehyde		291
"	ZnO	acetone	400°, 1 atm	208
"	$ZnHPO_4$ on C	acetaldehyde	250°	187
"	Cd phosphate on glass wool	acetaldehyde	350°, 1 atm, 95% yield	268
"	Cd or Zn phosphate + Ag and Cu compounds, on quartz or glass	acetaldehyde or acetone		267
"	$CdCrO_4 \cdot 2H_2O$ on acid clay	acetaldehyde	300°, 1 atm, 88% yield, possibly 31% conv.	163

Table 25—*Continued*

Reactant	Catalyst	Product	Conditions	Author
Acetylenes—continued				
Acetylenes	Zn tungstate on Al_2O_3	aldehydes or ketones	350–370°, 1 atm, 95% yield	45
Ethers				
Diethyl ether	Al_2O_3	ethanol	330°, 1 atm	128
" "	Al_2O_3	ethanol	250°, 1 atm	201
" "	Al_2O_3	ethanol	250°, 1 atm, 12% conv.	49
$(CH_2{=}CHCH_2)_2O$ and homologs	$CuSO_4$ on Al_2O_3	$CH{=}CHCH_2OH$ and homologs	190°, 1 atm, 29% conv.	46
Diphenyl ether	ThO_2	phenol	50% conv.	218
Miscellaneous				
Ethylene oxide	Ag_2O on Al_2O_3	ethylene glycol	170–172°, 1 atm, 20–30% conv.	42a
Methyl acetate	Cd, Ag or Zn acetate on SiO_2	methanol + acetic acid	230–300°, 1 atm, 49% conv.	99
2-Chloro-2-butene	H_3PO_4 on SiO_2 or Al_2O_3	methylethyl ketone	200–400°, 1 atm	5

* Taken from a review by Aries,[10] covering catalysts tested in England and the U.S.A. up to 1947.
† Taken from a bibliography by Nieuwland and Vogt[194] covering the literature up to 1938.
Note that for each of the reactants which appear in the table the authors are listed in chronological order.

hered to. A literature search has failed to reveal any mention of its use on a large scale, and we may wonder if there are practical difficulties yet to be solved.

Most of the orthodox dehydration catalysts such as Al_2O_3, W_2O_5, ThO_2 etc. are too slow in action to be of economic importance (Sanders and Dodge[235]). Yet one at least of the recent patents is based on a W_2O_5 catalyst (Thomson and Greenhalgh[258]). Apparently the mode of preparation is critical. WO_3 is formed into pellets and then reduced with ethanol at about 250°C[211]. High pelleting pressures are advantageous.

Mills, Weller, Hindin and Milliken[185] have shown that an alumina catalyst increases 60-fold in activity for C_2H_4 hydration as its temperature of ignition is increased up to 650°C. The reverse of this phenomenon is possibly responsible for the decline in activity of hydration catalysts with use. Mills *et al.* also noted that water poisoned their catalyst. It is not surprising that a high level of catalytic activity is difficult to achieve, with a feed which is about one third water, at the high pressures employed in large-scale hydration.

In the process operated by the Shell Company[139], ethylene and steam are passed over H_3PO_4 supported on celite, at 300°C and 70 atm pressure with a water to ethylene ratio of 6:10. At pressures much above 70 atm polymerization of ethylene becomes troublesome (see for example Sanders and Dodge[235]). The conversion per pass is 4.2 per cent of the ethylene and 7 per cent of the water. As well as ethanol a little ether is formed together with minor amounts of polymer and other products (Johnson and Nelson[139]).

Although the conditions described above seem to have been generally agreed upon as the best compromise, and to be the basis of operation of large-scale plants, a recent I.C.I. patent[258] suggests that much higher pressures may yet become practicable. The following experimental results at 300 atm pressure are of considerable interest in demonstrating that an 87 per cent yield of ethanol can be attained in spite of increased polymerization (Table 26).

TABLE 26. HYDRATION OF ETHYLENE AT 300 ATM PRESSURE ON A TUNGSTEN OXIDE CATALYST

(From Thomson, Greenhalgh and I.C.I. Ltd.[258])

	Temp., °C		
	300	320	345
Ethylene feed rate, kg/l. cat./hr.	0.029	0.043	0.085
Mole ratio of water to ethylene	53.6	36.1	17.9
Ethanol space time yield, kg/l. cat./hr.	0.011	0.020	0.040
Ethylene polymerized, kg/l. cat./hr.	0.001	0.01	0.04
Ethylene conversion to ethanol, %	23.3	28.2	28.5
Ethylene conversion to all products, %	26.8	51.5	75.5
Ethanol yield, %	87	55	38

Propylene to 2-Propanol. According to an I.C.I. patent (Levy[169]) equal amounts by weight of propylene and water are passed over W_2O_5 at 270°C and 250 atm, with a 16 per cent conversion to 2-propanol. A 15 per cent yield after passing for 1 to 4 hr is claimed by Lukasiewiez, Denton and Plank[171], using as catalyst SiO_2 supported on alumina, and a temperature and pressure of 250° and 100 atm respectively. Muller and Waterman[188] use a silico-tungstate catalyst at 160 to 220°C and 14.5 to 37 atm, with the results shown in Figures 7 and 8, which clearly demonstrate the need for careful control of the operating conditions. Under the conditions of pressure, space velocity and ratio of reactants applicable in Figure 7, an increase in temperature beyond 180°C leads to considerable loss in the form of polymer and side products.

Butenes to Butanols. Dale, Sliepcevich and White[54] describe the hydration of 2-butene to 2-butanol with a conversion of about 8.5 per cent at 385°C and pressures up to 612 atm, with a boron phosphate catalyst.

Somewhat better results are claimed in an I.C.I. patent[168]. The same conversion is obtained at only 230 to 270°C and 250 atm, using a W_2O_5 catalyst on graphite. In the same patent, with the same catalyst, is described the hydration of isobutene to tert-butanol, with a conversion of 14.3 per cent at 201°C and 250 atm.

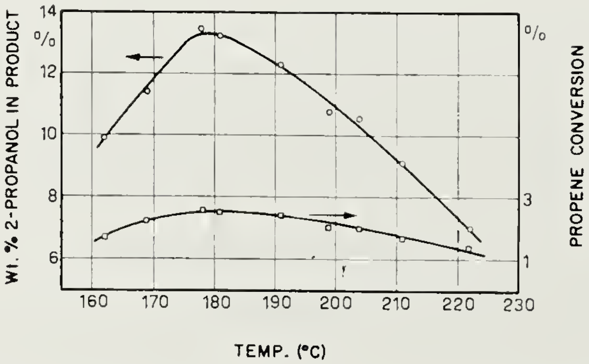


Figure 7. Hydration of propene to 2-propanol on a silico-tungstate catalyst. Dependence of propene conversion on temperature. Pressure 14.5 atm; mole ratio of C_3H_6 to H_2O is 1.7 (approx.); space velocity, approx. 4750 l./l. cat./hr. (From Muller and Waterman[188])

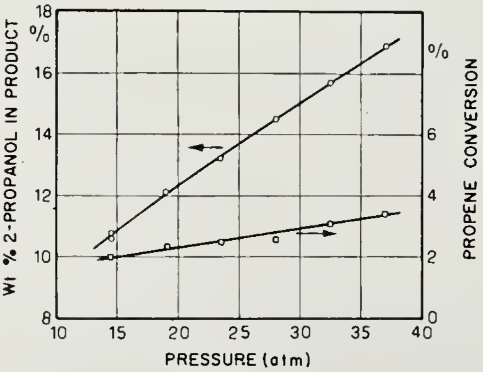


Figure 8. Hydration of propene as in Figure 7. Dependence of propene conversion on pressure, at 200°C. (From Muller and Waterman[188])

Acetylene to Acetaldehyde. That acetylene can to some small extent be hydrated on alumina at 160 to 250°C was demonstrated by Boswell and Dilworth[33] in 1925. Although a number of patents have been taken out in the intervening years, the author has found no description of a gas-phase process which is currently in operation (except as the first step in acetone synthesis). Usually the catalyst recommended contains zinc or cadmium, and almost all patents claim aldehyde yields of 90 to 95 per cent without resort to high pressures. Dissipation of the heat liberated during the reaction, and the prevention of acetone formation, are possibly the major practical problems in what appears to be an attractive process.

A catalyst consisting of $H_3PO_4 + ZnHPO_4 + CuHPO_4$ on carbon is described by Yakubovich, Danilevich and Medzykhovskaya[287]. The conversion claimed is high for a process of this type—48.5 per cent at 250°C. A Swedish patent[187] describes a similar method in which acetylene and steam in the ratio 1:4 are passed over zinc phosphate, supported on carbon, at 250°C. In another Swedish patent, Topsoe[267] uses either a zinc or a cadmium phosphate catalyst, supported on glass wool and activated with silver and copper compounds. In Japan one of the most active catalysts tested is said to be $CdCrO_4 \cdot 2H_2O$ supported on acid clay[163]. The conversion is 31 per cent at 300°C, with an ultimate yield of 88 per cent. An earlier Japanese patent[195] claimed a 95 per cent yield at the same temperature, using as catalyst a mixture of cadmium and calcium compounds.

Zinc tungstate on alumina is used in a German patent[45] for production of aldehydes or ketones from acetylenes in general. The yield is 95 per cent at 350 to 370°C.

Acetylene to Acetic Acid. Although an appreciable amount of acetic acid is still produced by the liquid-phase hydration of acetylene in the presence of mercury salts, it is now more commonly manufactured by the oxidation of acetylene. Little attention has been given to the gas-phase synthesis of acetic acid by hydrating acetylene.

Acetylene to Acetone. Possibly the origin of the present-day large-scale process, a Lonza patent[73] of 1923 described the gas-phase hydration[181] of acetylene to acetone at 350 to 450°C on a catalyst which consisted of one of a variety of thorium compounds supported on burnt clay or on pumice. A very large number of catalysts has since appeared in the patent literature. Practically all of the elements in the periodic table have been cited, apparently with the object of escaping the implications of the early patents. The I.G. Farbenindustrie for example claimed in one patent[119] the use of oxides, carbonates and acetates of alkaline earth metals and of zinc, tin, aluminum and magnesium, or basic salts of these, or the metals themselves. Also claimed were finely divided lead or iron, calamine, bauxite, V_2O_5, MnO_2, and Cr-Tl compounds, as well as various mixtures (quoted from Nieuwland and Vogt[194]).

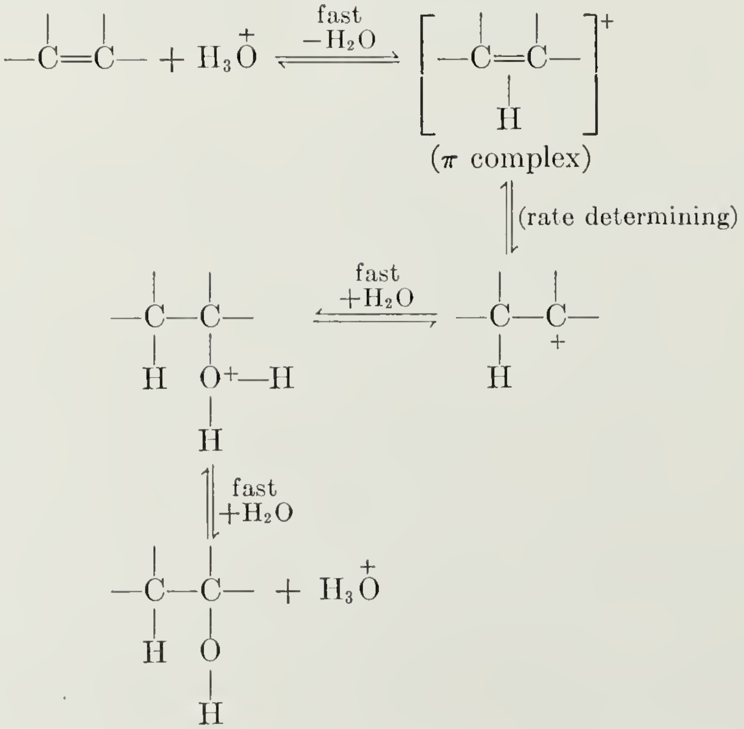
In large-scale production the catalysts generally used are mixtures of iron and zinc oxides. The Reppe Synthesis used in Germany during World War II[106] depended on a ZnO catalyst and temperatures around 400°C, without use of high pressures (Randall[208]). In the process operated by Shawinigan Chemicals Ltd., acetylene and steam in the ratio 1:10 are led over $Fe_2O_3 + ZnO$ at 420°C[71], probably at a pressure of 1 atm[243]. The mechanism is thought to be (Dyck[71])

$$\begin{tikzcd}
2C_2H_2 \arrow[r, "+2H_2O"] & 2CH_3CHO \arrow[d, "+2H_2O-2H_2"] \\
CH_3COCH_3 & 2CH_3COOH \arrow[l, "-H_2O-CO_2"']
\end{tikzcd}$$

Hydrations in General. Judging from the recent patent literature and descriptions of industrial hydration processes, the successful catalysts are most frequently phosphates, tungstates or zinc oxide. There is a marked tendency to use them mixed with carbon. A critical discussion of the rationale of these choices would be welcomed.

Mechanism of Hydration

Taft's[253] suggestion that the hydration transition states of olefins in aqueous acid are free from firmly bound water molecules has been mentioned briefly in connection with dehydration mechanisms. Taft's scheme is



Rates of hydration are claimed[252] to be proportional to Hammett's[103a] activity function H_0, but not to the acid concentration itself. H_0 is used in the form

$$H_0 = pK_a + \log_{10} (C_B/C_{BH+})$$

where C_B is the concentration of the neutral base B, C_{BH+} the concentration of its conjugate acid $B\overset{+}{H}$, and pK_a is the acidity constant $(-\log_{10} K_a)$.

Moiseev and Syrkin[186] also assume that the transition complex consists of the olefin with a proton attached. In the hydrolysis of acetic anhydride Koskikallio[159] assumes that the anhydride exists in the solution in two different forms and that the transition complex is solvated.

The mechanism of by-product formation in hydration processes, especially those based on acetylene, is complex and difficult to study. A conception of the large variety of compounds obtainable can be gained from a paper by Benson and Cadenhead[17] describing the Shawinigan liquid phase hydration of acetylene.

Very little indeed has been written about hydration mechanisms at a solid surface, too little in proportion to the potential economic value and in relation to the volume of fundamental research on other aspects of catalysis.

In the hydration of ethylene oxide, water and ethylene glycol are adsorbed more strongly on the silver oxide catalyst than is the ethylene oxide. The following mechanism is proposed (Cartmell *et al.*[42a]):

$$\begin{tikzcd}
Ag_2O + H_2O \arrow[r, rightleftharpoons] & Ag_2O[H_2O] \arrow[d, shift left, harpoon, "+C_2H_4O"] \\
Ag_2O + (CH_2OH)_2 & Ag_2O[(CH_2OH)_2] \arrow[l] \arrow[u, shift left, harpoon]
\end{tikzcd}$$

The activation energy for hydration of ethylene to ethanol is about 30 kcal/mole, according to Mace and Bonilla[172], at a silico-tungstate surface with a temperature of 330°C and a pressure of 130 atm. The catalysis proceeds without preferential adsorption of ethylene or water, and without retardation by strong adsorption of water.

Thermodynamics of Hydration-Dehydration

In designing a hydration process it is usually necessary to make use of the thermodynamic functions which govern the hydration-dehydration equilibrium, as an aid toward finding the optimum working conditions. This is particularly true for the heterogeneous hydration of olefins. The reactions are exothermic and the maximum conversion per pass is of the order of 1 per cent at 200°C and 1 atm pressure (Appleby, Glass and Horsley[9]). The struggle toward achieving an economic process was at first largely a struggle to measure or to calculate the equilibrium constants as a function of temperature. Much of the information now available is summarized in Table 27 and the equations given below.

The earliest attempts to calculate the change in free-energy (ΔF) and in enthalpy (ΔH) for the equilibrium between an olefin or ether and the corresponding alcohol were greatly in error, due to the lack of accurate values for the thermodynamic functions of the reactants and products. Some of the experimentally determined equilibrium constants were also misleading, because of experimental difficulties associated with low conversions and slow-acting catalysts.

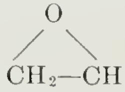
The most recent values in Table 27 are probably close to correct. They

TABLE 27. THERMODYNAMIC FUNCTIONS FOR HYDRATION—DEHYDRATION REACTIONS

Equilibrium	ΔH (kcal/mole)	ΔF (kcal/mole)	$\log_{10} K_p$	Temp. (°K)	Authors
$C_2H_2 + H_2O \rightleftharpoons CH_3CHO$	−40				125a
$C_2H_2 \rightleftharpoons H_2O \rightleftharpoons \frac{1}{2}CH_3COCH_3 + \frac{1}{2}CO_2$	−42.5				125a
$C_2H_4 + \frac{1}{2}H_2O \rightleftharpoons \frac{1}{2}(C_2H_5)_2O$	−11.5				12
$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$	−9.6			418–523	249
			−3.0	653	235
	−9.9			448–548	9
			0.49	298	114
			−0.58	400	114
			−1.81	500	114
			−2.6	600	114
			−3.2	700	114
	−10.964			423	10
			1.12	300	10
			−0.81	400	10
			−2.02	500	10
			−2.8	600	10
	−7				12
	−10.72*			298	14
	−10.55			298	14
$CH_3CH = CH_2 + H_2O \rightleftharpoons CH_3CH_2CH_2OH$	−9.3*	−0.14*	0.1*	298	70
$CH_3CH = CH_2 + H_2O \rightleftharpoons (CH_3)_2CHOH$	−9			448–523	249
$CH_3CH_2CH = CH_2 + H_2O \rightleftharpoons CH_3CH_2CHOHCH_3$	−8.45			423–523	249
$(CH_3)_2C = CH_2 + H_2O \rightleftharpoons (CH_3)_3COH$	−9 (approx.)			423–448	249
$(CH_3)_2C = CH_{2_{aq}} + H_2O_l \rightleftharpoons (CH_3)_3COH_{aq}$	−11.6	$\Delta S = -21$		298–308	72
$(CH_3)_2 = CH_{2_g} + H_2O_l \rightleftharpoons (CH_3)_3COH_{aq}$	−15.76	$\Delta S = -45.3$	0.74 (moles l^{-1} atm^{-1})	323	254

			0.41	333	254
			0.13	343	254
$(CH_3)_2 = CH_{2_g} + H_2O_l \rightleftharpoons (CH_3)_3COH_l$	$\Delta H^\circ = -12.6$	$\Delta F^\circ = -1.3$		298	254
		$\Delta S^\circ = -37.9$		298	254
$CH_2 = CHCH = CH_2 + H_2O \rightleftharpoons CH_3CH = CHCH_2OH$		2.13*	−1.56*	300	95
		10.95*	−3.99*	600	95
		16.23*	−4.44*	800	95
$CH_2 = CHCH = CH_2 + H_2O \rightleftharpoons CH_3CHOHCH = CH_2$		11*	−3.0*	773	282
$CH_2 = CHCH = CH_2 + 2H_2O \rightleftharpoons CH_3CHO + C_2H_5OH$	−13				125a
$CH_3CHOHCH = CH_2 + H_2O \rightleftharpoons CH_3CHOHCHOHCH_3$		17*	−4.9*	773	282
$(C_2H_5)_2O + H_2O \rightleftharpoons 2C_2H_5OH$			−0.36	463	175†
	22	6.4		298	202
			−0.9	403	202
			0.18	548	202
			−0.9	523	49
			−0.54	498	138†
			−0.92	542	4†
			−0.89**	539	193
			0.64	392	273
			0.40	403	273
			0.24	413	273
			0.06	425	273
			−0.021	431	273
			−0.086	437	273
			−0.40	473	273
			−0.49	482	273
			−0.54	492	273
			−0.56	503	273
			−0.59	509	273
	9				12
	43.4				264

TABLE 27—*Continued*

Equilibrium	ΔH (kcal/mole)	ΔF (kcal/mole)	$\log_{10} K_p$	Temp. (°K)	Au-thors
$(CH_3CH_3CH_2)_2O + H_2O \rightleftharpoons 2CH_3CH_2CH_2OH$			-0.97^{**}	523	193
$(CH_3CH_2CH_2CH_2)_2O + H_2O \rightleftharpoons 2\ CH_3CH_2CH_2CH_2OH$			-1.06^{**}	523	193
 $CH_2{-}CH_2(O) + H_2O \rightleftharpoons C_2H_4(OH)_2$	-23^*	$\Delta F^\circ = -15.8^*$	11.60^*	298	42a
		$\Delta S^\circ = -24.9^*$		298	42a
			3.48^*	573	42a
	-25.1^*	-17.4^*	12.75^*	298	70
$CH_3COC_2H_5 + H_2O \rightleftharpoons CH_3CHOHCHOHCH_3$		34^*	-9.5^*	773	282
$CH_3NH_2 + H_2O \rightleftharpoons CH_3OH + NH_3$	5.7				125a
$CH_3CONH_2 + H_2O \rightleftharpoons CH_3COOH + NH_3$	4				125a
$HCOOCH_3 + H_2O \rightleftharpoons CH_3OH + HCOOH$	5.6				125a

* Calculated rather than experimental values.

† As calculated by Valentin[273] from results in the original reference.

** K_c rather than K_p .

For each reaction the authors are listed in chronological order.

refer to the gaseous state of both reactants and products, except when the authors have determined K_c (the equilibrium constant in terms of concentrations) or have failed to specify clearly their conditions. The latter is possibly the reason for the serious lack of agreement in ΔH values.

A number of semi-empirical equations have been offered which provide values of ΔF or log K_p as a function of temperature or size of alcohol molecule. Examples are:

Equilibrium: $C_nH_{2n_g} + H_2O_l \rightleftharpoons C_nH_{2n+1}OH_g$
ΔF (cal): $-\Delta F = 5320 - 815n - 17.2T + 0.5nT$
Authors: Francis and Kleinschmidt[85]

Equilibrium: $C_2H_{4_g} + H_2O_g \rightleftharpoons C_2H_5OH_g$
Kp: $\log_{10} K_p = 2159/T - 6.34$
Conditions: 448–548°K
Authors: Appleby, Glass and Horsley[9]

Equilibrium: $C_2H_{4_g} + H_2O_g \rightleftharpoons C_2H_5OH_g$
Kp: $\log_{10} K_p = 2100/T - 6.195$
Conditions: 418–523°K, 1 atm
Authors: Stanley, Youell and Dymock[249]

Equilibrium: $C_2H_{4_g} + H_2O_g \rightleftharpoons C_2H_5OH_g$
ΔF (cal): $-\Delta F = 9600 - 28.2T$
Kp: $\log_{10} K_p = 2100/T - 6.17$
Conditions: 593–651°K, 7–11 atm
Authors: Bliss and Dodge[23]

Equilibrium: $C_3H_{6_g} + H_2O_g \rightleftharpoons (CH_3)_2CHOH_g$
Kp: $\log_{10} K_p = 1950/T - 6.060$
Conditions: 448–523°K, 1 atm
Authors: Stanley, Youell and Dymock[249]

Equilibrium: $C_4H_{8_g} + H_2O_g \rightleftharpoons C_2H_5CH(CH_3)OH_g$
(*Normal butenes*)
Kp: $\log_{10} K_p = 1845/T - 6.395$
Conditions: 423–523°K, 1 atm
Authors: Stanley, Youell and Dymock[249]

T is the temperature in degrees Kelvin and n is the number of carbon atoms in the olefin. K_p has the dimensions atm^{-1}. ΔF is apparently the standard free energy change $\Delta F°$, although most authors have not stated explicitly which is intended.

Recently Barrow[14] has discussed the thermodynamics of ethylene hydration in detail. His plot of observed and calculated values of log K_p as a function of temperature is reproduced in Figure 1. How little discrepancy now remains between the two sets of values is well illustrated by the following:

$\Delta H^\circ_{298.2} = -10.72 \pm 0.3$ kcal as calculated from heats of formation of the participants in the equilibrium.

$\Delta H^\circ_{298.2} = -10.55$ kcal from experimentally determined equilibrium constants.

Entropies, enthalpies and specific heats may be obtained from Ribaud[212] for methanol, ethanol, acetylene, ethylene, propylene, water, ammonia, hydrogen sulfide and hydrogen cyanide; entropies, enthalpies and free energies from Dyatkina[70] for propanol, butanol, ethylene glycol, propylene and water. The free energies of formation of a number of unsaturated hydrocarbons are to be found in papers by Thacker, Folkins and Miller[257], and by Francis and Kleinschmidt[85].

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CHAPTER 3

HYDROCARBON OXIDATION

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Introduction

These chapters on catalytic oxidation are concerned with the vapor phase oxidation of substances at solid surfaces. They describe the catalytic oxidation of materials in the presence of oxygen, and in most cases air. Although there have been many studies of catalytic oxidation in the liquid phase, these matters are considered to be outside the scope of this presentation.

The field of catalytic oxidation is one which should be attractive to investigators interested in catalytic phenomena. It is usually possible to prepare oxidation catalysts reproducibly, and their activity often remains constant over a long period of time so that studies of reaction kinetics are not complicated by changes in catalytic activity with use. Recently papers have appeared which describe successful attempts to apply the results of magnetic susceptibility measurements and other properties of semiconductors to oxidation catalysts. Also, effective use has been made of isotopic tracers, principally O^{18}, in catalytic oxidation studies. There has been much less interest in the understanding of catalytic oxidations than in many other reactions so that this field might prove to be of interest to some investigators if only for that reason.

Since the appearance of the excellent monograph of Marek and Hahn on "The Catalytic Oxidation of Organic Compounds in the Vapor Phase"[108], many papers and patents have appeared on this subject. In the preparation of this chapter a search was made of the literature and patents on catalytic oxidation. Many of the references found were concerned with the qualitative aspects of the subject. Often they referred to the nature of the products formed by catalytic oxidation or to the qualitative nature and behavior of the catalyst used. Although the results obtained in a number of these investigations will be cited, it is preferred where possible to attempt to emphasize the quantitative nature of the information presented by a review of a smaller number of the references. Also, the opportunity is taken to discuss the future course which investigations might take, based on present knowledge, to advance the subject.

A great deal of work in the field of catalytic oxidation has been performed in the laboratories of industrial organizations. This has been quite fruitful in promoting the important interests of the chemical industry. In many cases it has not seemed desirable to report the results of these studies because they often fail to correlate the results obtained with fundamental catalytic properties or mechanisms. It is not the intention to minimize the importance of the work of the industrial research, but only to point out why it has not seemed appropriate to discuss in detail the many important investigations which have been carried out by such organizations.

The authors have had many opportunities to discuss the problems of catalytic oxidation with members of the staff of the Stamford Laboratories, American Cyanamid Company. It has not been possible in all cases to refer by name to the investigators who have been of assistance. In many cases we will refer to the work of our associates as "unpublished results, American Cyanamid Company." This opportunity is taken to express our appreciation for this assistance in making the present chapter possible.

Literature Survey

In order to prepare the material for these chapters, a literature survey on heterogeneous vapor phase catalytic oxidation was carried out. This survey was conducted by Miss Lucy E. Vandervort of the Technical Information Section of the Stamford Laboratories, Central Research Division, American Cyanamid Company. The authors are grateful for her assistance.

Fortunately, a literature survey entitled "Vapor Phase Oxidation of Hydrocarbons," prepared by R. M. Thomas, Westvaco Chlorine Products Corp., Research Department, South Charleston Division, dated November 4, 1942, was acquired and was considered to be an adequate coverage of the literature on hydrocarbon oxidations prior to 1940. This survey contains 781 references to articles which were published up to June 1942. Marek and Hahn in their book on "Catalytic Oxidation of Organic Compounds in the Vapor Phase" summarize the literature through 1931.

The search carried out by Miss Vandervort was limited to a survey of "Chemical Abstracts" for the period 1940 through 1956. Information was abstracted on the following subjects: kinetics, mechanisms, laboratory and pilot plant apparatus, and plant equipment, as well as on the subject of vapor phase oxidation catalysts and catalytic processes. The headings searched in the Subject Indices of *Chemical Abstracts* were the following: Oxidation, Oxygen, Air, Ammonia, Nitric Acid, Nitrogen Oxide, Carbon Monoxide, Sulfur Dioxide, Sulfuric Acid, Sulfur Trioxide, Acetylene, Acetylene Compounds, Benzene, Ethylene, Ethylene Oxide, Anthracene, Naphthalene, Xylenes, Hydrogen, Hydrocyanic Acid, Amines, Cycloalkanes, Toluene, Thiols, Mercapto Compounds, Aldehydes, Ketones, Alcohols, Catalysis and Catalysts. In addition, it is believed that most of the pertinent articles which appeared through 1957 have been included as a result of the authors' following of the literature.

From 700 references located in this search an attempt was made to select those having some important bearing on the subject of kinetics and mechanisms of catalytic oxidation. The references giving but little information other than of a qualitative nature were considered to be outside the scope of this review. The authors believe that the search as referred to above provided the necessary background material for the topics covered in these chapters.

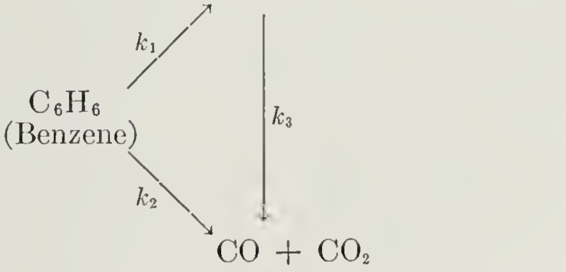
OXIDATION OF BENZENE

Introduction

Although the commercial production of maleic anhydride (MAA) by the catalytic oxidation of benzene has been in operation for over 20 years, only recently have data become available giving some insight into the reaction rates and mechanisms involved.

It has been suggested that the reaction proceeds through a number of intermediates including phenol[52, 131, 209], hydroquinone[131, 146] and quinone[131, 146, 179]. The presence of small amounts of formaldehyde and diphenyl has also been reported among the products[201]. However, MAA is the only product which has been obtained in economically attractive yields.

It has been found by a number of workers that the principal over-all reactions involved in the oxidation of benzene can be summarized by the scheme:



Both reactions (1) and (2) may proceed through a number of relatively short-lived intermediates.

Benzene and Maleic Anhydride (MAA)

Hammar[74] has studied the oxidation of benzene over a series of catalysts consisting of V_2O_5 and MoO_3 on aluminum. His data were in agreement with the reaction scheme outlined above. The effect of contact time (at constant feed concentrations and mass velocities) on the conversions to MAA and $CO + CO_2$ could be described by assuming that reactions 1, 2 and 3 were all first order with respect to the organic reactant involved. However, it has not been positively established that all of the reactions are exactly first order, since similar results might be obtained by other kinetic combinations.

TABLE 1. RELATIONSHIP BETWEEN GAS MASS TRANSFER RATE AND REACTION RATE IN THE OXIDATION OF BENZENE*

Catalyst = V:Mo:Al = 1.0:0.3:1.0
Temperature = 375°C
Air: Benzene (mole ratio) ~150
D_p (particle diameter) = 0.1 cm
$A_v = 30\ cm^{-1}$
$\mu = 0.00031$ g/cm/sec
$D_v = 0.256\ cm^2/sec$
$\rho = 0.544 \times 10^{-3}\ g/cm^3$
$\rho_b = 1.09\ g/cm^3$

Mass Velocity ($g/cm^2/hr$)	Pseudo First Order Rate Constants $(moles)(hr)^{-1}(g\ cat)^{-1}(atm)^{-2}$			k_g $moles/hr/atm/cm^2$
	k_1	k_2	k_3	
18.1	.065	.025	.036	.518
27.6	.069	.027	.038	.636
36.5	.088	.032	.038	.729
53.8	.096	.035	.043	.884

* Data from Hammar[9, 74].

In a single experiment in which the benzene inlet concentration was reduced by 50 per cent the first order rate constants for reactions 1 and 2 remained essentially constant while that for reaction 3 decreased by about 40 per cent. This result would indicate that whereas reactions 1 and 2 are first order with respect to benzene, reaction 3 is more nearly second order with respect to maleic anhydride. For all of the conditions investigated it was found that the ratio of $k_2/(k_1 + k_2)$ was 0.25 ± 0.03. The value of k_3 (first order rate constant) was found to be only 20 to 50 per cent as large as k_1 depending on the catalyst and the mass transfer rate for the gases passing over the catalyst. A comparison of the rate constants at 400°C with those at 375°C indicated an activation energy of 28 ± 4 kcal/mole for all three reactions.

The data of Hammar provide a good example of the influence which mass transfer rates may play in catalytic reactions. Table 1 shows the relationship which was observed between the mass velocity of the gas and the values of k_1, k_2 and k_3.

For any heterogeneous reaction the mass transfer rate to the catalytic surface may be expressed by

$$r = k_g A_v \frac{1}{\rho_b} (P - P_i) \tag{1}$$

where r = mass transfer rate (mole/hr^{+1}/g^{+1})
k_g = mass transfer coefficient (mole/hr^{+1}/atm^{+1}/cm^{+2})
A_v = surface area per unit volume of catalyst (cm^{-1})
ρ_b = bulk density of catalyst (g/cm^{+3})
P = partial pressure in the gas phase (atm)
P_i = partial pressure at the surface of the catalyst (atm).

Following Hougen and Watson[79], k_g can be expressed as

$$k_g = \frac{G}{M_m P_{fg}} \left(\frac{\mu}{\rho D_v}\right)^{-2/3} \cdot j_d \tag{2}$$

where G = mass velocity (g/cm^{+2}/hr^{+1})
M_m = average molecular weight (g)
μ = viscosity of gas (g/sec^{+1}/cm^{+1})
ρ = density of reaction mixture (g/cm^{+3})
D_v = diffusivity (cm^2/sec^{+1})

and

$$P_{fg} = \frac{(\pi + \delta_A P_A) - (\pi + \delta_A P_{A_i})}{\ln \left(\dfrac{\pi + \delta_A P_A}{\pi + \delta_A P_{A_i}}\right)} \tag{3}$$

where π = the total pressure in the system
P_A = the partial pressure of reactant A in the gas phase
P_{A_i} = the partial pressure of reactant A at the catalyst surface
δ_A = the change in the number of molecules when one molecule of A is reacted.

under the conditions of interest in this work where $P_A \ll \pi$ and δ_A is fairly small, then $P_{fg} \approx \pi$. Then,

$$k_g = \frac{G}{M_m \pi} \left(\frac{\mu}{\rho D_v}\right)^{-2/3} \cdot j_d \tag{4}$$

where $j_d = 1.82\, R_e^{-0.51}$ for $R_e < 350$ and R_e = Reynolds number (based on particle diameter). The values of k_g listed in Table 1 were calculated using Eq. (4) for the conditions at the entrance of the reactor. In Figure 1, k_1, k_2 and k_3 are plotted as a function of k_g. It is apparent that k_1 and k_2 vary directly with k_g while k_3 is less dependent on k_g.

Since the reaction rate constants k_1 and k_2 vary directly with k_g, Hammar concluded that the reaction rates for reactions (1) and (2) are equal to the mass transfer rates. This being the case one would expect the surface concentration of benzene to be very low. However, if one substitutes the observed reaction rate for the mass transfer rate in Eq. (1), values of P_i very nearly equal to P are observed. Hammar concludes that this result indicates that only a small fraction of the total surface area is active for reaction. If one assumes that the partial pressure of benzene at the surface is small—i.e., $P_i = 0$—and calculates A_v from Eq. (1), values of the active surface of the order of 4×10^{-3} of the total surface are obtained.

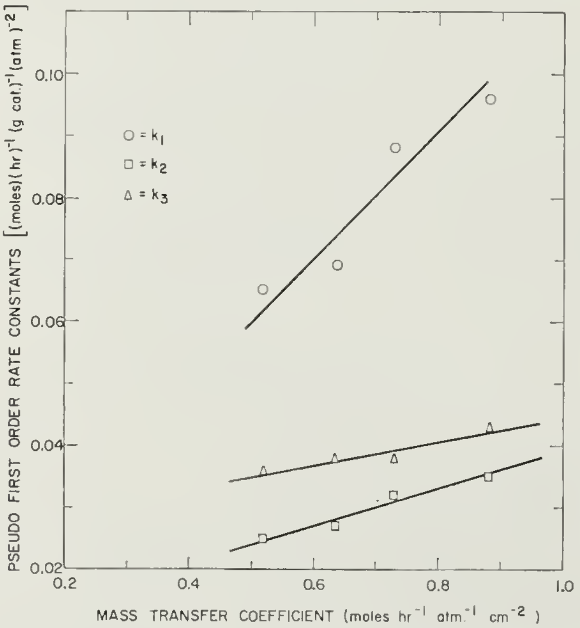


Figure 1. Effect of mass transfer rate on the pseudo first-order rate constants in the oxidation of benzene.[74] (Reprinted courtesy of Svensk Kemisk Tidskrift.)

The activation energy of 28 ± 4 kcal/mole appears to be so high as to be inconsistent with the idea that the mass transfer is the rate-determining step. It is suggested by Hammar that the marked increase in reaction rate with temperature may be related to the fact that at the higher temperature the catalyst is in a more highly oxidized and therefore more active state, that is, the activation energy is concerned with a process involving the oxidation of the catalyst surface.

Steger[2] studied the oxidation of benzene using a catalyst consisting of Ag_2O, V_2O_5, MoO_3 and Al_2O_3 on silicon carbide in a fixed bed. Contact times were varied by using different catalyst bed lengths at constant feed rates (and therefore constant mass transfer rates). From the percentage conversion-contact time data it was concluded that the rate of benzene oxidation (by reactions 1 and 2 combined) was approximately first order with respect to the benzene concentration. Reaction 2 was found to account for 30 per cent of the benzene oxidized over a considerable range of conditions. The first order rate constants for benzene disappearance were found to be approximately constant over a range of inlet concentrations from 1.2 to 2.4 mole per cent and a range of superficial gas velocities from 4 to 11 ft/sec. In contrast to the results of Hammar[74], these data indicate no dependence of the reaction rate on the mass transfer rate. An activation energy of about 15 kcal/mole was observed over a range of temperatures from 450 to 530°C.

Steger[2] also studied the oxidation of maleic anhydride over the same catalyst as was used in the study of the benzene oxidation. The order of the reaction as determined from the effect of initial MAA concentration (in the range 1.5 to 3.0 mole per cent in air) on initial rate was approximately one-half. However, at a given initial concentration, the observed changes in concentration with increasing contact time indicated zero order kinetics. Contact times were varied by changing the space velocity at constant bed length. The addition of products to the feed had no effect on the reaction rate. No reason for the discrepancy between the kinetics determined by the two different techniques is apparent.

The rate of oxidation of MAA was found to be essentially independent of the oxygen partial pressure down to partial pressures of about 0.03 atm. However, at very low O_2 partial pressures there was a marked fall off in rate. Over the temperature range from 400 to 500°C, an activation energy of 16 ± 1kcal/mole was observed.

It is apparent that Steger's data are in agreement with the reaction scheme outlined on p. 185. Reactions 1 and 2 are both first order with respect to benzene with $k_2/(k_1 + k_2) \sim 0.3$. Reaction 3 appears to be about half-order with respect to MAA and approximately zero order with respect to O_2 over the range of O_2 partial pressures from about 0.03 to 0.2 atm.

Mars and Van Krevelen[118, 119] studied the effect of benzene partial pressure on the rate of benzene oxidation in a small fluid catalyst bed. It was found that at benzene partial pressures below about 6 mm Hg (0.8 per cent at atmospheric pressure) the rate was approximately proportional to the benzene concentration but at higher pressures, the reaction rate became essentially independent of the benzene pressure. At O_2 partial pressures above about 300 mm Hg the rate was independent of O_2 pressure but varied directly with O_2 pressure at partial pressures below about 200 mm Hg.

The oxidation of benzene, phenol, quinone and maleic anhydride over a fixed bed catalyst of V_2O_5 precipitated on ⅛ in. Norton "Alundum" (alumina) pellets has been the subject of a recent dissertation by Holsen[77]. Measurements were made over a temperature range from 325 to 450°C at an inlet concentration of 1.9 per cent benzene in air. It was observed that at temperatures above 450°C the selectivity of the catalyst was permanently changed leading to somewhat higher maleic anhydride yields. However, this effect was not studied in detail.

The oxidation of benzene yielded mainly maleic anhydride, carbon monoxide and carbon dioxide with small amounts of quinone and phenol. Both the total benzene conversion and the conversion to maleic anhydride were approximately first order with respect to the benzene inlet concentration in the range 0.9 to 1.9 mole per cent. Contact times were varied by changing the space velocity from 1.19 to 0.16 $\sec^{-1}$ at constant catalyst volume. First order rate constants calculated from these data were approximately constant but did show a slight decrease with decreasing mass transfer rate. For purposes of comparing rates at different temperatures, first order kinetics have been assumed. The results indicate an activation energy for benzene disappearance of 19 to 20 kcal/mole.

The oxidation of MAA to CO and CO_2 was also investigated over the temperature range from 325 to 450°C. No data were presented from which the kinetics of the reaction could be determined. Assuming first order kinetics, the results indicate an activation energy of about 8 to 9 kcal/mole below 375°C, increasing to 13 to 14 kcal/mole in the range 375 to 450°C. This increase in activation energy may correspond to the onset of a pyrolysis of the MAA in addition to the oxidation reaction. This idea is substantiated by the fact that the ratio of $CO:CO_2$ also increased with temperature.

The conversions to MAA observed in the oxidation of benzene are in good agreement with those calculated using the equation

$$\frac{\text{MAA}}{\phi_0} = \frac{k_1}{k_3 - (k_1 + k_2)} [e^{-[(k_1+k_2)t]} - e^{-k_3 t}]$$

where k_1 = first order rate constant for benzene oxidation to MAA

k_2 = first order rate constant for direct oxidation of benzene to CO + CO_2

k_3 = first order rate constant for MAA oxidation

$$\frac{k_1}{k_1 + k_2} = 0.7.$$

ϕ_0 = Initial benzene concentration.

This indicates that both the oxidation of benzene and the oxidation of MAA are approximately first order and that, of the benzene oxidized, 70 per cent goes initially to MAA. This factor appears to be essentially independent of temperature and, within the range investigated, of benzene inlet concentration. These observations are in good agreement with those of Steger[2] and Hammar[74]. The fact that the maximum MAA yields observed by Holsen were not as high as those reported by Steger and Hammar appears to be due to a higher ratio of k_3/k_1 rather than to a difference in the relative amount of MAA formed in the initial oxidation step.

Table 2. Kinetics of the Catalytic Oxidation of Benzene

	Author			
	Hammar	Steger	Mars and Van Krevelen	Holsen
	Catalyst			
	V_2O_5, MoO_3 on Aluminum	Ag_2O, V_2O_5 MoO_3, Al_2O_3 on SiC	V_2O_5, K_2SO_4 on SiO_2	V_2O_5 on Al_2O_3
Temp. Range (°C)	375–400	450–530	375 (?)	325–450
Partial Pressure (mm Hg)				
Benzene	2.5-5.0	$\sim$10–20	<6 >6	7–14
O_2	150	$\sim$170	<200 >300	150
Kinetic Order re				
Benzene[a]	$\sim$1	1	1 <1	$\sim$1
Benzene[b]	$\sim$2	1	1 0	$\sim$1
O_2	—	<1		—
Dependence of Rate on Mass Transfer	Yes	No	—	—
Activation Energy (kcal/mole)	28 ± 4	15	—	19–20
Ratio $k_1/(k_1 + k_2)$	0.75 ± .03	0.7	—	0.7
Ratio k_3/k_1	0.2–0.5	0.1[c]	—	2–10

[a] Based on the relationship between conversion and contact time.

[b] Based on the relationship between initial rate and initial concentration.

[c] Reactions (1) and (3) of different order. Initial rates at corresponding inlet concentrations of 1.5 mole per cent are compared.

Rafikov *et al.*[154] have found phenol, hydroquinone, quinone and MAA among the products of the oxidation of benzene on V_2O_5 or $Sn(VO_3)_4$. Phenol and hydroquinone are reported to readily undergo further oxidation whereas quinone and maleic anhydride are more stable.

The available data on the kinetics of the oxidation of benzene and MAA are summarized in Tables 2 and 3. Most authors have found that, in the range of interest in commercial application, the oxidation of benzene is first order with respect to the benzene concentration. The fact that Hammar has found the rate to be mass transfer dependent whereas Steger did not may indicate that the catalyst used by Steger had a larger active surface area. The total area of the catalyst used by Steger was about 1 to 2 m^2/g *vs.* only .003 m^2/g for that used by Hammar. In both cases the transfer of material to the total catalyst surface should be more rapid than the reaction rate.

At low partial pressures the oxidation of MAA has been found to be approximately first order, whereas at higher pressures Steger found a somewhat lower order. It is possible that had he worked at MAA partial pressures below about 3 mm Hg, Steger would also have observed a higher order kinetics.

Table 3. Kinetics of the Oxidation of Maleic Anhydride

	Author		
	Hammar	Steger	Holsen
	Catalyst		
	V_2O_5, MoO_3 on Aluminum	Ag_2O, V_2O_5, MoO_3, Al_2O_3 on SiC	V_2O_5 on Al_2O_3
Temp. Range (°C)	375–400	400–500	325–450
Partial Pressure (mm Hg)			
MAA	0–3	14–28	0–2
O_2	150	>25	150
Kinetic Order re			
MAA[a]	1	0.0	1
MAA[b]	1	0.5	—
O_2	—	0	—
Dependence of Rate on Mass Transfer	No	No (?)	—
Activation Energy (kcal/mole)	28 ± 4	16	8–9 (325–375°C) 13–14 (375–450°C)

[a] Based on the relationship between conversion and contact time.

[b] Based on the relationship between initial rate and initial concentration.

Phenol and Quinone

Holsen[77] has made a limited study of the oxidation of phenol. The data indicated that the initial products were 50 to 60 per cent MAA and quinone and 40 to 50 per cent ($CO + CO_2$). The phenol conversion was essentially complete at 375°C and above at a 0.3-sec contact time. No kinetic data were presented. If one assumes first-order kinetics for the purpose of comparing rates at different temperatures, then a comparison of the rates at

325 and 350°C indicates a high activation energy, in the neighborhood of 60 kcal/mole for phenol disappearance. This value appears to be unreasonably high and further study of the reaction would be desirable.

If one assumes that in the initial oxidation of benzene, x moles of phenol are formed per mole of benzene oxidized, and further that all of the reactions involved are first order with respect to the organic reactant, then the conversion of benzene to phenol at any time, t, is given by

$$\frac{p}{\phi_0} = \frac{xk_1}{k_4 - k_1}[e^{-k_1 t} - e^{-k_4 t}]$$

where k_1 = rate constant for benzene disappearance,

k_4 = rate constant for phenol disappearance, and

$\frac{p}{\phi_0}$ = moles of phenol at time t per mole of benzene fed.

From this calculation one concludes that at 325 to 350°C, only about 1 to 5 per cent of the benzene oxidized goes through phenol as an intermediate —i.e., $x = 0.01$ to 0.05.

The main products from the oxidation of quinone were found to be MAA and ($CO + CO_2$). The results indicated that the initial oxidation step yielded about 80 per cent MAA and 20 per cent $CO + CO_2$. As in the case of phenol no data on the kinetics of the reaction are presented. If first order kinetics are assumed for the purpose of comparing results at different temperatures, the data indicate an activation energy of about 17 to 18 kcal/mole in the range 325 to 375°C, decreasing to 10 to 11 kcal/mole in the range of 375 to 400°C. This decrease in activation energy may be indicative of a transition from a chemically controlled rate at the lower temperatures to a mass-transfer controlled rate at higher temperatures. Using the same reasoning and assumptions as in the case of phenol, one concludes that of the benzene oxidized, only about 10 to 20 per cent passes through quinone as an intermediate, the remainder going directly to MAA, CO and CO_2.

These data indicate that while phenol and quinone may indeed be intermediates in the oxidation of benzene to MAA, at least under the conditions used by Holsen only a relatively small fraction of the total benzene oxidized passes through these intermediates.

In summary, it may be concluded that the reaction scheme outlined on p. 185 gives a fairly good description of the benzene oxidation. The exact kinetics appear to depend on the reaction conditions. It is striking that three investigators using quite different catalysts have all observed approximately the same value (0.7) for the ratio of $k_1/(k_1 + k_2)$. No good agreement was found concerning the activation energies of the reactions involved. It may be that changes in temperature are exerting a greater or lesser influence on the activities of the various catalysts in addition to the usual influence on reaction rates.

Miscellaneous Factors in Benzene Oxidation

A number of papers and patents have appeared which do not deal with the kinetics of the oxidation of benzene but which have contributed to the technology of benzene oxidation. Two main products, MAA and phenol, are formed in these processes.

Fukuda[61] has studied the oxidation of benzene to MAA at 430°C over catalysts consisting of V_2O_5 and MoO_3 on pumice. Studies of the effect of inlet concentration on reaction rate have indicated that the reaction is first order with respect to benzene at low concentrations, but less than first order at higher concentrations. Decreasing the ratio of vanadium to molybdenum resulted in a decrease in catalytic activity.

Kiprianov and Shostak[93] have studied the effect of varying the MoO_3 to V_2O_5 ratio in a catalyst on the optimum MAA yields which can be obtained in the oxidation of benzene. Although all of their MAA yields were rather low, the studies show a maximum in catalytic efficiency when the catalyst consists of 70 to 85 per cent V_2O_5 and 15 to 30 per cent MoO_3. Catalysts consisting of vanadates of bismuth, tin, or silver and a mixture of vanadium and nickel were also tested but all were found inferior to the mixed oxides of vanadium and molybdenum.

Although the addition of oxides of iron, nickel, chromium or manganese to a catalyst consisting of 70 per cent V_2O_5 and 30 per cent MoO_3 was either without effect or lowered the MAA yield, the addition of 5 per cent of the oxides of cobalt to such a catalyst resulted in an increase in MAA yield.

Wilken-Jorden[205] has studied the vapor phase catalytic oxidation of hydrocarbons with a manganese vanadate catalyst. With benzene, *p*-benzoquinone was formed as an intermediate product along with biphenyl. With toluene, the product obtained at high temperature contained benzaldehyde and bibenzyl.

Darby[49] has claimed that yields of MAA from the oxidation of benzene may be improved by treating the steel equipment with ammonia or ammonium carbonate at 400 to 600°C. The pretreatment is reported to reduce the oxidation or destruction of the MAA formed by the catalytic oxidation of benzene.

A number of patents dealing with the oxidation of benzene to MAA are summarized in Table 4.

Although the direct oxidation of benzene to phenol would be economically very attractive, only limited success has been attained in attempts to develop this process. The foregoing discussion of the kinetics of benzene oxidation on catalysts used for MAA production has shown that with these catalysts phenol is very readily oxidized to benzoquinone and MAA. Only at low benzene conversions are detectable amounts of phenol produced.

The literature which has appeared since 1930 on the vapor phase catalytic oxidation of benzene to phenol is summarized in Table 5. It is apparent that phenol yields of 50 to 80 mole per cent can be obtained but only by operating at benzene conversions of 10 per cent or lower.

TABLE 4. PATENT LITERATURE ON THE OXIDATION OF BENZENE TO MAA

Catalyst	Temp. (°C)	Remarks	Ref.
$V_2O_5 + MoO_3$ on Alundum (alumina) promoted with Al_2O_3 or MgO	475–525	Promoter in amounts of 5–10% by weight of catalytic oxides.	150
V_2O_5	580–650	Catalysts modified with the following, either singly or in mixtures; Na, K, Li, Ca, Mg, Be, Mn. Optimum concentrations of modifiers exist: e.g., 0.6–0.9% Na; 0.1–0.4% K; 0.1–0.9% Li, based on V_2O_5 present.	200, 202
Aluminum vanadate		Suggests use of a series of converters with product being condensed out but no additional air added between each.	88
V_2O_5		Catalyst prepared by hydrolysis of butyl vanadate with H_2O in presence of porous catalyst carrier.	105
70% V_2O_5 + 30% MoO_3 on carrier of silica bonded with refractory glass		MAA yield = 70%w (PAA yield 85%w in oxidation of naphthalene).	14
$V_2O_5 + MoO_3$ on alumina impregnated with lithium or sodium salts		MAA yield = 65–70% based on benzene consumed.	10
V_2O_5		Coated on carrier of finely ground silica and "Pyrex" glass. Particle size of pellets reported to be critical.	50

The work of Moyer[129] points out that the homogeneous vapor phase oxidation of benzene to phenol is inhibited by packing the reaction vessel with an "inert" packing. However, if the packing is coated with B_2O_3, conversions equivalent to those in the unpacked reactor are obtained. It is probable that the B_2O_3 prevents the breaking of free radical chains on the surface of the packing and thus facilitates the homogeneous oxidation rather than acting as a positive catalyst.

NAPHTHALENE OXIDATION

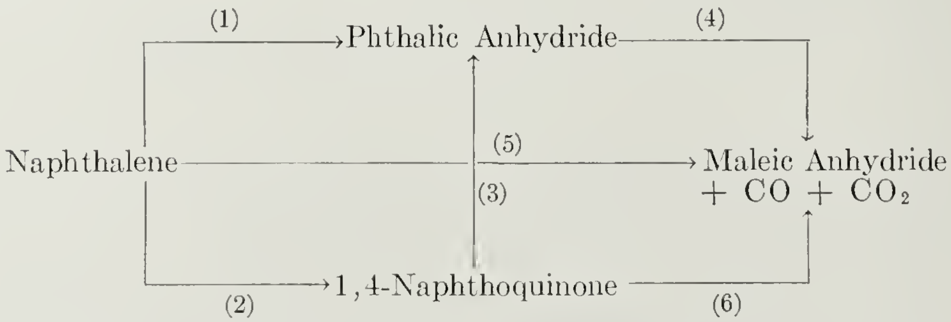
Kinetics

The oxidation of naphthalene to phthalic anhydride is commercially one of the most important vapor-phase catalytic oxidations. Nevertheless, important contributions to the understanding of the kinetics and mechanism of this reaction have been published only recently.

TABLE 5. THE VAPOR PHASE HETEROGENEOUS CATALYTIC OXIDATION OF BENZENE TO PHENOL

Catalyst	Temp. (°C)	Contact Time (sec)	Other Conditions	Benzene Conversion to Phenol (mole %)	Phenol Yield (mole %)	Ref.
10% $CoSO_4$	500		Pressure = 207 psi	10	77	155
2.8% $AgNO_3$ on Al_2O_3	480		27 moles benzene + 18 moles SO_2 + 60 moles Air	8.6	71	
Acid catalyst: e.g., sodium metaphosphate on Al_2O_3	700	~7	50:50 mixture of air and benzene	6	50	19
Vanadium oxide	371–427		20% benzene in air. Pressure = 20–34 atm	1–9	—	163
B_2O_3 on inert carrier	650–800		50:50 mole ratio of benzene to air	1–5	50–60	129

The major reactions involved in the oxidation of naphthalene are outlined below[18, 48, 82].



Reactions (1) and (2) are the most important primary reactions involved in the oxidation of naphthalene. As is discussed later their rates are approximately equal and considerably greater than that of reaction (5). Of the 1,4-naphthoquinone (NQ) initially formed, a large fraction is oxidized further to phthalic anhydride (PAA) and some to maleic anhydride, CO and CO_2. A portion of the PAA formed by reactions (1) and (3) is subsequently oxidized according to reaction (4).

Naphthalene Disappearance. *Variation of Initial Rates with Initial Concentrations of Naphthalene and Oxygen.* Using a catalyst consisting of 9 per cent V_2O_5 and 21 per cent K_2SO_4 on silica gel, Mars and Van Krevelen[118, 119] have shown that at 337°C, with naphthalene partial pressures below about 4 mm Hg, the initial rate of naphthalene oxidation is approximately proportional to the naphthalene partial pressure. However, at naphthalene partial pressures above about 8 mm the initial rate appears to increase only slowly with increasing naphthalene concentration. Similarly, at oxygen pressures up to 300 to 400 mm Hg, the rate of naphthalene disappearance is proportional to the oxygen pressure, but at higher pressures the oxygen dependence decreases.

Using a commercial vanadium catalyst at temperatures of 310 to 360°C, Calderbank[34] has confirmed that with naphthalene pressures between 15 and 76 mm Hg, the initial reaction rate is independent of the naphthalene partial pressure, and with oxygen pressures between 40 and 150 mm Hg, the initial rate is almost first order with respect to the oxygen pressure.

Ioffe and Sherman[81] have studied the kinetics of the oxidation of naphthalene using a thin layer of a mixed vanadium potassium sulfate catalyst coated on a thermometer bulb. Their data have shown that with naphthalene pressures in the range 4.9 to 11.4 mm Hg the initial rate depends on the initial naphthalene pressure to about the 0.4 order. With oxygen pressures from 80 to 375 mm Hg, the rate varies with the oxygen pressure to approximately the 0.75 power.

The oxidation of naphthalene has been used by Franklin *et al.*[58] to demonstrate a statistical method of determining the optimum conditions for a multivariable catalytic reaction. Effects of contact time, temperature and naphthalene inlet concentration were studied using a fluidized bed of V_2O_4, K_2SO_4 on silica gel catalyst. Optimum phthalic anhydride yields of about 85 mole per cent were obtained with attendant yields of 2 to 5 per cent MAA, 2 to 5 per cent NQ and about 10 per cent $CO + CO_2$.

Pinchbeck[145] has interpreted the data obtained in the foregoing statistical study in terms of the kinetics of the reaction. It was shown that the rate was the same on 40 to 80 mesh catalyst particles as on 100 to 150 mesh particles, indicating that the over-all reaction rate is not limited by diffusion into the catalyst pores and that surface kinetics are rate-controlling. An activation energy of 26 to 28 kcal/mole was observed below 400°C, with a marked decrease in activation energy at higher temperatures.

The yield data were in agreement with an over-all reaction scheme similar to that outlined above with the rate of naphthalene disappearance having a kinetic order between 0.8 and 0.9.

As can be seen from the summary in Table 6, all the above data are in essential agreement. Mars and Van Krevelen have shown that they can be explained as follows. Let us assume that two reactions are involved in the oxidation of naphthalene:

$$\text{Naphthalene} + \text{oxidized catalyst} \rightarrow \text{products} + \text{reduced catalyst} \quad \text{(I)}$$

and,

$$\text{Reduced catalyst} + O_2 \rightarrow \text{oxidized catalyst} \quad \text{(II)}$$

Assuming the rate of reaction (I) to be first order with respect to the partial pressure of the naphthalene and proportional to the degree of occupation of the surface by oxygen, θ, then

$$-\frac{dP_N}{dt} = k_{\text{I}} \cdot P_N \theta. \tag{1}$$

The rate of reoxidation of the surface reduced in reaction (I) may be assumed to be proportional to some power of the oxygen partial pressure and to the catalyst surface not covered by oxygen, i.e.:

$$-\frac{dP_{O_2}}{dt} = k_{\text{II}} P_{O_2}^n (1 - \theta) \tag{2}$$

If β molecules of O_2 are required for the oxidation of one molecule of naphthalene, then

$$-\beta \frac{dP_N}{dt} = -\frac{dP_{O_2}}{dt} \tag{3}$$

so that for the steady state

$$\beta k_{\text{I}} P_N(\theta) = k_{\text{II}} P_{O_2}^n (1 - \theta) \tag{4}$$

Solving (4) for θ and substituting in (1) gives

$$-\frac{dP_N}{dt} = \frac{1}{\dfrac{1}{k_{\text{I}} P_N} + \dfrac{\beta}{k_{\text{II}} P_{O_2}^n}} \tag{5}$$

At constant P_{O_2}, Eq. (5) can be rearranged to

$$-\frac{dP_N}{dt} = \frac{k_{\text{I}} P_N}{1 + k_{\text{I}} C P_N} \tag{6}$$

where

$$C = \frac{\beta}{k_{\text{II}} P_{O_2}^n}$$

Eq. (6) shows that at low P_N, the rate should be first order re P_N, and at high P_N should approach zero order in agreement with the data in Table 6. Similarly, at constant P_N, Eq. (5) predicts a dependence of the rate on $P^n_{O_2}$ at low pressures approaching zero dependence at high oxygen pressures. The data in Table 6 indicate $n \sim 1$.

Mars and Van Krevelen report that their data fit the integrated form of Eq. (5) but do not state the conversions at which the data were obtained.

Variation of Naphthalene Concentration with Contact Time. Several investigators have measured the change in naphthalene concentration with time during a single experiment. These data have been used to determine the kinetics of naphthalene disappearance using the integrated forms of the various rate equations. Although there is also a decrease in oxygen concentration as the oxidation proceeds, most of these studies have been made using low naphthalene concentrations so that the changes in oxygen concentration were small in comparison with the changes in naphthalene concentration. The results are summarized in the last column of Table 6.

TABLE 6. KINETICS OF NAPHTHALENE DISAPPEARANCE IN THE OXIDATION OF NAPHTHALENE

Author	Catalyst	Partial Pressure Range (mm Hg)		Order[a] re		Order[b] re Naphthalene
		Naphthalene	O_2	Naphthalene	O_2	
Mars and Van Krevelen	9% V_2O_5 21% K_2SO_4 70% SiO_2	0–4 8	300 400	1 0	1 1	
Calderbank	"Commercial V_2O_5"	15–76	40–150	0	.96	1 (350°C)
Ioffe and Sherman	V_2O_5, K_2SO_4	4.9–11.4	80–375	0.4[c]	0.75	0.5 (350–400°C)
Farkas	Fused V_2O_5	1.5–2.3	160			1
Booth and Fugate	10% V_2O_5 45% $K_2S_2O_7$ 45% SiO_2	7.6	160			0.5–1.0
Pinchbeck	V_2O_5, K_2SO_4 on SiO_2	0–35	160			0.8–0.9

[a] Based on initial rate *vs.* initial pressure.
[b] Based on change of naphthalene conc. with contact time.
[c] Calculated by the writer from the data of Ioffe and Sherman[81, 82].

It is apparent that the order re naphthalene as determined by the integrated equations is somewhat higher than that determined from the variations of initial rate with initial concentration. Ioffe and Sherman[81] attribute this difference to an inhibition of the reaction by the products so that as the reaction proceeds the rate drops off more rapidly than might be expected based on the changes in naphthalene concentration. However, it may be pointed out that, based on the analysis of Mars and Van Krevelen, as the naphthalene pressure decreases one enters the region where the dependence of rate on naphthalene pressure is most marked and, consequently, the rate decreases with decreasing naphthalene pressure.

Relative Rates of Reactions to PAA, NQ, and MAA + CO_2. Using an unpromoted, fused V_2O_5 catalyst, Farkas *et al.*[48] observed that in the initial reaction approximately 40 per cent of the naphthalene was converted to naphthoquinone, 40 per cent to PAA and about 20 per cent directly to MAA, CO and CO_2. These ratios were not changed by changing the temperature over the range 340 to 475°C. It was concluded that the over-all activation energies of all three reactions were in the range 28 to 30 kcal/mole.

TABLE 7. THE RELATIVE RATES OF OXIDATION OF NAPHTHALENE TO NAPHTHOQUINONE, PHTHALIC ANHYDRIDE AND CO_2

Author and Ref.	% Naphthalene Initially Converted to:			Activation Energy (kcal/mole) for Reaction to:		
	NQ	PAA	MAA + CO + CO_2	NQ	PAA	MAA + CO + CO_2
Farkas[48]	40	40	20	28–30	28–30	28–30
Calderbank[34]	60	35	small	26	26	
Ioffe and Sherman[81, 82]	40	60	small	14	14	
Booth and Fugate[18]	50	50	small	29	29	
Pinchbeck[145]	—	—	—	27	27	

Similar results were obtained with an Alundum (alumina)-supported V_2O_5 catalyst except that the branching of the initial reaction step yielded PAA, NQ and MAA + CO + CO_2 in the approximate ratio of 0.5:0.4:0.1. With a catalyst consisting of V_2O_5 impregnated on γ-Al_2O_3, approximately 20 per cent of the naphthalene was converted to MAA, CO and CO_2 in the initial step. A limited number of experiments were made with a fluidized catalyst consisting of 10 per cent V_2O_5 and 33 per cent K_2SO_4 on silica gel. These data indicated that all of the PAA may be formed via NQ as an intermediate.

As can be seen from the data in Table 7, most of the literature indicates a branching in the initial reaction step with an approximately equal split between PAA and NQ.

Calderbank[34] has shown that over the range of conditions studied the ratio of the initial rate of formation of α-naphthoquinone to the initial rate of formation of PAA was about 1.75. The activation energy of both reactions was about 26 kcal/mole. No data were given on the rate of reaction (5), but presumably it was slow.

Booth and Fugate[13] also observed that the initial attack on naphthalene resulted in about 50 per cent NQ and 50 per cent PAA; both reactions had an activation energy of about 29 kcal/mole.

The data of Ioffe and Sherman[81, 82] indicated that the initial attack leads to about 60 per cent PAA and 40 per cent NQ. However, in contrast to the results of the other workers the activation energy of both reactions was found to be only about 14 kcal/mole. The amount of direct complete oxidation of naphthalene was small.

One may speculate that the products of the initial reaction depend on the point of attack on the ring. Initial attack on an α-carbon may lead to naphthoquinone, on a β-carbon to PAA and on a bridge carbon to complete combustion.

Diffusion Effects in Naphthalene Oxidation. Korneichuk *et al.*[95] have studied the oxidation of naphthalene over a single piece of a technical fused V_2O_5 catalyst, 0.86 cm thick and 2.34 cm in diameter. The piece of catalyst was sealed in a tube and an air-naphthalene mixture circulated past one side. The gases on both sides of the diaphragm were analyzed for CO, CO_2 and partial oxidation products. Whereas at 385 to 410°C PAA, CO and CO_2 were found in the circulatory part, only CO and CO_2 were present in the gas which had diffused through the diaphragm. The data indicate that for catalyst pellets as large as 0.86 cm thick, losses of PAA yields might be expected due to overoxidation of PAA formed deep in the catalyst pore structure. As mentioned above, Pinchbeck[145] concluded that there was no diffusion limitation of the reaction on 40 mesh and smaller particles.

Measurements were also made[95] of the extent to which a catalyst pellet (7 mm diameter x 10 mm long) heated up during naphthalene oxidation. A much greater temperature difference (ΔT) between the catalyst and the gas was observed at gas temperatures around 410 to 420°C than at lower temperatures. This was interpreted as indicating the passage of the reaction into the "extra-diffusion area" which would promote a decline in the selectivity of the catalyst. However, a plot of their observed values of $\log \Delta T$ vs. $1/T$ gives a straight line with a slope corresponding to an activation energy of 30 to 35 kcal/mole. It may be that the observed increase in ΔT with temperature is merely a reflection of the normal increase in reaction rate with increasing temperature.

The Oxidation of Naphthoquinone; Reactions (3) and (6). Ioffe and Sherman[81, 82] have studied the oxidation of 1,4-naphthoquinone on a vanadium, potassium sulfate, silica gel catalyst. The results indicated that about 50 to 70 per cent of the naphthoquinone was converted to PAA and 30 to 50 per cent to MAA, CO and CO_2. An activation energy of about 11.5 kcal/mole was observed as compared with *ca.* 14 kcal for the oxidation of naphthalene. However, at 350 to 400°C, the rate constant for the oxidation of naphthoquinone was somewhat less than that for the oxidation of naphthalene to naphthoquinone.

Although first order kinetics were assumed in the treatment of the data, the kinetics were not established.

Farkas *et al.*[48] also reported that on the fused V_2O_5 catalyst the oxidation of naphthoquinone (NQ) resulted in an approximately 75 per cent conversion to PAA with 25 per cent being converted to MAA, CO and CO_2.

The data of Booth and Fugate[18] on the oxidation of naphthalene indicated that on oxidation, naphthoquinone was converted largely to PAA with not more than a small amount of complete oxidation.

The Oxidation of Phthalic Anhydride; Reaction (4). Ioffe and Sherman[81, 82] have studied the rate of oxidation of PAA and MAA over a range of temperatures from 350 to 480°C. No kinetic analysis was made but for the purpose of comparing rate constants, first order kinetics have been assumed. Their data have indicated that the activation energy for the oxidation of phthalic anhydride is about 26 kcal/mole whereas for the oxidation of MAA it is only about 10.5 kcal/mole. At 350 to 400°C the rate constant for the oxidation of naphthalene to PAA and NQ is about 30 times that for the oxidation of PAA to CO + CO_2. The data are summarized in Table 8.

TABLE 8. THE OXIDATION OF PHTHALIC ANHYDRIDE AND MALEIC ANHYDRIDE

Author and Ref.	Activation Energy for the Oxidation of:		k_N/k_ϕ [(a)]	k_M/k_ϕ [(b)]	Oxidation of PAA, Order re:	
	PAA (kcal/mole)	MAA (kcal/mole)			PAA	O_2
Ioffe and Sherman[82]	26	10.5	30 (350–400°C)	22 (350–400°C)		
Booth and Fugate[18]	29		35 (325–375°C)		1	0.5–0.8
Farkas[48]			20			

(a) $\frac{k_N}{k_\phi} = \frac{\text{first order rate constant for naphthalene disappearance}}{\text{first order rate constant for PAA oxidation at } P_{O_2} = 160 \text{ mm Hg}}$

(b) $\frac{k_M}{k_\phi} = \frac{\text{first order rate constant for oxidation of MAA}}{\text{first order rate constant for oxidation of PAA}}$

Booth and Fugate[18] have also studied the kinetics of the oxidation of PAA. Based on the change of initial rate with initial oxygen pressure they found that the order with respect to oxygen is approximately 0.8 in the range P_{C_2} = 80–160 mm Hg. From the integrated rate equations it was concluded that the rate was somewhat less than first order with respect to the phthalic anhydride concentration and half order with respect to the oxygen concentration. The observed activation energy was about 29 kcal/mole. These results are similar to those discussed above for the oxidation of naphthalene.

Farkas *et al.*[48] has also reported that the rate constant for the oxidation of PAA was only about $\frac{1}{20}$ of that for the oxidation of naphthalene to phthalic anhydride and naphthoquinone.

In contrast to the work of Booth and Fugate,[18] Hughes and Adams[80a] have reported that, with a catalyst of fused V_2O_5 on silicon carbide in a temperature range from 500 to 575°C, the rate of oxidation of phthalic anhydride to maleic anhydride and carbon monoxide was independent of the partial pressure of oxygen above 0.1 atm but varied with the phthalic anhydride partial pressure in a manner expected for a unimolecular surface reaction. The results were explained by assuming a fast adsorption of phthalic anhydride on the catalyst to form a vanadium oxide-phthalic anhydride complex. This adsorption is rapid, being either an irreversible or an equilibrium adsorption, although the data did not provide evidence for determining which alternative is correct. The slow step in the reaction mechanism was shown to be the desorption of the catalyst-phthalic anhydride complex. After desorption of the complex, the catalyst is reconverted to the higher valence state of vanadium by a fast oxidation. Using this proposed mechanism, it was possible to determine the energies and entropies of activation for the adsorption of the phthalic anhydride and for the decomposition of the surface complex. For this latter step, which is the slowest one in the over-all process, the activation energy was found to be 44 kcal.

TABLE 9. PRODUCT DISTRIBUTION FROM PHTHALIC ANHYDRIDE OXIDATION AT 550°C, 0.1 SEC, AND VARIOUS OXYGEN PRESSURES*

Initial oxygen pressure, atm	0.211	0.101	0.044	0.034
Phthalic anhydride oxidized, mole per cent	20	22	37	62
Phthalic anhydride converted to:				
CO_2, mole per cent	49	47	57	78
CO, mole per cent	35	38	30	17
MAA, mole per cent	10	12	10	4

* Data of Ref. 80a.

No attempt was made to correct the results for the oxidation of maleic anhydride on the catalyst. Table 9 shows the distribution of the products as a function of oxygen pressure at 550°C. If measurements of the maleic anhydride decomposition had been obtained, as a function of contact time, it might have been possible to correct the product distribution for the maleic anhydride oxidation. In this way it might have been shown that the product distribution was independent of oxygen pressure. This would agree with the results reported elsewhere in this chapter in which it is suggested that the product distribution is essentially independent of the extent of conversion of the hydrocarbon in some instances. Obviously, it would be important to have much more information regarding this point, namely, to find out whether the decomposition of the surface complex leads to the same distribution of products regardless of the extent of conversion and even the catalyst composition.

The unusual observation was made that at oxygen partial pressures below about 0.1 atm the rate of phthalic anhydride oxidation varied inversely with oxygen partial pressure. The authors explained this apparent anomaly by suggesting that the more highly reduced oxides of vanadium are intrinsically more active than the more highly oxidized.

TABLE 10. MAIN REACTIONS IN OXIDATION OF NAPHTHALENE

Reaction	Order re:		Activation Energy (kcal/mole)	Ref.
	Organic Compound	O_2		
Naphthalene → PAA	0.5–1.0	0.7–1.0	26–30	18, 34, 48
			14	81, 82
Naphthalene → NQ	0.5–1.0	0.7–1.0	26–30	18, 34, 48
			14	81, 82
NQ → PAA	—	—	29	18
			12–14	81, 82
PAA → MAA + CO + CO_2	1.0	0.5–0.8	29	18
			26	81, 82
MAA → CO + CO_2			10.5	81, 82

In summary, the best estimate of the state of our knowledge of the kinetics of the main reactions involved in the oxidation of naphthalene under conditions of importance in industrial application is presented in Table 10. In general, all of the reactions seem to depend on the concentrations of both oxygen and the organic reactant to an order intermediate between 0.5 and 1.0. The apparent kinetics depend on the partial pressures of the reactants and consequently may be expected to change with changes in the total pressure in the system.

The best values for the activation energies for the oxidation of naphthalene and PAA are about 26 to 30 kcal/mole. That for the oxidation of naphthoquinone may be about the same, but this value is less well established than that for naphthalene oxidation.

At this point a word of caution may be introduced regarding the validity of applying kinetic data obtained at one temperature to the operation of a unit at a different temperature. The treatment of Mars and Van Krevelen assumes that the reactants and catalyst are in equilibrium and that for a given set of reaction conditions, θ, the degree of occupation of the surface by oxygen, is constant. It seems probable that θ is related to the state of reduction of the catalyst, a high θ corresponding to a highly oxidized catalyst. It is known from experience that on short-term operation below the optimum temperature, an equilibrium state of reduction is not reached and probably kinetic data obtained under these conditions are not representative of results which would be obtained at equilibrium. This fact may be at least partly responsible for the apparent change in kinetics of naphthalene disappearance with temperature which was observed with Booth and Fugate's data.

Ushakova *et al.*[187] have made a study of the changes in oxidation state of vanadium during the oxidation of naphthalene similar to that reported by Simard *et al.*[171, 172] on the oxidation of *o*-xylene (see p. 215). Using 7-mm pellets, lower oxides were found at the periphery while inside the catalyst was generally present as the pentoxide. Apparently diffusion of naphthalene into the catalyst pores is not sufficiently rapid to result in uniform reduction throughout the pellet. As reported by Simard, partial reduction of the pentoxide was found to markedly increase both the electrical conductivity and catalytic activity of the catalyst. The observation that the oxidation of phthalic anhydride is very strongly inhibited by naphthalene vapor has not been reported by other workers in the field.

Catalysts and Conditions Used in Naphthalene Oxidation

No attempt will be made to list all of the papers and especially all of the patents dealing with the oxidation of naphthalene which have been issued since 1930. However, in addition to those papers which have already been discussed, dealing with the kinetics of naphthalene oxidation, there are several of greater or lesser commercial interest which are summarized in Table 11.

Marisic[117] has studied the use of fused V_2O_5 and heteropoly acids for naphthalene oxidation over a range of space velocities, inlet concentrations and temperatures. The best catalysts tested were found to be fused V_2O_5, and those prepared from ammonium phosphovanadotungstate and phosphomolybdic acid. The optimum yields are summarized in Table 11.

Brown and Frazer[30] studied the oxidation of naphthalene over a molybdo-tungsto-silicic acid catalyst. Maximum yields of PAA of about 60 per cent and of MAA of about 10 to 15 per cent were obtained. It was reported that the addition of CO_2 reduced the oxidation of PAA to MAA. Since the oxidation of 1,4-naphthoquinone gave only low yields of PAA, it was concluded that 1,4-NQ is not a major intermediate in the oxidation

TABLE 11. THE OXIDATION OF NAPHTHALENE

Catalyst	Temp. (°C)	Naphthalene Inlet Conc. (mole %)	Contact Time (sec)	Remarks	Ref.
			Naphthalene to PAA		
40–70% SiO_2 20–50% $K_2S_2O_7$ 3–25% V_2O_5 0.5–5% Ag_2O + CeO_2	350–400	0.5–2.0	3–20	Fluid-bed catalyst.	59, 60
$SnCl_2 + V_2O_5$				PAA yield = 97#/100# naphthalene.	134
$V_2O_5 + MoO_3 + P_2O_5$				Presence of 2–20% P_2O_5 decreases violence of reaction.	149
$SnO_2 + V_2O_5$	290		0.3	90%w PAA yield at 59% naphthalene conversion. Air: naphthalene ratio = 3 times theoretical.	39
9% V_2O_5 5% asbestos fiber 86% kaolin	325–400			Optimum yield = 40%w.	182
V_2O_5 on silicon carbide				PAA yield ~ 85 mole %.	159
V_2O_5 microspheres				Fluid bed of microspheres. PAA yield = 84–87%w.	199
Fused V_2O_5 spheres	565	0.8%		PAA yield = 87%w MAA yield = 10%w "Fluidized Bed." Beads of V_2O_5 poured through gaseous reactants and the PAA steam stripped off the beads.	106
$V_2O_5 + SnO_2$ on pumice (5–15% SnO_2 based on V_2O_5)	540–550	1%	0.25	Yield ~ 79–82%w.	25

TABLE 11.—*Continued*

Catalyst	Temp. (°C)	Naphthalene Inlet Conc. (mole %)	Contact Time (sec)	Remarks	Ref.
			Naphthalene to PAA—*Continued*		
Approximately 20% V_2O_5 on SiO_2 gel. Fluid bed	400–550		0.05 to 0.5	PAA yield = 50–80 mole%. Claim the presence of steam improves the yield.	7
Fused V_2O_5	~500	0.2–1.2	<0.5	Maximum % conversion to PAA = 75–80%w	117
Phosphomolybdic acid, ammonium phosphovanadotungstate	470–500 420–470	0.2–1.2 0.2–1.2	<0.5 <0.5	Maximum % conversion to PAA = 70–80%w Maximum % conversion to PAA = 80%w	
Catalyst containing a zeolite				PAA yields up to 85–90% of theoretical are claimed.	89
$TiO(VO_3)_2$				Atomic ratio of V:Ti should be between 1.5 and 3.0.	167
			Naphthalene to Naphthoquinone		
12.5% V_2O_5-25% K_2SO_4 on kieselguhr				15%w Yield of naphthoquinone	56
V_2O_5 + either Al_2O_3, ZrO_2, or ThO_2 on SiO_2	290–330	1–2%	8–13	Naphthoquinone yield = 19–34%w Phthalic anhydride yield = 45–60%w Unconverted naphthalene = 20–45%w	28
V_2O_5, $K_2S_2O_7$, Ag_2O on SiO_2	275–380	1–4%	5	Naphthoquinone yield up to 35%w Use of continuous regeneration of catalyst	183

of naphthalene to PAA. This conclusion is not in agreement with those of other workers and discussed in the preceding section.

THE OXIDATION OF TOLUENE, ETHYLBENZENE, BENZYL ALCOHOL AND BENZALDEHYDE

The data on the oxidation of toluene which were published prior to 1932 have been reviewed by Marek and Hahn[108] and will be considered only briefly here. The principal products, other than CO and CO_2, are benzaldehyde and benzoic acid along with some maleic anhydride and traces of anthraquinone. Marek and Hahn concluded that the relative proportions in which the products are obtained depends in part on the temperature to which the reaction mixture of toluene and air is subjected. High temperatures and short contact times as well as high temperatures and mild catalysts are said to be conducive to benzaldehyde formation. With V_2O_5, oxidation begins at 280 to 300°C, but long contact times are required and benzoic acid is the principal product. At 400 to 450°C the reaction is more rapid, permitting shorter contact times, and benzaldehyde becomes the main product. Under these conditions small amounts of anthraquinone have also been reported. With MoO_3 as a catalyst temperatures of 450 to 530°C are required to obtain good yields, and benzaldehyde is the primary product. In general, the oxides of molybdenum, tungsten, zirconium and tantalum promote oxidation to the aldehyde whereas V_2O_5 is particularly active in promoting the oxidation of benzaldehyde to benzoic acid, so that high conversions to the acid may be obtained by its use.

Before reviewing the more recent literature, the results of Maxted[122] will be considered briefly. The oxidation of toluene, ethylbenzene, benzyl alcohol and benzaldehyde were all studied using a tin vanadate catalyst. Unfortunately, only weight per cent conversions of reactant to benzoic acid were reported so that no kinetic analyses of the reactions can be made. Conversion-temperature data at constant reactant concentration in air and constant space velocity were reported for all of the reactants except toluene. The data are summarized in Figure 2. It is stated that a temperature of 290°C was found to be satisfactory for toluene oxidation at a toluene inlet concentration of 2.4 mole per cent.* A brief study of the effect of space velocity on conversion to benzoic acid was made under these conditions. A maximum conversion of 50 to 57 %w per pass was reported at a space velocity of 700 hr^{-1}. Bath temperatures only, and no catalyst temperatures, were reported throughout.

Although rather widely different inlet concentrations and space velocities were used for the different reactants, maximum conversions to benzoic acid were obtained at about the same temperature (±10°C) for all four reactants and, indeed, the maximum conversions were about the same (±5 per cent). This result may indicate that the rate of formation of benzoic acid from all four reactants is controlled by a common step such as the chemisorption of oxygen on the catalyst. The maximum obtainable yield of benzoic acid may be limited by the rate at which it is further oxidized to CO and CO_2.

Suvorov *et al.*[177] have studied the nature of the products in the oxidation of toluene, benzyl alcohol and benzaldehyde on V_2O_5 catalysts. The principal

---

* Calculated assuming equilibrium in the vaporizer.

products in each case are summarized in Table 12. Assuming that the reactions proceed through intermediate hydroperoxides, the authors proposed a mechanism to account for the observed products. It may be noted that no benzyl alcohol was found among the products of the toluene oxidation and that toluene was the only reactant which gave anthraquinone (AQ). It is suggested that anthraquinone is formed by the oxidation of anthracene resulting from the oxidative dehydrocondensation of 2 moles of toluene. There was some indication that the yields of benzoic acid obtainable in the oxidation of benzyl alcohol and benzaldehyde were increased by the addition of steam to the reaction mixture.

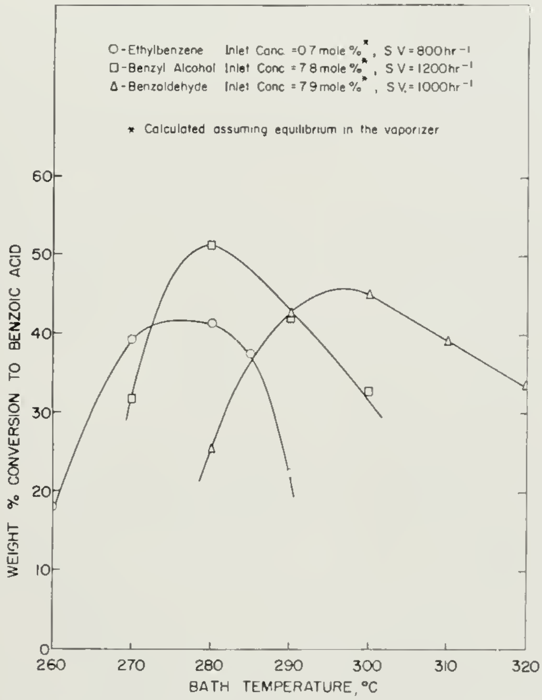


Figure 2. The oxidation of ethylbenzene, benzyl alcohol and benzaldehyde.[122] (Reprinted courtesy of *Journal of Society of Chemical Industry.*)

TABLE 12. PRODUCTS FROM THE OXIDATION OF TOLUENE, BENZYL ALCOHOL AND BENZALDEHYDE

Reactant	Products Found								
	CO_2	H_2O	Benzal-dehyde	Benzoic Acid	Quinone	MAA	AQ	Phenol	H_2CO
Toluene	×	×	×	×	×	×	×	×	×
Benzyl alcohol	×	×	×	×	×	×		×	×
Benzaldehyde	×	×		×	×	×		×	×

Parks and Katz[140] studied the catalytic activity of a number of compounds and mixtures at various temperatures in the vapor phase oxidation of toluene. Their results were recorded as the percentage of the input oxygen that was consumed in partial and complete oxidation. The best conversion of toluene to benzaldehyde was 20 per cent but no other directly determined yields of benzaldehyde or benzoic acid were given.

The work of Parks and Katz was extended by Parks and Yula[141]. Studies were made using cerium molybdate and uranyl, iron, calcium, zinc and silver vanadates as well as with V_2O_5 on silica, granular alumina and "Alfrax" (alumina). Only the results with V_2O_5 are reported in detail since unsatisfactory yields were obtained with the other catalysts. It was found that at 500°C, silica gel (without V_2O_5) causes a significant oxidation of toluene to CO and CO_2. The other supports were much less active. The most satisfactory catalysts were obtained by the decomposition of ammonium metavanadate on an Alfrax support.

The effect of toluene inlet concentration on conversions to benzaldehyde, total acids (benzoic + maleic) and CO + CO_2 was studied over the range 0.5 to 1.25 mole per cent toluene in air. The measurements were made using a catalyst consisting of 7.7 per cent V_2O_5 on Alfrax, a temperature of 420 to 425°C and a contact time of 0.5 sec. At inlet concentrations below about 0.8 mole per cent, the conversions to total acids and CO + CO_2 were approximately independent of concentration. At higher concentrations, the conversions decreased somewhat with increasing inlet concentration indicating a kinetic order less than unity. Over the whole range, the conversions to benzaldehyde increased slightly with increasing concentration. However, since benzaldehyde is probably being formed and oxidized simultaneously, it is not possible to draw significant conclusions concerning the kinetics of these reactions from the limited data available.

A series of curves of conversion to total acids *vs.* temperature were presented for catalysts containing from 2 to 16 per cent V_2O_5 on Alfrax. The data showed a trend toward higher optimum temperatures with decreasing V_2O_5 content of the catalyst. No marked differences in optimum acid yields with V_2O_5 content were observed.

The effect of varying the contact time between 0.2 and 1.0 sec on the conversion of toluene to benzoic and maleic acids was studied using a catalyst of 6.2 per cent V_2O_5 on Alfrax, a temperature of 415°C and a toluene inlet concentration of about 0.8 mole per cent. The optimum conversion to benzoic acid was about 30 to 35 per cent with an attendant conversion to MAA of about 15 per cent at contact times of 0.7 to 0.8 sec.

Mars[119] has shown that toluene oxidation follows a kinetic scheme similar to that which has been outlined for the oxidation of naphthalene and other aromatic compounds. With a catalyst consisting of a mixture of V_2O_5 and

MoO_3 on Al_2O_3, the principal products were benzaldehyde and benzoic acid with traces of anthraquinone.

The work of Kuznetzov and Stepanenko[101] has indicated that excellent yields of benzaldehyde and benzoic acid can be obtained in the oxidation of toluene by operating under conditions where the toluene conversion is low. Their data are summarized in Table 13. Using MoO_3 as the catalyst, benzaldehyde was the main product. Using tin vanadate as the catalyst, the yield of benzoic acid was much higher than that of benzaldehyde. The total yield of useful products is seen to decrease markedly with increasing toluene conversions.

Sasayama[161] has reported obtaining a 47 per cent yield of MAA in the oxidation of toluene using a tin vanadate catalyst at 300°C. It was suggested that the formation of MAA proceeds through the following sequence of reactions:

Table 13. The Oxidation of Toluene Over Molybdenum Oxide and Tin Vanadate[101]

Catalyst	Temp. (°C)	Toluene Inlet Conc. (mole %)	Contact Time (sec)	Total Toluene Conversion (mole %)	Conversion to:		Yield*	
					ϕCHO (mole %)	ϕCOOH	ϕCHO (mole %)	ϕCOOH
MoO_3 on pumice	475	16	2	9.8	8.6	0.4	88	4.6
MoO_3 on asbestos	525	—	5–7	13.7	5.5	4.1	40	30
MoO_3 (solid)	500	1.2	3	42.3	23.3	2.1	55	5
Tin vanadate	290	6.2	—	20	1.4	18	7	90

* Based on toluene converted.

$$\text{toluene} \rightarrow \text{benzaldehyde} + \text{benzoic acid} \rightarrow \text{benzoquinone} \rightarrow \text{MAA}.$$

Bigalli[16] studied the oxidation of toluene over a number of catalysts. The highest yield of benzaldehyde obtained was 47 per cent using a catalyst consisting of 4.1 per cent V_2O_5 and 5.8 per cent V_2O_4 on sintered Al_2O_3 at 446°C and an air to toluene weight ratio of 1.87.

Green[66] studied the oxidation of toluene over MoO_3 on pumice. Benzaldehyde yields as high as 60 per cent were obtained but at conversions in the range of 0.5 to 3 per cent. Winslow[206] has reported that conversions of toluene to benzaldehyde of over 50 per cent may be obtained at 630°C with a contact time of 0.15 sec using a cerium molybdate catalyst.

Pargal[139] has investigated the oxidation of several aromatic hydrocarbons over beds of fluidized catalysts. The catalysts included silica gel, and Pt, V_2O_5, CuO and Ag on silica gel. The oxidation of toluene over the vanadia catalyst resulted in the formation of benzaldehyde, formaldehyde, benzoquinone, MAA, CO_2 and H_2O. Similar products were obtained in the oxidation of benzyl alcohol and benzaldehyde. The addition of a few per cent of di-*t*-butylperoxide or benzoylperoxide to the reactants resulted in the formation of similar products but at somewhat lower temperatures. No experiments were made with peroxides in the absence of solid catalysts, so it is difficult to conclude whether or not there was any synergistic effect between the catalysts and the peroxides. Similar products were obtained in the oxidations of the xylenes, ethyl benzene, benzene, benzyl alcohol and benzaldehyde.

It was suggested that the primary function of the solid catalyst may be to initiate free radical chains by the abstraction of a hydrogen atom from the hydrocarbon. A subsequent free radical scheme, involving the formation and decomposition of hydroperoxides, is proposed which is quite similar to that commonly accepted for liquid phase oxidation reactions and suggested by Bretton, Wan and Dodge[20] for the oxidation of four-carbon hydrocarbons (see p. 257).

Although they are somewhat outside the scope of this chapter, the data of Kreshkov[100] may be mentioned briefly. Toluene was oxidized using chlorine and steam over catalysts of V_2O_5 and MoO_3 on pumice, tile etc. It was reported that toluene conversions up to 78 per cent per pass with toluene losses to complete combustion of only 3.5 per cent could be obtained. Yields of up to 12.5 per cent benzyl alcohol, 75 per cent benzaldehyde and 15 per cent benzoic acid were obtained at 360 to 380°C. By varying the conditions the yield of benzoic acid could be increased to 72 per cent and that of benzyl alcohol and benzaldehyde correspondingly decreased. No organic chlorides or anthraquinone were found among the products.

The Oxidation of *o*-Xylene

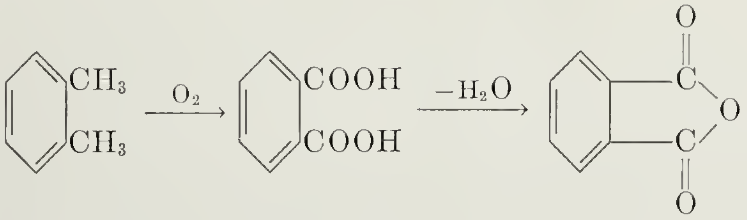
The oxidation of *o*-xylene is of importance because of the fact that xylene may be substituted for naphthalene in the production of phthalic anhydride[35, 38]. In principle, 140 lb of phthalic is attainable per 100 lb of starting xylene, as against only 116 lb/100 lb of naphthalene. However, in practice, it has not appeared possible to attain yields of phthalic better than 50 to 60 mole per cent of theoretical in the case of xylene, whereas naphthalene oxidation yields are quite commonly 85 to 90 mole per cent.

No complete discussion of the kinetics of this reaction has yet appeared in the literature. The most extensive work reported is that of Parks and Allard[142] who have reviewed the prior literature and studied the yields of phthalic anhydride and *o*-tolualdehyde under a number of conditions of temperature, contact time, xylene-air ratios, and catalyst composition. They do not report the presence of maleic anhydride as a product. They found that with air-xylene ratios of 1.5 to 5.0, tolualdehyde could be produced exclusively, whereas higher ratios favored phthalic anhydride. Some catalysts, such as the various metal vanadates, were capable of producing either phthalic anhydride or tolualdehyde, while others, such as oxides of zirconium, molybdenum, and tungsten, appeared capable of producing only tolualdehyde. The maximum yields (per pass) of phthalic reported were only 18 per cent, although yields based on converted xylene were in the 50 to 60 per cent range, with one value as high as 84 per cent. The experiments carried out with V_2O_5 as a catalyst involved contact times of a few tenths of a second, temperatures in the range 450 to 530°C, and air-xylene weight ratios ranging from 3 to 60.

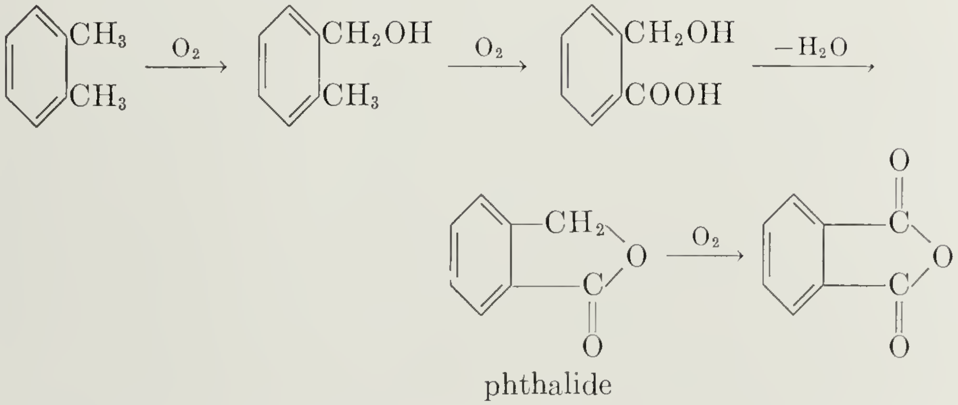
In more recent work, employing a V_2O_5 catalyst, Gulati and Bhattacharyya[67, 68] have reported yields of 60 per cent phthalic anhydride and 10 per cent maleic anhydride at temperatures of 360 to 480°C and air-xylene ratios ranging from 250 to 425. No significant amounts of aldehyde were found by these investigators.

Recently, Levine, in a review article on *o*-xylene oxidation[103], proposed two possible reaction mechanisms:

(1)

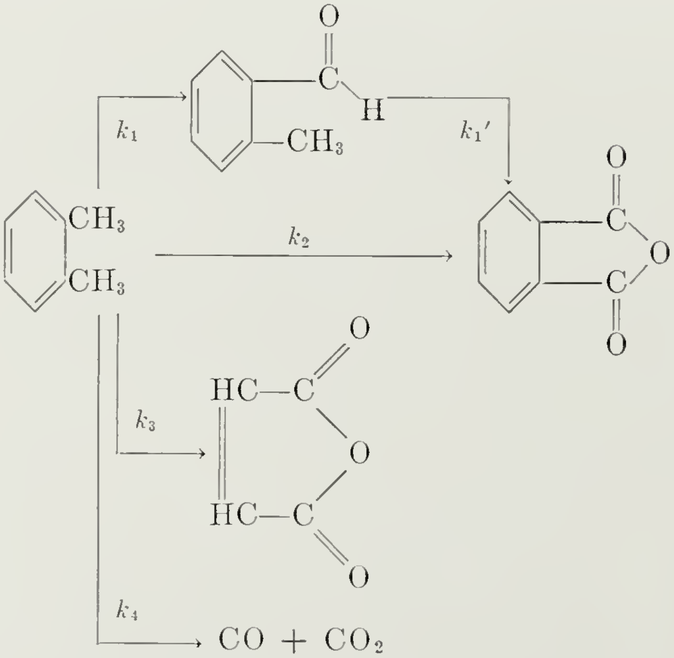


(2)



The second route was suggested as the principal one for the case of *o*-toluic acid oxidation where good yields of phthalic anhydride have been reported. Presumably in each case, the step involving the catalyst is the first one, but these schemes are not adequate to explain the fact that tolualdehyde rather than phthalide (see above) is a major isolatable partial oxidation product.

In an unpublished investigation[171], Simard *et al.* carried out a study of the kinetics of *o*-xylene oxidation at conversions below 25 per cent over a SiC-supported V_2O_5 catalyst. The following kinetic scheme was observed to be followed at 400 to 450°C, contact times of .01 to .06 sec and xylene concentrations in air of 0.4 to 1.4 per cent:



Reactions k_1 and k_1' were found to be first order with respect to *o*-xylene and *o*-tolualdehyde, respectively, while reactions k_2, k_3, and k_4 were all zero order. All reactions showed a square-root dependence on oxygen pressure. Under the low conversion conditions employed, yields of *o*-tolualdehyde were 10 to 40 per cent, depending upon the initial xylene concentration. The product phthalic anhydride is known to be stable to further oxidation under the conditions of these experiments. The kinetic results lead to the conclusion that the various oxidation reactions to form phthalic anhydride, maleic anhydride, and carbon oxides respectively are independent reactions occurring on the catalyst surface, involving transfer of catalyst oxygen to the adsorbed xylene followed by desorption of the products. The rate-determining step is oxidation of the catalyst by gaseous oxygen. In particular, chemisorption of oxygen would be expected to show a square-root dependence on pressure. This behavior is not unlike that which is observed in the case of naphthalene oxidation. The formation of aldehyde, involving as it does the least oxygen transfer of any of the xylene oxidation reactions, may occur through reaction of the gaseous hydrocarbon with a chemisorbed oxygen atom, which would result in the observed kinetics.

Simard *et al.*[172] have also investigated the phase composition of a vanadium oxide catalyst during the oxidation of *o*-xylene. Under normal operating conditions (1.1 per cent *o*-xylene in air, bath temperature = 460°C, contact time = 0.26 sec) the catalyst was found to consist of a mixture of V_2O_4, $V_2O_{4.34}$ and V_2O_5. Under more severe reducing conditions (3.3 per cent *o*-xylene) V_2O_3 may also be observed. Since V_2O_3 and V_2O_4 were found to be catalytically inactive for the production of phthalic anhydride or intermediates, it was concluded that consideration of the active catalyst can be limited to V_2O_5, $V_2O_{4.34}$ and to intermediate structures which may exist on the surface.

Exposure of the oxidized catalyst to a feed of 1 mole per cent *o*-xylene in prepurified nitrogen resulted in the formation of the normal oxidation products with simultaneous reduction of a portion of the catalyst to $V_2O_{4.34}$ and V_2O_4. The role of gaseous oxygen in the catalytic oxidation appears to be a secondary one with the reaction proceeding through the following steps:

1. The chemisorption of hydrocarbon on the catalyst surface.
2. The reaction of the chemisorbed hydrocarbon with oxygen ions of the catalyst.
3. Desorption of intermediate or final products.
4. Replenishment of oxygen to the catalyst from the feed air.

Margolis and Plyshevskaya[109] measured the rate of adsorption of oxygen on V_2O_4 and V_2O_5 and found it to be faster on the former. They also studied the rate of exchange of O_2 with V_2O_4, V_2O_5 and $MgCr_2O_4$ catalysts, but were not able to establish any clear relationship between the activity of the catalyst for oxidation and the O^{18} exchange rate.

In another investigation[11], electrical measurements were utilized to gain more detailed information about the role of vanadium pentoxide in the catalytic oxidation of *o*-xylene. The oxide was studied in the form of coarse powders, thin films (220 to 1600Å thickness), and a polycrystalline pellet under various partial pressures of oxygen. One per cent mixtures of *o*-xylene in air or oxygen were used to simulate conditions where the solid acts as a catalyst. The electrical measurements, made on the samples at various temperatures, included d.c. resistance, a.c. resistance at frequencies up to 5×10^5 cps, and thermoelectric emf. From these data, the specific conductivity, activation energy for conduction, Fermi level and charge carrier concentrations were calculated.

Analysis of electrical properties was used to formulate a picture of the defect structure of the solid. Under ordinary partial pressures of oxygen, the solid contained fewer than the number of oxygen atoms required for stoichiometry. As a result, there are oxygen vacancies in the solid lattice. These defects form electron donor levels which, from the electrical measurements, lie ~0.42 ev (9.7 kcal) below the conduction band. Consequently, V_2O_5 is an *n*-type (electron excess) semiconductor. Under most conditions the number of donor levels is sufficient to make V_2O_5 a fairly good conductor (Sp. cond. = 10^{-1} to 10^{-3}). The defects are apparently quite mobile in the surface region even below 180°C, but are mobile in the bulk only above 350°.

Conductivity and thermoelectric power data were also used to follow changes in the solid under catalytic conditions. The measurements were made on a coarse V_2O_5 powder in both 1.3 per cent *o*-xylene-air and 1.3 per cent *o*-xylene-oxygen streams at various temperatures. Thermoelectric power values at low temperature were the same as measured in air or oxygen, indicating the electronic energy levels in the bulk of the solid to be unaffected by the xylene. In contrast, the electrical conductivity of the sample was greatly increased, even at temperatures far below those where catalytic oxidation is first detected. Chemisorbed *o*-xylene evidently donates electrons to the solid very easily at all temperatures and with an apparently small activation energy.

Once catalytic temperatures were reached, both the conductivity and the thermoelectric power increased rapidly. The extent of increase in the value of the latter indicated that the Fermi level of the electrons in the oxide had dropped to about 0.72 ev (16.6 kcal) below the conduction band. This change indicated that the whole solid was affected by the reaction at the surface and defect equilibrium may be reached throughout the whole oxide. It is imagined that as an *o*-xylene molecule is oxidized at the surface an oxygen deficient region containing defects is formed. At catalytic temperatures the defects are mobile in the solid and can move around from one place to another. They may migrate into the solid from one point on the surface and subsequently reappear at another. Chemisorption of oxygen at this point could then annihilate the defect and regenerate the pentoxide. Thus the catalyst is pictured as a rapidly changing series of defect structures continually being reduced during the oxidation of an *o*-xylene molecule and subsequently being reoxidized by oxygen either migrating from neighboring regions of the solid or being chemisorbed directly from the gas phase. The sites active for oxidizing the hydrocarbon are probably on one portion of the surface at one moment, and another portion at the next moment. The catalyst would then be one where all of the surface is catalytically active part of the time. Since all of the surface is potentially active, a very rugged catalyst results which is quite resistant to poisons, for a large percentage of the surface would probably have to be covered before the solid becomes catalytically inactive.

Alternating current electrical resistances of thin V_2O_5 films (220 to 1600Å thickness) supported on quartz slides were measured at various frequencies.

The resistance showed a rapid decrease or "dispersion" at a current frequency of $\sim 10^4$ cps. This dispersion indicated that the films were electrically inhomogeneous. Electron micrographs of portions of the films stripped from the slide showed that they consisted of small crystallites separated by grain boundary material. Subsequent measurements after subjecting the films to a hydrocarbon-air stream at catalytic temperatures showed that both the electrical inhomogeneities and the crystallite structure decreased and finally disappeared. The comparison of resistance data with the electron micrographs indicated that the initial attack of the hydrocarbon was probably at the grain boundaries. This disordered material is probably quite reactive, for it can tolerate an excess of oxygen which would not fit into the ordered structure in the interior of a crystallite. As the boundary material is reduced, sintering appears to take place between the grains. The distinct barriers are no longer apparent in the films and the sample becomes electrically homogeneous.

Kinetic studies[171] showed the production of phthalic anhydride directly from *o*-xylene to be zero order with respect to xylene partial pressure and to have a square-root dependence on oxygen pressure. The uptake of oxygen is thus believed to be the rate-determining step of the reaction. If an electron transfer is involved, the initial chemisorption of oxygen would include a transfer of one or two electrons from the solid to the chemisorbed layer.

$$\tag{1} \tfrac{1}{2}O_{2(g)} + \ominus \rightarrow O^{-}_{(ads.)}$$

or

$$\tag{2} \tfrac{1}{2}O_{2(g)} + 2\ominus \rightarrow O^{-2}_{(ads.)}$$

Under catalytic conditions, the vanadium pentoxide is partially reduced, and there are a large number of electrons available for either one of these reactions. The first is the most probable initial reaction. The uptake of oxygen is in Hauffe's nomenclature an "ejection" reaction, where an electron goes from the solid to the chemisorbed layer. If this is true, a quantitative correlation might be realized between the electrical properties of the solid and its catalytic activity. Much work, both theoretical and experimental, remains to be done before such an attempt would be valid.

THE OXIDATION OF POLYNUCLEAR AROMATIC HYDROCARBONS

Anthracene

It has been recognized for some time that good yields of anthraquinone may be obtained by the catalytic vapor phase oxidation of anthracene[108]. Although this process has found commercial utilization in Europe[144], the lack of a source of anthracene has so far made it economically unattractive in America.

Since 1930 a series of patents was issued to Jaeger[90] on catalysts for the oxidation of anthracene to anthraquinone. Yields of 85 to 90 per cent were claimed. The commercial process in Europe used a catalyst consisting of V_2O_5, K_2SO_4 and Fe_2O_3 on pumice. The catalyst was supported in thin layers with heat exchangers between the catalyst layers. The oxidation was carried out at temperatures of 320 to 390°C in the reactor. The inlet anthracene concentrations in air were around 0.3 mole per cent. Anthraquinone yields of 95 to 97 weight per cent (82 per cent of theoretical) were obtained. Phthalic anhydride, maleic anhydride, CO and CO_2 were the main by-products. When operating below the optimum temperature, unconverted anthracene and some highly colored impurities were present. However, when operating at temperatures at or above the optimum, anthraquinone of greater than 99 per cent purity was readily obtained by simply washing the crude product with hot water to remove the phthalic and maleic anhydrides which were formed as by-products.

It has recently been found by West[203] that yields of anthraquinone equal to those reported above can be obtained by the oxidation of anthracene in a fluid catalyst bed using the same catalyst as for the oxidation of naphthalene to phthalic anhydride.

Yatani[207] has reported that yields of anthraquinone of 90 to 95 per cent may be obtained by the oxidation of anthracene over a vanadium catalyst promoted with salts of potassium, rubidium or cesium.

Goftman and Golub[64, 65] have studied the oxidation of anthracene fractions of varying degrees of purity over a fused vanadium pentoxide catalyst. With a "redistilled, washed anthracene fraction" containing approximately 50 per cent anthracene and 50 per cent phenanthrene, the total yield of acid product based on the phenanthrene content of the feed was 112 per cent, 79 per cent of which was phthalic anhydride, the remainder being maleic anhydride. In addition to the acid products, anthraquinone was obtained with a yield of 63 per cent of theoretical, based on the anthracene content of the feed. Phthalic anhydride, maleic anhydride and anthraquinone were also the major products formed in the oxidation of an "unwashed, first anthracene fraction" containing a number of polynuclear aromatic hydrocarbons.

The only publication dealing with the kinetics of the anthracene oxidation is that of Mars and Van Krevelen[118, 119]. It was found that the reaction rate was essentially independent of the anthracene partial pressure at pressures above about 1 mm Hg. The rate showed some dependence on O_2 partial pressure over the whole range up to 1 atm. Mars and Van Krevelen concluded that, as with benzene and naphthalene (pp. 185 and 196), the data could be explained by assuming that the oxidation takes place in two steps, i.e.:

$$\text{anthracene} + \text{oxidized catalyst} \rightarrow \text{oxidation product} + \text{reduced catalyst} \quad (1)$$

and

$$\text{reduced catalyst} + O_2 \rightarrow \text{oxidized catalyst} \quad (2)$$

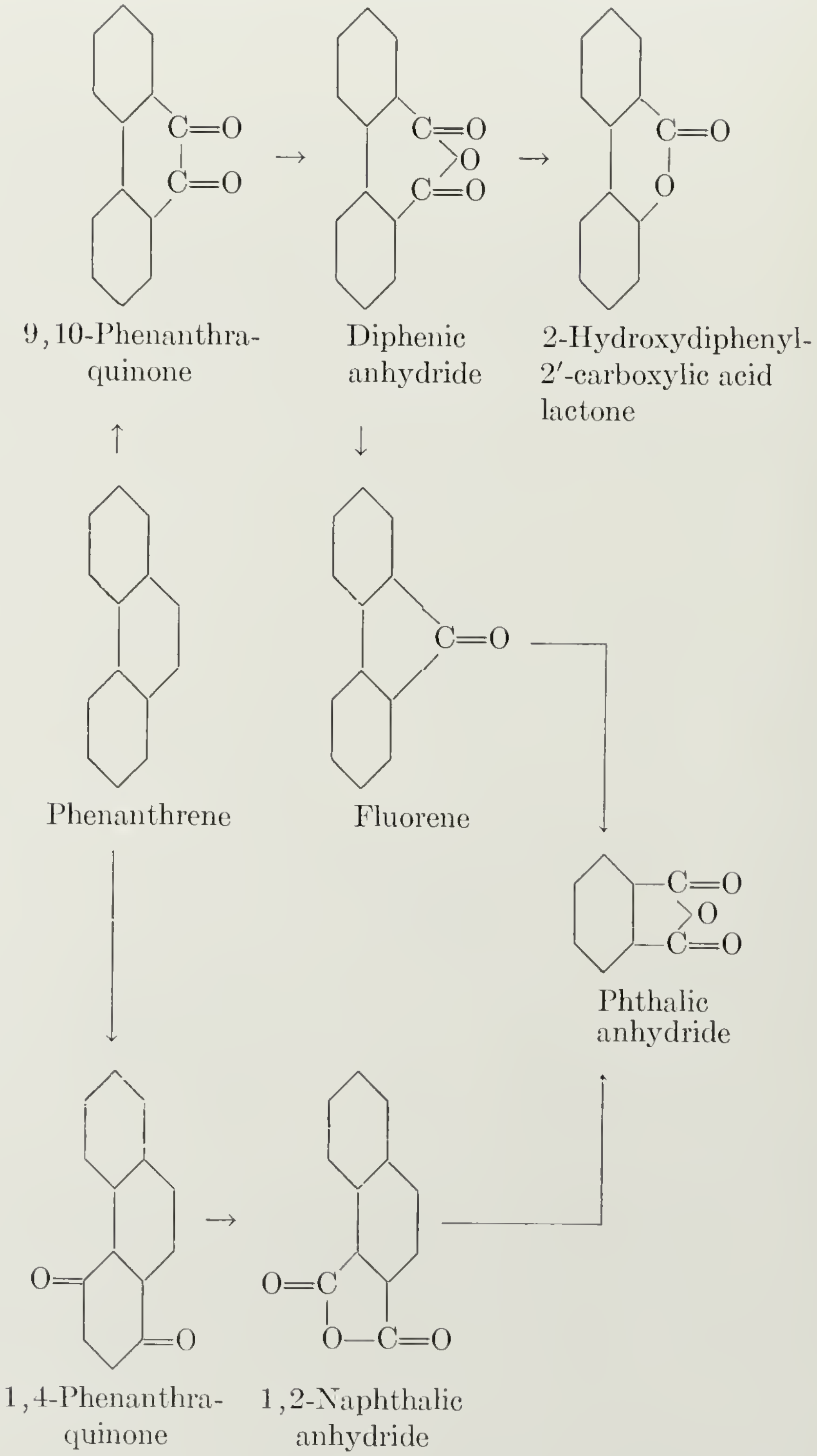
Table 14. The Oxidation of Phenanthrene

Catalyst	Temp. (°C)	C.T. (sec)	Product	% Yield	Remarks	Ref.
V_2O_5 on pumice	370	4	PAA	12		208
$V_2O_5 + UO_2$ on pumice	430–440	1.2	PAA + diphenic acid	41	H_2O added to feed	
V_2O_5	—	—	Acids calculated as PAA	75		191
$V_2O_5 + MoO_3$	400	—	Phenanthraquinone	7		
10% V_2O_5 65% SiO_2 23% K_2SO_4	400	—	PAA	18		99
7.5% V_2O_5 on Al_2O_3	425	—	PAA	35		
Tin vanadate on asbestos	420	0.35	PAA + traces of 1,4-phenanthraquinone	22		41
Fused V_2O_5	—	—	Mixed acids	70–80 (calculated as PAA using crude phenanthrene 70–80% pure)		174

Phenanthrene

Marek and Hahn[108] have reported that phthalic anhydride (PAA) is the main product of the oxidation of phenanthrene. Small yields of phenanthraquinone are also obtained. The results of a number of more recent studies of the oxidation are summarized in Table 14. Mixtures of PAA and other acids have been obtained, with total acid yields generally below 40 per cent.

Brooks[29] has studied the oxidation of phenanthrene over catalysts consisting of V_2O_5 on silica gel with and without K_2SO_4. Depending upon the reaction conditions the main product was found to be either PAA (maxi-


9,10-Phenanthraquinone
Diphenic anhydride
2-Hydroxydiphenyl-2′-carboxylic acid lactone
Phenanthrene
Fluorene
Phthalic anhydride
1,4-Phenanthraquinone
1,2-Naphthalic anhydride

mum yield = 56 per cent) or 2-hydroxydiphenyl-2′-carboxylic acid lactone (HDL) (maximum yield = 45 per cent) and 1,2-naphthalic anhydride. It is suggested that the oxidation of phenanthrene may proceed by two alternate routes, as shown below, both of which result in the formation of phthalic anhydride. Goftman and Golub[64, 65] have demonstrated the existence of hydroxy compounds as intermediates in the oxidation of phenanthrene.

Acenaphthene and Fluorene

Little has been contributed to our knowledge of the oxidation of acenaphthene since Marek and Hahn's monograph[108] was written. The main products are known to be acenaphthylene, acenaphthoquinone, naphthaldehydic acid, naphthalic anhydride and maleic anhydride. Jaeger[91] has claimed good yields of naphthalic anhydride by the oxidation of acenaphthylene at 375 to 400°C over a catalyst containing a compound of vanadium, molybdenum, tungsten, uranium, chromium or iron.

Fluorene may be oxidized to diphenylketone in good yields over a V_2O_5 catalyst.

THE OXIDATION OF SUBSTITUTED AROMATIC HYDROCARBONS

Hydrocarbon Substituents

The reader is referred to pp. 207 and 212 for discussions of the oxidation of toluene, xylene, ethyl benzene, benzyl alcohol and benzaldehyde. The data which have appeared since Marek and Hahn's monograph[108] on the oxidation of substituted aromatic compounds are summarized in Table 15.

Rafikov and Suvorov[153] found *p*-toluic acid and terephthalic acid as the main products from the oxidation of *p*-cymene over V_2O_5. Other products which were identified included *p*-methylacetophenone, *p*-isopropylbenzaldehyde, quinone, etc. *p*-Tolualdehyde and *p*-isopropylbenzoic acid were absent. A complete scheme of oxidation is proposed in which a variety of products is derived from a primarily formed hydroperoxide. Morrell *et al.*[128] have reported yields of phthalic anhydride of 85 per cent in the oxidation of *o*-toluic acid over a vanadium catalyst.

The oxidation of methylnaphthalene yields phthalic and maleic anhydrides, although in considerably poorer yields than are obtained from naphthalene[2].

It has been reported[188] that good yields of benzaldehyde along with some benzoic acid can be obtained by refluxing dibenzyl over a catalyst such as MnO_2 in the presence of air at 180 to 230°C. The oxidation of biphenyl over V_2O_5 or MoO_3 catalysts at 400 to 550°C is reported to yield maleic anhydride[57].

Aniline

Brown and Frishe[31] have studied the vapor phase catalytic oxidation of aniline over a thallic oxide catalyst at temperatures of 250 to 500°C. The main products were phenazine and azobenzene. An optimum conversion of aniline to azobenzene of 30 %w was obtained at 350°C with a mole ratio of O_2 to aniline of about 8:1. Under the same conditions an optimum conversion to phenazine of 15 %w was obtained. Under the above conditions the yields were approximately constant over a range of space velocities from 100 to 600 hr^{-1}. Over this range the total aniline conversion was essentially 100 per cent. For space velocities greater than 600 hr^{-1}, both the total aniline conversions and the conversions to the individual products decreased.

Table 15. The Oxidation of Substituted Aromatic Compounds

Reactant	Catalyst	Inlet Conc. (mole %)	Temp. (°C)	Contact Time (sec)	Principal Product[a]	Yield (mole %)	Ref.
p-Cymene	V_2O_5	—	—	—	*p*-Toluic acid		153
					Terephthalic acid		
	V_2O_5	—	300–550	—	Toluic acid	1–4	138
					Cumaldehyde	<3	
					p-Hydroxyisopropylbenzoic acid	<3	
Methylnaphthalene	Ag_2O-V_2O_5	1.0	420–445	0.4–0.6	PAA	40	2
					MAA	10	
α-Methylnaphthalene or β-Methylnaphthalene	10% V_2O_5 25% K_2SO_4 65% SiO_2	1.0	350–400	5	PAA	50	
					MAA	15	
α-Methylnaphthalene or β-Methylnaphthalene	V_2O_5 on Al_2O_3	—	415–425	—	PAA	35	
					MAA	5	
Styrene	Tin vanadate	—	285–400	0.08	Benzaldehyde	up to 8	
				0.1	Benzoic acid	" " 58	
					MAA	" " 17	
α-Methylstyrene	Tin vanadate	—	310–390	0.08	Acetophenone	" " 9	
				0.10	Benzoic acid	" " 61	
					MAA	" " 24	

[a] PAA = Phthalic anhydride; MAA = Maleic anhydride.

Cislak *et al.*[45] have reported the formation of carbazole by the oxidation of *o*-phenylaniline over vanadium or tungsten catalysts.

THE OXIDATION OF NAPHTHENES AND TERPENES

The Oxidation of Naphthenes and Related Compounds

The results which have appeared in the recent literature on the oxidation of naphthenes and related compounds are presented in Table 16. In general the monocyclic compounds have yielded principally maleic anhydride and the bicyclic, principally phthalic anhydride. The yields are generally lower than can be obtained by the oxidation of benzene and naphthalene respectively.

Chowdhury and Saboor have obtained a mixture of aldehydes and acids by the oxidation of cyclohexane using a tin vanadate catalyst[40]. The oxidation of methylcyclohexane over a silver catalyst is reported to yield methylcyclohexanone[193].

The Oxidation of Terpenes

Only a few papers have appeared in the literature on the oxidation of terpenes. The data are summarized in Table 17. Although a wide range of products have been reported[152], the main ones appear to be maleic anhydride, *p*-toluic acid, tolualdehyde and H_2CO. Clark and Hawkins[46] have reported an optimum maleic anhydride yield of about 30 per cent and total aldehyde yields (calculated as H_2CO) of 30 to 60 per cent.

THE OXIDATION OF HETEROCYCLIC COMPOUNDS

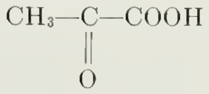
Substituted Pyridines

The literature on the oxidation of substituted pyridines is summarized in Table 18. The oxidation of picolines results in three main products depending on the catalysts and conditions used. Catalysts consisting principally of V_2O_5 or vanadates lead to the formation of the corresponding pyridine carboxylic acids or pyridine itself. Presumably pyridine is formed by the decarboxylation of the acids. On the other hand, catalysts containing molybdena lead to the formation of pyridoin or substituted pyridoins. It is probable that these result from the condensation of two moles of the corresponding pyridine aldehydes. An interesting parallelism may be noted between the oxidation of toluene and the picolines. In both cases vanadium catalysts tend to give primarily carboxylic acids whereas molybdenum catalysts favor the formation of the corresponding aldehydes.

Furfural and Related Compounds

The data which have appeared in the recent literature on the oxidation of furfural and related compounds are summarized in Table 19. Maleic anhydride is the principal product. Whereas Steger[2] obtained only relatively poor yields using a standard benzene oxidation catalyst, other workers

TABLE 16. THE OXIDATION OF NAPHTHENES AND RELATED COMPOUNDS

Reactant	Catalyst	Temp. (°C)	Product	Wt. % Yield	Remarks	Ref.
Cyclohexane	Tin vanadate	250–420	CH_3CHO $CH_2{=}CH{-}CHO$ CH_3COOH  $CH_3{-}\underset{\underset{O}{\Vert}}{C}{-}COOH$ Unsaturates Peroxides			40
Cyclohexane		300–350	MAA			204
Cyclohexane	V_2O_5 on SiO_2 gel	315	MAA	Improved yield by pretreating catalyst at 430°C in pure cyclohexane		169
Cyclohexane Cyclohexene Cyclohexanone Cyclopentane Cyclopentadiene			MAA	15–32		127
Methylcyclohexane	Ag_2O	400–500°C	Methylcyclohexanone		C.T. = 0.3 sec	193
Cyclooctatetraene	V_2O_5 MoO_3	370	Benzoic acid	70		156
Methylcyclopentane	MoO_3, Al_2O_3, V_2O_5 and Ag_2O on SiC	470	MAA	36	Inlet conc. = 0.8% Contact time = 0.7 sec	2
Indene Hydrindene	V_2O_5 on Al_2O_3	430–480	PAA	"Good"	Inlet conc. = 0.5–1.0% Contact time = 0.4 sec	175
Bicyclic nonyl Hydrocarbons	V_2O_5 on pumice	300–360	PAA	40–80	30–60 l. of air/g hydrocarbon C.T. = 0.4 sec	192

Bicyclic hydrocarbons (indene)	V_2O_5 on SiC		PAA			8
Tetrahydronaphthalene and decahydronaphthalene	V_2O_5		PAA, NQ Naphthalene			176
Tetrahydronaphthalene and decahydronaphthalene	V_2O_5	310–430	PAA, NQ Naphthalene CO_2	Up to 7% naphthalene from tetrahydronaphthalene	No tetrahydrophthalic anhydride or 1-naphthol	151
Tetrahydronaphthalene	Ag_2O, V_2O_5 MoO_3, Al_2O_3 on Silicon carbide	450–500	PAA	79		2
			MAA	9		
Decahydronaphthalene	V_2O_5, K_2SO_4 on SiO_2	360–375	PAA	92–95	Contact time = 4.7 sec inlet concentration = 1.1 mole %	2
			MAA	trace		

TABLE 17. OXIDATION OF TERPENES

Reactant	Catalyst	Temp. (°C)	Inlet Conc.	Other Conditions	Products	Yields	Ref.
α-Pinene	V_2O_5 on pumice	390–515		C.T. = 0.7 to 0.84 sec. O_2 : hydrocarbon ratio = 20–115	MAA	Opt. = 29% at 426°C, 0.13 sec, and ratio of O_2 : hydrocarbon = 112	46
					H_2CO + tolualdehyde	30–60% calc. as H_2CO	
Dipentene *p*-cymene	Similar to above						165
α-Pinene, dipentene	V_2O_5				*p*-Toluic acid Terephthalic acid Benzoic acid Acetic acid *p*-Tolylmethylketone Quinone H_2CO Benzaldehyde Hydroquinone Cumaldehyde *p*-Cresol		152
α-Pinene	Ag_2O V_2O_5 $K_2S_2O_7$ on SiO_2	325–400	1 mole % in air	C.T. = 4 sec	*p*-Toluic acid MAA	20–30% acid calculated as *p*-toluic	2

TABLE 18. OXIDATION OF SUBSTITUTED PYRIDINES

Reactant	Catalyst	Temp. (°C)	Reaction Conditions	Principal Product	Yield (%)	Remarks	Ref.
2-Picoline	NiO on kaolin	180		Pyridine	3.4–6.2	Rapid loss of activity	83
	V_2O_5 on pumice	465–475		Pyridine	8–10	No loss of activity	
	$V_2O_5 + CrO_3$, WO_3 or MoO_3	400-600		Pyridine	37–40		
2-Picoline	V_2O_5 on pumice	300–450	C.T. ~3 sec; 0.05 ml picoline/300 ml air	Pyridine	—		84
Picoline Lutidene Nicotine	$V_2O_5 + Fe_2O_3$ on SiO_2	400	Wt. ratio of air:organic = 30	Corresponding pyridine-carboxylic acid	—		43 42 44
3-Picoline etc.	Vanadates of Sn, Ba, K, Fe or Ag	275	Mole ratio of O_2: picoline = 9	Nicotinic acid etc.	23	Best with tin vanadate	104
4-Picoline	$V_2O_5 + MoO_3$, CrO_3 or WO_3	—	—	Isonicotinic acid	—	—	86
4-Ethylpyridine	$Sn(VO_3)_4$ or promoted V_2O_5 on pumice	350 (300–400)		Isonicotinic acid	20–30		85
2-Picoline	V_2O_5, MoO_3 on SiO_2	380–400		α-Pyridoin and 2-pyridine aldehyde			121
2,6-Lutidene	$MoO_3 + WO_3$ and V_2O_5 on pumice			6,6′-Dimethyl-α-pyridoin			87
Quinaldine	$MoO_3 + WO_3$ and V_2O_5 on pumice	450–480		Quinaldoin			
Methylquinolines	V_2O_5, MoO_3 on SiO_2	380–400		Corresponding quinoline aldehydes	35–45		120

TABLE 19. THE OXIDATION OF FURFURAL AND RELATED COMPOUNDS

Reactant	Catalyst	Temp. (°C)	Reaction Conditions	Product	Yield (%)	Remarks	Ref.
Furfural	MoO_3, Al_2O_3, Ag_2O, V_2O_5 on carborundum	360–380	I.C. = 1.4 mole % C.T. ~ 0.7 sec.	MAA	26		2
Furfural	V_2O_5 + MoO_3 + promoters, e.g. $(NH_4)_3PO_4$ W, Al, Fe, As, B etc.	270	I.C. ~ 1 mole % C.T. = 0.2–1.0 sec	MAA	70–80 mole %	Claim advantage of using Ni reactor rather than iron or steel.	133
Furfural	V_2O_5 + MoO_3 + iron molybdates on Al_2O_3			MAA	57–72	Fluid catalyst.	136
Furfural, furan etc.	V_2O_5, MoO_3 on pumice	290–320	C.T. = 3 sec I.C. = 1–2 mole %	MAA	20–25		126
	(Description of apparatus for introducing furfural as fine liquid spray)						
Dihydrofuran, Tetrahydrofuran	V_2O_5 or MoO_3	250–450		MAA			53
Dihydrofuran, Tetrahydrofuran	V_2O_5	300–400	1–1.5% H.C.* in air; C.T. = 0.3 sec	MAA	32		2

* H.C. = hydrocarbon reactant.

have claimed yields as high as 75 to 80 per cent of theoretical, using catalysts which are active at lower temperatures.

ACETYLENE OXIDATION

The oxidation of acetylene in air at very low acetylene concentrations is of considerable importance in the commercial production of liquid oxygen. If the small amount of acetylene normally present in air is not removed, it may be concentrated in the liquid oxygen to the point where it forms a separate solid phase and constitutes an explosion hazard.

Rushton and Krieger[160] have presented a rather detailed account of the work which has been done in this field through 1950. This work will be reviewed and more recent papers discussed.

A large number of metallic oxides and salts, both supported and unsupported were screened for their activity in acetylene oxidation in the range of acetylene concentrations around 5 ppm. Most of the tests were run at 150°C, a space velocity of 100,000 hr^{-1} (S.T.P.) and a pressure of 100 psig. The air was saturated with water vapor at this pressure and temperatures of 53 or 65°C.

Promoted hopcalites (mixtures of MnO_2 and CuO) were found to be quite active and the most satisfactory catalyst reported by Rushton and Krieger was prepared by mixing 90 per cent Hopcalite* (60 per cent MnO_2 + 40 per cent CuO) and 10 per cent Ag_2O. All the catalysts underwent a gradual loss of activity on use. The activity can be partially restored by regeneration in air at 200°C. However, complete regeneration is never effected and the loss in activity is paralleled by a loss in surface area and a growth in crystal size.

Fastovskii and Malyusov[55] have studied the use of a number of catalysts. With MnO_2 at 150°C, the order of the reaction with respect to acetylene concentration was always less than unity but approached 1 at low acetylene concentrations. At 180°C the order was approximately unity over a considerable range of concentrations. It is suggested that the adsorption of either acetylene or a product of the reaction is high at the lower temperature.

Roiter and Rusov[158], using an "active" MnO_2, found the order with respect to acetylene concentration to vary from 0.5 at 142°C to 0.75 at 190° and 1.0 at 220°C and above. The corresponding activation energies were 16, 5 and 0 kcal/mole. They interpret the results to reflect a change from a diffusion-limited process at 220°C to a reaction-limited process at 142°C.

Krieger[98] studied the oxidation of acetylene on catalysts consisting of silver nitrate supported on alumina. With a high (132 m^2/g) area support,

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* Mine Safety Appliance Co.

concentrations of silver up to about 5 per cent were inactive while between 5 and 10 per cent the activity rose abruptly to a high value and leveled off. A similar phenomenon was observed with a low (0.2 m^2/g) area support, but at much lower silver nitrate concentrations. The maximum activity of the catalyst was independent of the area of the support and it is believed that only the external surface of the granules are active and that the $AgNO_3$ in the pores is not accessible for reaction. X-ray diffraction patterns indicated that crystalline silver nitrate was absent at low silver concentrations. It is believed that a certain minimum crystal size is required for catalytic activity. At silver concentrations above about 5 per cent on the high area catalyst, the area decreased with increasing silver content with no attendant change in activity. The loss of area is believed due to a filling or blocking off of the catalyst pores. That there is no loss of activity is taken as support for the theory that only the external surface is active. It would be of interest to check this idea directly using catalysts which are otherwise identical but with different external areas—i.e., different particle sizes.

The active catalyst is believed to be a mixture of crystalline silver nitrate with the partially decomposed salt causing a certain number of lattice distortions. The temperature of activation for maximum activity is somewhat higher than that for maximum silver nitrate crystallinity. Further, the promoting effect of small quantities of samarium and aluminum nitrates may be due to the formation of lattice distortions. The samarium compound also acts to prevent sintering. Pretreatment of the catalysts at higher than optimum temperatures leads to further decomposition, an increase in surface area, and a decrease in catalytic activity.

Kirsch and Krieger[94] have studied the adsorption of acetylene on silver nitrate catalysts at temperatures below those at which oxidation takes place. The sorption was found to be irreversible. The adsorbed acetylene could not be removed by continued outgassing at very low pressures. The rate of sorption varied inversely with the initial acetylene pressure. The total amount of acetylene sorbed was independent of pressure over the range studied, but increased slightly with temperature.

Approximate calculation of the geometric surface area of the silver nitrate showed that the amount of acetylene sorbed at saturation was about one thousand times that required for a monolayer. Consequently, it was concluded that penetration of the solid occurs. In addition, it is suggested that the adsorbed acetylene undergoes polymerization (or dimerization) which inhibits further penetration of the lattice. At relatively high pressures a more dense population of acetylene molecules results in the formation of a more impenetrable layer of polymer than is formed at lower pressures.

By use of radioactive tracer techniques, Johnson and Krieger[92] were able to follow accurately the acetylene adsorption on the catalyst and CO_2 production as a function of time. At 125°C only adsorption occurred. At and above 149°C, the first acetylene fed to the system was adsorbed without reaction. At some critical surface concentration, oxidation began abruptly, accompanied by CO_2 production and an exotherm in the catalyst bed. The amount of sorption required to initiate oxidation decreased with increasing temperature. The activity then decreased gradually due to the slow decomposition of the silver nitrate. X-ray studies of catalysts exposed to acetylene gave evidence of the presence of a compound of the type $Ag_2C_2 \cdot AgNO_3$. It is suggested that the oxidation proceeds by a bimolecular reaction of acetylide surface complexes. Data in the literature[160] show that diacetylenes are formed from cuprous acetylides under mild oxidizing conditions. Further, results have been obtained in the oxidation of acetylene-nitrogen mixtures with silver nitrate catalysts which show that the course of the reaction is similar to that observed when oxygen is present. The oxygen in the CO_2 may come from the silver nitrate while the oxygen in the air serves to regenerate the silver compounds to nitrate or oxide.

The postulated reaction mechanism may be summarized as follows:

Acetylene oxidation:

$$nC_2H_2\ (\text{gas}) \xrightarrow[\text{AgNO}_3]{} \underset{\text{sorbed}}{(C_2H_2)n} \xrightarrow[\text{AgNO}_3]{} CO_2 + H_2O + AgNO_x\ (x < 3)$$

Catalyst regeneration (in air:)

$$AgNO_x + O_2 \rightarrow AgNO_3$$

Catalyst decomposition:

$$AgNO_3 \rightarrow Ag + \text{oxides of nitrogen}$$

$$AgNO_x \rightarrow Ag + \text{oxides of nitrogen.}$$

THE PREPARATION OF FORMALDEHYDE

The manufacture of formaldehyde represents one of the more highly developed commercial applications of vapor phase catalytic oxidation. The estimate of United States annual production for 1956 is 1.4 billion lb. of 37 per cent formaldehyde. While the catalytic oxidation of methanol remains the principal source of formaldehyde, increasing amounts (estimated at 25 per cent of total in 1957) are being prepared by the direct oxidation of hydrocarbons.

The Oxidation of Methanol

Two types of catalysts are currently used commercially for methanol oxidation. The classic procedure uses a silver or copper catalyst and employs a rich mixture of methanol with air at approximately atmospheric pressure. The second method makes use of an oxide catalyst, such as iron-molybdenum oxide, and employs a lean methanol-air mixture. Whereas the classic procedure operates at a methanol conversion level of 60 to 70 per cent, the oxide-type catalysts operate at substantially complete methanol conversion and yield a methanol-free product.

Metallic Catalysts. As early as 1868 Hofmann reported the preparation of formaldehyde by the oxidation of methanol in the presence of a hot platinum spiral. The subsequent developments in the oxidation of methanol over metallic catalysts have been reviewed by Walker[195] and by Marek and Hahn[108].

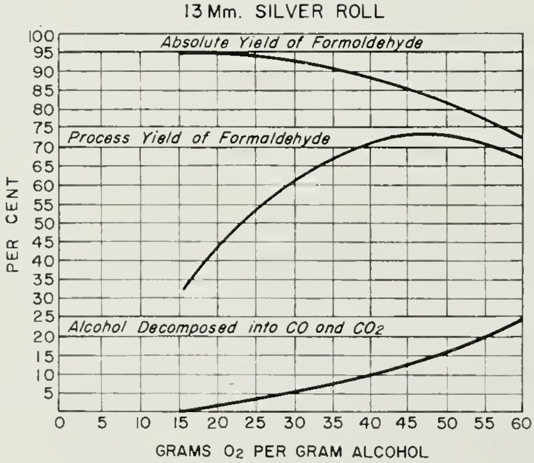

Figure 3. The effect of oxygen to alcohol ratio on the oxidation of methanol to formaldehyde.[180] (Reprinted courtesy of the *Journal of the American Chemical Society.*)

Thomas[180] has reported the results of laboratory-scale studies of the oxidation of methanol in the presence of copper, silver and gold catalysts. His results on silver catalysts are in general agreement with those reported for commercial operation by Homer[78]. Thomas[180] studied the oxidation using rolls of copper, silver and gold gauze approximately 13 mm in diameter and 100 mm long. Weight ratios of O_2 to CH_3OH were varied from about 0.15 to 0.60 and air rates were varied from about 90 to 200 l./hr. Whereas the inlet gas temperatures were in the range of 350 to 565°C, temperatures in the center of the gauze varied from 530 to above 900°C. Data from these experiments were compared at constant air flow rates. It was felt that, since under these conditions the rate of oxygen supply to the system was constant, the temperatures were most likely to be constant.

Typical results obtained using a silver gauze are presented in Figure 3. The data are presented in terms of process yield (per cent conversion to H_2CO based on CH_3OH feed), absolute yield (per cent conversion to H_2CO

based on CH_3OH reacted) and per cent alcohol decomposed to CO and CO_2. As the weight ratio of O_2 to CH_3OH is increased from about 0.15 to 0.50, the process yield rises from about 30 per cent to about 70 to 75 per cent. There is an attendant drop in absolute yield from 95 to about 80 per cent and an increase in conversion to $CO + CO_2$ from about 3 to 15 per cent. At the same time, the H_2 content of the product gas decreases from 12 to 13 per cent to about 8 to 9 per cent. It may be noted that 0.5 g O_2/g CH_3OH is required for the reaction

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow H_2CO + H_2O \tag{1}$$

Thus, over most of the range investigated there was insufficient O_2 present to oxidize all of the methanol. This is especially true since some of the O_2 was consumed in the complete oxidation to CO_2.

Little effect of flow rate at constant composition was observed, in spite of the fact that higher flow rates produced higher temperatures. This may not be too surprising when one considers that, in general, the reaction is being operated under conditions of complete O_2 consumption. Hence the major effect of higher temperatures might be to increase the decomposition of H_2CO. This temperature effect may have been largely compensated for by the decreased residence time in the reaction zone at the higher flow rates.

Similar results were obtained with copper and gold gauzes. However, they were both somewhat less active and caused more formaldehyde decomposition than silver. Consequently, the absolute yields were somewhat lower. With the gold roll the presence of 1.7 per cent acetone or 10 per cent water in the alcohol did not appreciably affect the process. Other workers[186, 195] have reported that the addition of 20 to 40 per cent water (based on methanol) gave improved yields of formaldehyde based on the alcohol oxidized.

Thomas[180] suggests that the fundamental reactions involved under the above conditions are

$$CH_3OH \rightarrow H_2CO + H_2$$

and

$$H_2CO \rightarrow H_2 + CO$$

followed by the oxidation of the hydrogen and carbon monoxide until all of the oxygen is consumed. He suggests that the functions of the oxygen may be to

1. Remove hydrogen to maintain a favorable equilibrium;
2. Maintain the necessary temperature;
3. Keep the catalyst active, possibly by oxidizing and removing "poisons" or by maintaining the catalytic surface in the proper physical conditions.

The chemical nature of the surface may also be affected by the chemisorption of oxygen.

Newton and Dodge[132] have studied the equilibrium relations for the dehydrogenation of methanol to formaldehyde. They conclude that at atmospheric pressure, the equilibrium conversions of methanol to formaldehyde would be about 50 per cent at 400°C, 90 per cent at 500° and 99 per cent at 700°C. LeBlanc and Plashke (see Ref. 16) obtained only a 27 per cent yield of formaldehyde by the dehydrogenation of methanol over a copper spiral at 600 to 700°C in the absence of air. The yield fell off gradually to about 4 per cent as the experiment was repeated but the activity of the metal could be restored by oxidizing and reducing it. Thus, as Thomas[180] has concluded, the function of the oxygen, aside from maintaining the necessary temperature, seems to be to keep the catalyst active by oxidizing and removing any "poisons" or to keep the surface of the metal in the proper chemical and physical state.

On the other hand, Walker[195] has concluded from the work of Sator[162] that the silver-catalyzed process may depend exclusively on dehydrogenation and that the only function of the oxygen is to maintain the necessary temperature by the oxidation of hydrogen. Sator's results indicate that the catalyst temperature is more important than the ratio of oxygen to alcohol in determining the alcohol conversion and that, to a considerable extent, a decrease in O_2 concentration may be compensated for by preheating the feed gases or insulating the reactor. However, a certain amount of O_2 is required since preheating of the feed must not exceed temperatures at which the decomposition of methanol and formaldehyde becomes excessive.

Vlodavets *et al.*[190] have studied the oxidation of methanol over 2-mm silver spheres. Temperatures were varied from about 300 to 517°C. The product stream consisted mainly of H_2CO, CO_2, N_2, H_2O and some CO. The work was directed mainly toward a study of the variation of O_2 concentration with flow rate or contact time. With an initial mole ratio of methanol to oxygen of 2, the rate of oxygen consumption was found to be first order with a rate constant of $\sim 0.77 \text{ sec}^{-1}$ at 302°C and an activation energy of 16 kcal/mole. They have proposed the following reaction scheme:

$$(1)\quad O_2 + Ag \rightarrow Ag[O_2]$$
$$(2)\quad CH_3OH + Ag[O_2] \rightarrow CH_2O + H_2O + Ag$$
$$(3)\quad CH_2O + Ag[O_2] \rightarrow CO_2 + H_2 + Ag$$
$$(4)\quad H_2 + Ag[O_2] \rightarrow H_2O + Ag$$

It is assumed that:

1. The reactants, except O_2, and the products are not adsorbed.
2. The oxygen is chemisorbed and the rate of oxygen chemisorption is the rate-determining step.

3. The rate of desorption of oxygen is small relative to the rates of reactions (1) to (4); and
4. The oxidation reactions are irreversible.

Hader *et al.*[73] have published a review of the commercial processes currently in use for formaldehyde manufacture. In commercial operation with silver catalysts conversions of methanol to formaldehyde are generally about 60 per cent. An additional 3 to 5 per cent of the methanol is converted to CO and CO_2 so that absolute yields of formaldehyde are over 90 per cent. It has been found that with down-flow operation virtually all of the conversion occurs near the top of the catalyst bed and that the principal function of the additional catalyst is to dissipate the large amounts of heat released. The temperature drop between the upper edge of the catalyst and a point below the catalyst support is 150 to 200°C. The actual reaction temperature is normally about 600°C.

Hader also reports that extreme care must be taken to remove extraneous materials from the feed. For example, as little as 0.1 g of iron deposited on on a converter's catalyst will promote the carbonization of methanol and kill the catalyst activity completely in only 12 hr.

Payne and Vail[143] have reported that the addition of 5 to 100 ppm of an organic sulfur compound to the methanol results in a 1 to 3 per cent increase in formaldehyde yield in both the metal catalyzed and oxide catalyzed processes.

Oxide-Type Catalysts. Adkins and Peterson[1] have studied the oxidation of methanol over iron oxide, molybdenum oxide and mixtures of the two oxides. Most of the studies were made using a bed of catalyst 15 cm in length and 3 cm^2 cross-sectional area and with feed rates of 10 g of methanol in 93 l. of air/hr.

With pure MoO_3, approximately 100 per cent H_2CO yields based on the alcohol oxidized were obtained. However, the percentage conversion decreased from about 60 per cent to a steady value of about 32 per cent after 12 to 24 hr operation at 400°C. Raising the catalyst bath temperature from 360 to 400°C raised the steady state conversion level only from about 24 to 32 per cent. With pure iron oxide under similar conditions, almost all of the methanol was oxidized to CO_2 with the formation of little or no formaldehyde.

The most satisfactory catalyst was found to be an equimolar mixture of iron oxide and molybdenum oxide. With this catalyst the percentage conversion to H_2CO increased from an initial value of about 82 per cent to an equilibrium value of about 91 per cent when feeding 10 g of CH_3OH in 93 l. of air at 373°C. Decreasing the length of catalyst bed from 15 to 5 cm gave the same conversion of methanol to H_2CO but a somewhat higher yield of H_2CO. Decreasing the feed rate (at constant methanol to air ratio) resulted in a loss in H_2CO yield due to over-oxidation. Similarly, at temperatures of 353, 373 and 400°C, conversions of methanol to H_2CO of 85.2, 91.8 and 91.9 per cent were obtained. However, at 400°C some loss in yield due to over-oxidation of the H_2CO was observed.

In 1933 a patent was issued to Meharg and Adkins[125] disclosing essentially the process outlined above. The preferred conditions were: bath temperature = 250°C, contact time = 0.01 to 0.03 sec, a reactant mixture of 8 to 10 %w methanol in air and an 8-mesh catalyst consisting of about 8 to 20 per cent Fe_2O_3 and 80 to 92 per cent MoO_3. A 95 per cent conversion of methanol to H_2CO with 5 per cent going to CO and CO_2 is claimed. Hader *et al.*[73] have reported that the du Pont Company is currently employing the process described by Adkins and Peterson[1] for the commercial production of formaldehyde.

Table 20. Oxidation of Methanol with Oxide-Type Catalysts

Feed Conc. CH_3OH in Air (% w)	Temp. (°C)	Contact Time (sec)	Mole % Conversion to H_2CO	Remarks	Ref.
10	260–310	10-15	72	Total methanol conversion ~ 83% Catalyst-1:1 mole ratio of WO_3:MoO_3	5
	285		93–95	Mole ratio of WO_3:MoO_3 = 1.22	5
	305		97–100		
6	310	0.4		Catalyst of 99% V_2O_5 + 1% MgO on silica gel	47
15–20 (mole %)	300–450	0.5 to 1.5	90	Catalyst of 1–10% CeO in MoO_3	24

Simultaneous studies of the variations in the electronic and catalytic properties in going from iron oxide to molybdenum oxide to mixtures of the two might provide an insight into the details of the mechanism of the oxidation of methanol on these catalysts. The system may be sufficiently simple to provide an excellent opportunity for a fundamental investigation of the mechanism of oxidation reactions over oxide type catalysts in general.

Suvorov *et al.*[178] studied the oxidation of methanol over a tin vanadate catalyst at 310°C. Using 50 l. of air/g of methanol and contact times of 0.1 to 0.2 sec, the products were mainly formaldehyde and carbon monoxide. No formic acid was found in the oxidation of either methanol or formaldehyde. The oxidation of methanol in the presence of ammonia was reported to give HCN in yields up to 90 per cent.

Other patents claiming the use of metal oxide catalysts are summarized in Table 20.

Hydrocarbon Oxidation

The direct oxidation of methane and higher hydrocarbons to formaldehyde would be economically very attractive if sufficiently high formaldehyde yields could be obtained. Many of the studies directed to this end have involved noncatalytic processes or the use of homogeneous catalysts. However, some work has also been done on the use of heterogeneous catalysts.

Schonfelder[164] reported 55 to 58 per cent conversions of methane to formaldehyde by the passage of a mixture of methane, air and steam over copper or silver at 500°C. Campbell[36] investigated the use of a number of supported metal catalysts for methane oxidation. Formaldehyde was the principal intermediate product.

Formaldehyde may be produced by the oxidation of ethylene over boric or phosphoric acids or their salts supported on clay or diatomaceous earth[21]. Walker has studied the oxidation of natural gas over mixed catalysts comprising aluminum phosphate and metal oxides at pressures of 7 to 20 atm and temperatures of 430 to 480°C. Typical liquid products contained 34 to 36 per cent methanol, 20 to 23 per cent formaldehyde, and 5 to 6 per cent acetaldehyde[194].

Oxidation of Ethylene to Ethylene Oxide

The oxidation of ethylene to ethylene oxide is unique as compared with most of the oxidations discussed in this chapter, in that one of the principal products of the oxidation, namely ethylene oxide, is formed from the ethylene by the addition of only one atom of oxygen. Most of the other cases which will be dealt with in detail involve the consumption of more than one oxygen atom in producing the final product. The production of ethylene oxide by catalytic vapor phase oxidation is the basis for large industrial installations. For this reason there is a large body of literature describing the over-all results of the industrial technological programs. Much of this work, however, does not lead to conclusions that are particularly valuable in understanding the kinetics or catalyst behavior. Sherwood[168] has recently published a brief review of some of the technological aspects of ethylene oxide synthesis. In order to obtain some understanding of the mechanism and kinetics of this oxidation reaction one is indeed fortunate in having the excellent fundamental work of G. H. Twigg[184, 185]. There are however a number of elements in the catalyst behavior which need additional study and some suggestions are made below which indicate the direction which future studies might take.

Before considering the studies of Twigg and other workers on the mechanism, it is desirable to describe the general nature of the work which has been carried out on this oxidation. There is obviously some matter of choice in the paper to which one might refer for an over-all picture of the catalytic oxidation of ethylene. We prefer to present the results of McBee, Hass and Wiseman[124]. These workers carried out their oxidations on a tabular alumina coated with about 21 per cent silver oxide to which was added some 2 per cent barium peroxide promoter. The alumina in this case was essentially corundum, the high-temperature form of aluminum oxide. These authors varied the temperature, the air-ethylene ratio and the contact time in their studies. Typical data are presented in Figures 4 and 5.

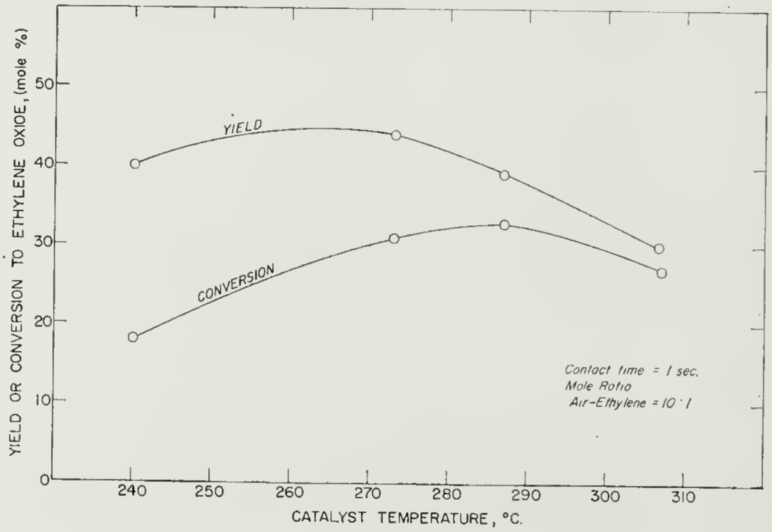

Figure 4. Effect of temperature on the catalytic oxidation of ethylene oxide.[124] (Reprinted from *Industrial & Engineering Chemistry*, **37**, 432 (May 1945). Copyright 1945 by the American Chemical Society and reprinted by permission of the copyright owner.)

From their experiments they conclude: (a) A high air-ethylene mole ratio of the order of 10 to 20 is most favorable for obtaining good yields and conversions. Under optimum conditions the yields and conversions are of the order of 40 to 60 per cent. (b) As the catalyst ages it becomes less and less efficient for the conversion of ethylene to ethylene oxide. (c) On continued use, the temperature of the catalyst must be raised if maximum efficiency for the production of ethylene oxide is to be maintained. The optimum temperature for *conversion* (based on ethylene fed) to ethylene oxide is around 265°C and the temperature of optimum *yield* (based on total ethylene converted) is about 20° lower than the temperature for optimum conversion.

At the early stages of the development of the catalytic oxidation of ethylene to ethylene oxide on a commercial scale, an outstanding contribution was made by G. H. Law *et al.*[102]. It was noted that the addition of organic halogenated compounds was effective in increasing the yields of ethylene oxide. As has been pointed out above, the silver catalyst gradually loses activity with use. The addition of small quantities of ethylene dichloride to the air-ethylene mixture improves the yield and conversion. Data of McBee, Hass and Wiseman[124] showing the effect of different amounts of ethylene dichloride on the relative conversion of ethylene to ethylene oxide are presented in Figure 5. These workers have presented additional data on the effect of ethylene dichloride addition showing, among other things, that the use of too much ethylene dichloride in the feed gas will deactivate the silver catalyst. A catalyst which has been deactivated with ethylene dichloride may be reactivated fairly easily by simultaneously raising the temperature and passing the reactants over the catalyst. There are many other references[13], principally in the patent literature, on the use of other halogenated compounds as additives to the ethylene-air mixture. Likewise, the effects of impurities and changes in catalyst composition are covered in large numbers of references[37]. A discussion of these important improvements to the industrial technology will not be covered at this point. Some reference to this subject, however, will indicate how these findings might point the way to future fundamental studies on the catalytic oxidation processes.

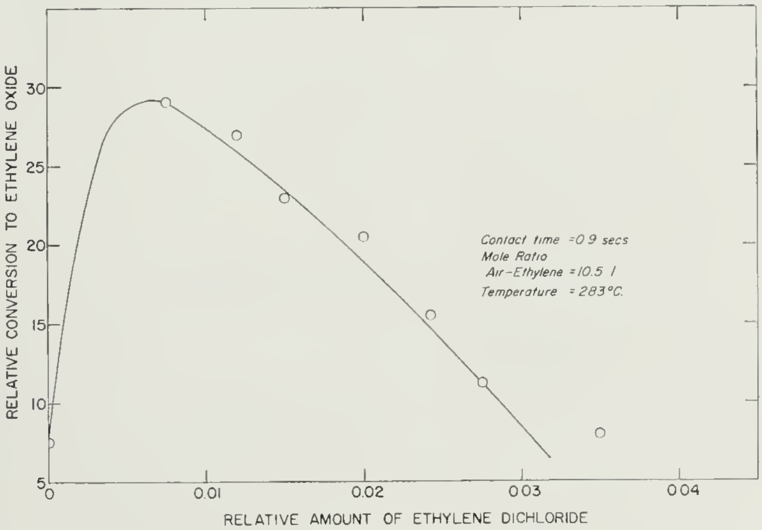

Figure 5. Effect of ethylene dichloride on the oxidation of ethylene to ethylene oxide.[124] (Reprinted from *Industrial & Engineering Chemistry*, **37**, 432 (May 1945). Copyright 1945 by the American Chemical Society and reprinted by permission of the copyright owner.)

The use of fluidized catalysts has become increasingly important in oxidation reactions. One of the earliest references, if not the earliest, is due to

S. B. Becker[9]. It will be recalled that Becker was apparently the originator of the idea of using fluidized vanadium oxide catalysts for oxidation of naphthalene to phthalic anhydride. The patent just referred to claims the use of fluidized beds of catalyst, principally silver catalyst, for oxidation of ethylene to ethylene oxide. This suggestion has recently been verified by Venkataraman, Gulati and Bhattacharyya[189].

In connection with the oxidation of hydrocarbons containing four carbon atoms, Wan[197] has obtained empirical information on the oxidation of ethylene to ethylene oxide on a silver-tabular alumina catalyst. Although his equations were developed for a specific catalyst, the nature of his correlations appear to be worth noting. Wan was interested in finding the number of gram-moles of ethylene oxide produced per gram of catalyst under different conditions of contact time and partial pressure of the reactants, namely oxygen and ethylene. Wan assumes the following over-all equation for the production of ethylene oxide:

$$dn/d\theta = kP^a_{C_2H_4}P^b_{O_2}$$

where n = gram-moles of ethylene oxide/g of catalyst, a, b and k = constants, θ = time of contact with catalyst (hr), and P = partial pressure (atm).

Table 21. Effect of Contact Time on Oxidation of Ethylene to Ethylene Oxide[197]

Catalyst = Ag_2O on Tabular Al_2O_3

$$\frac{dn}{d\theta} = kP^a_{C_2H_4}P^b_{O_2}$$

n = gram moles oxide formed/g catalyst

θ = Time of contact of gases with catalyst (hr)

a, b, k = Constants

P = Partial pressure (atm)

	Temp. (°C)		
	230	240	260
a		0.365	0.316
b		0.667	0.677
k	0.00472	0.00708	0.0141

Wan then performed sufficient experiments to determine the three constants in the above equation and their relationship to temperature. He also showed that the temperature coefficient of the over-all reaction velocity constant, k, was 19.3 kcal/mole. The results of his study are shown in Table 21. This type of three-constant empirical relationship is of value in the design of large-scale industrial equipment.

In his first paper on the catalytic oxidation of ethylene, Twigg showed that at 200 to 350°C, oxygen was chemisorbed as atoms and that none of the other reactants was adsorbed. Twigg was also able to show that he could measure the fraction of the silver surface covered by oxygen by means of electrical conductivity measurements. In this way he had a means of estimating the quantity of oxygen adsorbed on the silver surface. The adsorption and desorption of oxygen were slow, activated processes, and he was able to carry out reactions of various gases with adsorbed layers of oxygen on silver. Thus the individual steps in the reaction chain were isolated and studied separately. He showed that ethylene can be oxidized by adsorbed oxygen atoms either to ethylene oxide or directly to CO_2 and water. Ethylene oxide may undergo isomerization to acetaldehyde which is then rapidly oxidized to CO_2 and water.

On a clean surface the ethylene oxide was simultaneously isomerized to acetaldehyde and also converted back to ethylene and adsorbed oxygen, which could react to form CO_2 and water. Twigg also showed that ethylene oxide and acetaldehyde, but not ethylene, are adsorbed on a clean surface to form a nonvolatile layer on the catalyst. This layer was composed of carbon, hydrogen and possibly oxygen combined in indefinite and varying proportions.

In addition, Twigg studied the oxidation of ethylene in a flow system. From this study of the effects of contact time, reactant concentrations and temperature he concluded that the following reactions were involved:

$$\text{(1)}\quad C_2H_4 + O(\text{ads.*}) \rightarrow C_2H_4O$$

$$\text{Rate} \propto P_{C_2H_4} \text{ and } \theta(O_2)$$

$$\text{(2)}\quad C_2H_4 + 6O(\text{ads.}) \rightarrow 2CO_2 + 2H_2O$$

$$\text{Rate} \propto P_{C_2H_4} \text{ and } [\theta(O_2)]^2$$

$$\text{(3)}\quad C_2H_4O + 5O(\text{ads.}) \rightarrow 2CO_2 + 2H_2O$$

$$\text{Rate} \propto P_{C_2H_4O}\text{ ; independent of } \theta(O_2)$$

where $\theta(O_2)$ is the fraction of the catalyst surface covered by adsorbed oxygen.

It was concluded that the reaction mechanism involves first the chemisorption of oxygen atoms on the catalyst surface followed by the reaction of gaseous or weakly adsorbed ethylene molecules either with one oxygen atom to form ethylene oxide or with two atoms to form products that are oxidized rapidly to CO_2 . The ethylene oxide may isomerize to acetaldehyde which is readily oxidized to CO_2 and water.

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* Ads. = adatoms

The mechanism proposed by Twigg has been confirmed in some recent work by Murray[130]. He found that the oxidation of ethylene to ethylene oxide involved an activation energy of 12 kcal, whereas the corresponding reaction to carbon dioxide has an activation energy of 15 kcal. It is also of interest to note that Murray found that the oxidation of propylene with oxygen on the same sort of catalyst produced only carbon dioxide and water. As pointed out elsewhere in this chapter, this probably means that the propylene oxide is much less stable than ethylene oxide and is consequently destroyed faster than it is formed.

Additional studies of the kinetics of the oxidation of ethylene over silver catalysts have been reported recently by Andrianova and Todes[4]. It was concluded that ethylene oxide is an intermediate in the oxidation of ethylene to carbon dioxide. Over the range of conditions investigated, the rates could be described by the following equations:

(1) Oxidation of ethylene:

$$\frac{-d(C_2H_4)}{dt} = 100\ e^{-\frac{13,000}{RT}}\ (u)^{1/2}[O_2]^{1/2}$$

where u = volumetric gas flow rate; and

(2) Oxidation of ethylene oxide:

$$\frac{-d(C_2H_4O)}{dt} = 4 \times 10^5\ e^{-\frac{21,000}{RT}}\ [C_2H_4O][O_2]$$

Both reactions are reported to be rapid and at least partially diffusion-controlled under the conditions studied. Mazzolini[123] has also considered the influence of mass transfer in controlling reaction rates in ethylene oxidation.

Kummer[96] has studied the oxidation of ethylene over single crystals of silver. The rate of reaction and ratio of ethylene oxide to carbon dioxide were found to be independent of the crystal face. The presence of sulfur or chlorine on the surface decreased the total reaction rate and increased the selectivity to ethylene oxide. It was found that the rate of oxygen chemisorption was comparable to the reaction rate. Based on the reaction rate per unit area of silver surface and the observed activation energy, it was concluded that the reaction is between chemisorbed oxygen and physically adsorbed ethylene in agreement with Twigg's proposed mechanism.

A recent paper by Wilson, Voge, Stevenson, Smith and Atkins[205a] describes some new physical techniques for the study of silver catalyst used for the oxidation of ethylene. These authors prepared evaporated silver films which contained crystals randomly oriented, or with (110) planes parallel to the support on which they were deposited. They found that both types were about equally active and selective. This appears to be in agreement with the results of Kummer[96] who found no clear-cut differences in catalytic activity between (211), (111), and (110) crystal faces. Wilson *et al.* showed that during the oxidation of ethylene at 250 to 280°C, the oriented films of silver recrystallized in a few hours to a randomly oriented material, thus indicating that in this oxidation unusual crystal faces would not be expected to persist during catalytic use. This type of rearrangement to a random orientation might be expected to take place in investigations involving specific crystal faces, for example, in the work on single copper crystals as reported by Gwathmey.

In addition to their studies of the effect of crystal orientation, Wilson *et al.*, showed that many of the typical silver catalysts contained appreciable amounts of carbon, oxygen, hydrogen and sulfur compounds. This, of course, emphasizes the difficulty in preparing pure metallic oxide or metallic catalysts for study. This brings to mind the difficulties that the present authors have had in studying the properties of vanadium pentoxide catalysts, where the presence of traces of residual ammonia left on decomposition of ammonium vanadate, made measurements of oxygen adsorption rates extremely difficult and variable. Wilson *et al.* also made some measurements which showed the possible utility of measuring the surface potential of the silver catalyst relative to a gold electrode in air. The chemisorption of phosphorus, sulfur or chlorine compounds on the silver catalyst they studied changed the surface potentials measured in this way by appreciable amounts. This may open up new methods of studying catalysts similar to silver in order to determine the effects of impurities, etc., on catalytic behavior.

Orzechowski and MacCormack[137] have recently published the results of a detailed study of the oxidation of ethylene on a silver catalyst. It was found that the catalyst activity and selectivity were dependent on the conditions of previous treatment and that the catalyst may have to be operated for up to 150 hr before reaching a steady state. All runs were made after an extended pretreatment under standard conditions. A series of check runs were made during the program to permit corrections for slight variations in catalytic activity.

The kinetics were studied at atmospheric pressure over a range of O_2 concentrations from 9.9 to 79 per cent and ethylene concentrations from 2.35 to 9.4 per cent, the remainder being nitrogen. Flow rates, which were always in the region of laminar flow, were varied to give contact times of 0.05 to 1.0 sec. Temperatures of 234 and 274°C were studied. The initial rates of formation of ethylene oxide and CO_2 were measured; no acetaldehyde was observed.

It was concluded that the data were best represented by

$$r_o = \frac{k}{1 + \dfrac{a}{P_E} + \dfrac{b}{P_o}}$$

where r_o = initial rate of ethylene oxidation*; P_E = initial pressure of ethylene (mm Hg); P_o = initial pressure of oxygen (mm Hg). The values of a, b and k are listed in Table 22.

In agreement with Twigg it was concluded that both ethylene oxide and carbon dioxide were primary products of the ethylene oxidation. The selectivity for ethylene oxide at zero conversion was found to be 50 to 52 per cent at 274°C and 60 to 64 per cent at 234°C, approximately independent of the reactant composition. In contrast to Twigg, the conversion to carbon dioxide was not found to be linear with time.

The oxidation of ethylene oxide was studied under conditions similar to those used in the ethylene oxidation. It was concluded that the data were best fitted by

$$R_o = \frac{A}{1 + \dfrac{B}{P_x} + \dfrac{C}{P_o}}$$

TABLE 22. KINETIC CONSTANTS IN THE OXIDATION OF ETHYLENE

Temp. (C)	k*	a	b
234	0.048	45	240
274	0.200	86	225

where R_o = rate of ethylene oxide oxidation; P_x = partial pressure of ethylene oxide (mm Hg); P_o = partial pressure of oxygen (mm Hg); and at 274°C, $A = 0.032$, $B = 90$, and $C = 270$. Little or no decomposition of ethylene oxide to ethylene + O_2 was observed. The isomerization of ethylene oxide to acetaldehyde was studied using mixtures of ethylene oxide and nitrogen with no oxygen. The results indicated that isomerization is not the rate-determining step in the oxidation of ethylene oxide. It was suggested that the oxidation involves the reaction of gaseous or weakly adsorbed ethylene oxide with chemisorbed oxygen atoms.

In contrast to Twigg, it was concluded that the two primary reactions—i.e., to ethylene oxide and to CO_2—probably proceed through the same type of, if not a common, step. Twigg had proposed the following reactions:

$$C_2H_4(\text{gas}) + O(\text{ads.}) \rightarrow C_2H_4O$$

and

$$C_2H_4(\text{gas}) + 2O(\text{ads.}) \rightarrow CO_2 + H_2O$$

Orzechowski and MacCormack suggest that the reaction proceeds by the following scheme:

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* r_o and k in arbitrary units; see Ref. 137, p. 426.

$$\begin{tikzcd}
C_2H_4 + O\text{-}Ag \arrow[d, shift right, "k_1"'] & & C_2H_4 + O\text{-}Ag \arrow[d, shift right, "m_1"'] \\
C_2H_4 - O\text{-}Ag \arrow[u, shift right, "k_1'"'] \arrow[rr, leftrightharpoons, "i"'] \arrow[d, shift right, "k"'] & & Y\text{-}Ag \arrow[u, shift right, "m_1'"'] \arrow[d, shift right, "m"'] \\
C_2H_4O + Ag \arrow[u, shift right, "k'"'] & & Y + Ag \arrow[u, shift right, "m'"']
\end{tikzcd}$$

where Y is isomeric with ethylene oxide and is very rapidly oxidized to CO_2 and H_2O. It is suggested that Y is acetaldehyde. Thus the "direct" oxidation of C_2H_4 to CO_2 may proceed by either the steps k_1, i and m or m_1, m. In both cases only single adsorbed oxygen atoms are proposed. No discussion of the exact mechanism by which Y is converted to CO_2 and H_2O is given.

In agreement with Orzechowski and MacCormack, Kurilenko *et al.*[97] have concluded that the kinetics of ethylene oxidation over a silver catalyst depends on the prior history of the catalyst and in particular on the amount of oxygen adsorbed in the layer of silver adjacent to the surface. For the catalyst in a steady state, the rates of ethylene oxidation to both ethylene oxide and to CO_2 can be described by equations of the form

$$\frac{-d[C_2H_4]}{dt} = \frac{k[C_2H_4]}{[C_2H_4O] + k'[CO_2]}$$

The following mechanism is suggested which is similar to that proposed by Orzechowski and MacCormack, but in addition Kurilenko *et al.* suggested that the unidentified intermediate "Y" may be $CH_2{=}CHOH$.

$$O_2 + 4\ e^- \rightarrow 2O^{--}$$

$$O^{--} + C_2H_4 \rightarrow C_2H_4O + 2\ e^-$$

$$O^{--} + C_2H_4 \rightarrow CH_2{=}CHOH + 2\ e^-$$

$$CH_2{=}CH_2OH + 2\tfrac{1}{2}\ O_2 \rightarrow 2CO_2 + 2H_2O$$

An integral form of the kinetic equation representing the course of the process in a flow system is also given.

Smeltzer *et al.*[173] measured adsorption rates and volumes of adsorbed oxygen on technical silver catalysts at temperatures from 180 to 300°C. There is an initial rapid rate of adsorption, which increases with increasing temperature, followed by a slower adsorption reaching equilibrium after about 25 minutes. At constant pressure the volume of oxygen finally adsorbed is larger at lower temperatures, indicating that a state of equilibrium exists between the adsorbate and the gas phase.

Surface area determinations show that each silver atom of the surface is associated with approximately one oxygen adatom for a monolayer coverage. Abrupt changes in the adsorption-time curves occur at approximately half coverage of the catalyst surface. This suggests that the surface is rapidly covered by oxygen so that each oxygen atom is associated with two silver atoms. Slow rearrangement of adatoms may then occur to permit further adsorption until one oxygen atom is associated with each silver atom.

The oxidation of ethylene on a magnesium oxide-chromium oxide on asbestos catalyst produces no ethylene oxide and essentially all carbon dioxide and water. This work, which was carried out by Todes[110, 181], leads to an activation energy for the production of carbon dioxide on this catalyst of 22.4 kcal/mole in the range from 285 to 350°C. This same magnesium oxide-chromium oxide catalyst was active in the oxidation of ethylene oxide to CO_2 and H_2O. When copper oxide was substituted for the magnesium oxide analogous results were obtained.

These authors also compared the results of the oxidation on the magnesium oxide-chromium oxide catalyst with those obtained on a silver catalyst. They found that on the silver catalyst the oxidation of ethylene to ethylene oxide is faster than the oxidation of ethylene oxide to carbon dioxide. The converse is true on the magnesium oxide-chromium oxide catalyst. Consequently, on a silver catalyst, the formation of ethylene oxide through oxidation of ethylene will outstrip the consumption of ethylene oxide as long as enough ethylene is present. Oxidation of ethylene oxide will gradually catch up with its formation as the consumption of ethylene progresses and the amount of ethylene oxide in the product will pass through a maximum. This conclusion of Todes is in agreement with the mechanism proposed above by Twigg. However, Todes' conclusion that all of the CO_2 is produced by the secondary oxidation of ethylene oxide is not in agreement with the conclusions of most of the other workers in the field. The fact that ethylene oxide does appear on the oxidation of ethylene on silver but does not on magnesium oxide-chromium oxide, is due in the latter case simply to the more rapid oxidation of ethylene oxide, as compared with the velocity of oxidation of ethylene, on the chromium oxide catalyst. The rapid oxidation of ethylene oxide on this catalyst thus destroys the intermediate product and it is not detected.

Bolme[17] studied the oxidation of ethylene at 200 and 220°C in a differential reactor using a catalyst of silver on silicon carbide. The most striking observation in this work was that the rate of ethylene oxidation was markedly inhibited by the addition of CO_2 to the reaction stream. The rates, to both ethylene oxide and CO_2, varied approximately linearly with the oxygen concentration. While the rate increased with increasing ethylene concentration at low partial pressures it was found to be essentially constant at ethylene concentrations above about 5 mole per cent.

In contrast to the conclusion of Twigg[184, 185] and others, these data indicate that the rate-controlling step is the reaction of chemisorbed ethylene with either gaseous or weakly adsorbed oxygen. As mentioned above, Kurilenko *et al.*[97] also report that the rate of ethylene oxidation on a silver catalyst is inhibited by CO_2 but in contrast to Bolme[17] find the rate to vary directly with the ethylene concentration.

Margolis and Roginskii[116] have studied the oxidation of mixtures of ethylene with ethylene oxide, acetaldehyde and formaldehyde over a silver catalyst. The ethylene was tagged with C^{14} and, by measuring the C^{14} content of the products, conclusions could be drawn regarding the nature of the intermediates in the reaction. It was concluded that in the oxidation of a mixture of ethylene and ethylene oxide at 220°C, about 80 per cent of the CO_2 comes directly from ethylene, bypassing ethylene oxide, and that only about 20 per cent is formed via ethylene oxide. By studying the oxidation of mixtures of ethylene with formaldehyde and acetaldehyde, it was concluded that the presence of the aldehydes increases the rate of formation of ethylene oxide slightly but decreases the rate of CO_2 formation. Consequently, it is concluded that these aldehydes cannot be the chief intermediate products in the formation of CO_2 either from ethylene, bypassing ethylene oxide, or from ethylene oxide itself. Similar studies were also made using a V_2O_5 catalyst at 350°C[115].

Schultze and Thiele[166] have carried out studies on the oxidation of ethylene over a silver catalyst. They state that the oxidation of ethylene is inhibited by its oxidation products, primarily water. Their paper also suggests that the surface temperature of the catalyst is a determining factor in the oxidation, and not the temperature of the gas stream. The possibility of a difference between these two temperatures is one which has concerned almost every investigator in the catalytic oxidation field. Schultze was interested in confirming the postulate of Twigg's that adsorbed atomic oxygen is a rate-determining factor. Schultze attempted to cover the silver surface with atomic oxygen by using nitrous oxide (N_2O) as a source of oxygen. In this case his results were inconclusive. He then attempted to produce atomic oxygen on the surface, by first passing oxygen over the catalyst, then nitrogen, followed by nitrogen and ethylene, and finally again by nitrogen. In this way he hoped to react the mixture of ethylene and nitrogen with the atomic oxygen formed on the surface. However, he did not find any preferential indication of reaction of the ethylene with the adsorbed atomic oxygen on the silver surface. Schultze explained this by concluding that the adsorbed oxygen was taken up by the silver surface, partly physically and partly as chemically adsorbed atomic oxygen. He concluded that the primary product in the oxidation of both ethylene and ethylene oxide may, therefore, be a peroxidic complex $C_2H_4O_2$.

A survey of the literature indicates that many methods of preparing catalysts for oxidation of ethylene to ethylene oxide have been tested. Likewise, almost countless promoters, inhibitors and catalyst supports have been tested and many specific examples of the effects of these variations on yields or conversions are quoted. Essentially all of the successful catalysts referred to contain silver as the main active component, and include mixtures of these alloys with other metals or metal oxides as promoters. The catalysts have been used in the form of finely divided metallic powders, thin sheets of metal, various dispersions of metals on multitudinous supports of all kinds of porosity and crystal structure. Of metals which have been mentioned as excellent promotors are gold, copper, iron and manganese. Additional metals that have been tried include antimony, barium, beryllium, cadmium, calcium, cerium, cobalt, lithium, magnesium, nickel, palladium, platinum, sodium, strontium, thorium, tin and zinc. Alpha-alumina has been found to be the best support for the silver catalyst although many others have been reported. There is some indication that different kinds of alumina may show different degrees of activity when coated with silver. It is also notable that barium oxide is often quoted as being an excellent promoter for silver. Mention has already been made of the effect of addition of chlorinated hydrocarbons to the ethylene-air mixture in promoting the activity of silver catalysts. The effect of these halogenated compounds is quite important and striking. The results of these many investigations of the industrial aspects of ethylene oxidation lead to certain proposals for future study of the fundamentals of this catalytic oxidation.

It should be relatively easy to correlate the electrical properties of silver catalysts with their catalytic behavior. Undoubtedly one may prepare a surface coated with a silver film as a satisfactory catalyst to oxidize ethylene to ethylene oxide. Thus a catalyst containing a film of silver is not only easy to prepare for studying electrical conductivity of the catalyst during its operation, but the results obtained may be correlated with much information on silver catalysts that are recorded in the literature. Reference has already been made in this chapter to the effects of electronic properties of the catalyst on catalyst performance. A consideration of the electronic factors which might be of importance in the operation of a silver catalyst during oxidation of ethylene, leads to the following proposed experiments:

1. Thin silver films should be deposited on quartz slides, for example, for measurements of the electrical conductivity of the film in air. Measurements should be made under various partial pressures of oxygen, *and under*

reaction conditions where the silver film would be acting as a catalyst. The conductivity studies would reveal whether there is a net flow of electrons in or out of the metal under catalytic conditions. The direction of the flow of electrons should indicate the charge of the surface-activated complex, which in turn would determine the change in work function of the silver that is required theoretically to increase the catalytic activity.

Lyubanskii[107] has made a start in this direction. Electrical measurements were made during the oxidation of ethylene over silver films ($\sim 10^{-5}$ mm thick) deposited on glass filaments 5 to 7μ in diameter. It was found that adsorption of oxygen on the catalyst causes a transfer of electrons from the catalyst to the adsorbed oxygen resulting in a decreased conductivity. When the oxidation reaction is taking place a dynamic equilibrium exists and the conductivity remains constant and has a relatively high value, close to the value for the films in a reducing atmosphere.

2. Sufficient experimental work on the addition of promoters to silver catalyst has been reported in the published patent literature to enable testing of the theory of how these promoters affect a silver catalyst. It is likely that it may be necessary to perform electrical conductivity measurements as well as catalytic oxidation-conversion experiments on the same film. Additions of gold, iron and copper in small concentrations as promoters have been found to increase the activity, while the addition of potassium hydroxide or calcium hydroxide has been found to reduce the activity to practically zero. Determination of the electrical properties of the silver films containing these impurities would provide crucial information regarding the nature of the catalytic processes taking place during the oxidation of ethylene.

3. Twigg's experiments indicate that the best catalyst probably has to be a compromise in that it should not give a total conversion if optimum yields are to be produced. Twigg's work reveals that by increasing the flow rate of the gaseous reactant stream over the catalyst the total ethylene conversion decreases while the production of carbon dioxide decreases, and the production of ethylene oxide remains essentially constant. These observations may indicate that certain steps in the reaction are controlled by mass transfer phenomena rather than by chemical reaction kinetics. This possibility would bear further investigation. In addition electrical conductivity measurements on silver films while in use for the oxidation of ethylene, using different gas flow rates in the experiments, would be of interest.

4. Very little information is available that provides any indication of the reason for the outstanding effect of compounds like ethylene dichloride on the performance of the catalyst. Here again electrical conductivity measurements carried out on films while operating in the absence and presence of ethylene dichloride would be of critical importance.

The Oxidation of Propylene and Higher Olefines

Although a number of patents have appeared during the last 10 years on the oxidation of propylene to acrolein, we are limited largely to the Russian literature for reports of more fundamental studies of this process. Most of the patents recommend the use of cuprous oxide supported on either silica or silicon carbide as catalysts. The more important features of many of these are summarized in Table 23. Similar patents on the oxidation of higher olefines are listed in Table 24.

Margolis *et al.*[113] have studied the oxidation of propylene over a series of oxide catalysts. MnO_2, NiO, $MgCr_2O_4$ or $CuCr_2O_4$ (all 30 per cent on Al_2O_3) were found to yield essentially only CO_2 and water. Ten per cent V_2O_5 on Al_2O_3 gave some aldehydes (formaldehyde and acetaldehyde) and acids but mainly CO and CO_2. MoO_3, WO_3 and UO_3 on Al_2O_3 gave somewhat poorer yields of aldehydes and acids than did V_2O_5. Of the catalysts tested, only Cu_2O on Al_2O_3 gave a substantial yield of acrolein. The significance of these observations, in the light of the electronic structure of the catalysts, is discussed on p. 349.

Margolis[111, 112, 114] has also studied the kinetics of the oxidation of propylene over V_2O_5 on SiO_2. The rate of formation of aldehydes, CO and CO_2 was found to be first order in oxygen and independent of the propylene concentration. The activation energies for the formation of the various products were found to be 4 to 5 kcal/mole for the aldehydes, 2 kcal/mole for CO and 22 kcal/mole for CO_2. Under similar conditions the decomposition of acetaldehyde was found to be first order with respect to the aldehyde concentration with an activation energy of 7 kcal/mole. The oxidation of acetaldehyde was approximately 0.2 order with an energy of activation of 5 to 6 kcal/mole. In addition, studies were also made of the oxidation of ethylene and propylene over V_2O_4, V_2O_5 or $MgCr_2O_4$ using oxygen containing O^{18}. From the distribution of O^{18} among the products, conclusions were drawn concerning the participation of the oxygen contained in the catalyst, as distinguished from the gas phase oxygen, in the formation of the various reaction products.

Andrianova and Roginskii[3] have also shown that the oxidation of propylene on a silver catalyst proceeds almost to completion with conversion of all three carbon atoms of propylene to carbon dioxide. With a vanadium pentoxide catalyst small amounts of aldehydes and acids were formed, the main products again being CO and CO_2.

Butyagin and Elovich[32, 33] have studied the complete oxidation of propylene to CO_2 at temperatures from 0 to 200°C and pressures of 0.1 to 2 mm Hg using a Pt on $BaSO_4$ catalyst. It is suggested that the first step in the reaction involves the chemisorption of O_2 on the platinum. The propylene then reacts with the chemisorbed oxygen to give a surface compound.

Catalyst	Temp. (°C)	Contact Time (sec)	Mole Ratio $C_3H_6:O_2$	% Propylene Conversion	Acrolein* Yield	Remarks	Ref.
Cu_2O on SiO_2, SiC, or Al_2O_3	250–450	0.1–2.0	4–10		65%	4–8% O_2 by volume, consume 20–80% of O_2.	75
Cu on SiO_2, pumice or SiC	370			14	65		22
Cu + Se on Al_2O_3						Yields improved by presence of Se.	23
CuO on SiO_2 + Se			0.5	40	65	Improved yield in presence of Se.	70
CuO + Al_2O_3 + Se			2% C_3H_6 in air		80	Catalyst more active if precalcined at 850 than at 1000°C.	80
Fe, Co, Ni, Mn, Ce or Cr promoted with Se	200–400				10–20		71
TeO_2 on Al_2O_3	310–340	~6	10% C_3H_6 in air	5			157
CuO					30	More active catalyst if prepared from Cu phthalocyanine than from $Cu(NO_3)_2$.	6
CuO on SiO_2	300	~7	10% propylene in air	49	40		27
Cu_2O on SiC	460	~1	2		50–60	Addition of 0.05 mole % isopropyl chloride improves yield. Uses steam dilution.	76
2.1% Cu_2O on SiC	375	~1	20% C_3H_6 20% air 60% steam	70% of O_2 consumed	70	Pressure = 30 psig.	26
Cu_2O						Regeneration of catalyst by periodic interruption of O_2 flow. Burn off carbon with O_2 + inert gas. Use olefine purified of CO.	51

* Based on propylene converted.

The surface compound may then be oxidized by O_2 from the gas phase to give CO_2 or may escape from the surface to yield partially oxidized intermediates.

It is noted that with a platinum surface which is covered with O_2, the slow process is the oxidation of the intermediate with gas phase O_2. Under these conditions the rate may be zero order with respect to O_2 and temperature independent over the range from 80 to 180°C.

CATALYTIC OXIDATION OF FOUR-CARBON HYDROCARBONS

Introduction

Maleic anhydride is being made on a large scale in industry by the catalytic vapor phase oxidation of benzene. Since maleic anhydride is a material of much industrial importance there have been many attempts to prepare it from raw materials other than benzene. It has always been obvious that it might be made by oxidation of hydrocarbons containing four carbon atoms. Consequently, there is much information in the literature on the catalytic oxidation of such four-carbon hydrocarbons[54, 108]. Unfortunately, however, most of the literature which is devoted to this subject is concerned with the practical phases of the oxidation of such hydrocarbons. The information available does not appear to be of great importance in understanding the catalytic oxidation processes involved. Also, many of the literature references are concerned with studies carried out in such a way that the conversion of the hydrocarbon was relatively high, in most cases 100 per cent, and therefore there is but little information that aids in understanding the kinetics of oxidation processes involved.

Table 24. The Oxidation of Higher Olefines

Catalyst	Reactant	Temp. (°C)	Mole Ratio Olefine: O_2	% Conversion of Olefine	Substituted Acrolein Yield*	Remarks Ref.
CuO + Se	Isobutylene	300–400	0.5	10	70	69
CuO on SiO_2 + Se	Diisobutylene	320	Products contain: 11% α-Methylacrolein 28% Reactant 15% Residue 32.5% C_8 monoolefinic aldehydes			72

* Based on olefine consumed.

An important contribution to the oxidation of four-carbon hydrocarbons has been made by Bretton, Wan and Dodge[20]. In their studies these workers usually carried out their oxidations in such a way that the conversion of the hydrocarbon under study was essentially complete. They obtained little information or understanding of the effect of the nature of the catalyst upon the oxidation processes. In spite of these drawbacks their contribution is important because it outlines quantitative methods of analysis for the products formed, and a review of the information obtained should be of interest in pointing the way toward further developments. This paper also attempts to develop a free radical mechanism to explain the composition of the products of oxidation, and it is believed that these authors may have made a valuable start in formulating mechanisms for catalytic oxidation processes.

During the oxidation of four-carbon hydrocarbons the following materials are obtained: formaldehyde, acetaldehyde, α-methylacrolein, glyoxal, methyl vinyl ketone, maleic anhydride and acetic acid. These will be discussed in the following.

Oxidation over Silver Catalysts

Bretton *et al.*[20] studied the oxidation of four-carbon hydrocarbons over silver catalysts in which the silver or silver oxide was deposited on activated alumina or on Alfrax, essentially fused aluminum oxide. This latter carrier is essentially α-alumina or corundum. With these silver catalysts the four-carbon hydrocarbons gave only CO_2 and water, and no intermediate products of interest.

It will be recalled that in the oxidation of ethylene to ethylene oxide one is able to obtain yields of ethylene oxide of the order of 50 to 60 per cent of theory by careful control and selection of conditions of oxidation. Bretton's work, however, indicates that with the four-carbon hydrocarbons in the presence of silver catalysts, which work so well with ethylene oxidation, one obtains no intermediate oxidation products. Considerable attention was paid to control of conditions so as to attempt to obtain intermediate products in the oxidation of the four-carbon hydrocarbons. In spite of this the amounts of intermediate products were negligible. Since large amounts of ethylene oxide are obtained in the oxidation of ethylene one might conclude that the intermediate products from the four-carbon hydrocarbons are quite unstable as compared with ethylene oxide which is formed in the ethylene oxidation. It is noted elsewhere in this chapter that acetaldehyde is an intermediate in the oxidation of ethylene and that its stability on a silver catalyst such as used by Bretton is quite low, that is, it is rapidly transformed into CO_2. It will also be recalled that in the oxidation of ethylene the chief product, ethylene oxide, is rapidly isomerized to acetaldehyde. This isomerization is responsible for loss of yield since the aldehyde is rapidly converted to CO_2. It is not certain that one might obtain much information of value as regards mechanism by further study of the four-carbon hydrocarbons on silver catalysts. However, it might be possible to learn something about catalyst behavior by seeking catalyst inhibitors or impurities which would slow down the decomposition or transformation of the intermediate products.

Oxidation over Vanadium Pentoxide Catalysts

Most of the work of Bretton was carried out on a vanadium pentoxide catalyst which was supported on a fused alumina carrier (corundum). These investigators studied the oxidation of butene-2, butene-1, butane, isobutylene and butadiene. In general the oxidation experiments were carried out over a range of contact times from 0.1 up to 2 sec. The air: hydrocarbon ratio (volume basis) was varied from around 30 up to around 90. Temperatures were of the order of 300 to 500°C. The hydrocarbon fed to the converter was often not completely converted. Yields of the principal products identified were determined in a quantitative manner. In the oxidation of hydrocarbons, carbon monoxide, hydrogen, acetaldehyde and formaldehyde were important products; hence the catalytic oxidation of these materials was also studied.

TABLE 25. OXIDATION OF FOUR-CARBON HYDROCARBONS-V_2O_5 ON α-ALUMINA; WORK OF BRETTON, WAN AND DODGE[20]

Substance Oxidized	Products Formed
Isobutylene	40–80% $CO + CO_2$, 5% HCHO, 10–30% acetic acid, α-methylacrolein
2-Butene	CO, CO_2, HCHO, acetic acid, maleic acid, acetaldehyde
1-Butene	CO, CO_2, HCHO, acetic acid, maleic acid, acetaldehyde, methyl vinyl ketone
Butadiene	CO, CO_2, HCHO, maleic acid
n-Butane	CO, CO_2, HCHO, maleic acid, acetic acid, acetaldehyde
Acetaldehyde	80% CO, 7% CO_2, 5% HCHO, 8% acetic acid
HCHO	CO (no CO_2), trace HCOOH
CO and H_2	No reaction.

The products formed during the oxidation of the four-carbon hydrocarbon over the vanadium pentoxide catalyst are summarized in Table 25. The products from oxidation of acetaldehyde, formaldehyde, CO and hydrogen are also shown in this table. It is significant that CO and hydrogen were not oxidized over this catalyst, whereas the two aldehydes gave mostly CO and relatively little CO_2. It is necessary to emphasize that even though CO and hydrogen failed to oxidize on this catalyst this does not necessarily mean that when these materials were formed during the hydrocarbon oxidation and thus produced in an activated state on the catalyst that they did not oxidize during the hydrocarbon oxidation process. Carbon monoxide, for example, produced in an activated state in the hydrocarbon oxidation might be susceptible to oxidation to CO_2 before it could leave the surface.

In the case where the attempt was made to oxidize CO alone it might never have been adsorbed in an activated state and thus it may be incorrect to conclude that it does not oxidize on the catalyst. Conversely, we are inclined to believe that the CO_2 produced during the oxidation of hydrocarbons might be formed by the oxidation of an activated CO molecule.

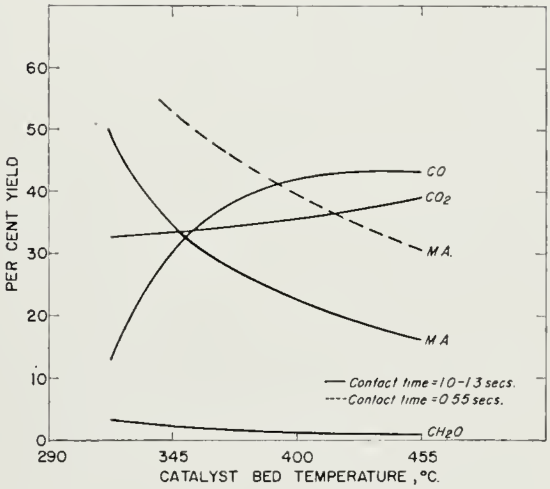


Figure 6. The effect of temperature on the oxidation of butadiene.[20] (Reprinted courtesy of *Industrial & Engineering Chemistry*.)

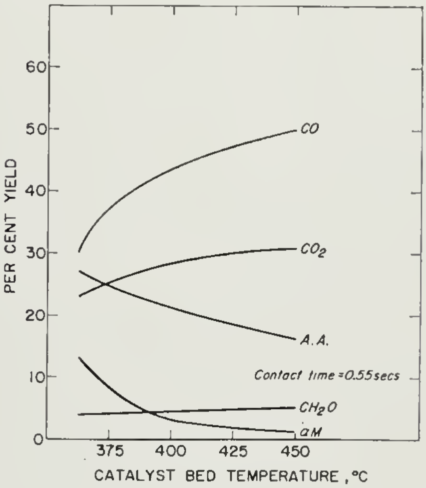


Figure 7. The effect of temperature on the oxidation of isobutylene.[20] (Reprinted courtesy of *Industrial & Engineering Chemistry*.)

It is of interest to present in Figures 6 and 7 some of the results of Bretton *et al.* on the oxidation of butadiene and isobutylene in order to indicate how the yields of the different products were influenced by the catalyst temperature. There are other important diagrams given by Bretton to illustrate the effects of other variables, for example, hydrocarbon-air (volume) ratio, on yields of products during the oxidation of these hydrocarbons. Reference to the paper of Bretton *et al.* indicates that in a fairly large number of cases the percentage yield of a product did not change greatly with temperature. This is illustrated in the case of formaldehyde and carbon dioxide during oxidation of butadiene as shown in Figure 6. Also, in Figure 7 for the oxidation of isobutylene the yields of formaldehyde, acetic acid, and CO_2 do not change materially with catalyst temperature.

It was also found that on changing the air-hydrocarbon ratio in some of the oxidations the amounts of products did not change materially. The amount of formaldehyde formed in this work was usually less than 10 per cent. It is likely that any formaldehyde formed as an intermediate on the catalyst surface was instantly converted to carbon monoxide, and it is suggested that the amounts observed resulted from inability of the formaldehyde formed in the gas phase to diffuse to the surface fast enough in order to obtain complete oxidation in all cases. That is, mass-transfer rates rather than reaction rates may be limiting. One wonders also in some of the other instances where the yields were less than 10 to 20 per cent whether the products observed were the result of processes limited by diffusion rather than true chemical reaction. For example, why should acetaldehyde which breaks down on the catalyst very rapidly remain nearly constant over a threefold change in air-hydrocarbon ratio or over a considerable range of temperature during the oxidation of the two butenes? For these hydrocarbons the yields of acetic acid, CO_2, maleic acid, acetaldehyde and formaldehyde were nearly constant as the air-hydrocarbon ratio changed over a threefold ratio. Could we be observing in this case a problem in mass transfer rather than surface reaction?

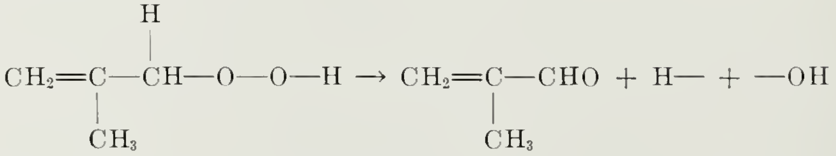
As the temperature was changed during oxidation of these four-carbon hydrocarbons, the amount of unconverted hydrocarbon decreased. When the amount of unconverted material was accounted for the products of reaction did not vary appreciably over some 100 to 200°C change in temperature. The notable exception to this qualitative statement is the increase of carbon monoxide and in a few instances of carbon dioxide with increase in temperature. If one could conclude that mass transfer effects are not involved in these oxidations, then the constancy of the yield of the products during variation of temperature, contact time and hydrocarbon-air volume ratio would indicate that the kinetics of oxidation to produce these different products are the same. It would appear worthwhile to make further studies of these reactions utilizing the splendid analytical procedures and information given by Bretton *et al.* especially *at low conversions* in order to obtain valuable information on catalytic oxidation processes. Bretton has proposed certain mechanisms for these oxidations which are presented below. It appears that additional studies would be important in attempting to substantiate these mechanisms.

Mechanism of Oxidation of Four-Carbon Hydrocarbons

Bretton, Wan and Dodge[20] have suggested mechanisms for the catalytic oxidation of four-carbon hydrocarbons, which are similar to those currently accepted as correct for liquid phase homogeneous oxidation of certain hydrocarbons. These reaction schemes for the liquid phase were suggested by Waters and others[62, 63, 196-198] and have been adapted by Bretton to explain the vapor phase catalytic oxidation over vanadium pentoxide catalysts. In explanation of the oxidation at a surface, Bretton *et al.* assume that the catalyst abstracts hydrogen from the hydrocarbon, possibly by reaction with oxygen at or on the surface. Once the initial hydrogen atom is removed from the hydrocarbon it is assumed that the reactions which will be described below do take place. It is obvious that many of the assumptions made need verification, and actually it is easy to think up experiments which might test the reaction mechanisms proposed. But in any case, it appears worthwhile and desirable to describe the kinetic mechanisms summarized by Bretton *et al.* It appears best to quote from their paper in order to indicate the nature of their proposals on mechanisms:

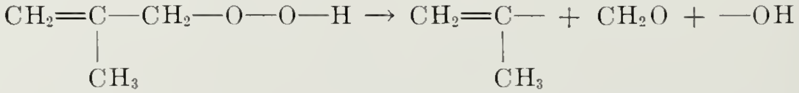
> The products found in the vapor phase oxidation of the four-carbon hydrocarbons over a vanadium pentoxide catalyst can for the most part be explained by a scheme of atomic dehydrogenation and peroxidation similar to that suggested by Waters[198], and by peroxide decomposition. The first step in this scheme would be the removal of a hydrogen atom from the hydrocarbon forming a free radical which then could react with a molecule of oxygen to form a peroxide radical. This last product could then become a peroxide by gaining a hydrogen atom. In the scheme proposed by Waters the peroxide radical abstracts a hydrogen atom from another hydrocarbon molecule and the reaction proceeds in a chain fashion. In the present system of heterogeneous catalysis, the vanadium pentoxide catalyst evidently plays an important role, the nature of which is not disclosed by the results of this investigation. To explain the results which have been reported it is suggested that the catalyst be considered as a hydrogen atom abstractor and donator. This role of the catalyst is then represented by the reaction
>
> $$\mathrm{RH} + \mathrm{X} \rightarrow \mathrm{HX} + \mathrm{R}\text{—} \tag{1}$$
>
> $$\mathrm{R}\text{—} + \mathrm{O_2} \rightarrow \mathrm{R{—}O{—}O}\text{—} \tag{2}$$
>
> $$\mathrm{R{—}O{—}O}\text{—} + \mathrm{HX} \rightarrow \mathrm{ROOH} + \mathrm{X} \tag{3}$$
>
> where X represents the catalyst.
>
> The mode of decomposition of the peroxides of saturated hydrocarbons has been discussed by Walsh[196], and George and Walsh[63]. The little information available on the decomposition of peroxides of unsaturated hydrocarbons has been summarized by Farmer[62]. Evidence indicates that decomposition of peroxides occurs by scission at the O—O bond followed by scission of an adjacent C—H bond or of the weakest adjacent C—C bond.

The presence of α-methylacrolein and methyl vinyl ketone in the products of oxidation of isobutylene and 1-butene, respectively, indicate that the initial point of oxidative attack on the mono-olefins may be at the α-methyl or methylenic carbon atom. With this initial point of attack, an attempt will now be made to explain the results obtained in the oxidation of isobutylene. The first step would involve the formation of the hydroperoxide by Equations 1, 2, and 3, the peroxide group being attached to one of the α-carbon atoms. The second step would involve the decomposition of this peroxide. Scission of the O—O bond and adjacent C—H bond could lead to α-methylacrolein.



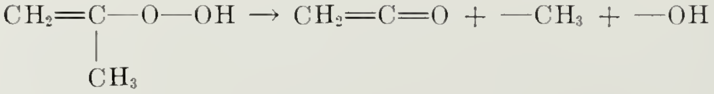
$$\mathrm{CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}\overset{\substack{H\\|}}{C}H{-}O{-}O{-}H \rightarrow CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}CHO + H{-} + {-}OH} \qquad (4)$$

If scission at the adjacent C—C bond rather than at the C—H occurs, formaldehyde and another radical could result.



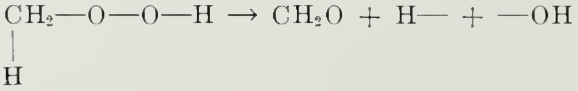
$$\mathrm{CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}CH_2{-}O{-}O{-}H \rightarrow CH_2{=}\underset{\substack{|\\CH_3}}{C}{-} + CH_2O + {-}OH} \qquad (5)$$

This new radical would then by Equations 2 and 3 be converted to a peroxide which could decompose.



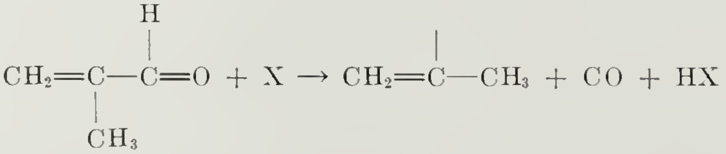
$$\mathrm{CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}O{-}OH \rightarrow CH_2{=}C{=}O + {-}CH_3 + {-}OH} \qquad (6)$$

Any ketene formed by Equation 6 would be hydrated to acetic acid in the final product. Formaldehyde could also be produced by peroxidation of the methyl radical and subsequent decomposition of the peroxide.



$$\mathrm{\underset{\substack{|\\H}}{C}H_2{-}O{-}O{-}H \rightarrow CH_2O + H{-} + {-}OH} \qquad (7)$$

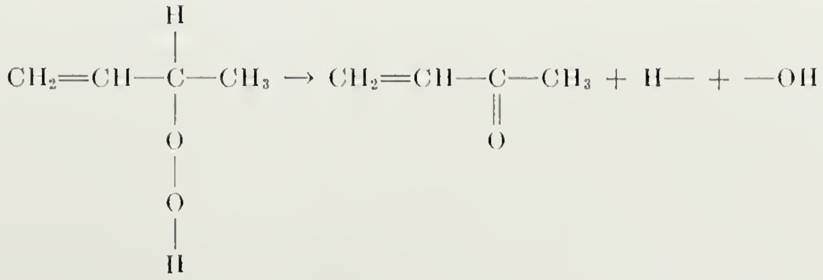
The results of the work with acetaldehyde and formaldehyde indicate that aldehyde oxidation results in the formation of large amounts of carbon monoxide. This reaction for α-methylacrolein could be represented by



$$\mathrm{CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}\overset{\substack{H\\|}}{C}{=}O + X \rightarrow CH_2{=}\overset{|}{C}{-}CH_3 + CO + HX} \qquad (8)$$

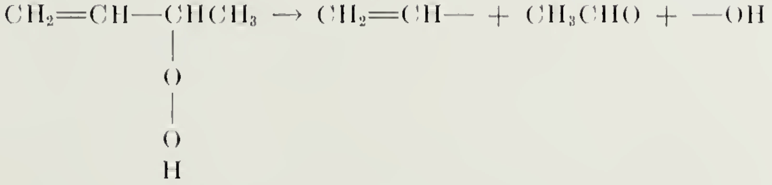
Oxidation of the radical would then proceed by reactions given above. This scheme would account for the products of oxidation of isobutylene.

In a reaction similar to Equation 4 methyl vinyl ketone could be formed from the peroxide resulting from the oxidation of 1-butene.



$$\mathrm{CH_2{=}CH{-}\overset{\displaystyle H\atop |}{\underset{|\atop {O\atop {|\atop {O\atop {|\atop H}}}}}{C}}{-}CH_3 \rightarrow CH_2{=}CH{-}\underset{\|\atop O}{C}{-}CH_3 + H{-} + {-}OH} \qquad (9)$$

Another mode of decomposition would be



$$\mathrm{CH_2{=}CH{-}\underset{|\atop {O\atop {|\atop {O\atop H}}}}{C}HCH_3 \rightarrow CH_2{=}CH{-} + CH_3CHO + {-}OH} \qquad (10)$$

This would account for the acetaldehyde found.

The mechanisms proposed by Bretton *et al.*[20] do not seem adequate to describe the method by which carbon dioxide is formed during oxidation. They also avoid any attempts to provide an exact mechanism for the formation of maleic acid or maleic anhydride. However, it is known that an explanation of the formation of maleic anhydride in the vapor phase is also difficult, as has been made evident by a recent paper of Norrish and Taylor[135] in which they describe their work on the oxidation of benzene.

The mechanism proposed by Bretton *et al.* seems to be in accord with our own ideas that the catalyst removes the hydrogen from the hydrocarbon to form a radical which combines with oxygen striking it from the gas phase. Decomposition of the resulting peroxy-radicals would then lead to other radicals which in turn might combine with oxygen from the gas phase. The mechanisms of Bretton *et al.* do not provide any requirement for reaction of radicals or molecules on the surface. This is in accord with our own ideas on the subject.

Effect of Hydrocarbon Structure on Catalytic Oxidations

Reference has been made elsewhere in this chapter to the effect of hydrocarbon structure on catalytic oxidation, especially in connection with the oxidation of aromatic hydrocarbons to form phthalic anhydride. Also, some reference has been made to the different products which are obtained upon oxidation of C_4 hydrocarbons. Certain aspects of the effect of structure on oxidation seem worthy of review in more detail at this point. In some instances the information used as a source was obtained from the literature[20, 170], and in others from work carried out in the authors' laboratories[2].

We are inclined to emphasize the latter since these results were obtained under comparable conditions; this, for the present discussion, is most important.

Table 26 presents the effect of hydrocarbon structure on yields of phthalic and maleic anhydrides during oxidations on a vanadium pentoxide catalyst.

TABLE 26. EFFECT OF HYDROCARBON STRUCTURE ON OXIDATION[2]

Molybdenum-Aluminum-Vanadium Oxide Catalyst; 450–500°C.
Contact Time = 1–2 sec.
1% By volume hydrocarbon in air.

Hydrocarbon	Yields Under Optimum Conditions, % of Theoretical Maleic Anhydride	 Phthalic Anhydride
Naphthalene 100%	10	70
Tetrahydronaphthalene	10	70
Decahydronaphthalene (100% *trans*-)	14	62
Decahydronaphthalene (*cis-trans*)	14	62
Methylnaphthalene (97%)	20	49
ortho-Xylene (100%)	16	49
meta-Xylene (99%)	54	—
para-Xylene (95%)	29	—
Benzene	56	—
Methylcyclopentane	31	
Furfural	26	

TABLE 27. MALEIC ANHYDRIDE YIELDS FROM DIFFERENT HYDROCARBONS

Vanadium Catalyst; 300–400°C; Optimum Yields
1–1.5% Hydrocarbon in Air; 0.3-sec Contact Time.

Hydrocarbon	Yield of Maleic Acid in % of Theory Ref. (2)*	 Ref. (20)†
Butadiene	45	50
Butene-2	16	20
Butene-1	22	12
Isobutylene	3	small
Tetrahydrofurane	32	
Butane	small	small
Benzene	47	

* 1 to 1.5% Hydrocarbon in air at 0.3 sec contact time. Vanadium on silicon carbide catalyst. Ref. 2.
† Vanadium on Alfrax alumina catalyst. Varying conditions about as in *.

Table 27 presents information on the effect of the structure of a C_4 hydrocarbon on product yields of maleic acid. These results are also compared with corresponding data for 5 and 6-membered ring compounds; namely, tetrahydrofurane and benzene. The results shown in these tables were obtained in oxidations carried out essentially to completion. The interpretation or conclusions drawn from these results are, therefore, open to the same criticism as any others where conversion is high. It is apparent that these experiments might well be repeated with low conversions. In the case of benzene it is known (p. 186) that at low conversions yields in per cent of theory of maleic anhydride based on the benzene converted are nearly independent of the degree of conversion. Although this might also be the case for the other hydrocarbons, it remains to be proved.

It is interesting that in the oxidation of naphthalene, tetrahydronaphthalene and decahydronaphthalene, the yields of phthalic and maleic anhydrides are essentially independent of the hydrocarbon structure. It is quite true that in the case of decahydronaphthalene the yield is somewhat lower, but in view of the considerably greater number of hydrogen atoms that have to be removed in decahydronaphthalene as compared with naphthalene, the slightly lower yield does not seem to be too important.

Furthermore, in the case of decahydronaphthalene the heat liberated during oxidation is more critical, and a closer control of this variable during oxidation might actually prove that the yields for decahydronaphthalene are nearly the same as those for tetrahydronaphthalene and naphthalene. It is probable that tetrahydronaphthalene and decahydronaphthalene may dehydrogenate before oxidation of the ring takes place.

In the case of oxidation of *ortho*-xylene there are 6 hydrogens on the methyl groups and 4 ring hydrogens which are available for attack during oxidation. If all these hydrogens are equivalent as regards reactivity in oxidation, one would expect that the amount of products from oxidation of the methyl groups would be 50 per cent greater than from oxidation of the ring compound. Since oxidation of methyl groups would be expected to lead to phthalic anhydride, and attack of ring hydrogens to the formation of maleic anhydride, the amount of phthalic anhydride would be expected to be 50 per cent greater than the yield of maleic anhydride. Actually the yield of phthalic anhydride is considerably more than this, thus suggesting that the hydrogen atoms on the methyl groups are much more susceptible to attack than those on the ring.

During the oxidation of methylnaphthalene one would expect to form both maleic and phthalic anhydrides by oxidation of the ring containing the methyl group. Also there is the possibility that methyl phthalic anhydride would form by oxidation of the ring containing no methyl group. So far as we know, there have been no reports in the literature on careful studies of the products of this reaction in order to determine the extent of formation of methyl phthalic anhydride. However, it is our belief that this substituted phthalic anhydride does not form to any considerable extent. It is probable, therefore, that as in the case of *ortho*-xylene, the hydrogen atoms on the methyl group on methyl naphthalene are quite reactive, and as soon as they are attacked, phthalic anhydride, maleic anhydride and/or CO_2 form by subsequent rapid reactions. One might also conclude that the attack of the methyl group does not lead to formation of phthalic anhydride but only to formation of maleic anhydride and CO_2. This assumption would explain the low yields of phthalic anhydride which are observed during oxidation of this substituted naphthalene.

In the oxidation of *ortho*-xylene, a small fraction of the "maleic anhydride" is citraconic acid[2], that is, methyl maleic acid. Here we are observing a stability to some extent of the methyl group as compared with the ring hydrogens. In the oxidation of *meta*- and *para*-xylene, existence of citraconic acid in the maleic acid is not known to the authors, and some study should be directed toward direct detection of this impurity, especially at low conversions. In oxidizing *meta*-xylene, for example, maleic anhydride cannot be formed except in such a way that the methyl groups are present in the final product provided the methyl group is not oxidized off. Since evidence is lacking on this point it would be very important to know whether *meta*- and *para*-xylenes form citraconic acid to any extent during the oxidation of these hydrocarbons.

Bhattacharyya *et al.*[15] have studied the oxidation of the three isomeric xylenes over a series of promoted and unpromoted vanadium oxide catalysts. Phthalic and maleic anhydrides were the principal products from the oxidation of *o*-xylene, as observed by other workers (p. 260). Only traces of terephthalic and *p*-toluic acids were produced in the oxidation of *p*-xylene. Conversions to maleic anhydride up to about 30 per cent were observed with attendant conversions to *p*-tolualdehyde as high as 10 per cent. With *m*-xylene, only maleic anhydride and *m*-tolualdehyde were observed in substantial quantities. It is possible, that in all of these products, a portion of the material reported as maleic anhydride may, in fact, have been citraconic acid.

There is one matter to note in connection with the aromatic hydrocarbons; namely, in the case of naphthalene, tetrahydronaphthalene, decahydronaphthalene, methylnaphthalene and the xylenes, once oxidation begins one does not have to go to a much higher temperature before the reaction accelerates rapidly and, due to the exotherm, the reaction is nearly complete over a short temperature range. In the case of benzene, however, one can control the extent of oxidation readily. The conversion of benzene does not complete itself until one reaches temperatures considerably higher than where initial oxidation begins. This indicates that benzene is a much more "stable" material to oxidation than the other hydrocarbons, and this can be attributed to the difficulty in extracting hydrogen from benzene as compared with hydrogens on the other aromatic compounds cited.

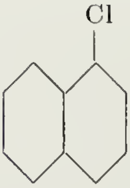
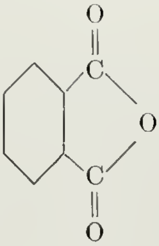
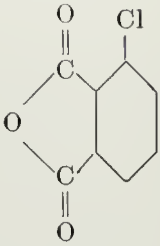
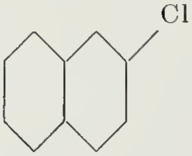
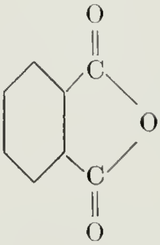
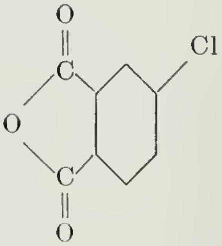
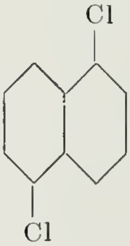
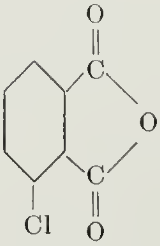
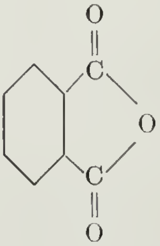
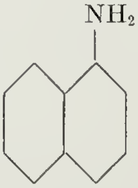
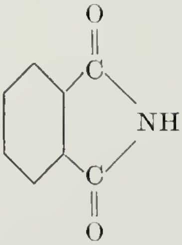
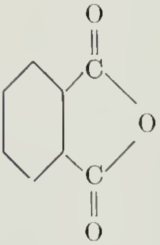
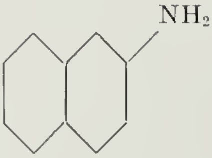
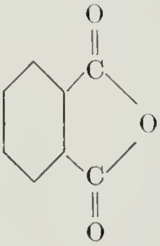
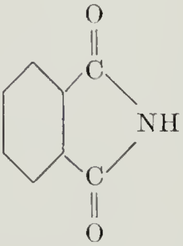
A study of the oxidation of the three isomeric xylenes would be particularly interesting in explaining the mechanism of catalytic oxidation. When these compounds oxidize it is only possible to obtain phthalic anhydride from the *ortho*-isomer. By tagging the side chain and ring carbon atom it should be possible to determine which carbon atoms are concerned in the formation of maleic anhydride. These isomers should be tagged, oxidized and the products analyzed chemically and by tagging methods to determine which carbons are responsible for maleic formation. This would, of course, indicate where the most probable points of attack are on these three isomers, and as a result of considerations of structural organic chemistry one would expect to obtain important information regarding the initial and subsequent steps involved in the catalytic oxidations. This is the type of tagging work carried out by Pines on the isomerization of hydrocarbons[147].

If the oxidation of naphthalene to phthalic anhydride should involve the transfer of electrons to and from the catalyst it should be possible to learn a great deal concerning the initial step in the oxidation by studying the oxidation of naphthalene with substituents in the ring. Thus, if the substituents in the ring were of different electronegativities then one might determine from the oxidation results how the electronic structure of the naphthalene ring influences the oxidation, possibly by the ease of transfer of electrons from the ring to the surface. A paper by Pongratz[148] dealing with this matter has appeared. This paper describes in a semiquantitative manner the nature of the products obtained during oxidation of α and β-chloronaphthalene, 1,5-dichloronaphthalene, α and β-nitronaphthalenes, α-naphthylamine, β-naphthylamine, α and β-cyanonaphthalene, and α and β-hydroxynaphthalene. In this work the amounts of different kinds of phthalic anhydride formed during oxidation of these compounds were determined in a quantitative manner. There is question as to whether the analytical procedures used to determine the products quantitatively were satisfactory. For this reason only a few of the results which were reported are presented in Table 28, but they will serve to indicate in a semiquantitative manner the nature and amounts of products formed.

Table 28 shows the effect of a chlorine substituent on the naphthalene ring oxidation. When the substituent is in the β-position, the ring containing this substituent appears to be more stable than when it is in the α-position. The same is true when the substituent is an NH_2 group. This result is a little surprising since the chlorine and amino groups have different electronegativities and one might expect them to have opposite effects on the oxidation. Thus, if the chlorine group makes the ring unstable one would expect the amino group to make it more stable whereas actually the reverse is the case. It is also surprising to note that chlorine atoms are removed during the oxidation of the dichloronaphthalene. This interesting paper of Pongratz suggests that further work should be done of a similar nature, improving the identification and quantitative determination of the nature of the reaction products.

Table 28. Effect of Chemical Structure on Oxidation Products

TiO_2-V_2O_5 catalyst; 350°C (approximate)

Compound Oxidized	Composition and Percentage of Solid Product			
	97			3
	53			47
	80			20
	90			10
	62			38

INITIATING TEMPERATURE FOR CATALYTIC OXIDATION OF HYDROCARBONS

Discussions are presented elsewhere in this chapter on the few facts that are known on the structure of oxidation catalysts. These discussions describe how the electronic structure of the surface and of the reacting materials influence the course of oxidation. In the case of *ortho*-xylene, for example, it is suggested that there is a transfer of an electron from the hydrocarbon to the solid surface and simultaneously a transfer of an electron from the catalyst to adsorbed oxygen. This suggests that in order to determine the effect of chemical structure on catalytic oxidation it would be of interest to compare the behavior of a series of hydrocarbons at a catalytic surface as regards the temperature at which oxidation begins. This might shed some light on the question as to how the electronic structure of the hydrocarbon affects the reaction on a given catalyst.

Unpublished data[2] were obtained on the initial temperature of oxidation of butadiene, butane, two butenes and benzene using a typical vanadium oxide catalyst under the usual conditions of oxidation in a fixed-bed catalyst system. By referring to the sections on the oxidation of these particular hydrocarbons, further typical experimental details for such systems are outlined.

By measuring the concentration of CO_2 in the exit gases by infrared absorption and by determination of changes in concentration of the reacting hydrocarbon by ultraviolet absorption it was possible in the case of benzene to detect as little as 4 per cent reaction. For butene-2 the limit of detection for reaction was of the order of 2 to 5 per cent. By simultaneous measurement of temperature in the catalyst bed and conversion, it was found that a measurement of temperature rise was capable of detecting the initial temperature for oxidation in the above cases to within ±5°C, thus making it feasible to measure an extent of reaction of 2 to 5 per cent by means of the oxidation exotherm. With slowly rising temperature it is likely that the catalytic surface was mostly V_2O_5, but there is no guarantee that the surface did not contain enough deficiencies of oxygen atoms to provide lattice defects that might have been required for catalysis.

The results of experiments are reported in Table 29. It will be observed that on a given catalyst the oxidation of butadiene, butene-2, and butene-1 all commenced at about the same temperature. There were some small differences in temperature noted which are not considered significant since the reproducibility of the experiments was only ±5°C. It will also be noted that benzene did not start oxidizing until the temperature was some 35 to 75° higher than for the butenes. Likewise, butane was exceedingly stable and proved to be very difficult to oxidize. It will be observed further that the addition of molybdenum oxide to a silver oxide-vanadium oxide catalyst raised the temperature required for initial oxidation of any hydrocarbon. The addition of Al_2O_3 to the three-component catalyst had little effect on initiating temperature.

TABLE 29. EFFECT OF HYDROCARBON STRUCTURE ON INITIAL OXIDATION TEMPERATURE

Hydrocarbon	Catalyst	Estimated Initial Oxidation Temp. (°C)
Butadiene	Ag_2O-V_2O_5	315
“	Ag_2O-MoO_3-V_2O_5	~370
“	Ag_2O-MoO_3-Al_2O_3-V_2O_5	355
Butane	Ag_2O-MoO_3-V_2O_5	~475–500
Butene-1	Ag_2O-V_2O_5	315
Butene-2	Ag_2O-V_2O_5	315
“	Ag_2O-MoO_3-V_2O_5	365
“	Ag_2O-MoO_3-Al_2O_3-V_2O_5	365
Benzene	Ag_2O-V_2O_5	400
	Ag_2O-MoO_3-Al_2O_3-V_2O_5	400

TABLE 30. TEMPERATURE FOR INITIATION OF OXIDATION OF CERTAIN HYDROCARBONS

Hydrocarbon	Catalyst	Initiation Temp. for Oxidation (°C)	Principal Product	Ref.
Toluene	V_2O_5	280°	øCOOH	Marek and Hahn[108] Maxted[122]
“	MoO_3	450°	øCHO	
“	Sn-V_2O_5	290°	øCOOH	
Butenes	Ag_2O-V_2O_5	315–360	MAA	Cyanamid[2]
Butane	Ag_2O-V_2O_5	475	CO_2	
Butadiene	“	315–350	MAA	
Benzene	“	400	MAA	
Naphthalene	“	375	PAA	
Tetrahydronaphthalene	“	375	PAA	
Decahydronaphthalene	“	375	PAA	
Methyl naphthalene	“	400	PAA	
Xylenes	“	400	PAA	
Butenes	Ag_2O	150–200	CO_2	Bretton, Wan, Dodge[20]
Ethylene	“	200–300	C_2H_4O	

One may compare the results in Table 29 with those of other authors in Table 30. Here the initiating temperatures and main products are listed for a series of hydrocarbons on MoO_3, V_2O_5 and Ag_2O catalysts. It is evident that the aromatic and hydroaromatic rings require temperatures around 400°C for oxidation to begin. However, unsaturated hydrocarbons start at a lower temperature, 300 to 375°C. Toluene appears to act like an unsaturated hydrocarbon (280°C) and *ortho*-xylene like an aromatic compound. Butane is very stable (475°C). Although the results in Table 29 are strictly comparable, those in Table 30 are from different sources and need repetition.

In the case of the oxidation of xylene it is pointed out elsewhere in this chapter that the transfer of an electron from the xylene to the catalyst surface or to the catalyst lattice takes place[12]. If we make the assumption that the oxidation of the C_4 hydrocarbons proceeds by a similar mechanism then we have to account for the fact that at the same temperature butane and benzene will not oxidize whereas the butenes do oxidize. It is presumed that the activation of oxygen would be the same for all systems. This suggests that a transfer of electrons from the more easily oxidized materials takes place more readily, therefore, oxidation initiates at a lower temperature. Furthermore, we see that the lattice or surface of vanadium oxide may be modified by addition of molybdenum so that the electron transfer from the hydrocarbon to the surface is hindered. One further comment is in order, namely: in the oxidation of the butadiene and the butenes it is very difficult to control the oxidation in such a way that conversion is not complete. One usually finds that the reaction is nearly uncontrollable, and without considerable care all of the hydrocarbon is oxidized. In the case of benzene this is not true. It is relatively easy to carry out the oxidation of benzene so that any given degree of conversion to products is obtained. Since the benzene reaction takes place on the same catalyst as that for the butenes, one might conclude that there are some factors involved in the electronic structure of the benzene which are considerably different than those for the C_4 hydrocarbons.

In the oxidation of naphthalene, benzene and other aromatic compounds it is difficult to determine much effect of catalyst composition on yields, especially since most work on this matter has been carried out at fairly high conversions. Thus, addition of for example 10 per cent MoO_3 to V_2O_5 has but little effect on yield or conversion of naphthalene to phthalic anhydride. This makes the measurement of yield and/or conversion a poor means of studying differences between catalysts. However, the results in Table 29 suggest that the initiating temperature may be a more sensitive procedure for evaluating differences between catalysts and between hydrocarbon structures, and this problem would appear worthy of more study in the future.

So far as the authors know, few good attempts have been made to modify the structure of the hydrocarbon in some regular manner, so that a better interpretation can be given to results similar to those cited above. Some information on this point is presented in connection with the effect of hydrocarbon structure on yields, but the data are obviously scant. For example, it is obvious that the substitution of chlorine or nitro groups (in other words electrophilic groups) in benzene would influence its electronic structure. It would be quite important to determine how such substitutions would affect the temperature of initial oxidation. This kind of experiment could provide very important information on this oxidation process. Furthermore, since the temperature of initial oxidation is easily observed, it might be possible to carry out such experiments in a very simple manner and obtain a great deal of information that is presently lacking in this field. The effect of catalyst structure on initial temperature of oxidation has not been studied extensively. It is obvious that the electrical conductivity techniques discussed elsewhere in this chapter should be applied to catalysts such as those mentioned in Table 29 in order to determine, for example, how and why molybdenum alters the surface. These correlations would illustrate how the molybdenum affects electron transfer between the catalyst and the reacting hydrocarbon. This would aid in interpretation of results like those shown in Table 29.

Oxidation of Hydrocarbon Mixtures and Effects of Additives on Oxidation

In studying catalytic oxidations at solid surfaces it has always been of interest to attempt to explain the mechanisms of such reactions in terms of current theories for gas phase and liquid phase oxidation reactions. The theories for these latter systems are more highly developed than those for the heterogeneous reactions. Bretton, Wan and Dodge[20] have made such attempts to apply these theories to the oxidation of C_4 hydrocarbons and a discussion of this subject is given on p. 257. In the gas and liquid phase reactions, many types of reaction inhibitors or modifiers have been employed for changing the course of these reactions. The very fact that the additives affect the yield and reaction kinetics in these cases has often provided some insight into the mechanisms involved. Likewise, in the gas and liquid phase systems, it has often been possible to react mixtures of materials instead of pure compounds in order to obtain additional information regarding reaction mechanisms. For example, in the thermal decompositions of hydrocarbons and in the oxidation of hydrocarbons in the gas phase, the composition of the reacting materials has often been varied in order to obtain special information regarding the course and kinetics of the reactions taking place. The information gained in homogeneous systems suggested that the techniques just mentioned might well be applied to catalytic oxidations at solid surfaces.

Considerable unpublished work[2] has been carried out in the laboratories of the authors on these matters. This work may be divided into two main parts. First of all, studies were made on the yields obtained upon oxidizing mixtures of hydrocarbons in order to compare the yields of the products with those obtained when oxidizing the pure compounds alone. Second, studies were made to determine the effects of small percentages of oxidation inhibitors or additives on the yields obtained during the oxidation of hydrocarbons. In some few instances it appears that the results that have been obtained are at variance with those reported in the patent literature. However, the results in our laboratories have been checked frequently and with great care, and where our results have seemed to differ from those reported in the literature we are convinced that our own are probably essentially correct.

Effect of Feed Composition on Catalytic Oxidation of Hydrocarbons

For reasons indicated above, experiments were carried out on the oxidation of hydrocarbon mixtures. It was assumed that the yields of products obtained by oxidizing pure hydrocarbons were known. If, then, a mixture of two hydrocarbons was oxidized, was the yield of product obtained the same as that calculated from the results for the pure reactants? For example, let a and b be the yields of phthalic anhydride obtained by oxidizing pure orthoxylene and naphthalene, respectively, and let x = fraction of xylene in a mixture of the two fed to the catalyst:

$$\text{Calculated yield of phthalic anhydride based on yields from pure reactants} = ax + b(1 - x)$$

Does this calculated yield equal observed yield of phthalic anhydride from the mixture?

When mixtures of methylnaphthalene and naphthalene were oxidized under optimum operating conditions on a vanadium oxide catalyst the yields of phthalic anhydride and maleic acid observed were a linear function of feed composition as shown in Figures 8 and 9, respectively. Since reaction was essentially complete in all cases, the yields of ($CO + CO_2$), which were the only other products, were also a linear function of composition. These results show that the calculated and observed yields were in agreement, or in other words, the addition of one hydrocarbon to another produced no synergistic effect on the yields. It would be difficult to state that the ratio of CO/CO_2 can be predicted since this factor is variable in time and quite difficult to hold constant.

The oxidation of mixtures of pure *o*-xylene and pure naphthalene was studied on a vanadium oxide catalyst under optimum conditions of operation. As noted above for the naphthalene-methylnaphthalene case the yield of phthalic anhydride produced was a linear function of the composition as will be observed in Figure 10. Likewise the yield of maleic anhydride formed during the oxidation of these mixtures was a linear function of the composition.

Butadiene may be oxidized in the presence of air on a vanadium oxide catalyst supported on an inert carrier with molar yields of maleic anhydride around 40 to 50 per cent. Experiments were carried out starting with 1.2 to 1.4 per cent butadiene in air in order to determine the effect of other hydrocarbon additives on this oxidation. The nature of the results on the oxidation of butadiene have been described above in connection with the summary of the work of Bretton *et al.*[20]. The results which were obtained with additives in this laboratory were quite similar to those obtained by Bretton. It was noted experimentally that the addition of two parts of butene to one

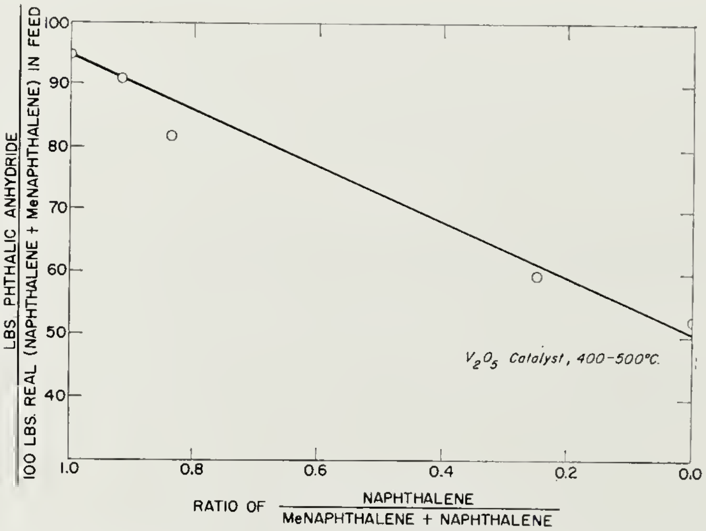


Figure 8. Yields of phthalic anhydride in the oxidation of mixtures of naphthalene and methylnaphthalene.[2]

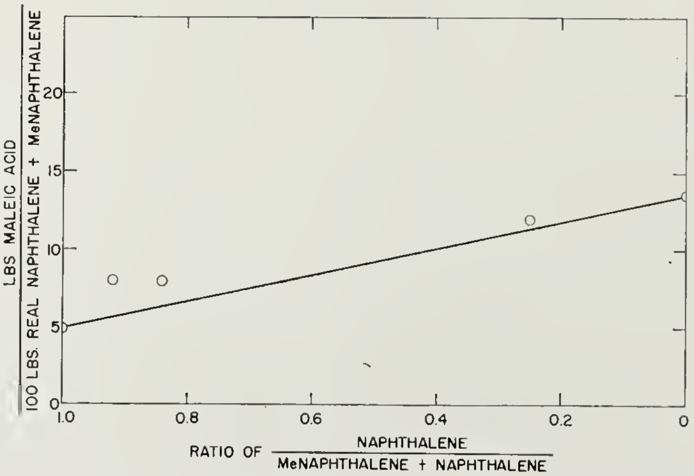


Figure 9. Yields of maleic acid in the oxidation of mixtures of naphthalene and methylnaphthalene.[2]

of butadiene had but little effect on the yield of maleic anhydride which was calculated from the yields obtained with the pure components. In a similar manner the addition of a large amount of butane had but little effect on the yield of maleic anhydride that might have been expected from the behavior of pure components on this vanadium catalyst. A large number of other experiments were performed with other mixtures of C_4 hydrocarbons: namely, mixtures of butene, isobutylene, butane and butadiene. Again, it was concluded that one can predict the yield of maleic anhydride from the behavior of the pure components.

In the homogeneous gas phase oxidation of hydrocarbons one would expect mixtures of hydrocarbons to give products which would not be calculable from the behavior of the pure components. The reaction chains involved in these cases would be expected to involve all or most of the hydrocarbons present, depending, of course, upon the specific reaction rates and other factors. In any case, however, the yield would not be expected to be a linear function of composition in most cases. The oxidation of a hydrocarbon at a catalytic surface involves the transformation of the original hydrocarbon through a number of steps to the final product. In the oxidation of the hydrocarbons mentioned above the number of atoms of oxygen involved is fairly large and the number of atoms removed as water and CO_2 is also quite large. If the radicals which must be formed in the oxidation are mobile on the surface and if there are two kinds of hydrocarbons oxidizing then one might expect that there might be reaction between the intermediate radicals from the different hydrocarbons; thus, one might expect the products to be

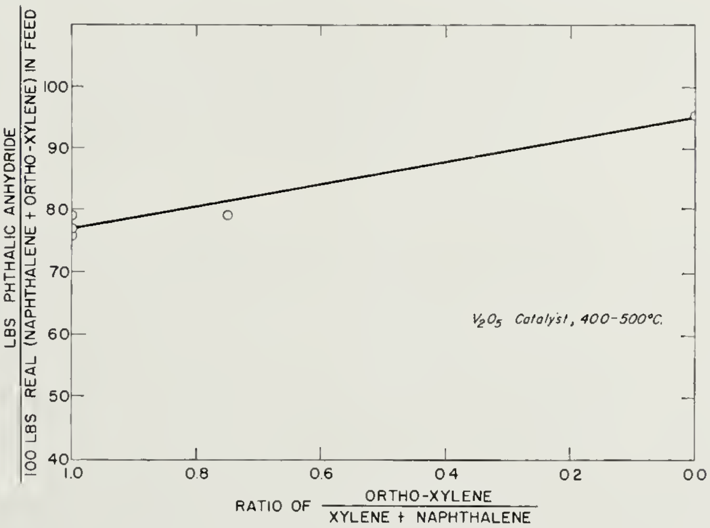


Figure 10. Yields of phthalic anhydride in the oxidation of mixtures of *o*-xylene and naphthalene.[2]

influenced by the composition of the mixture. Since such effects are not found, it is concluded that these experiments indicate that once the oxidation reaction starts, the composition of the final product is fixed by the initial oxidation step, and cannot be interfered with by similar oxidations taking place on other molecules. During the oxidation of a hydrocarbon it might undergo its initial oxidation attack, and the resulting intermediate might remain adsorbed on the surface. Furthermore, one might assume that the adsorbed radical would then react with a hydrocarbon adsorbed on an adjacent part of the surface, or might even be transformed by a hydrocarbon molecule striking it from the gas phase. The products obtained might then depend on whether a pure compound or a mixture is oxidized, and certainly the yield might not necessarily be expected to be a linear function of the composition. As indicated, no synergistic effects were observed. Again this emphasizes that once the original oxidation step takes place the molecule is then transformed by further attack by oxygen either from the gas phase or on the surface to form the final product or products which then desorb. There is no evidence, therefore, for a chain-type reaction in catalytic oxidations.

In the section on the oxidation of the C_4 hydrocarbons, Bretton, Wan and Dodge suggested a mechanism for the oxidation. They propose that certain radicals are formed on the surface in a manner similar to that which is involved in liquid phase oxidation. The mechanism, however, does not assume any reaction between radicals or intermediate oxidation products. If there had been postulated such reactions between components present in low concentration on the surface, one might then assume that in the reaction of mixtures, the radicals or intermediates from one starting material might be involved in reactions with those from another starting material. Actually the evidence just presented indicates that this does not take place. The mechanism of Bretton *et al.* does not postulate the occurrence of such reactions and hence there is apparently no inconsistency between their postulated mechanicms and the above results on the oxidation of mixtures.

Effect of Additives for Reaction Initiators on Xylene Oxidation

For reasons indicated above it was of interest to study the effect of certain additives on the catalytic oxidation of *o*-xylene. Those additives were chosen which are of influence in gas or liquid phase homogeneous oxidations. Several recent publications have suggested pronounced effects of introducing up to 2 mole per cent of nitroalkanes in the homogeneous oxidation of aromatics, e.g., cumene. It is stated that these nitroalkanes influence the composition of the products, such as acetophenone and carbinols. Likewise in the homogeneous oxidation of propylene and higher homologs to the corresponding acroleins, the use of as little as 0.4 mole per cent of allyl chloride or similar substances has been described as effective in controlling the yield. In the high pressure oxidation of benzene to phenol by oxygen, a number of promotors have been suggested to increase yields and to decrease oxidation temperatures: namely, 1 per cent of cyclohexanol, cyclohexane, ether, turpentine, amyl nitrite, aniline, carbon bisulfide and tetrahydronaphthalene. In this oxidation of benzene these promoters are believed to promote peroxide formation readily, or to serve as sources of free radicals which dehydrogenate the benzene at lower temperatures than can pure oxygen.

In view of this special literature and the more general literature on the effects of additives on homogeneous oxidations, it seemed of interest to attempt to find the effect of initiators or modifiers on the course of the oxidation of *o*-xylene on a typical vanadium oxide catalyst. In the experiments carried out the amounts of additives were varied from 0.25 to 2 per cent of the xylene. By holding the amount of additive to less than 2 per cent, its effect on determination of yields was essentially negligible, and only a small correction had to be made to the phthalic anhydride yield for any acidic products formed from the additives. In general, the experiments were carried out under conditions known to give optimum oxidation of the *o*-xylene to phthalic anhydride. Using 1 per cent of *o*-xylene in air, the amount of total acid without additive usually averaged some 65 to 70 mole per cent. This figure for the yield of phthalic anhydride was not altered significantly by the addition of cyclohexane, cyclohexanol, turpentine, isoamylnitrite, nitromethane and amyline. The results are shown in Table 31.

TABLE 31. EFFECT OF ADDITIVES ON YIELDS OF PHTHALIC ANHYDRIDE FROM ORTHOXYLENE VANADIUM OXIDE CATALYST: ORTHOXYLENE IN AIR[2]

Additive	% of Additive in Xylene	Yield of Total* Acids (mole %)	Yield Increase Over Result for No Additive
No additive	0.0	67.8	
Cyclohexane	1.0	68.4	+0.6
Cyclohexanol	1.0	67.2	−0.6
Turpentine	1.0	66.5	−1.3
Isoamylnitrite	1.0	68.5	+0.7
Isoamylnitrite	1.0	67.4	−0.4
Nitromethane	0.5	68.5	+0.7
Aniline	1.0	69.1	+1.3
"	1.0	68.1	+0.3
"	2.0	67.5	−0.3

* 90 per cent phthalic anhydride and 10 per cent maleic anhydride.

It was expected that some of the additives would produce materials like nitric oxide, if only in trace amounts, which are known to be of considerable influence on homogeneous gas phase oxidations. It is concluded that the oxidation of *o*-xylene does not start at the surface and then proceed out into the gas phase, otherwise some influence of the additive on yield would have been noted. For example, a small formation of nitric oxide would have influenced any gas phase reaction and thus should have altered its course sufficiently to produce a detectable change in the final product.

In the oxidation of methanol on a catalyst consisting of a gold gauze the presence of 1.7 per cent acetone or 10 per cent water in the methanol did not appreciably affect the yields[180].

It was pointed out in connection with the oxidation of toluene with air on vanadium catalysts that Pargal[139] had found the addition of a few per cent of peroxides to the reactants caused the lowering of the operating temperature of the catalyst without affecting the nature of the products. This appears to be an effect more on the catalyst operation rather than on the nature of the products.

During the oxidation of ethylene to ethylene oxide on a silver catalyst, the catalyst loses activity and the yield of ethylene oxide gradually decreases. In the section of this chapter dealing with this oxidation reaction it is mentioned that the addition of ethylene dichloride counteracts these effects. Although it appears that this and similar additives may affect the catalyst surface, there is no information which would explain this important phenomenon.

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CHAPTER 4

OXIDATION OF AMMONIA, AMMONIA AND METHANE, CARBON MONOXIDE AND SULFUR DIOXIDE

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Ammonia Oxidation on Platinum Gauze

Experimental Observations

The catalytic oxidation of ammonia to form nitric oxide and subsequently nitric acid is one of the most efficient and important catalytic processes operated on an industrial scale. It has been studied intensively in plant equipment and has also been the subject of numerous fundamental investigations. It is of particular interest to discuss this process here because it represents a low contact time reaction which is not often encountered in other catalytic operations.

The oxidation of ammonia proceeds by the way of three alternative routes.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (2)$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \qquad (3)$$

Reactions (1) and (2) are strongly exothermic, by 217 and 303 kcal, respectively, at 25°C, and the reactions should proceed to completion according to thermodynamic calculations. The observed temperature increase during oxidation agrees with that calculated from the heats of reaction[121] and the yields obtained in reactions (1) and (2).

Although the oxidation of ammonia on platinum catalysts was first observed in 1839 by Kuhlmann[80], it was not until 1900–1913 that Ostwald[97] worked out methods of carrying out the oxidation on a technical scale. It was in 1926 that Andrussow[2], working in Bodenstein's laboratory, carried out the first of his studies on this reaction and he was able to formulate the complicated mechanism of this oxidation for the first time. Andrussow studied the oxidation as a function of the temperature, the contact time, and the ratio of ammonia to air in the mixture fed to the platinum gauze. He evaluated the amount of nitric oxide, ammonia and nitrogen in the exit gases. Andrussow realized that the decomposition of ammonia in the absence of oxygen might be one factor involved in the reaction, and therefore measured the rate of decomposition of ammonia on his platinum catalyst as a function of temperature. He also realized that the nitric oxide formed in the reaction might interact with any unoxidized ammonia, and therefore he passed mixtures of these gases over his platinum catalyst in order to measure their rate of reaction. Finally, he proposed that the oxidation of ammonia involved a series of chemical reactions.

He postulated that the primary reaction step led to formation of nitroxyl, that is, HNO. One may also refer to the original paper of Andrussow to find references to earlier work on this important oxidation. On the basis of further evidence presented below, one can make certain comments regarding the work of Andrussow. His results suggest that the decomposition of nitric oxide on platinum gauze in the absence of air is high at temperatures usually employed in oxidizing ammonia. Also he found the decomposition of ammonia on the gauze to be appreciable. However, with multilayer (30 layers) gauzes most of the nitric oxide is formed on the first one or two gauzes, and yet it does not decompose appreciably on the remaining layers of gauze because nitric oxide yields are over 90 per cent. Since most of the ammonia is oxidized on the first one or two gauzes producing high yields of nitric oxide, the ammonia decomposition cannot be important even if it is appreciable in the absence of O_2.

Andrussow has more recently[4, 6] studied the oxidation of ammonia under high velocity conditions. For example, in streaming the reacting gases through a fine platinum capillary, he concluded that this oxidation and a number of other fast catalytic reactions take place so that the concentration of reactants at the catalytic surface is quite small. Under such conditions the reaction rate is governed by the rate of diffusion of the reactants to and from the surface rather than by their usual steady state concentration in the gas phase. Essentially he proposes that the reaction kinetics of the ammonia oxidation are governed by mass transfer or diffusional effects rather than by the classic considerations of kinetics. This does not appear to be an unreasonable view of this fast reaction, but it may not necessarily make the postulated steps of the reaction as indicated above incorrect. It does, however, suggest that the application of the usual Langmuir-Hinshelwood methods of formulating the reaction mechanism is not valid.

In some recent work, Krauss[74, 75] attempts to work out equations for the reaction kinetics of the ammonia oxidation based on further work on the oxidation carried out at low pressures. In view of the suggestion of Andrussow that the reaction is diffusion-controlled, one wonders whether Krauss is justified in attempting to calculate reaction velocity constants for this complicated reaction if diffusion to, as well as chemical reaction at the surface is involved.

The oxidation of ammonia on a commercial scale is usually carried out on a gauze catalyst containing principally platinum or 90 per cent Pt-10 per cent Rh[54]. The reaction has been conducted on pellets or granules of iron oxides promoted with bismuth, but the information on the operation of such oxides is so scant that it will not be discussed here[132].

On platinum gauze catalysts, the operating temperature is usually in the range from 750 to 950°C at contact times of 1 to 5×10^{-4} sec and linear gas velocities of around 1.0 ft/sec. Under these conditions with around 8.0 to 9.0 per cent by volume of ammonia in air some 90 to 100 per cent, and usually 94 to 98 per cent, of the ammonia is oxidized to NO with but little of the ammonia remaining unoxidized. The ammonia lost appears as N_2 according to reaction (2). The platinum gauze gradually loses metal and simultaneously the wires in the gauze develop sprouts of fine crystals which give them the appearance of tinsel. Also, the wires show crystal growth.

The appearance of the fine crystals on the surface and the intergranular crystal growth suggest that the highly exothermic reactions produce higher temperatures on the wire surfaces than are actually measured. This point of speculation obviously needs some experimental confirmation.

The usual industrial process operates at 100 per cent conversion where yields of NO are around 95 per cent of theory. (Yield and efficiency of oxidation are used synonymously in this section.) Conditions are not often varied sufficiently to obtain information required for specifying reaction kinetics and mechanism. However, the industrial experience will be cited to emphasize certain critical factors in the catalytic processes involved which otherwise would remain obscure in the kinetic analysis to follow[10, 11].

Figure 1 presents the effect of temperature on yield of NO for a single layer, 0.0024 in., 80 mesh, 90 per cent Pt-10 per cent Rh gauze, with upflow. The contact time was 0.54×10^{-4} sec and the linear gas velocity (at NTP) 0.45 ft/sec. In calculating contact times it has been assumed that the thickness of the contact zone is equal to the wire diameter of the gauze.

The volume of the contact zone has been corrected for the volume of the wire. The linear gas velocity is actually the velocity of approach, that is, the velocity in the space ahead of the catalyst.

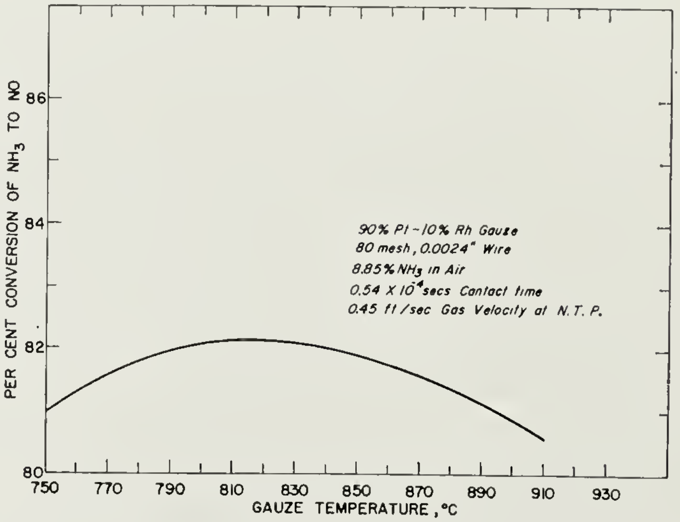


Figure 1. The effect of temperature on the oxidation of ammonia to nitric oxide.[1]

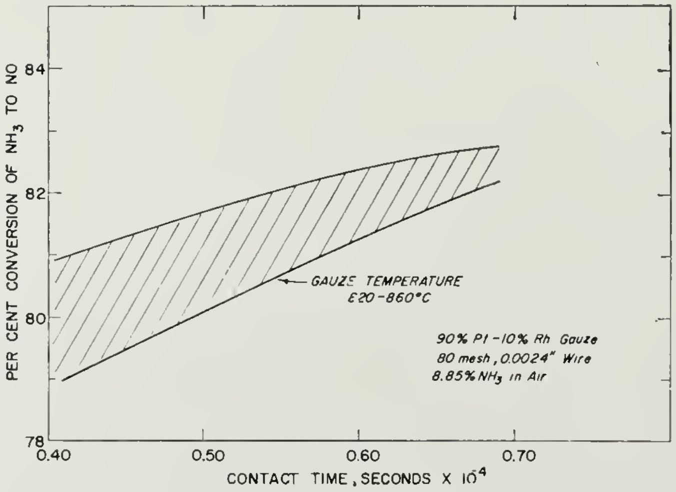


Figure 2. The effect of contact time on the oxidation of ammonia to nitric oxide.[1]

The effect of contact time on yield and the effect of gauze temperature on the percentage of unoxidized ammonia are shown in Figures 2 and 3. The results in Figures 1 through 3 summarize data which indicate but little effect of gauze temperature and contact time on yields of NO and on the unconverted NH_3[1]. Over a wider range of conditions these variables might become important, however, especially at lower linear gas velocities. Since ammonia and NO_2 (or HNO_2) react readily at low temperature, one cannot be sure that some unoxidized ammonia is not destroyed by NO_2, a product of the oxidation, during the sampling procedure[45]. Figure 2 shows

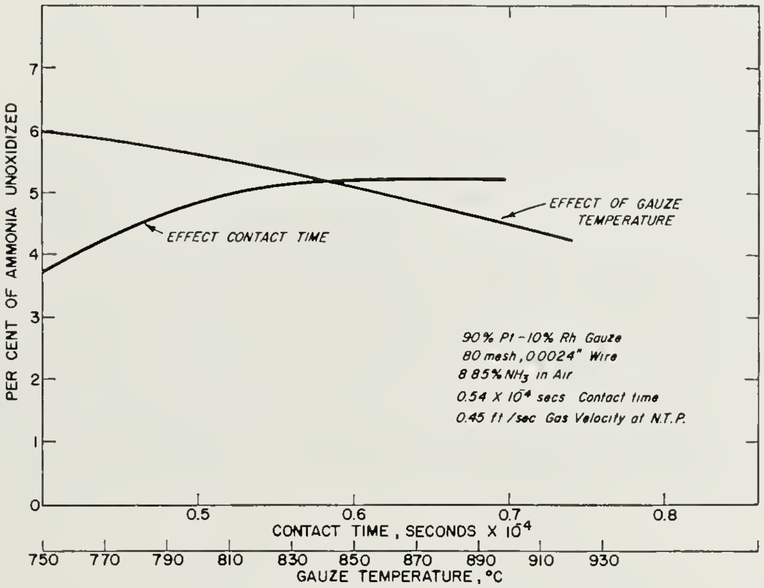


Figure 3. The effect of contact time and temperature on the percentage of unoxidized ammonia.[1]

Table 1. Oxidation of Ammonia by Air on Gauze Catalyst

10% Rhodium-90% Platinum
9% by volume NH_3 in Air, about 815°C.
Gas Up-flow, Linear Gas Velocity = 0.45 ft/sec (NTP)

Linear Gas Velocity (ft/sec)	Gauze Combination			Contact Time (sec × 10^{-4})	Unoxidized NH_3 (%)	Per Cent Conversion of NH_3 to NO	Geometric Platinum Surface Area (Sq in./Sq in. of Gauze)
	No.	Mesh	Wire Diam. (in.)				
0.42	1	80	0.0024	0.54	5.0	83	1.21
0.42	1	80	0.0024				
	1	150	0.0016	0.86	0.3	99	2.72
	3	80	0.0030	1.88	0.4	98	4.53
	4	80	0.0030	2.51	0.1	99	6.04

the effect of contact time on the percentage of ammonia oxidized to NO at 820 and 860°C. Additional data on the influence of a number of gauzes on yield of NO is shown in Table 1. (See also Refs. 10 and 11.) From the results presented in Figures 1 through 3 and Table 1, it is evident that with a contact time of the order of 10^{-4} sec, the reaction forming NO is 83 per cent complete on one gauze and essentially 100 per cent on two or more gauzes. At even 140°C lower than the optimum (860°C), the reaction is still complete, but the yield of NO drops to 92 per cent and the unoxidized NH_3 is negligible. Again, one wonders whether at for example 720°C the unoxidized NH_3 reacts with the NO_2 in the sampling system. Would an infrared analysis of the exit gases at 500 to 700°C, for example, show the presence of unconverted NH_3 ?

Many large-scale operations of the oxidation of ammonia are carried out with as many as 20 layers of platinum gauze and with linear gas velocities that are high. Under such conditions, there is probably little back diffusion or mixing of the gas and the contact time is of the order of 10×10^{-4} sec (see Table 1) and yields of nitric oxide are about 95 to 100 per cent. Under conditions of high linear gas velocity, the amount of unoxidized ammonia passing through the first or second gauze would be appreciable—e.g., greater than 15 per cent. Apel'baum and Temkin[8] show this to be the case at linear gas velocities of 6 ft/sec on 6 to 8 layers of gauze. Under such conditions, therefore, there would be ample opportunity for nitric oxide and ammonia to react according to the following equation:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

If the reaction of nitric oxide and ammonia were important, one would expect this reaction to decrease yields appreciably under operation with, for example, 20 gauzes. Actually, the observed yields of nitric oxide are still of the order of 95 to 100 per cent and, therefore, it is safe to conclude that the reaction of nitric oxide and ammonia is not appreciable under reaction conditions usually employed. With high linear gas velocities it is necessary to employ a large number of gauzes. In commercial practice one does not need the large number of layers just to complete the reaction. Actually, one wishes to use a number of these gauzes as mechanical support for those which first come in contact with the oxidizing ammonia. The oxidation disintegrates the first few layers of gauze relatively rapidly and, if a large number of layers is employed, there is no need for shutting down the operation in order to replenish those which do disintegrate.

When the oxidation is carried out with the 20 layers of gauze, for example, the yield of nitric oxide is not appreciably lower than that obtained with a smaller number of gauzes. This is a clear indication that the decomposition of nitric oxide to oxygen and nitrogen as shown by the following reaction is not important under normal conditions of operation:

$$2NO \rightarrow O_2 + N_2$$

In fact, one may go to temperatures appreciably higher than those required for yields of better than 95 per cent without experiencing any drop in efficiency, thus again indicating that the nitric oxide decomposition to nitrogen is not an important reaction.

It is interesting to note that Andrussow reported poor yields as he increased his contact time from less than 5×10^{-4} sec to above 5 to 10×10^{-4} sec. The data in Table 1 indicate that the yields with these contact times should be quite high. It is concluded that Andrussow carried out his work under such conditions that he was obtaining considerable back-diffusion of the nitric oxide, and other reaction products formed at the first gauze back into the ammonia-air mixture. This would lead to appreciable losses in yield by reaction of NO_2 and ammonia at low temperatures in the gas phase. Falk and Pease[45], for example, show that the reactions of NO_2 and NH_3 take place at very low temperatures. The curves shown by Andrussow for yield *vs.* temperature at different contact times are often quoted in the literature, but there is some question as to whether they are valid for all conditions of operation. That is, under other conditions of higher linear velocity the yields might be considerably different than shown by Andrussow[2].

With 9 per cent NH_3 the heat of oxidation raises the gas temperature some 650°C, thus leading to gauze temperatures of 700°C or higher. Under these conditions, non-noble metals soon disintegrate, probably due to the same causes that produce the tinsel effect on platinum gauze. Apel'baum and Temkin[8] state that the first in a series of gauzes may be some 50°C higher in temperature than the last, thus indicating the possibility of surface overheating.

In view of the completeness of the reaction in a short contact time, it is of interest to calculate certain factors that might be of interest in the kinetics. The first of these is the ratio of the space between wires to the mean free path of the gaseous molecules. The space between wires is about 0.01 in., the mean free path of an average molecule at 800°C for 9 per cent NH_3 in air $= 15 \times 10^{-6}$ inch.

$$\frac{\text{Space between wires}}{\text{Average mean free path at 800°C}} \sim 600$$

Hence, every molecule should experience gas phase collision before reaching the surface.

One next inquires as to whether the diffusion from between the wires would account for the observed reaction rate. By assuming no mixing and an effective ammonia concentration equal to that in the inlet gas, and by taking the diffusion coefficient of NH_3 at 0°C and correcting to 800°C, one can calculate that

Number of moles NH_3 diffusing = 0.041 moles/sq in. surface area/min.
Amount of NH_3 reacting = 0.024 moles/sq in. surface area/min.

$$\frac{\text{Rate diffusion of } NH_3 \text{ to surface}}{\text{Rate reaction of } NH_3 \text{ on surface}} = 1.75$$

The calculation ignores gas turbulence which is believed to be important in gas flow through gauzes, hence we can conclude that diffusion might be an important factor in the oxidation. In a private communication, Dr. Hugh Hulburt[60] has indicated that his hydrodynamic calculations show the gas flow through the gauze openings to be laminar. In any study of kinetics it is necessary to consider the problems of diffusion and gas turbulence. This would be true even in studies in which conversion is low. Apel'baum and Temkin[8] conclude that the rate of reaction is determined by diffusion and relate their calculations of diffusion rates to heat-transfer data.

One might speculate that the oxidation starts at the surface and then propagates out through the gas phase. There is not much evidence on this matter. If the distance of propagation were of the order of a gauze wire diameter, then one might expect two layers of gauze to behave differently than one. Table 2 shows that there is actually but little difference, the second layer serving principally to oxidize unconverted NH_3. The time between gauzes is of the order of 10^{-4} sec, thus suggesting any chain propagated ends in that period of time. The effect of gauze separations of ¾ and 2 in. is not important, as shown in Table 2, indicating that any chain reaction in the gas phase over long distances is not likely. Vainshtein and Polyakov[126] carried out analogous experiments with separated gauzes and reached the contradictory conclusion that the oxidation is a hetero-homogeneous reaction.

Vladov[130] has compared the temperature downstream from a platinum-rhodium catalyst wire during the time ammonia is being oxidized with the temperature in the oxygen stream alone or in the ammonia stream alone. It was concluded that in a mixture of 10 per cent NH_3 in oxygen, about 60 per cent of the total heat of oxidation of the ammonia was liberated in the gas phase downstream from the catalyst.

There are many references to the use of noble metals other than pure platinum for this oxidation. Table 3, for example, indicates that addition of 10 per cent Rh increases the yield of NO a few per cent. (See also Ref. 8.) Although this is of great importance in an industrial operation, it provides little help in explaining the nature of the catalytic operation. It would be desirable to have data on the effect of metal composition on yields of NO and N_2 at low conversion, perhaps on a single electrically heated wire rather than gauzes. This might help clear up the nature of the surface reaction. It should be noted that modern instrumental methods would permit carrying out the determination of small amounts of H_2O, NO, NO_2 in large amounts of NH_3 and air, thus permitting work to be done at low conversions.

TABLE 2. EFFECT OF GAUZE SEPARATION ON EFFICIENCY OF OXIDATION OF NH_3 TO NO

10% Rh-90% Pt Gauze
8.7% by volume NH_3 in Air
Contact time about 0.5–1.0 × 10^{-4} secs.
Gauze temp. = 820°C.

Gauze Combination	Separation	Unoxidized NH_3 (%)	NH_3 Oxidized to NO (%)
1–80 mesh, 0.0024″	—	5.0	83
2–80 " 0.0030″	None	0.3	99
1–80 " 0.003″		1.6	94
1–30 " 0.007″ 1–80 " 0.003″	¾″	1.6	94
1–30 " 0.007″ 1–80 " 0.003″	None	1.2	92
1–80 " 0.003″ 1–30 " 0.007″	2″	1.2	92

TABLE 3. EFFECT OF RHODIUM CONTENT ON PLATINUM GAUZE EFFICIENCY

Each gauze combination 1–150 mesh, 0.0016″ wire gauze
1–80 " 0.0024″ " "
Up-flow; Contact Time = 0.9 × 10^{-4} secs.

% Rh in Pt Gauze	Best Gauze Temp. (°C)	Best Yield (%)	Best NH_3 Conc. in Air (%)
0.0	865	96	7.0–8.5
10.0	815	99	8.3–9.5

Handforth and Kirst[54] were among the first to call attention to the importance of the effect of linear gas velocity through the gauze as a factor governing yields. Their patent covering this important point suggests that the linear gas velocity is important because it prevents diffusion of nitrous gases from the gauze back into the ammonia-air stream. They summarized the conditions of operation in a number of well-known ammonia oxidation processes as follows:

	Rate (lb NH_3/oz of cat./day	Gauze Weave		No. of Layers	Contact Time (sec)	Velocity (ft/sec)
		Mesh	Wire			
	—	80	.0024	4	.0006	2.7
United Alkato Co. G.B.	50 to 100	80	.0026	4	.0018 to .00036	5 to 10
Landis, U.S.A.	60	60	.005	2–4	.00019	9 to 18
Parsons Jones	97	80	.0026	4	.00018	9.5
Bamag, Ger.	50 to 150	150	.0016	2	.00013 to .0004	1.3 to 4
Fauser, Fr., atm	50	150	.0015	2	.00018	2.8
Fauser, pressure (50 psi)	250	150	.0015	2	.00022	2.3
DuPont, atm.	100	80	.003	4	.00016	12–8
DuPont, pressure (100 lb)	100	80	.003	4	.0012	1.6
Handforth and Kirst, atm	100	80	.003	16	.00016	48
Handforth and Kirst, atm	100	150	.0015	16	.00019	21
Handforth and Kirst, 100 lb pressure	800	80	.003	16	.00015	49
Handforth and Kirst, 100 lb pressure	800	150	.0015	16	.00018	21

Polyakov[101] states that "preliminary reaction" takes place on the vessel walls ahead of the gauze and states that the maxima in Andrussow's curves disappear if the wall reaction is minimized. The reaction is postulated to be partly homogeneous and partly heterogeneous. Atroshchenko[10] states that oxidation of NH_3 on the walls of the vessel decreases yields as much as 6 per cent at 620°C under his conditions of study. If this takes place the yield decreases and, therefore, high linear gas velocities are required to prevent just such side reactions. When the products of reaction are permitted to circulate back into the ammonia-air stream, then reactions of NO_2 with ammonia take place at relatively low temperatures and also on the walls of the converter prior to the hot gauze[45]. The side reactions taking place lower the over-all yields and lead to conclusions about catalyst operation and reaction kinetics which are probably erroneous. It has been stated before that in Andrussow's early work, where he found yields of 0 to 70 per cent of nitric oxide at temperatures of 500 to 800°C, he was working with contact times of 15 to 100 $\times$ 10^{-4} sec and therefore presumably with linear velocities of some 15 to 100 times lower than now used industrially. Under these conditions it is most probable that he may have been working at the gauze surface with not an ammonia-air mixture, but with ammonia-air-NO_2-NO in which the NO and NO_2 were very appreciable. His conclusions based on this work may have been complicated by the side reactions. It should be noted, however, that in recent years Andrussow has pointed out the importance of diffusion and gas mixing so that he too would be led to modify his very earliest conclusions on this reaction.

Theories of Ammonia Oxidation

The theories of ammonia oxidation arise from the work of Raschig[102], Andrussow[2], Bodenstein[18] and others[56]. According to Raschig the oxidation proceeds by the following reaction (imide) scheme:

$$NH_3 + O = NH + H_2O \tag{1b}$$

$$2NH + 2O_2 = 2HNO_2 \rightarrow NO + NO_2 + H_2O \tag{2b}$$

$$NH + NH_3 = N_2H_4 = N_2 + 2H_2 \tag{3b}$$

$$N_2H_4 + O_2 = N_2 + 2H_2O$$

$$NH + NH = N_2H_2 = N_2 + H_2$$

$$NH + O = HNO \tag{5b}$$

$$2HNO = N_2O + H_2O \tag{6b}$$

Bodenstein formulated another reaction scheme as a result of analysis of work carried out by Andrussow[2] at atmospheric pressure. This theory is known as the nitroxyl (HNO) theory.

$$NH_3 + O_2 = HNO + H_2O \text{ (or } NH_3O) \tag{1a}$$

$$HNO + O_2 = HNO_3 \tag{2a}$$

$$4HNO_3 \rightarrow 2H_2O + 4NO + 3O_2 \tag{2c}$$

$$HNO + NH_3 = N_2H_2 + H_2O = N_2 + H_2 + H_2O \tag{3a}$$

$$HNO + HNO = N_2O + H_2O \tag{4a}$$

Following the work of Andrussow at higher pressures, Bodenstein and Büttner[19] and Krauss[74, 75] studied the oxidation on platinum "wire" at low pressures (10^{-2} mm Hg) in order to eliminate reactions in the gas phase of products formed on the hot surface and evaporating therefrom. These products were frozen out on surfaces cooled to liquid air temperatures, thus stabilizing the intermediates formed on the hot wire. Nitrous acid (HNO_2) and hydroxylamine (NH_3O or NH_2OH) and N_2 were shown to be principal products of the catalytic oxidation. Reactions in the gas phase were shown to destroy NH_3O and form more HNO_2. Little hydrazine was observed as a product of reaction when oxygen was present, and but little in the absence of oxygen.

These findings led to the following modified formulation of the hydroxylamine mechanism by Bodenstein[18, 19]

$$NH_3 + O = NH_3O \tag{1c}$$

$$NH_3O + O_2 = HNO_2 + H_2O \tag{2c}$$

$$NH_3O + NH_3 = N_2 + H_2O + 2H_2 \tag{3c}$$

$$NH_3O + O = HNO + H_2O \tag{4c}$$

$$2HNO = N_2O + H_2O \tag{5c}$$

$$NH_3O + HNO = N_2 + 2H_2O \tag{6c}$$

$$HNO_2 + NH_3 = N_2 + 2H_2O \tag{7c}$$

$$4HNO_2 = 4NO + 2H_2O + O_2 \tag{8c}$$

Bodenstein published a variation of the above scheme which need not be discussed here because it merely complicates discussions of two already complicated theories. Epshtein[42] and Apel'baum and Temkin[9] describe work at low pressures which agrees in general with the mechanisms and conclusions presented here.

An important objection may be raised against certain reactions presented in the reaction schemes outlined above. In particular, for example, reactions (3c), (6c) and (8c) do not appear reasonable because they involve either the production of more than two molecules and/or the reaction of more than two molecules. It is improbable that one could have a reaction such as (8c) involving four molecules since this would require the proximity of four such partners adjacent to each other on the surface simultaneously. Since this is an unlikely event, it is evident that reaction (8c) is an improbable one and, if it is correct over-all, it really involves a series of steps which are not yet defined. In reaction (3c) four molecules are formed by the reaction of two. If one were to observe the models for the reactants, it would be noted immediately that the probability of being able to form four molecules in one single reaction step is very small. For these reasons, it appears that the reaction schemes presented need further revision and perhaps simplification so that they involve the reaction of only pairs of molecules or the production of pairs of molecules.

In his paper in 1937 in the *Trans. Electrochem. Soc.*[20], Bodenstein summarized his work with Andrussow, Büttner and Krauss. He concluded that (1) hydroxylamine, NH_3O, is a primary product of the surface reaction as shown in (1c). (2) Nitrous acid, HNO_2, forms on the surface or in gas phase by reaction (2c). (3) Hydrazine is not an important product of reaction by a process $NH + NH_3 \rightarrow N_2H_4$ and hydroxylamine is not formed by a reaction $NH + H_2O \rightarrow NH_3O$ as might be concluded from work of Christiansen *et al.*[29]. (4) In the low-pressure experiments of Krauss he found the decomposition of NH_3 on the platinum, $2NH_3 \rightarrow N_2 + 3H_2$ is comparable in extent to the oxidation of NH_3, and at low oxygen pressures the decomposition overrides the oxidation and the hydrogen burns in the gas phase to water. Bodenstein concluded that decomposition of NH_3 to N_2 and H_2 rather than the reaction (3c) accounts for nitrogen formation. It is pointed out above that this reaction (3c) is improbable based on the large number of molecules involved. Polyakov, Urizko and Galenko[101] studied the oxidation up to 1040°C on platinum gauze and concluded that the decomposition of NH_3 at high temperatures and long contact times causes the maximum in the yield of NO.

In 1949, Wendlandt[136] compared laboratory and commercial results in order to clarify the above mechanisms and described industrial experience of the kind summarized at the beginning of this section (Figures 1–3, Tables 1–3). As a result of the presentations of Bodenstein *et al.*, Wendlandt arrived at the following conclusions: (1) Failure to observe N_2H_4 in the low pressure experiments of Büttner[19] and Krauss[75] seems to rule out the imide mechanism of Raschig, that is, reactions (1b–5b). With no O_2 present, the decomposition of NH_3 on the platinum wire did produce small amounts of N_2H_4 in the low pressure experiments of Krauss. (2) If the imide (NH) theory holds, then the work of Bodenstein and Büttner[19] requires that it react to form NH_3O by a reaction $NH + H_2O \rightarrow NH_3O$. The latter should be influenced by the concentration of water vapor. Wendlandt states that commercial operation with excess water has no effect on yields, suggesting that this reaction does not occur. (3) In work *at low pressures* most of the NH_3 was decomposed to N_2 whereas commercial operations at high pressures give essentially all NO, uninfluenced by factors such as temperature, contact time, etc. Bodenstein explains this as due to ammonia decomposition on a surface nearly free of adsorbed oxygen due to the low pressures of oxygen in the low-pressure experiments. Wendlandt calculates that the amount of reaction per unit surface in "full-scale" is 300 to 1500 times that in the low pressure, wire experiments. Wendlandt argues that the ratio of surface to oxidized NH_3 ($= NH_3O$) is large at low pressures and, therefore, the NH_3O is constantly exposed to fresh NH_3.

Krylov, Roginskii and Tret'yakov[78] state that oxygen forms an unstable oxide, Pt_3O_4, on platinum, but that the formation of this oxide does not increase the activity of the platinum. The oxidation activity involves adsorbed oxygen rather than the unstable oxide, although an attempt to define the difference between these may not be really meaningful.

The technical ammonia oxidation mechanism proposed by Bodenstein which appears to be most acceptable is as follows:

$$\left.\begin{array}{l} NH_3 + O = NH_3O\ (NH_2OH) \\ NH_3O + O_2 = HNO_2 + H_2O \xrightarrow{+O_2} HNO_3 \end{array}\right\} 95\,\%\ \text{yield NO}$$

At low pressures the HNO_2 escapes from the surface without reaction and is recovered as such.

$$\left.\begin{array}{l} NH_3O + NH_3 \xrightarrow{O_2} N_2 + 3H_2O \\ HNO_2 + NH_3 \longrightarrow N_2 + 2H_2O \end{array}\right\} 5\,\%\ \text{yield } N_2$$

$$NH_3O + HNO_2 = N_2O + 2H_2O \qquad \text{Traces } N_2O^{28}$$

It is most likely that reaction of NH_3 occurs with adsorbed oxygen atoms, or an oxide film on the platinum. It is not too important what the exact state of the oxygen is, for reaction might be

$$NH_3 + \text{Pt-active } O_2 \rightarrow NH_3O + PtO$$

$$PtO + NH_3 \rightarrow NH_3O$$

Ammonia Oxidation on Metallic Oxide Catalysts

The section on the oxidation of ammonia on platinum gauze catalysts refers to the formation of nitrous oxide as a product of the reaction. On metallic platinum catalysts, however, under most conditions of operation only traces of nitrous oxide are formed. Zawadzki[141] has recently described conditions under which nitrous oxide does form on gauze catalysts.

In 1930 von Nagel[133] showed that an iron-bismuth oxide catalyst was able to form nitrous oxide in good yields at temperatures around 300°C. Here again conclusions regarding mechanism seem uncertain based on the information presented, but it appears that this would be an ideal reaction for further study especially at low conversions where it might be possible to obtain valuable information regarding the kinetics and mechanism of the reaction. As will be pointed out below, Krauss[76] has carried out some very interesting work which is of interest in explaining the mechanism of this reaction.

The work of von Nagel[133] was repeated by Kobe and Hosman[72] and the reader is referred to this more recent report for information on this reaction. For example, with 11 per cent ammonia and 89 per cent oxygen, the conversion of ammonia to nitrous oxide was of the order of 40 per cent, with a maximum being obtained at around 225°C on a bismuth-iron oxide catalyst. The space velocity, the concentration of ammonia in oxygen, and the time of operation of the catalyst were found by Kobe and Hosman to be of importance, and reference to their article will indicate the effects of these variables on the performance of the catalyst. The recent report of Zawadzki[141] also summarizes further information on the effects of variables in this reaction (Figure 4). This work of Zawadzki *et al.* shows the effect of temperature on the yields of nitrous oxide, nitric oxide, and nitrogen at three different gas flow rates.

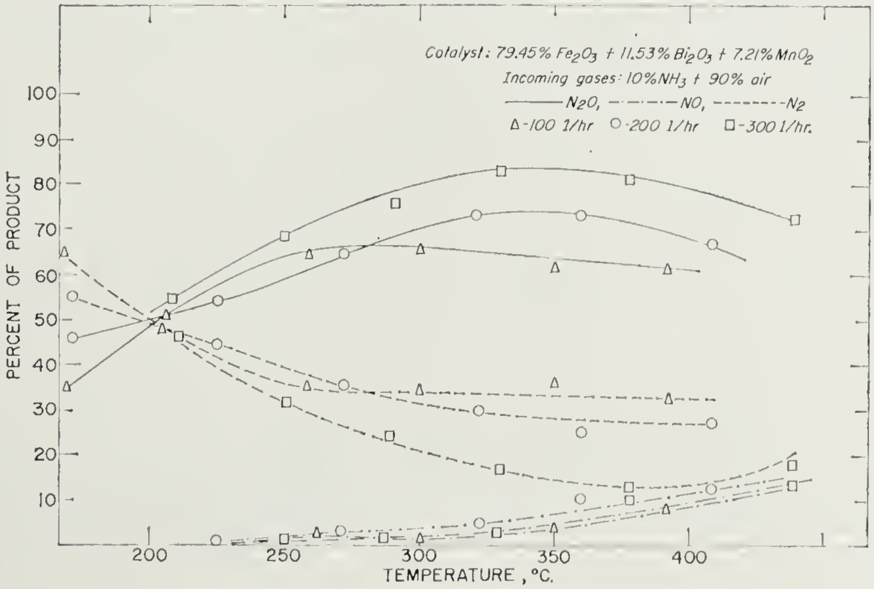


Figure 4. The effect of temperature on the oxidation of ammonia over a bismuth-iron oxide catalyst.[141] (Reprinted courtesy of the Faraday Society.)

Table 4. Oxidation of NH_3 with Air on Oxide Catalysts
Conditions: 10 per cent NH_3 in air.
Other conditions as given by Zawadzki.[141]

Oxide Catalyst (percentages)	Optimum Yields N_2O (%)	at Temp. (°C)	NO (%)	at Temp. (°C)
$36CuO$-$64MnO_2$	60	300–400	>40	>400
$80Fe_2O_3$-$12Bi_2O_3$-$8MnO_2$	80	300–400	>20	>400
$100Bi_2O_3$	8	450–500	>40	>550
$45CuO$-$45MnO_2$-$10CaCO_3$	60	300–400	>50	>500

Zawadzki indicates that a number of different oxides or oxide mixtures are active in forming nitrous oxide in yields approaching 80 per cent (Table 4). The yield of the nitrous oxide passes through a maximum at around 400°C. The nitric oxide yield, however, increases with temperature and presumably its maximum yield would be found at a temperature considerably in excess of 500°C. In view of the recent results of Kobe and Hosman[72], there is some question as to whether the results reported by Zawadzki would not be found to change with time of operation of the catalyst.

From the description of the work of Krauss which follows, it will be noted that some understanding has been obtained of the nature of the mechanism and of certain factors which govern the performance of the catalyst itself. A more systematic study should be made of the effect of catalyst composition on the results, especially relating these changes in composition to the electronic or semiconducting properties of the oxides tested. This might be an ideal reaction for studying the electrical conductivity properties of a thin film of oxide simultaneously with a determination of catalytic formation of nitrous oxide.

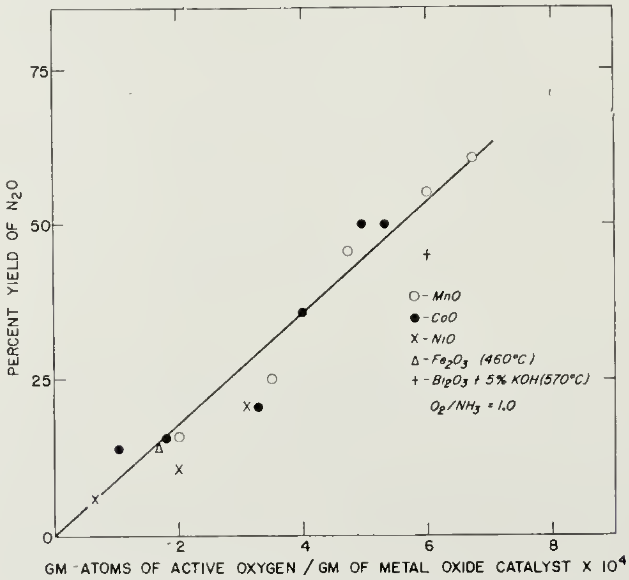


Figure 5. The effect of excess oxygen in the catalyst on the rate of oxidation of ammonia to nitrous oxide.[75] (Reprinted courtesy of the Zeitschrift fur Electrochemie)

In the usual oxidation of ammonia on platinum gauze catalysts, only traces of nitrous oxide form. By use of oxide catalysts, however, von Nagel[133] obtained N_2O in good yields (conversions per pass) at around 300°C. The recent work of Krauss[76] suggests that the oxides of Mn, Ni, Co, Cu, Fe, etc., which contain excess oxygen as defects in the lattice, operate to form N_2O in good yields because of this active oxygen. Krauss measured the active oxygen by a titration procedure and correlated it with the yields of N_2O (conversions per pass) as a function of time of oxidation, type of oxide and $NH_3{:}O_2$ ratio (Figures 5 and 6). By mixing active BaO_2 with inactive CuO, Krauss showed that the yield of N_2O varied with temperature and catalyst composition as in Figure 7. Krauss concluded that oxygen from the gas phase quickly establishes equilibrium with the surface.

$$\tfrac{1}{2}O_2 \leftrightharpoons O\text{ ads.} \leftrightharpoons O^{=}$$

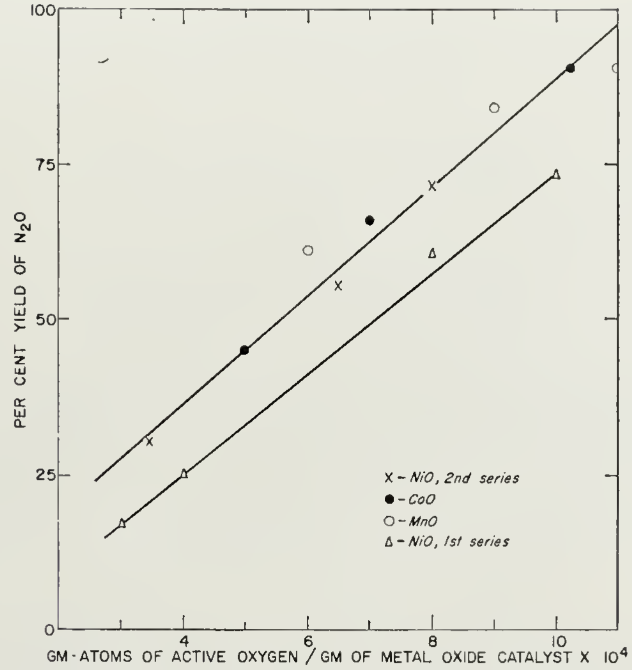


Figure 6. The effect of excess oxygen in the catalyst on the rate of oxidation of ammonia to nitrous oxide.[75] (Reprinted courtesy of the Zweitschrift fur Elektrochemie)

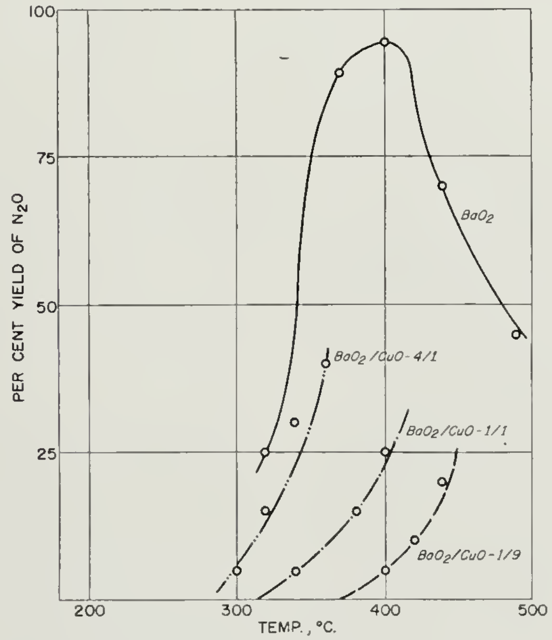


Figure 7. The effect of temperature and catalyst concentration on the oxidation of ammonia to nitrous oxide.[75] (Reprinted courtesy of the Zeitschrift fur Elektrochemie)

The adsorbed oxygen or $O^=$ reacts with either NH_3 or NH_3O

$$NH_3 + O^= \rightarrow NH_3O$$

or

$$NH_3O + O^= \rightarrow HNO + H_2O$$

which in turn reacts as follows with HNO:

$$NH_3O + HNO \rightarrow N_2 + 2H_2O$$

$$HNO + HNO \rightarrow N_2O + H_2O$$

With high concentrations of $O^=$, any NH_3O on the surface tends to react to give HNO. When high concentrations of HNO prevail it reacts to form N_2O. Some HNO reacts with NH_3O to form N_2. With an oxide catalyst it is presumed that any O_2 striking the surface does not react as follows:

$$NH_3O + O_2 = HNO_2 + H_2O \rightarrow NO$$

since little NO is observed, but reacts with the surface to form oxygen atoms or ions. Using the data of Roginskii *et al.*[105], Krauss estimates that a platinum surface has an equilibrium atom concentration of 10^{-15} gram-atoms of oxygen/cm^2, whereas MnO_2 has a concentration of 7×10^{-7} gram-atoms of oxygen/cm^2. The figure for MnO_2 is not readily understood when it is realized that approximately 10^{-9} gram-atoms of oxygen/cm^2 would constitute a monolayer. However, it may well be true that the chemisorbed oxygen atom concentration on MnO_2 is several powers of 10 higher than the concentration on platinum.

Krauss also showed that for MnO, CoO and NiO the equilibrium O concentration in the lattice is proportional to $Po_2^{\frac{1}{2}}$, thus suggesting that the oxygen is adsorbed as atoms. The correlation of these results with the electrical conducting properties determined by Wagner *et al.*[134, 135] was not clearly established. Future work in which active oxygen, electrical conductivity, N_2O yields, etc. are studied simultaneously, preferably on thin films, would be important.

Johnstone and his co-workers[62] have studied the catalytic oxidation of ammonia with air in the presence of rare earth oxides and on a mixture of manganese-bismuth oxides. This work which was carried out in a reactor with a fixed bed catalyst caused oxidation of the ammonia to nitrogen and to nitrous oxide. Experiments were made in the temperature range from 180 to 400°C. The effects of temperature and of the oxygen and ammonia pressures were determined in order to evaluate the kinetics of the reaction.

It was concluded that the rate of oxidation with these oxide catalysts is a function of the amount of active oxygen on the surface of the catalyst. The amount of active oxygen is related to the number of active centers on the catalyst surface. They concluded that the rare earth oxide, Pr_2O_3, contains but few active centers on the surface, thus accounting for the fact that this catalyst requires temperatures of 340 to 380°C to give appreciable reaction of the ammonia. Also, because of the small amount of active oxygen present, the surface is essentially saturated with ammonia and, therefore, the rate is independent of the ammonia pressure and only dependent on the oxygen pressure.

The manganese oxide-bismuth oxide catalyst was active at low temperatures, 180 to 220°C. The reaction rate was dependent not only on the pressure of oxygen but was first order with respect to the ammonia pressure, thus indicating that in contrast with the rare earth oxide catalyst the surface is not saturated with ammonia. The activation energy for the reaction on manganese-bismuth oxide catalyst is 19 kcal/mole while that on the rare earth oxide is 25 kcal/mole. With both catalysts the reaction mechanisms obey a Langmuir-type adsorption-kinetic equation, and there is good evidence that the oxygen is present on the surface as atomic oxygen, the latter being responsible for the oxidation reaction.

When one employs a *p*-type solid catalyst, which contains an excess of oxygen, the latter acts as the active initiator for the oxidation of ammonia. This is consistent with the hypothesis advanced earlier for platinum gauze catalysts that an oxygen atom is the trigger for the oxidation. The manganese-bismuth oxide mixture which Johnstone used is a *p*-type oxide, and thus it is quite active in oxidizing ammonia. With the *n*-type catalyst, however, there is a deficiency of oxygen and an excess of metal. With the praseodymium oxide one is dealing with an *n*-type lattice and the metal is in excess. In this case there is little active oxygen present to accumulate at the surface for initiating the oxidation of ammonia. In this case, therefore, the catalyst is a relatively inactive one as compared with the manganese-bismuth oxide which is the opposite type of semiconductor. From this comparison Johnstone *et al.* concluded that the *p*-type oxides are more active than the *n*-type oxides for the ammonia oxidation.

The oxidation of ammonia in the presence of manganese oxide-bismuth oxide catalyst supported on alumina was studied at low temperature by Johnstone, Batchelor and Shen[63]. Their catalyst was prepared in a form suitable for carrying out studies in a fluidized state, but the experiments were conducted not only with the catalyst fluidized, but also with gas velocities just below incipient fluidization. The rate of oxidation in the range from about 200 to 250°C without fluidization was found to be proportional to the pressure of ammonia and to the amount of oxygen adsorbed in the form of atoms. Appreciable quantities of nitrous oxide as well as nitrogen were formed in the oxidation. With the catalyst under fluidizing conditions, the reaction rate was faster than in the fixed bed at the same space velocity. The activation energy for the reaction, however, was the same for both types of catalyst operation, namely 14.8 kcal/mole. It was concluded also that the reaction rate in a fluidized bed can be divided into two parts: the part that is related only to the chemical kinetics can be predicted from the rate of reaction in a fixed bed; the part that depends on mass transfer conditions in the fluidized catalyst is a function of the gas velocity and is independent of the particle size of the catalyst.

THE SYNTHESIS OF HYDROCYANIC ACID

The partial oxidation of a mixture of methane and ammonia to HCN forms the basis of several large commercial installations both in this country and Europe[67, 100]. The process was first described by Dr. Leonid Andrussow[5] and bears his name.

The reaction

$$NH_3 + CH_4 + 1.5O_2 \rightarrow HCN + 3H_2O$$

is exothermic to the extent of about 115 kcal. The commercial process, which bears much similarity to that for the oxidation of NH_3 to NO, is essentially as described in Andrussow's original patent[5]. The preferred conditions, originally disclosed, describe the passage of a mixture of about 10 to 12 per cent ammonia, 13 per cent methane and 75 per cent air over a fine-meshed wire gauze catalyst consisting of platinum containing 1 to 10 per cent rhodium. At a flow velocity of 200 to 400 l./hr/cm^2 of catalyst (2 to 4 ft/sec linear velocity at 0°C), 60 to 65 per cent of the ammonia fed is converted to HCN with some 25 to 30 per cent remaining unconverted. The remaining 10 per cent of the ammonia is converted to nitrogen. The reaction operates essentially adiabatically and, depending on the detailed reaction conditions, the exotherm is sufficient to bring the reaction temperature to something in the range 900 to 1100°C.

Andrussow's work has been described in greater detail in more recent papers[4, 7]. He states that the best gauzes are those of platinum-iridium (2 to 3 per cent Ir), then those of platinum-rhodium. Those of platinum alone are stated to be inferior. During use, the gauzes tend to recrystallize or form threads on the surface, as in ammonia oxidation[67]. Platinum losses are on the order of 1 g/metric ton of HCN; the life of the gauzes is several months. A 63 per cent conversion of NH_3 to HCN is claimed using a feed stream consisting of 11.2 per cent NH_3, 11.7 per cent CH_4, 0.3 per cent C_2H_6, 15.6 per cent O_2 and 61.2 per cent N_2.

In agreement with the results of Andrussow, Mihail[91] has found that optimum HCN yields are obtained at a methane:ammonia ratio of about 1.0. Mihail summarizes the published data of several authors. There is general agreement that with gauze catalysts, optimum HCN yields of 60 to 65 per cent are obtained with a methane:ammonia mole ratio of 1.05, and an oxygen:ammonia mole ratio of about 1.5. Attendant conversions of ammonia to N_2 of 10 to 20 per cent were reported with the remainder of the NH_3 being unconverted. Reaction temperatures were generally about 1000°C.

Houpt and Smith[58] have reported somewhat higher HCN yields by operating at 2 to 3 atm pressure rather than at atmospheric pressure. Their data are summarized in Table 5.

It has been found[81, 91] that HCN can be produced from CH_4, NH_3, and O_2 in two stages. In the first stage NH_3 is catalytically oxidized to NO and in the second NO and CH_4 are reacted over a supported platinum catalyst to yield HCN. Bond and Harris[81b] found that yields of HCN, based on NO used, of about 60 to 70 per cent could be obtained by passing a methane-NO mixture over a supported Pt-Rh catalyst at about 1100°C and a contact time of a few hundredths of a second.

TABLE 5. EFFECT OF PRESSURE ON HCN YIELDS[58]

Mole Ratio $NH_3:CH_4$ = 0.9–1.0
Mole Ratio $O_2:CH_4$ = 1.2
Gas Velocity (at 0°C) = 51–53.4 cm/sec

Pressure (atm)		1.1	1.9	2.5	3.0
Mole % Conversion of NH_3 to	HCN	62.5	67.2	68.5	64.1
	.N_2	17.9		10.0	

Based on the nitroxyl theory for the oxidation of ammonia, Andrussow[4] suggests that the formation of HCN proceeds through the following sequence of reactions:

$$NH_3 + O_2 \rightarrow NH_3 \cdot O_2 \rightarrow HNO + H_2O$$

$$HNO + CH_4 \rightarrow HNO \cdot H_2CH_2 \rightarrow HN\text{-}CH_2 + H_2O$$

$$HN\text{-}CH_2 \rightarrow HCN + H_2$$

or

$$HN\text{-}CH_2 + O_2 \rightarrow HCN + H_2O.$$

A similar reaction scheme has been proposed by Wendlandt[136]. During operation a portion of the methane is oxidized to CO and H_2O, possibly via H_2CO as an intermediate. The possibility is suggested that some HCN may be formed through the methylenimine intermediate: i.e.,

$$H_2CO + NH_3 \rightarrow H_2CNH + H_2O.$$

The reactions leading to the formation of HCN, like those involved in the oxidation of ammonia to NO, are very rapid, contact times of the reactants with the gauze being on the order of 10^{-4} sec. Accordingly, the over-all reaction rate may be limited to a considerable degree by mass transfer rates to and from the catalyst surface. Andrussow has considered this problem with regard to ammonia oxidation[3, 4]. However, his treatment of the problem suffers certain shortcomings. One of the boundary conditions used in his theoretical analysis of the problem assumes an infinitely rapid reaction at the surface. Experimentally, the apparatus was not such as to assure one of having purely laminar flow in the capillaries and, in addition, temperature control and measurement were quite crude. Thus, while it is not unlikely that these reactions are at least in part mass transfer limited, much work remains to be done to fully describe the details of the rate processes involved.

The use of supported platinum or platinum-rhodium catalysts has also been described in the literature[87, 117] and is known to be in commercial use in certain installations.

Stiles[117] suggests the use of an alumina-zirconia porcelain base, whereas Merrill and Perry[89] recommend the use of natural beryl (beryllium aluminum silicate) coated with platinum or a platinum alloy. Maffezzoni[87] has reported conversions of NH_3 to HCN of 60 per cent with an HCN yield based on NH_3 converted of 85 per cent using a platinum catalyst supported on porcelain, pumice or Al_2O_3. As in work with gauze catalysts, the methane to ammonia mole ratio was about 1.06 with about 11.5 to 13.5 mole per cent NH_3 in the feed gas. With a catalyst bed 40 to 45 mm thick, the gas flow rate was 450 standard liters/hr/cm^2 and the reaction temperature was in the range 1150 to 1200°C.

Luckey *et al.*[85] have claimed higher HCN yields and longer catalyst life by using a platinum-rhodium gauze in combination with a beryl supported Pt-Rh catalyst than with either catalyst separately. HCN yields in the range 68 to 70 per cent are claimed with a useful catalyst life of at least 60 days.

Sasaki[112] has reported HCN yields in the range of 65 to 80 per cent (based on NH_3 fed) in the oxidation of a methane-ammonia mixture over a catalyst of either pure Co_3O_4 or Co_3O_4 mixed with alumina, magnesia or beryllium oxide. Methane and ammonia were fed in roughly equivalent amounts but the oxygen concentration was reduced by diluting the air with approximately an equal volume of nitrogen. The reaction temperature was about 800°C.

Comparable reactions have been reported for the synthesis of nitriles by the partial oxidation of a hydrocarbon-ammonia mixture. Notably, benzonitrile may be synthesized by the partial oxidation of a toluene-ammonia mixture[32]. Similarly, acrylonitrile may be formed by the partial oxidation of a propylene-ammonia mixture[31].

The Catalytic Oxidation of Carbon Monoxide

General Review

The reaction of carbon monoxide with oxygen to form carbon dioxide occurs readily at high temperatures. However, the reaction has been found to be catalyzed at lower temperatures by many oxides. The most active catalysts which include MnO_2, CuO, CoO, and NiO have been found to initiate the reaction as low as room temperature. Mixtures of oxides such as those of nickel, cobalt and iron have been found very effective as multicomponent catalysts. Hopealite is a particularly active 4-component mixture of MnO_2, CuO, Co_2O_3, and Ag_2O[46]. The mixture of 60 per cent MnO_2 and 40 per cent CuO is also a very effective hopealite-type catalyst. Recently the use of $AgMnO_4$ with metallic oxide promoters has received considerable attention.

Katz[66] in 1953 prepared an extensive review of the subject of the heterogeneous oxidation of carbon monoxide. In this summary he presents a detailed review of the literature on different types of catalysts which have been studied for this oxidation and a list of references on the subject. He also describes the use of the so-called kinetics of the adsorption wave theory for evaluating the activity of activated silver permanganate catalyst for carbon monoxide oxidation. This appears to be a useful tool in the scaling up of the design of catalytic converters for this and other heterogeneous reactions.

The simplicity and the wide range of conditions under which it is catalyzed has made this reaction a particularly attractive one for fundamental investigations of oxidation catalysis. Some of these investigations are summarized here with emphasis on the interpretation of results in accordance with recent advances in catalytic theory. A number of recent reviews include detailed information on this subject[12, 35, 55, 98, 119].

Heterogeneous oxidation of carbon monoxide in the presence of an oxide catalyst might possibly occur through one of two general mechanisms: (1) The oxygen and carbon monoxide are chemisorbed on the oxide surface. Reaction occurs in the chemisorbed layer and CO_2 is produced. The carbon dioxide is then desorbed and the process repeated. This mechanism implies that the surface is not greatly changed by the reaction occurring on it. However, it is quite possible that some parts of the surface are much more active catalytically than others. Catalysis under these conditions will be described by the active site theory which postulates that part of the surface is catalytically active all of the time. (2) Another possibility is that when carbon monoxide is chemisorbed it reacts with the surface lattice oxygen. Now, when carbon dioxide is desorbed, the surface is left in a partly reduced state. Oxygen from the gas phase is then taken up to restore the surface to its original condition. Under this mechanism the surface of the solid is an active participant in the oxidation reaction. Oxidation-reduction cycles are continually occurring in the surface region and it is probable that all of the surface is catalytically active part of the time. Oxidation on vanadium oxide is probably one of the clearest examples of this type of mechanism as has been shown by Hughes and Hill[59].

Isotopic exchange experiments utilizing O^{18} have been carried out to investigate under which mechanism catalysis by various oxides operates. Under different sets of conditions both (1) and (2) have been observed. As a general conclusion, reaction occurs in the chemisorbed layer at low temperature, and at high temperature the carbon monoxide actually reacts with the surface lattice oxygen.

Application of semiconductor theory to this system also shows the catalysis to follow certain general rules. The reader should consult the section on Electronic Properties of Oxidation Catalysts for additional information on semiconductor theories. *p*-Type (electron deficient) oxides have been found the most active and initiate the reaction at the lowest temperatures. The *n*-type oxides are active at moderate temperatures and insulators catalyze the reaction only at fairly high temperatures. Electron transfer between the solid and one of the reactants is more probable in the first two cases. This is then apparently important for the reaction to proceed.

Kinetic studies have also emphasized the difference in the high and low temperature reactions when catalyzed by a single oxide. The reaction tends toward first order dependence on oxygen pressure at the lowest temperature and changes to the first order with respect to carbon monoxide pressure at the highest temperature. Also, the activation energy of reaction at low temperature is small (2 to 5 kcal) while it is considerably larger (12 to 20) at higher temperatures.

Comparison of Different Oxides

The catalytic oxidation of carbon monoxide to carbon dioxide over oxide catalysts involves a complicated mechanism which has been explained to a very considerable degree by Garner and his associates[51], as well as others. In a qualitative way, one may arrange the oxide catalysts in the following order of activity. The most efficient catalysts are the *p*-type oxides and these are usually active even below 50°C. The second most active group of oxides consist mainly of *n*-type oxides and these are usually active in the range from 150 to 400°C. Table 6 records the metallic ion in the oxide, the number of unpaired *d*-electrons in the metallic ion, the order of activity and the type of semiconductor involved.

At low temperatures the *n*-type oxides shown in Table 6 do not adsorb appreciable amounts of oxygen external to the lattice. In the presence of carbon monoxide, however, there is a transfer of electrons from the carbon monoxide to the catalyst, and hence carbon monoxide is chemisorbed on the surface. Under the influence of the carbon monoxide one has the formation of a carbonate ion taking place as shown in the following reactions:

$$O_2 + 2(e) \rightleftharpoons 2O^-$$

$$CO(\text{gas}) + 2O^-(\text{ads.}) \rightleftharpoons CO_3^=(\text{ads.})$$

$$CO_3^=(\text{ads.}) \rightleftharpoons O^= + CO_2$$

TABLE 6. THE CATALYTIC ACTIVITY OF OXIDES FOR THE OXIDATION OF CARBON MONOXIDE

Metallic Ion in Oxide	Unpaired *d* Electrons	Order of Activity	Electronic Type
Co^{+2}	3	Below 150°C	*p*
Cu^{+1}	0	“	*p*
Ni^{+2}	2	“	*p*
Mn^{+4}	3	“	*p*
Cu^{+2}	1	150–400°C	intrinsic semiconductor
Fe^{+3}	3	“	*n*
Zn^{+2}	0	“	*n*
Ce^{+4}	0	“	insulator
Ti^{+4}	0	“	*n*
Cr^{+3}	3	“	*p*-intrinsic semiconductor
Th^{+4}	0	“	
Zr^{+4}	0	“	
V^{+5}	0	“	*n*
Hg^{+2}	0	“	
Al^{+3}	0	“	insulator

Further different formulations of the reaction scheme shown above have been postulated by Hauffe[55]. Winter[138] has used the isotopes of oxygen and carbon to study the exchange reactions of carbon monoxide, carbon dioxide and oxygen with oxide catalysts, and subsequently the reaction of carbon monoxide with oxygen at these oxide surfaces. He formulates the reactions of carbon monoxide and oxygen slightly differently than proposed by Garner, indicating that the reactions may not be as simple as originally proposed by Garner and his associates. For example, Winter proposed the following reaction scheme for the carbon monoxide oxidation:

$$CO(\text{gas}) + 2O^=(\text{ads.}) \rightarrow CO_3^= + 2(e)$$

$$CO_3^= + O_2(\text{gas}) + 2(e) \rightarrow CO_2(\text{gas}) + 2O^=(\text{ads.}) + O(\text{ads.})$$

$$O(\text{ads.}) + 2(e) \rightarrow O^=(\text{ads.})$$

and, further the second step may involve

$$O_2(\text{gas}) + 2(e) \rightarrow O^= + O(\text{ads.})$$

$$CO_3^= \rightarrow CO_2(\text{gas}) + O^=(\text{ads.})$$

It is apparent that under certain conditions a complicated series of reactions involving chemisorption of the different products and/or reactants on the surface may possibly occur, as well as the reaction of the adsorbed gases with gases from the gas phase or on the surface, and further oxygen ions and electrons may be involved in the surface of the catalyst. It is not implied by these statements that all the permutations and combinations of these reactions are always possible, but it appears that detailed studies of the reactions are beginning to indicate that all of the possible reactions may be involved under certain conditions, as illustrated by Winter. In the case of nickel oxide, for example, which is a *p*-type conductor, a reaction may take place between chemisorbed oxygen external to the lattice and carbon monoxide to form say a carbonate ion which then poisons the surface. At 150 to 200°, however, the mechanism of the reaction may change due to the fact that the carbon monoxide may begin to attack the surface and produce anionic vacancies as occurs with *n*-type oxides. Also at this temperature, CO_2 begins to be desorbed so that it no longer acts as a poison. In this case the mechanism and kinetics of the reaction change. This type of change has been observed by Parravano and Boudart[98] where they obtained an activation energy of 2 to 3 kcal/mole at low temperatures, and 14 kcal at high temperatures.

Winter[139] in a recent excellent review of the reactions of oxygen with oxides presents detailed information and interpretation of his work on the interaction of oxygen with oxide surfaces. He discusses the oxidation of CO with O_2 on such surfaces and, in general, the mechanisms presented are similar to those which are reviewed in this section, although many details of the effects of oxide preparation, pretreatment, surface coverage, etc., are given. It is always of interest to note the differences in conclusions reached by several investigators due to these troublesome factors. Winter (Ref.[139], p. 210) also summarizes important information on the energetics of oxygen adsorption.

Reaction on Copper, Nickel and Chromium Oxides

Garner and his associates have been responsible for the principal studies of the oxidation of carbon monoxide on copper oxides and on cuprous oxide in particular[49, 50, 51]. They studied the oxidation of CO on crystalline Cu_2O over a range of temperatures, and also the electrical conductivity of the catalyst and the adsorption of CO, CO_2 and O_2 over a wide range of conditions. A brief summary of the results of these studies will assist in an explanation of the conclusions reached on the nature of this reaction at the catalytic surface.

Garner *et al.* measured the chemisorption of O_2 and CO on the same Cu_2O crystals. By use of electrical conductivity measurements it was found that the chemisorption of O_2 was faster (100 to 270°C) than the oxidation of Cu_2O to CuO. This indicated that the O_2 was adsorbed as a boundary layer and not throughout the lattice. It was also concluded from the kinetic results that the chemisorbed O_2 was more reactive for CO oxidation than O_2 incorporated in the Cu_2O lattice.

At room temperature, Garner, Stone and Tiley[51, 118] found that the adsorbed CO molecules reacted with chemisorbed oxygen atoms in the Cu_2O surface with the formation of CO_2 molecules. At 20°C the chemisorption of CO was reversible, or at least it could be completely desorbed by heating, and was faster than the chemisorption of O_2. This would make the kinetics nearly independent of P_{CO} and dependent on P_{O_2}.

On a clean surface of Cu_2O the adsorption of CO_2 is not appreciable, but, if the Cu_2O surface holds chemisorbed O_2, then the CO_2 reacts and is chemisorbed. Hauffe[55] reports that Garner *et al.* have suggested a mechanism involving a CO_3^- complex. Further work of the type reported by Eischens[39] (see below) may permit a decision between the alternatives. The mechanism favored by Hauffe is as follows:

$$(e) + \tfrac{1}{2}O_2(\text{gas}) \rightarrow O^-(\text{ads.})$$

$$CO_2(\text{gas}) \rightarrow CO_2^+(\text{ads.}) + (e)$$

$$CO_2^+(\text{ads.}) + O^-(\text{ads.}) \rightarrow CO_3(\text{ads.})$$

In a *p*-type semiconductor, such as Cu_2O, a transfer of electrons from the solid to an adsorbed gas such as O_2 results in an increase in the number of "positive holes" which are the current carriers. Garner *et al.* found that the electrical conductivity of Cu_2O was actually increased by adsorption of O_2 thus indicating the correctness of the reaction $(e) + \tfrac{1}{2}O_2(\text{gas}) \rightarrow O^-(\text{ads.})$ or $O^=$. Conversely, it was found that adsorption of CO on the Cu_2O decreased the conductivity thus indicating transfer of electrons from the CO to the Cu_2O.

$$CO(\text{gas}) \rightarrow CO^+(\text{ads.}) + (e)$$

The two reacting gases thus transfer electrons in opposite directions. It is a possible hypothesis that the adsorption of carbon monoxide might transfer the electron to the Cu_2O, the electron might move through the lattice and create a defect at the surface for adsorption of oxygen as an ion. Changes in electrical conductivity have been observed with other catalytic oxides, the direction of the change depending on the nature of the semiconductive properties of the solid. For the best catalyst one might imagine that the degrees and energies of exchange might have to correspond closely as suggested by Dowden[37].

The final form of the mechanism suggested by Garner was as follows:

$$\tfrac{1}{2}O_2(\text{gas}) + (e) \rightarrow O^-(\text{ads.})$$

$$2O^-(\text{ads.}) + CO(\text{ads.}) \rightarrow CO_3^=(\text{ads.})$$

$$CO_3^=(\text{ads.}) + CO(\text{ads.}) \rightarrow 2CO_2(\text{gas}) + 2(e)$$

With oxides other than Cu_2O, for example CuO, Cr_2O_3 and ZnO, one may adsorb O_2 up to a ratio of $\tfrac{1}{2}O_2{:}CO$ to form a complex. On CuO, for example,

$$CO + 2O^= + 2Cu^{+2} \rightarrow CO_3^= + 2Cu^+$$

Oxygen is then adsorbed

$$\tfrac{1}{2}O_2 + 2Cu^+ \rightarrow 2Cu^{+2} + O^=$$

and the net over all reaction is

$$CO + \tfrac{1}{2}O_2 + O^= \rightarrow CO_3^=$$

This illustrates the formation of the $CO_3^=$ complex in CO oxidation. Although the idea of formation of a $CO_3^=$ complex is old, the use of modern methods in strengthening the basis for concluding that such an intermediate is formed has advanced the art greatly. The work of Eischens in identifying surface complexes on NiO with CO and CO_2 by infrared will be referred to later, but application of such methods on the other types of catalysts, especially Cr_2O_3 and Cu_2O, would be desirable.

Parravano and Boudart[98] studied the CO oxidation over NiO and concluded that there is (a) a low temperature region where the rates of oxidation are high and irreproducible and (b) a higher temperature region where the rate is reproducible.

$$\text{Region (a), rate} = k(P_{O_2})^{0.5}(P_{CO})^{0.5}$$

$$\text{Region (b), rate} = k(P_{O_2})^{0.2}(P_{CO})$$

If the slow step is the removal of adsorbed O atoms by CO striking the surface, the high temperature rate equation (b) is obtained. In the low temperature region the reaction appears to involve adsorbed carbon monoxide with adsorbed oxygen, thus leading to the equation (a) shown above. The explanations advanced do not appear to be convincing proof that there are two kinds of O_2 adsorption as postulated by Parravano and Boudart. The authors suggest that the lack of reproducibility of catalytic behavior might indicate that impurities or diffusion phenomena are involved, which would make theoretical treatment of data difficult, if not impossible. The recent infrared data of Eischens *et al.*[39] indicate that NiO prepared from $NiNO_3$ contains Ni—O—N=O and hence if one were to prepare Ni or NiO catalysts by low temperature methods subsequent reactions on the surface might appear to be unusual in the presence of this complex. Parravano and Boudart consider that the low temperature oxidation involves O_2 chemisorbed in a way which does not involve transfer of electrons from the solid; the high temperature region does involve oxygen coupled with electrons supplied by the lattice. These we have referred to earlier as $O^=$ or $O_2^=$, etc.

At high temperatures the rate $= kP_{CO}P_{O_2}^{0.2}$, involves O_2 bound in the lattice by electron exchange. As a result of the work of Verwey, Wagner, etc., it was postulated by Parravano and Boudart[98] that the addition to NiO of impurities of higher and lower valence than +2 should influence the electronic structure of the NiO lattice and thus alter its catalytic behavior. Also, such influence on catalytic activity might then be correlated with current theories on electrical conductivity. In the low temperature region where Parravano postulated that there was no electron transfer from lattice to O, addition of impurities had little influence, which is as predicted. In the high temperature region, however, addition of impurities affected the activation energy of the reaction as shown in Table 7. Since addition of impurities with valence higher than two decreases the activation energy for the CO oxidation, one may conclude that the impurities affect the transfer of electrons from lattice to O_2 and hence oxygen ions are involved in the slow reaction step. This is in agreement with the kinetic analysis that the mechanism involves reaction of adsorbed O_2 with CO striking from the gas phase, thus leading to the kinetic equation

TABLE 7. ACTIVATION ENERGIES FOR CARBON MONOXIDE OXIDATION ON NICKEL OXIDE CATALYSTS[98]

Catalyst	Temp. (°C)	Activation Energy (kcal/mole)
NiO + 0.01 mole % WO_3	180–220	6.5
NiO + 0.01 mole % Cr_2O_3	160–220	7.9
NiO + 1 mole % $NiCl_2$	160–220	8.2
NiO + 0.01 mole % CeO_2	160–220	8.9
NiO	180–250	13.7
NiO + 0.01 mole % Ag_2O	180–250	14.9
NiO + 1 mole % Ag_2O	225–260	17.5
NiO + 0.01 mole % Li_2O	230–280	18.0

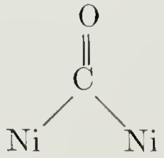
$$\text{rate} = kP_{CO}P_{O_2}^{0.2}$$

Schwab and Block[113] studied the oxidation of carbon monoxide on nickel oxide, and on mixtures of nickel oxide with other metal oxides with higher and lower valence. Their results in several cases were just the opposite of those shown by Parravano and Boudart (Table 7). The former authors[113] explain this by suggesting that their work was done at higher temperatures where the mechanism is different from that at the low temperatures employed by Parravano. Keier, Roginskii and Sazaonova[69] have studied in a similar way the effects of additives in the oxidation with results as shown in Table 8. These results appear to confirm those of Parravano and Boudart. A restudy of this interesting problem is needed with special care being taken to remove all traces of impurities from the catalysts since these might be responsible for the remarkably different results observed by the different investigators.

Eischens and Pliskin[39] have developed a new technique for study of catalytic reactions in which the infrared spectrum of a gas is determined while it is adsorbed on the catalyst before, during and after operation at catalytic conditions. With CO on Ni he arrived at the tentative conclusion that this gas forms the following bridge structures:

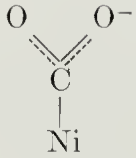
TABLE 8. ACTIVATION ENERGIES FOR CARBON MONOXIDE OXIDATION ON NICKEL OXIDE CATALYSTS[69]

Catalyst	Activation Energy (kcal/mole)
NiO	4.5
NiO plus up to 50 mole % MgO	4.5
NiO plus up to 0.82 mole % Li_2O	4.5–17.6
NiO plus Li_2O, plus 0.82% Fe_2O_3	17.6–4.5
NiO plus Cr_2O_3	4.5



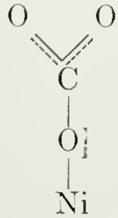
and Ni-C≡O

With CO_2 on nickel, a carboxylate ion structure was observed:



and at high enough temperatures this ion lost an O$^-$ and the reaction Ni-CO$_2^-$ → NiC≡O + O$^-$ took place. O$^-$ diffused into the Ni lattice.

With CO_2 on nickel oxide a bicarbonate ion is formed.



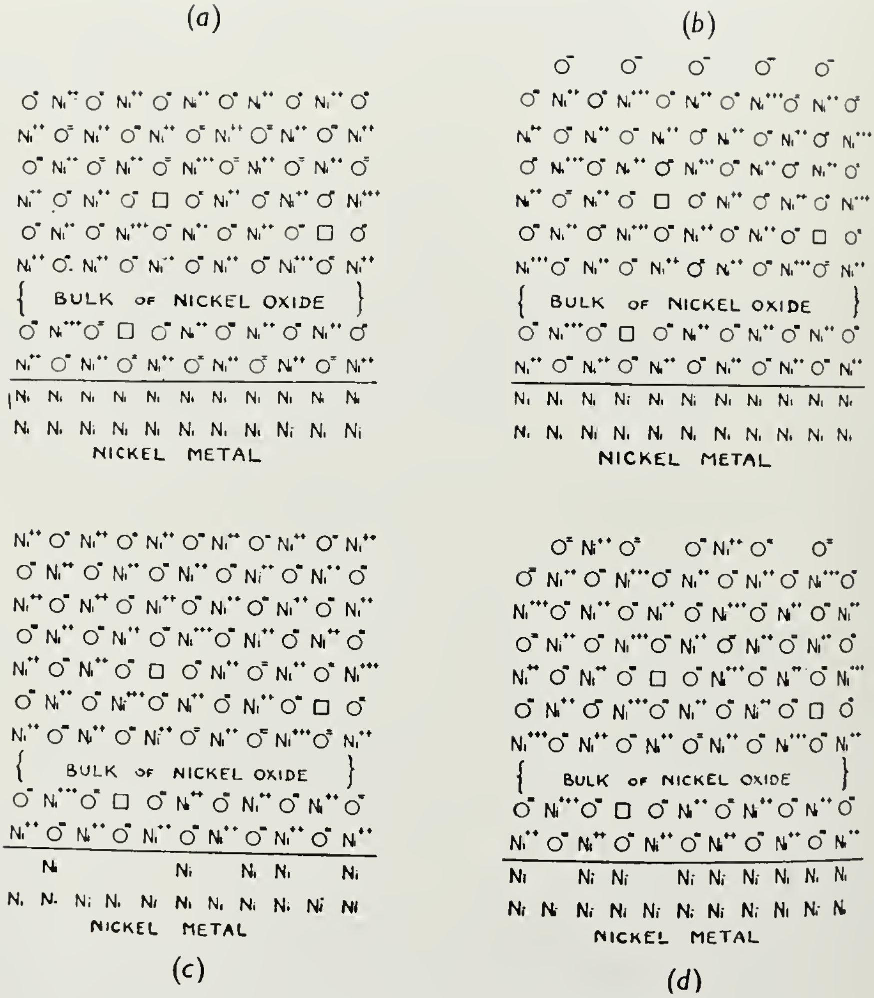
Dell and Stone[36] postulate a mechanism for the oxidation of CO on NiO based on their kinetic studies which suggests the formation of CO_3^- ion, but the work of Eischens and Pliskin[39] failed to substantiate this mechanism since he was unable to find the $(CO_3)^-$ ion under any conditions proposed by Dell and Stone. Although the mechanism is in doubt at present, it is evident that further use of these new techniques will assist in the development of a better understanding of the catalytic processes involved.

During the reaction of CO and O_2 on Ni-NiO catalyst, Eischens observed a band at 4.56μ which he attributes to a surface complex formed in the reaction. The structure of the complex suggested by Eischens was Ni-O-C-O. It is observed when NiO is reduced by CO at 200°C and at 25°C over nickel when oxygen is admitted prior to CO and when O_2 and CO are admitted simultaneously. When O_2 is admitted prior to CO, the spectrum of the adsorbed species is that of the bicarbonate structure shown above.

A more recent review of the infrared spectra of adsorbed molecules by Eischens and Pliskin[40] gives further details of the probable structure of adsorbed CO and CO_2 complexes on metals and metallic oxides (Pd, Pt, Fe, Cu, Ni). The interpretation is complicated by the effects of catalyst preparation, other gases, temperature, etc., but undoubtedly these studies will contribute to a more complete understanding of the mechanisms described in this section.

As discussed above, Parravano and Boudart concluded from their work on NiO catalysts for CO oxidation that there are two forms of chemisorbed oxygen, one of which does not involve electron transfer between the lattice atoms and oxygen. This mobile form of oxygen is presumed to be similar to that observed by Garner, Gray and Stone in their studies of oxygen adsorption on Cu_2O films.

The mechanism of the oxidation of CO on nickel oxide is similar in many respects to that involved in copper oxide catalysts. The recent paper of Dell and Stone[36] describes the mechanism in detail which they support with measurements of heats of adsorption of CO, CO_2 and O_2 on nickel oxide. They also gave a pictorial representation of certain steps in the mechanism of incorporation of oxygen in a nickel oxide lattice, which is reproduced in Figure 8.



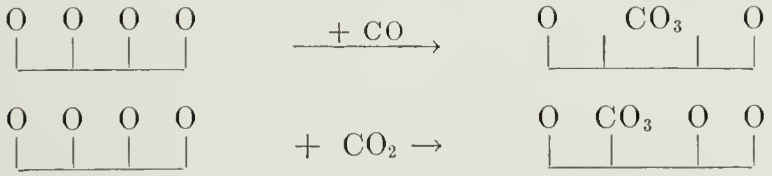
Diagrammatic Representation of the Chemisorption of Oxygen

Figure 8a illustrates an oxide layer on nickel with a surface free from chemisorbed gas. Chemisorption of oxygen on this layer at 20°C. leads to the state shown in Figure 8b, where the positive holes produced (here represented as Ni^{3+} ions) are distributed in the surface region. On heating, this chemisorbed gas is removed by "incorporation". If the temperature of baking-out is sufficiently high, nickel atoms from the underlying metal pass into the oxide layer and diffuse as ions via cation vacancies or grain boundaries to the surface. The electrons from these atoms reduce the surface Ni^{3+} ions to Ni^{2+} and the adsorbed oxygen becomes incorporated as O^{2-}, due to nickel ions occupying sites between the adsorbed oxygen. The surface is completely regenerated (Figure 8c) and the same number of sites is available for adsorption as in Figure 8a. At lower baking-out temperatures, regeneration is less complete. Figure 8d illustrates the case where only two adsorption sites are regenerated, compared with six in Figure 8c. Furthermore, the concentration of Ni^{3+} ions in the surface region after the low-temperature treatment is much higher. (Reprinted by Permission of The Faraday Society)

The heats of adsorption (studies of Dell and Stone) show that the following comparison between cuprous oxide and nickel oxide catalysts is obtained:

	Heats of Adsorption (kcal/mole)	
	Cu_2O	NiO
$CO(g) + O_2(g) = CO_3$ ads.	+116	+127
$CO(g) \rightarrow CO$ ads.	+20	+26
$2CO(g) + O_2(g) = 2CO_2(g) + 135$ kcal		
Therefore, CO ads. + CO_3 ads. = $2CO_2(g)$	−1	−18

From the above thermal equations it is evident that carbon dioxide is fairly strongly adsorbed on nickel oxide and, consequently, it serves as a poison for the catalytic oxidation of carbon monoxide. This probably accounts for the fact that Parravano and Boudart observed a change in the kinetics at around 150°C. Above this temperature the carbon dioxide was desorbed rapidly enough to eliminate it as a poison for the reaction. Dell and Stone also show that the carbonate ion, $CO_3^=$, is stable in the presence of carbon monoxide or oxygen and hence conclude that it cannot be an intermediate in the oxidation reaction. This indicates that the mechanism for the oxidation on nickel oxide is not the same as on the copper catalyst. It was also concluded that this CO_3 complex does not decompose at 220°C but does break down at 350°C. (It is for this reason that the pretreatment of the nickel oxide catalyst can be a determining factor in its subsequent behavior when used for kinetic studies.) Finally, it is of interest to note that when CO reacts with oxide ions on the surface it forms $CO_3^=$ and liberates one vacant site on the surface, whereas carbon dioxide reacts without formation of a free site.



All of these factors obviously complicate the problem of studying these reactions as a function of different temperatures and different pretreatments.

Winter carried out a series of experiments on the exchange reactions of oxygen with solid oxides, and in one of this series[138] he described experiments on the reactions of carbon monoxide, carbon dioxide and oxygen on cuprous oxide, nickel oxide, and chromium oxide catalysts. On nickel, the reaction proceeded with an apparent activation energy of 5.5 kcal, but for chromium oxide the activation energy was essentially zero. With both these catalysts the rate of carbon dioxide formation was dependent on the carbon monoxide pressure and inhibited by carbon dioxide. Using O^{18}, Winter showed that the reaction probably proceeds on a small fraction of the surface oxygen sites probably of the order of less than 2.5 per cent. The carbon monoxide removes a surface oxygen ion from the surface which is then rapidly replaced by oxygen from the gas phase. The rate-determining step on nickel and chromium oxides appears to be the reaction of oxygen gas with electrons in the surface to form a doubly charged oxygen ion and an adsorbed oxygen atom. Carbon monoxide, carbon dioxide, and oxygen exchange but little with the surface oxygen ions at temperatures of interest in the oxidation studies. The oxidation reaction on cuprous oxide proceeds by the same mechanism. In contrast with the other two catalysts there was a ready exchange of oxygen between the two oxides of carbon and the surface oxygen ions on copper oxide. The oxidation reaction has an apparent activation energy of 10 kcal and the exchange reactions with carbon monoxide and carbon dioxide have activation energies of 10 and 4 kcal, respectively. In further contrast with the chromium and nickel oxides the oxidation reaction proceeds on 10 to 40 per cent of the surface sites; the proportion increasing with rising reaction temperature. By using both C^{13} and O^{18} it was shown that no exchange of carbon occurred between carbon monoxide and carbon dioxide on the catalyst surface.

Turovskii and Vainshtein[124] also described the oxidation of carbon monoxide with oxygen on chromium oxide catalysts in which O^{18} was used to obtain information on the mechanism of the reaction. From their studies it was concluded that the alternate oxidation and reduction of the catalyst is not involved as a mechanism in the oxidation of the carbon monoxide, since oxygen exchange with the surface was not observed. This result appears to be contradictory to that obtained by Winter and undoubtedly might have arisen from differences in reaction conditions which are obviously of importance in such studies of exchange and oxidation. This points out, however, that careful defintion of conditions is obviously required to permit comparison between results and conclusions of different investigators. This may be emphasized by noting that in the recent work of Voltz and Weller[131] they found that in reducing Cr_2O_3 catalyst, hydrogen was strongly adsorbed and formed water subsequently when oxidation of CO on the reduced catalyst was studied. The latter was strongly held and affected the kinetics.

A recent paper of Lyashenko and Stepko[86] describes a new method of relating the work function and conductivity of copper oxides with catalytic activity. In this work the authors measured the change of conductivity and of the work function of thin layers of copper oxide as a function of temperature and during the adsorption of carbon monoxide, carbon dioxide, oxygen, and mixtures thereof. The temperature of the thin film was varied from 20 to 225°C and over this temperature range the conductivity and work function were measured. The curve of temperature *vs.* work function showed a marked change and the straight line relationship between conductivity and temperature also gave a sharp break which could be correlated with the onset of catalytic oxidation. Apparently catalysts which were not active in the oxidation did not show similar changes in the two electrical properties so that this appears to be an interesting method for studies of catalytic reactions. It should be possible in a detailed study of this reaction to carry out such electrical measurements in conjunction with kinetic measurements and oxygen exchange experiments so that the entire mechanism of the reaction can be worked out in detail and with considerable validity.

Oxidation on Manganese Dioxide

Early work on the oxidation of carbon monoxide was carried out by Benton[14] on manganese dioxide, and it was proposed that the mechanism involved the alternate oxidation and reduction of the active oxide catalyst. A series of Russian papers[41, 64, 65, 106, 107, 127] up to 1940 suggested that Benton's scheme for the reaction was inadequate. Several other Russian papers[65, 104, 108] have appeared in the meantime, and the latest of these summarizes the most recent information on this reaction in the presence of manganese dioxide and is cited since it will serve to indicate the value of the use of the O^{18} isotope as a means of studying catalytic reactions of this type.

In this most recent paper by Vasil'ev, Elovich and Margolis[129] the oxidation was carried out on active manganese dioxide at temperatures of the order of 20°C. O^{18} was used to determine the rate of exchange of oxygen, carbon monoxide and carbon dioxide with the manganese dioxide catalyst. Likewise, the kinetics of the reaction was studied by the usual static procedures. The kinetics of the exchange of CO_2 with the manganese dioxide was found to obey a first order law with a rate constant of 0.0020 min.^{-1}. The reduction of the surface by carbon monoxide showed a first-order reaction kinetics with a rate constant of 0.0027 min.^{-1}. The reaction of carbon monoxide with oxygen took place at the surface with a reaction kinetics obeying a first order law with a rate constant of 0.0215 min.^{-1} when the surface of the manganese dioxide was reduced about 5 per cent. These rate constants indicate that the rates of exchange and reduction of the surface are approximately equal, while the reaction rate constant for the oxidation is a power of 10 larger. Thus, the kinetics and isotopic data suggest that it is impossible to explain the mechanism of this oxidation on manganese dioxide at low temperatures by processes involving the alternate reduction and oxidation of the surface. These authors suggest that when the reaction is conducted at a higher temperature it may be possible that the relationship between the rates of the individual stages and reactions may be different in character.

It should be noted, however, that Vasil'ev, *et al.* have based their conclusions on adsorption experiments carried out with the single components which are then compared with the reaction in the presence of both components. Since the adsorption of oxygen and carbon monoxide influence each other and thus influence the rates of adsorption of the single components, it is possible that when both gases are present the adsorption rate constants found for each single gas alone may no longer hold. Therefore, the conclusions reached by these authors that their data show that the mechanism does not involve alternate oxidation and reduction may be in error.

Vainshtein and Turovskii[124, 127], however, performed similar work with heavy oxygen in the reaction of carbon monoxide with air on a manganese dioxide catalyst in which they found that there was little exchange between the catalyst containing O^{18} and a mixture of CO in air or CO_2 in air provided water was carefully excluded from the reaction system. These authors concluded that the reaction involves not merely a fraction of the surface of the manganese dioxide but its main mass.

It would seem desirable to extend the more detailed and extensive methods of Winter[138] (see p. 314) to the manganese dioxide system in order to determine more of the details of the reactions which are taking place with this interesting catalyst. There is also need for studies of not only the oxygen exchange but some of the electrical properties in connection with manganese dioxide catalysts. As in the case of reactions on nickel, chromium and copper oxides the findings of kinetic studies vary greatly depending on the pretreatment of the catalyst. In a recent study of MnO_2 for CO oxidation Shurmovskaya and Bruns[116] state that the rate increases with temperature in part at least due to desorption of water from the lattice as the temperature is increased.

Oxidation on Zinc Oxide

Keier and Chizhikova[71] studied the oxidation of carbon monoxide on (a) zinc oxide, (b) zinc oxide containing 0.5 to 1.2 atom per cent lithium and (c) zinc oxide with 1 atom per cent gallium. They found (1) the addition of Li increases the activation energy of conductivity of the zinc oxide, (2) the adsorption of oxygen decreases the conductivity by lowering the concentration of free electrons, (3) the addition of Li represses the adsorption of CO and its reaction with ZnO, and (4) the activation energy of CO oxidation on ZnO is increased by addition of Li, but is essentially unaltered by Ga. It was concluded that the mechanism of oxidation on ZnO is similar to that on NiO. The addition of Li affects the electron exchange properties of the zinc ions which are present as interstitial defects in ZnO, thus effectively decreasing the concentrations of free electrons. The results are interpreted to account for the effects of impurity addition which are referred to above. The oxygen adsorption, without being the rate-limiting step in the oxidation, exerts a considerable influence on the stage which determines the oxidation rate. This may be either the CO adsorption or the interaction of adsorbed oxygen with the CO from the gas phase. In the latter case, the increase in the activation energy of this interaction with an increase of lithium concentration leads to a decrease in the reaction rate.

Oxidation on Vanadium Oxide

Hughes and Hill studied the oxidation of CO on vanadium oxide[59]. Their results led to the following mechanism:

$$\text{Adsorption of CO: VO + CO} \rightarrow \text{VOCO}; \Delta E = 28.4 \text{ kcal}$$

$$\text{Desorption of CO}_2\text{: VOCO} \rightarrow \text{V + CO}_2; \Delta E = 6.2 \text{ kcal}$$

$$\text{Oxidation of V: V} + \tfrac{1}{2}\text{O}_2 \rightarrow \text{VO(fast)}$$

Under certain assumptions this mechanism leads to the following rate equation:

$$\text{rate} = k_1 P_{\text{CO}}/(1 + k_2 P_{\text{CO}})$$

which is consistent with their results which showed no effect of P_{CO_2} and P_{O_2} on the rate. It is likely that V_2O_5 would be a good catalyst to work with in studying simultaneously rates of reaction, O^{18} exchange, etc. As a word of caution, the authors of this chapter[1] have observed strong chemisorption of NH_3 on V_2O_5 prepared by NH_4VO_3 decomposition, thus leading to peculiar effects on subsequent adsorption studies of O_2 on this V_2O_5.

Magnetic Properties of Oxides for Carbon Monoxide Oxidation

The work of Mooi and Selwood[92] described the activity of a series of oxide catalysts made from manganese dioxide, copper oxide and iron oxide supported on γ-alumina for the oxidation of carbon monoxide at a series of concentrations of the active oxide on the alumina. Selwood at an earlier date had studied the effect of degree of dispersion or concentration on the magnetic susceptibilities of these oxides and consequently attempted to relate the magnetic susceptibilities to the activity for carbon monoxide oxidation. Table 9 shows the pertinent data obtained by Mooi and Selwood on this reaction for the three oxides in question. The second column shows the weight per cent of metal on the γ-alumina.

As the percentage of active oxide on the catalyst decreased, its degree of dispersion increased and the specific activity increased. (The specific activity was the activity after dilution with the γ-alumina to a standard concentration of metal on the aluminum oxide.) At a low concentration of the active oxide on the alumina, the activity passed through a maximum and then decreased as the concentration of oxide on the alumina decreased further. The increase in dispersion which occurred on decreasing the oxide concentration on the alumina had been shown by Selwood by means of earlier magnetic susceptibility measurements. That is, the degree of dispersion determines the magnetic susceptibility, and also the catalytic activity.

The maximum in the catalytic activity curve is not easily explained, but Selwood believes that at a very low concentration the oxide molecules are not grouped together sufficiently so that alternate oxidation and reduction of the active oxide is feasible. Thus, for example, with manganese dioxide the oxidation and reduction of the catalyst would be as follows:

TABLE 9. ACTIVATION ENERGIES FOR OXIDATION OF CO OVER OXIDE CATALYSTS

Catalyst	Wt. % Metal on γ-Al_2O_3	Temp. Range (°C)	Activation Energy (kcal/mole)
MnO_2	0.79–21.5	180–300	25.0 ± 0.4
Fe_2O_3	0.5 – 7.1	210–340	30.0 ± 0.5
CuO	0.5 –20.3	170–250	26.5 ± 0.6

$$2Mn_2O_3 + O_2 \rightleftharpoons 4MnO_2$$

Unless four manganese atoms are grouped together on a catalyst this reaction cannot take place. The activity of the catalyst should begin to decrease at the concentration where the number of quadruplets begins to fall. It was shown by Mooi and Selwood that the maximum in the activity curve was not due to solid solution of manganese in the aluminum oxide. They proved this point by carrying out proton relaxation studies on the catalyst as a function of manganese dilution. These measurements showed that the manganese was always on the surface. It would obviously be of interest to carry out exchange reaction studies with carbon monoxide, carbon dioxide and oxygen on the same catalysts as tested by Mooi and Selwood in order to relate these exchange reactions to Selwood's magnetic susceptibilities and other types of measurements on these catalysts.

Oxidation on Silver and Palladium Catalysts

Schwab and Gossner[114] have studied the oxidation of carbon monoxide on (1) silver, (2) palladium, and (3) silver-palladium alloy catalysts. The activation energies were determined by a dynamic method and the kinetic results were obtained in a static apparatus.

The activation energies were as shown in Table 10.

The velocity of the oxidation on palladium follows the rate equation

$$v = \frac{k \times P_{O_2}}{P_{CO}}$$

On the other hand, on silver catalysts, the rate is given by $V = kP_{CO}P_{O_2}$.

In the case of metallic silver, all of the 4*d* electronic orbits are filled, whereas only half of the 5*s* orbits are occupied. In the case of palladium, however, as compared with silver, there is one less 4*d* electron and the 5*s* electron is now in part in the 4*d* band. According to Pauling's theory of metals the *d* band in palladium is not completely filled and about 0.55*d* orbits are unfilled. Therefore, when one adds palladium to silver to make the silver-palladium alloy referred to above as a catalyst the number of *s* electrons decreases. Likewise, when one adds silver to palladium the *d* band deficiency of the palladium decreases. With the alloy consisting of 95 per cent silver and 5 per cent palladium, only about 95 per cent of the *s* band is filled.

TABLE 10. CARBON MONOXIDE OXIDATION ACTIVATION ENERGIES FOR Ag, Pd CATALYSTS

Catalyst	Temp. (°C)	Activation Energy (kcal/mole)
Ag	400–530	13.9
Pd	250–320	22.2
95 Atom % Ag- 5 Atom % Pd	300–450	11.6

Schwab and Gossner[114] are able to explain their results by assuming that in the case of silver the *s* electrons are transferred upon adsorption from the *s* shell to the oxygen. On the other hand, with palladium, the *s* shell contains comparatively few electrons, there are few available for transfer to the oxygen and adsorption of this gas is weak. The adsorption of carbon monoxide takes place by transfer of an electron from the carbon monoxide to the metal in the event that there are some unfilled levels in the *d* band. Since the silver and silver alloy contain but few vacancies, the adsorption of carbon monoxide on the two silver catalysts was very weak, as predicted by the theory. Also, the theory predicts that with palladium where there are *d* vacancies, the adsorption of carbon monoxide should be much stronger than on silver. Such was the case.

The classic rate equations developed by Langmuir for reaction of two gases would predict that the velocity is proportional to the product of the concentration of the two gases when they are weakly adsorbed, which is the case for silver and the silver-palladium alloy. On the other hand, the

Langmuir equations would predict that the rate would be proportional to the oxygen and inversely proportional to the carbon monoxide pressure in the event that the oxygen is weakly adsorbed and the carbon monoxide strongly adsorbed. This agrees with experiment. The picture developed from knowledge of the electronic structure of the metals leads to a correct prediction of the gas adsorptions and the rate equations which are quite satisfactory.

Miscellaneous Effects in Carbon Monoxide Oxidation

In this section mention will be made of certain effects reported in the literature which are of special interest in this oxidation reaction.

Keier and Roginskii[70] report that the activity of a nickel oxide catalyst prepared from nickel carbonate varies with the CO_2 pressure over the $NiCO_3$ during decomposition of the latter. If the CO_2 pressure is lower, the subsequent catalytic activity is greater. It is likely that the important factor might be the effect of CO_2 pressure on particle size of the NiO, but no results are quoted.

On quartz at high temperatures, Kondo and Toyama[73] report the rate-determining step in carbon monoxide oxidation is the bimolecular reaction of CO and O_2. The reaction is retarded by water and by CO_2 as in the case of the reaction on NiO and MnO_2. The reaction of mixtures of H_2 and CO with O_2 has been studied by Shurmovskaya, and Bruns[116], indicating the effects of water and CO_2 on these oxidation reactions on MnO_2.

Ritchey and Calvert[103] studied the photosensitized oxidation of carbon monoxide on cuprous oxide from 2500 up to 4100Å as a function of the light intensity, pressure and other factors. They conclude that light of wave length less than 4100Å transforms the cuprous ion in the cuprous oxide to cupric ions in the cuprous oxide lattice, thus releasing an electron in the conduction band of the cuprous oxide. This electron in the lattice then reacts with oxygen as has been indicated above according to the mechanisms proposed by Garner and his co-workers (see p. 307). By determining the surface area of cuprous oxide containing added amounts of sulfur and antimony, and simultaneously measuring the electrical conductivity of these samples, Ritchey and Calvert were able to obtain a good correlation between the rate of CO_2 formation per unit of surface area and conductivity as a function of the amount of sulfur and antimony added. They found that the rate of CO_2 formation was at a maximum with no added impurities. The electrical conductivity curve is a fairly exact analog of the one observed for the rate of CO_2 formation (see Figure 9), the conductivity being at a minimum with no added impurities. On adding impurities they conclude that the conductivity increases, thus lowering the amount of charge unbalance in the surface which the crystal can maintain at steady state.

The lower the population of electrons at the surface, the lower the photochemical rate. Ritchey and Calvert state that they are proceeding with additional measurements of this type in order to obtain information regarding the effect of lattice defects on catalytic reactions at surfaces.

Garvin[52] has shown that ozone oxidizes carbon monoxide in the presence of a silver catalyst, presumably by a mechanism involving formation of active oxygen on the surface of the silver as a result of a primary decomposition of the ozone. This active oxygen on the surface of the silver then reacts with carbon monoxide to form CO_2 and the silver atom is regenerated on the surface. Not only does the active oxygen on the silver oxidize carbon monoxide, but it also oxidizes the ozone in the gas mixture to oxygen, thus regenerating the silver surface.

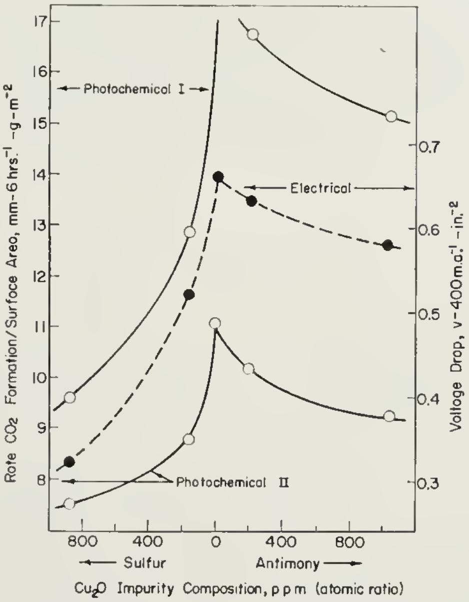


Figure 9. Effect of impurities in Cu_2O on its catalytic activity for the oxidation of carbon monoxide.[103] (Reprinted by permission of the *Journal of Physical Chemistry*)

Roginskii, *et al.*[109] prepared single crystals of copper and studied certain reactions, among them being the oxidation of CO to CO_2, on different faces of these single crystals. The face with the maximum atomic density was found to be least active, which is contradictory to the conclusions reached by Leidheiser and Gwathmey[82a] in his studies with single crystals of copper.

Erchak, Fankuchen and Ward[43] have identified the phases in the reaction of ferric oxide and barium carbonate at a series of compositions by x-ray methods, and then determined the catalytic activity of each mixture for the oxidation of CO to CO_2 with O_2. Catalytic activity was high when there was incipient formation of the compound $BaO \cdot 6Fe_2O_3$ or $BaO \cdot$

$2Fe_2O_3$, but decreased as the percentages of these crystalline phases increased. A compound with the formula $Ba_8Fe_8O_{21}$ was very active catalytically and activity increased as its concentration increased. In this compound only one-quarter of the iron atoms are in the valence state 4 and the lattice is deficient in oxygen atoms with respect to $Ba_8Fe_8O_{24}$ in which all the iron would be +4. During oxidation on this compound one has oxygen adsorbed, thus leading to the reaction.

$$Ba_8Fe_8O_{21} + O_2 \rightarrow Ba_8Fe_8O_{23}$$

followed by

$$Ba_8F_8O_{23} + 2CO \rightarrow Ba_8Fe_8O_{21} + 2CO_2$$

Actually it is not likely the situation is clear-cut, and probably the crystals in the catalyst are essentially "completely defective," being a disordered mixture of $Ba_8Fe_8O_{21}$ and $Ba_8Fe_8O_{24}$ with oxygen present in the lattice as randomly distributed O^- or $O^=$.

OXIDATION OF SULFUR DIOXIDE

Introduction

In terms of the tons per day of material produced, the oxidation of sulfur dioxide to sulfur trioxide is undoubtedly the most important vapor phase catalytic oxidation reaction. In fact, the manufacture of sulfuric acid is often used as a barometer for the economic climate in the entire chemical industry. The use of "contact" or catalytic oxidation processes for the manufacture of sulfuric acid increased from 5.6 million short tons per year in 1946 to 10.2 million short tons per year in 1953.

This section will not attempt to review every article which has been published on the oxidation of SO_2 to say nothing of the innumerable patents which have issued on the subject. Instead, after giving a brief summary and comparison of the various commercial processes, we shall consider some of the more important contributions to our understanding of the kinetics and mechanism of the reaction. For a more complete review of the entire process involved in the manufacture of sulfuric acid the reader is referred to a recent book edited by Duecker and West[38].

The thermodynamics of the reaction

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g)$$

has been the subject of several papers[110]. Table 11 presents values of the heats and free energies of formation of SO_2 and SO_3 and of the above reaction taken from the data of Evans *et al*[110]. Values of the equilibrium constant

$$K_p = \frac{(P_{SO_3})}{(P_{SO_2})\,(P_{O_2})^{1/2}}\,(\text{atm}^{-1/2}) \qquad (1)$$

Table 11. Thermodynamic Properties of SO_2, SO_3 and the Reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

Temp. (°K)	SO_2			SO_3			$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$			
	$\Delta H_f°$ (kcal/mole)	$\Delta F_f°$ (kcal/mole)	C_p cal/mole (°C)	$\Delta H_f°$ (kcal/mole)	$\Delta F_f°$ (kcal/mole)	C_p cal/mole (°C)	ΔH_T (kcal/mole)	ΔF_T (kcal/mole)	log K_p	K_p $(atm)^{-1/2}$
600	−86.58	−76.08	11.71	−110.00	−86.02	16.90	−23.42	−9.94	3.621	4180
700	−86.59	−74.32	12.17	−109.86	−82.04	17.86	−23.27	−7.72	2.410	257
800	−86.59	−72.57	12.53	−109.67	−78.08	18.61	−23.08	−5.51	1.505	32.0
900	−86.57	−70.81	12.82	−109.44	−74.15	19.23	−22.87	−3.34	0.811	6.47
1000	−86.55	−69.06	13.03	−109.16	−70.24	19.76	−22.61	−1.18	0.258	1.81
1100	−86.51	−67.33	13.20	−108.86	−66.37	20.21	−22.35	+0.96	−0.191	0.645
1200	−86.48	−65.58	13.35	−108.54	−62.51	20.61	−22.06	+3.07	−0.559	0.276

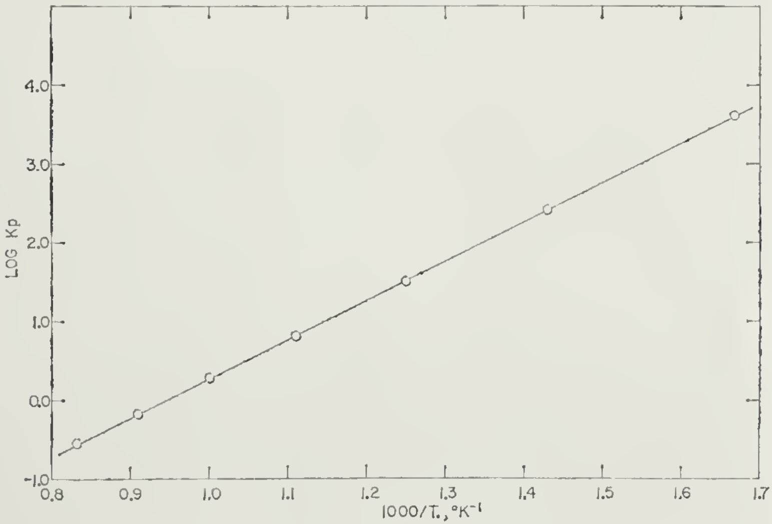


Figure 10. Effect of temperature on the equilibrium constant for the reaction $SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g)$.

are also given. Experimental values of K_p, determined by several workers[15] are in satisfactory agreement with the values listed in Table 11. Figure 10 shows a plot of log K_p vs. the reciprocal of the absolute temperature. A straight line is obtained, described by the equation

$$\log K_p = \frac{4{,}956}{T} - 4.678$$

The effect of temperature on the equilibrium conversion of SO_2 to SO_3 may be seen more graphically in Figure 11 which is obtained as follows.

Let a be the initial partial pressure of SO_2 (atm) in the burner gas obtained by the burning of sulfur in air, and y be the fraction of a remaining unconverted at equilibrium. Then, at equilibrium,

$$P_{SO_2} = \frac{2.00\,ay}{2.00 - a(1 - y)}$$

$$P_{SO_3} = \frac{2.00\,a(1 - y)}{2.00 - a(1 - y)}$$

$$P_{O_2} = \frac{0.42 - 3a + ay}{2.00 - a(1 - y)}$$

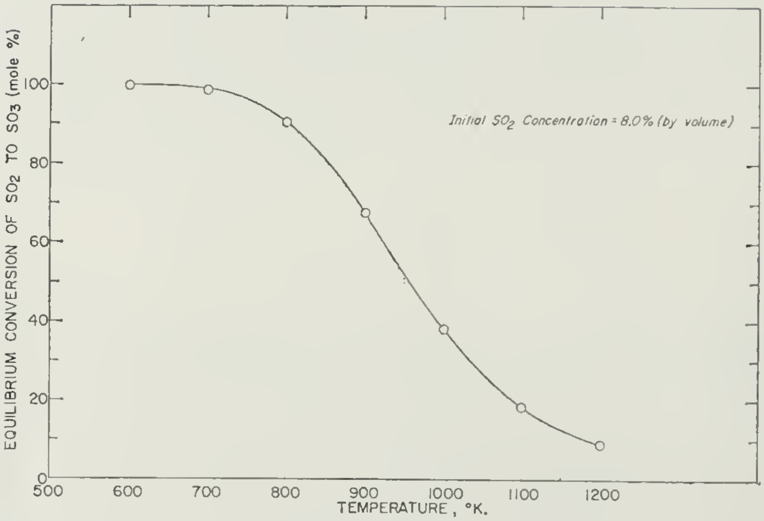


Figure 11. Effect of temperature on the equilibrium conversion of SO_2 to SO_3

Substituting in Eq. (1) and rearranging leads to

$$a(K_p^2 - 1)y^3 + [K_p^2(0.42 - 3a) - (2 - 3a)]y^2 + (4 - 3a)y - (2 - a) = 0 \tag{2}$$

For a burner gas containing 8.0 per cent SO_2 by volume, Eq. 2 reduces to

$$(K_p^2 - 1)y^3 + (2.25\,K_p^2 - 22)y^2 + 47y - 24 = 0 \tag{3}$$

Eq. (3) was solved for the values of K_p listed in Table 11 to obtain the data plotted in Figure 11. It is of interest to note that the solution of Eq. (3) for seven values of K_p, which would be a laborious process manually, was completed in less than 4 hr by a member of the Mathematical Analysis Group of the authors' laboratories using a Burroughs E-101 computer.

Increasing the SO_2 content of the feed results in a lower equilibrium oxygen concentration and a lower equilibrium conversion of SO_2 to SO_3 at any given temperature. It is seen that at temperatures below 500°C, conversions per pass of over 90 per cent are theoretically possible, but above 700°C, equilibrium conversions are below 50 per cent. Thus, commercially attractive catalysts should be active at temperatures in the neighborhood of 400 to 500°C.

Only two types of catalysts have gained widespread commercial acceptance. These are platinum, supported on one of a number of bases, and vanadium pentoxide, usually promoted with K_2SO_4 or $K_2S_2O_7$. The first mention of the use of a platinum catalyst for the oxidation of SO_2 to SO_3 dates back to 1831. However, commercial interest in and scientific investigation of the process did not take place until the latter part of the nineteenth century. In 1901, Knietsch disclosed much of the knowledge of the Badische Analin and Soda Fabrik concerning the process. With the presentation of this paper it became apparent that the general principles governing the manufacture of sulfuric acid by the contact process were quite well understood. On the other hand, the first suggestion of the use of V_2O_5 as a catalyst for SO_2 oxidation is attributed to R. Meyers in 1899. A number of other patents on the use of vanadium catalysts were issued in the early 1900's, but Fairlie[44] states that it is doubtful that any commercial plants were operating with this catalyst before about 1920.

Four somewhat different platinum catalysts have been widely used in the oxidation of SO_2. The "Badische" process uses a platinized asbestos containing from 8 to 10 per cent platinum, placed on numerous perforated trays in layers from ½ to ¾ in. deep. If proper care is taken to avoid contamination of the catalyst, especially arsenic poisoning, the catalyst life is of the order of 12 to 15 years. About 1923 a "low-ignition" platinum catalyst was developed which is active at considerably lower temperatures than the Badische catalyst described above. Whereas the process for manufacture of the Badische catalyst has been described in detail[44], the steps in the manufacture of the low ignition catalyst have been kept secret.

The Grillo Schroeder process employs a platinized magnesium sulfate catalyst. The process for its manufacture, which has also been described[44], involves impregnation of calcined granules of $MgSO_4$ (⅛ to ⅝ in.) with an aqueous solution of platinic chloride. In contrast to the platinized asbestos catalysts, which contain from 4 to 10%w platinum, this catalyst contains only 0.1 to 0.3 per cent platinum.

A platinized silica gel catalyst was developed by the Davison Chemical Company. This catalyst, which was prepared by the impregnation of washed, calcined silica gel with ammonium chloroplatinate, also contained about 0.1%w platinum. With a burner gas containing 7 per cent SO_2, conversion efficiencies of better than 95 per cent could be obtained at temperatures from about 425 to 550°C at a flow rate of approximately 1 l. of gas/hr/cc of catalyst. This catalyst is poisoned by chlorine and other halogens, but unlike the other platinum catalysts is claimed to be not susceptible to arsenic poisoning.

At least four somewhat different vanadium catalysts have found commercial application in SO_2 oxidation. The "Slama-Wolf" catalyst, which has been used by the Badische Co. and the General Chemical Co., is prepared by the impregnation of kieselguhr with ammonium metavanadate and potassium hydroxide followed by pelleting and calcining in the pressence of SO_2 and air. Part of the KOH undoubtedly reacts with the kieselguhr to form potassium silicate and the remainder is converted to K_2SO_4 or $K_2S_2O_7$ during the sulfating and calcining steps.

The "Monsanto" catalyst has been described as a vanadium pentoxide zeolite. Patent examples describe its preparation by the precipitation of silica gel, formed in the neutralization of potassium silicate with hydrochloric acid, in the presence of a solution of ammonium metavanadate and potassium hydroxide.

The base for the "Selden" catalyst is prepared by the addition of an aqueous solution of potassium silicate to kieselguhr. A solution of potassium aluminate is added to form a gel-like potassium aluminum silicate. This zeolitic mass is then coated with a complex vanadium compound prepared by the addition of ammonium vanadate to a solution of potassium aluminate and potassium silicate. The whole mass is then pelleted and calcined in a stream of SO_2 and air.

In the preparation of the K.F.I. catalyst, an aqueous solution of sodium hydroxide and vanadium pentoxide is added to a dry mixture of "Celite" diatomaceous earth, K_2SO_4 and gum tragacanth. The mixture is neutralized with H_2SO_4, dried, pelleted and calcined.

The advantages and disadvantages of platinum and vanadium catalysts in comparison with one another have been discussed by Fairlie[44]. His conclusions are summarized below.

The principal disadvantages of vanadium catalysts are: (a) they are normally operated with only 6 to 8 per cent SO_2 in the feed *vs.* about 10 per cent for platinum catalysts, and (b) when deactivated they have no salvage value. On the other hand, the advantages cited for vanadium catalysts include (a) longer life than platinum, (b) higher average conversion efficiency, (c) immunity to poisoning by small amounts of arsenic, chlorine etc., (d) greater physical ruggedness, and (e) greater availability to all countries in wartime.

Studies of the V_2O_5-Catalyzed Reaction

Boreskov *et al.*[23] have compared the catalytic activity for the oxidation of SO_2 of (a) pure V_2O_5, (b) one mole of V_2O_5 plus 8 moles of amorphous

SiO_2, (c) one mole of V_2O_5 + 0.1 mole of K_2SO_4, and (d) one mole of V_2O_5 + 8 moles of SiO_2 + 0.1 mole of K_2SO_4.

Using pure V_2O_5, the apparent activation energy was 38 kcal/mole. Even below 500°C there was apparently no reduction of the V_2O_5. The addition of 8 moles of SiO_2 per mole of V_2O_5 decreased the activity of the catalyst to $1/15$ that for pure V_2O_5 but left the activation energy unchanged. The addition of 0.1 mole of K_2SO_4 per mole of V_2O_5 (no SiO_2) resulted in a higher apparent activation energy than was obtained with pure V_2O_5. The reaction rate was lower below 490°C and higher at higher temperatures. In this catalyst some of the V_2O_5 was converted to $VOSO_4$, and it is suggested that the active catalyst between 495 and 510°C may be a mixture of V_2O_5, $VOSO_4$, K_2SO_4 and $K_2S_2O_7$. The V_2O_5-K_2SO_4-SiO_2 catalyst was approximately 20 times more active than pure V_2O_5 over the temperature range from 440 to 500°C and gave an activation energy of 27 kcal/mole. The increased activity is attributed to an increased dispersion of the active catalyst over the silica gel surface.

In an earlier paper, Boreskov[21] had reported that the rate of oxidation of SO_2 over a (commercial?) vanadium catalyst at 470°C was proportional to the O_2 concentration to the first power, to the SO_2 concentration to the 0.8 power and inversely proportional to the 0.8 power of the SO_3 concentration. An activation energy of 23 kcal/mole was found between 470 and 500°C.

Boreskov[22] also compared the catalytic activity of KVO_3, $NaVO_3$, $Ba(VO_3)_2$ and V_2O_5 at 480°C. All of the salts were more active than V_2O_5. At this temperature the V_2O_5 was very slowly reduced to $VOSO_4$. The addition of K_2O or K_2SO_4 to the V_2O_5 increased its activity, the active catalyst being a mixture of V_2O_5, $VOSO_4$, K_2SO_4 and $K_2S_2O_7$.

In addition, Boreskov[25] has studied the systems V_2O_5-K_2SO_4 and V_2O_5-$K_2S_2O_7$ by means of heating and cooling curves, x-ray analysis and chemical analysis. In the system V_2O_5-K_2SO_4 the formation of a compound was detected containing approximately equimolar quantities of the two components. It melted around 500°C and formed a eutectic with K_2SO_4 melting below 430°C at an approximate composition of 0.4 mole fraction V_2O_5. Mixtures of V_2O_5 and $K_2S_2O_7$ containing greater than 0.4 mole fraction $K_2S_2O_7$ possessed a low melting point. On heating mixtures of V_2O_5 and $K_2S_2O_7$, an exothermic effect was detected at 275°C, which is believed to be due to a compound formation.

Tandy[120] has recently considered the role played by the alkali metal sulfates in vanadium catalysts for SO_2 oxidation. The chemical composition of alkali metal sulfate-vanadium oxide mixtures in equilibrium with SO_2-SO_3-air mixtures was investigated. In the temperature range 440 to 600°C, a liquid product was produced consisting of vanadium compounds dissolved in an alkali pyrosulfate-sulfate mixture. The melting point of the mixture decreased with increasing atomic weight of the alkali metal used. The weight increases observed with an alkali sulfate/V_2O_5 molecular ratio of 2.5/1 suggest the formation of a normal pyrosulfate, $M_2S_2O_7$, and $VOSO_4$. The extent of reduction of the V_2O_5 is lower in the presence of alkali metals of higher atomic weight. It is suggested that this may account for the preference for the potassium salt over the sodium salt as a promoter in commercial catalysts. Unpublished results of the American Cyanamid Company have shown that the promoter effects of the alkali elements increases with their atomic weights.

Topsoe and Nielsen[123] have confirmed that, during SO_2 oxidation, vanadium pentoxide-alkali pyrosulfate catalysts consist of a highly viscous melt which covers the carrier with a film. Those alkali metals which can produce compounds with a higher sulfur trioxide content than pyrosulfates were shown to be the most suitable catalyst components. The metals concerned are potassium, rhubidium, cesium, and tellurium, whereas sodium, barium, and silver, which do not form compounds with higher sulfur trioxide content than pyrosulfates, make less active catalysts.

It was also shown[123] that a liquid melt consisting of a solution of V_2O_5 in a fused alkali pyrosulfate-sulfur trioxide solution constituted an active catalyst system for the oxidation of SO_2 to SO_3. This observation would seem to contradict the theory of Frazer *et al.*[47] (see p. 330) that the silica gel base plays an active role in the catalytic process. Weychert *et al.*[137] have studied the synthesis and decomposition of vanadyl sulfate between 360 and 630°C.

Kubo *et al.*[79] have reported that TiO_2 and V_2O_5-TiO_2 catalysts are strongly activated for the oxidation of SO_2 by x-rays of suitable intensity. It is suggested that the TiO_2 undergoes phototropy evolving active oxygen and that the reaction proceeds according to the equations

$$2TiO_2 + h\nu \rightarrow Ti_2O_3 + [O]$$

$$SO_2 + [O] \rightarrow SO_3$$

Conventional platinum catalysts and silicate-type carrier vanadium catalysts are not activated by x-rays.

Krichevskaya[77] studied the kinetics of the oxidation of SO_2 over a pure V_2O_5 catalyst at temperatures from 475 to 575°C. Rate measurements were made using mixtures of SO_2 (4 to 40 per cent), O_2 (5 to 40 per cent) and CO_2 (remainder) and at conversion levels from 18 to 71 per cent. The apparent activation energy for SO_2 formation was 34 kcal/mole in general agreement with the results of Boreskov[23]. The rate of decomposition of SO_3

was studied at 575°C and from these data, coupled with those from the SO_2 oxidation, it was concluded that

$$\frac{d[SO_3]}{dt} = \frac{k_1[SO_2]^{1/2}[O_2]^{1/2}}{[SO_3]} - \frac{k_2[SO_3]^{1/2}}{[SO_2]^{1/2}}$$

and

$$\frac{k_1}{k_2} = 13.4 \text{ at } 575°\text{C}.$$

The over-all reaction rate is believed to be determined by the rate of reaction between adsorbed SO_2 and adsorbed O_2. On the other hand, it is suggested that the rate of reaction on technical catalysts is determined by the rate of sorption of O_2 and by diffusion within the catalyst pores.

Calderbank[27] has studied the kinetics of the oxidation of SO_2 using a commercial V_2O_5 catalyst. This work was done in a flow reactor at relatively short contact times and low conversions. These conditions made it possible to study the reaction under essentially isothermal conditions and also to neglect the reverse reaction.

Based on studies of the variation of initial rate of oxidation with initial reactant concentration, it was found that the kinetics are described by:

$$r = KP_{SO_2}^{0.4}P_{O_2}^{0.8}$$

where r = rate of SO_2 oxidation and P_{SO_2} and P_{O_2} are the partial pressures of SO_2 and O_2, respectively. These data are not in agreement with those of other workers using commercial catalysts, summarized by Krichevskaya[77]. Calderbank suggests that the earlier workers may have failed to obtain isothermal conditions. As discussed above, Krichevskaya found

$$r = KP_{SO_2}^{1/2}P_{O_2}^{1/2}$$

using pure V_2O_5. However, Calderbank has pointed out that these results may have been influenced by the use of CO_2 rather than N_2 as the diluent gas.

The usual Arrhenius plot of Calderbank's data showed some tendency to curve toward a lower activation energy at the higher temperatures. However, using all of the data, an average activation energy around 29 kcal/mole was calculated by the writer.* This is in reasonable agreement with the value reported by Boreskov[23] for the V_2O_5-K_2SO_4-SiO_2 catalyst.

In addition to the kinetic study, Calderbank has also investigated the rate of chemisorption of SO_2 and O_2 on the catalyst and the adsorption

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* In a later paper[28], Calderbank calculated a value of 31 kcal/mole based on the same data.

isotherms for these systems. For both adsorbates, the isotherms are Langmuir in character. Both are reversibly chemisorbed, oxygen being weakly bound with a heat of adsorption of 6.4 kcal/mole and SO_2 strongly bound with a heat of 28.8 kcal/mole.

Measurements of the rate of adsorption on the clean surface indicate that, under conditions where the rate of desorption can be neglected, the rate of adsorption can be described by the equation:

$$\frac{d\theta}{dt} \approx k_1P(L - \theta)$$

where θ = moles of gas adsorbed/g of catalyst, L = moles of active centers/g of catalyst, and P = pressure of adsorbate. It is concluded that the chemisorption of O_2 involves the reaction of one molecule of gas with one active center of the substrate. On the other hand, the rate of SO_2 chemisorption indicates a third-order mechanism in which one molecule of gas reacts with two active centers. The isotherms, which were measured at higher temperatures than the rates of adsorption, indicate that at the higher temperatures, the active sites are sufficiently mobile that third-order kinetics are no longer valid. At a given temperature, the rate of O_2 chemisorption is much slower and the rate of SO_2 chemisorption much faster than the rate of SO_2 oxidation.

Based on considerations of both the kinetic and chemisorption data, Calderbank concluded that the oxidation involves the reaction of a chemisorbed SO_2 molecule with a gas-phase oxygen molecule. The steps in the oxidation are believed to be

(1) $$\underset{\text{gas}}{SO_2} + \underset{\substack{\text{active}\\\text{centers}}}{2e} \rightleftharpoons \underset{\substack{\text{chemisorbed}\\\text{complex}}}{SO_2^{=}}$$ (ΔH = -28.8 kcal/mole) [fast third-order chemisorption of SO_2]

(2) $$\underset{\text{gas}}{O_2} + \underset{\text{chemisorbed}}{SO_2^{=}} \rightarrow \underset{\text{chemisorbed}}{SO_3} + O^{=}$$ (slow second-order reaction)

(3) $O^{=} \rightleftharpoons \frac{1}{2}O_2 + 2e$ (ΔH = $+6.4$ kcal/mole) (fast desorption).

Both Frazer and Kirkpatrick[47] and Neumann[94] have considered possible mechanisms for the oxidation of SO_2 on vanadium catalysts. Neumann's mechanism assumes that the V_2O_5 is reduced to V_2O_4 by the SO_2, the silica acting as an inert support. The role of the alkali pyrosulfate is not mentioned.

Frazer *et al.* point out that under the reaction conditions, the pyrosulfate phase is liquid and can act as a solvent for the V_2O_5. They suggest that on reaction with SO_2 the vanadium is reduced to the trivalent state according to the equation

$$K_2S_2O_7 + V_2O_5 + 2SO_2 \rightarrow 2KV(SO_4)_2$$

The SO_3 is then liberated by the reaction

$$2KV(SO_4)_2 + 2SiO_2 \rightarrow V_2Si_2O_7 + K_2S_2O_7 + 2SO_3$$

and the vanadium returned to the pentavalent state by the oxidation of the vanadium silicate according to the equation

$$V_2Si_2O_7 + O_2 \rightarrow V_2O_5 + 2SiO_2$$

Thus it is concluded that both the $K_2S_2O_7$ and the SiO_2 play an active role in the oxidation reaction.

In a later paper, Calderbank[28] has applied the results of the foregoing kinetic study[27] to the calculation of the design of sulfuric acid converters. For this purpose, the observed rate equation for the oxidation of SO_2 is approximated by

$$r_1 = k_1 P_{SO_2}^{1/2} P_{O_2}$$

In addition, it is assumed that the rate of decomposition of SO_3 is described by an equation of the form

$$r_2 = k_2 \frac{P_{SO_3} P_{O_2}^{1/2}}{P_{SO_2}^{1/2}}$$

Combining these equations, one obtains for the over-all rate of SO_3 production,

$$\frac{d[SO_3]}{dt} = k_1 P_{SO_2}^{1/2} P_{O_2} - \frac{k_2 P_{SO_3} P_{O_2}^{1/2}}{P_{SO_2}^{1/2}}$$

From a knowledge of k_1 and the equilibrium constant for the reaction

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3$$

one can calculate values of k_2. Using these equations, calculations have been made of the minimum amount of catalyst required for a given duty and the optimum temperature distribution for a converter to insure maximum reaction rate at all points and a minimum size of the equipment.

From consideration of the stoichiometry involved in the oxidation of SO_2 to SO_3, Colette and Scheepers[30] have assumed that the rate of oxidation of SO_2 and SO_3 is given by the equation

$$\frac{dx}{dt} = k_1(a - x)^2(b - x) - k_2x^2 \qquad (4)$$

where $2a$ and b are the initial concentrations of SO_2 and O_2, respectively, and x is the fraction of a converted to SO_3. Values of k_1 and k_2 were calculated from measurements of the percentage conversion of SO_2 and SO_3 at a series of different temperatures but at constant feed ratios and catalyst volumes. However, no data are presented to show that the reaction rate is actually described by Eq. (4). Using these data, Salsas-Serra[111] has calculated the optimum conditions of temperature, feed rate, etc. for the operation of a commercial sulfuric acid plant.

Mars and van Krevelen[88] have recently reviewed the literature on the kinetics of the oxidation of SO_2. They concluded that most of the available data can be correlated by an equation of the form

$$\frac{k}{V_s} \cdot \frac{(\bar{P}_{O_2})^n}{(P_{SO_2})} = \alpha_{eq}\left(\ln \frac{1}{1 - \alpha'} - \alpha'\right) \tag{5}$$

where V_s = space velocity, $\bar{P}_{O_2}$ = avg. partial pressure of O_2, P_{SO_2} = initial partial pressure of SO_2, and α' = degree of conversion as compared to that at equilibrium = α/α_{eq}. This equation is derived on the basis that the reaction can be described kinetically by the following three steps:

$$SO_2 + \text{Cat-O} \rightarrow SO_3 + \text{Cat.}$$

$$\text{Cat.} + O_2 \rightarrow \text{Cat-O}$$

$$SO_3 + \text{Cat.} \rightarrow SO_2 + \text{Cat-O.}$$

For the gross reaction process the rate-determining step is the reoxidation of the catalyst. Eq. (5) is used to calculate optimum conditions for the operation of commercial fixed bed units for SO_2 oxidation.

Baron *et al.*[13] have studied the oxidation of SO_2 in porous tubular reactors impregnated with vanadium oxide catalyst. The reactors consisted of ½-in. ID and ¼-in. ID alundum tubes, impregnated with approximately 7 per cent potassium metavanadate. When the catalyst was first subjected to $SO_2 + O_2$, the SO_3 produced was absorbed until the catalyst tube contained about 7 moles of SO_3/mole of metavanadate. Thereafter, sulfur balances were 100 per cent.

Damköhler[33] has presented a mathematical analysis of first-order reactions in a tubular reactor. This treatment assumes rod-like, frictionless and nonturbulent flow through the reactor in which a constant volume, heterogeneous reaction occurs. Under these conditions, if one plots

$$\ln(Ce/Ca) \quad \text{vs.} \quad T = 4DL/Vd^2,$$

a series of straight lines are obtained having slopes = $kd/2D$. (See end of section for notation.) Baron *et al.* modified Damköhler's treatment to allow for reversible first-order reactions. They considered that the other assumptions involved in Damköhler's treatment were satisfied in their experiments.

Since plots of the data in the form of $\ln(Ce/Ca)$ vs. $4DL/Vd^2$ yielded straight lines, it was concluded that the reaction was first order with respect to the SO_2 concentration. Values of $kd/2D$ were obtained over the temperature range from 425 to 550°C. The maximum value of $kd/2D$ was less than 0.10, indicating that under the conditions of these experiments, the diffusional resistance to reaction is not more than a small fraction of the total resistance.

Specific reaction rate constants were calculated from the values of $kd/2D$ for the two different reactors and at a series of different temperatures. The $\frac{1}{4}$-in. reactor gave rate constants about 12 per cent higher than the $\frac{1}{2}$-in. reactor; it had a 20 per cent higher catalyst content per unit weight.

All of the experiments were made using a feed consisting of 7.8 mole per cent SO_2, 19.4 mole per cent O_2 and the remainder an inert gas, either helium, nitrogen or carbon dioxide. It was found that the nature of the inert gas had a profound effect on both the reaction rate and the activation energy. Over the temperature range investigated, the reaction rate was higher and the activation energy lower, the higher the molecular weight of the inert gas. Baron *et al.* have explained these observations by assuming that the limiting step in the oxidation of SO_2 is the desorption of the SO_3 formed in the reaction.

It was shown that the observed inert gas effects could be explained by considerations of the momentum transfer between gaseous molecules of inert gas and chemisorbed SO_3 molecules. Thus, a high molecular weight inert gas causes a more rapid desorption of SO_3, resulting in a higher reaction rate than is obtained with a low molecular weight gas.

Nomenclature:

Ce = Concentration of limiting reactant at exit of reactor.
Ca = Concentration of limiting reactant at entrance to reactor.
D = Diffusivity of limiting reactant.
L = Length of reactor.
V = Average velocity of gases in reactor.
d = Inside diameter of tubular reactor.
k = Specific reaction rate constant [moles converted/(cm^2)(sec)(moles/cc)].

Oxidation on Platinum Catalysts

In Bodenstein's[16, 17] classic work on the oxidation of SO_2 over a platinum catalyst, it was found that the reaction rate varied directly as the SO_2 partial pressure, inversely as the square root of the SO_3 partial pressure and, over a wide range, was independent of oxygen partial pressure. These observations can be explained by assuming that the mechanism involves the reaction of gaseous SO_2 molecules with chemisorbed oxygen. The inhibition by SO_3 is believed due to a strong chemisorption of SO_3 on the surface of the catalyst, thus limiting the number of sites available for reaction.

In 1927, Lewis and Ries[84] studied the kinetics of SO_2 oxidation under conditions similar to those used in commercial operation with platinum catalysts. The oxidations were done under essentially isothermal conditions using a 7 per cent platinized asbestos catalyst. In order to insure having only a small exotherm, the maximum concentration of SO_2 in the feed to the converter was 0.5 per cent and not more than 60 per cent was converted to SO_3. In some runs the feed contained a high ratio of SO_3 to SO_2 so that the product compositions corresponded to 96 to 97 per cent conversion of SO_2 to SO_3. All studies were made at constant total flow rate and constant volume of catalyst. Temperature and feed compositions were varied.

Whereas Lewis and Ries[83] had found that the data of Knietsch could be fitted by a rate expression derived from the ordinary mass-action equation, their own data, obtained with feeds containing only SO_2 and air, did not fit the expression. Nor were these data fitted by an expression of the form used by Bodenstein. However, the agreement was better than in the first case. The best fit was found to be a simple first-order rate with respect to SO_2, virtually independent of O_2 and SO_3 partial pressures.

Even in the runs in which the feed contained appreciable SO_3, the conditions were such that the extent of decomposition of SO_3 to $SO_2 + O_2$ was negligible. Under these conditions the data were best fitted by the equation

$$\frac{-d(\mathrm{SO_2})}{dt} = k[\mathrm{SO_2}]\left[\ln\left(\frac{\mathrm{SO_3}}{\mathrm{SO_2}}\right)_{\mathrm{eq}} - \ln\left(\frac{\mathrm{SO_3}}{\mathrm{SO_2}}\right)\right]$$

This equation also adequately fitted the results of the runs with no SO_3 in the feed.

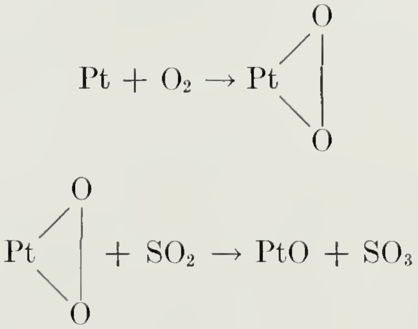
The discrepancy between these data and those of Knietsch is believed due to the fact that Knietsch was not operating under isothermal conditions. In addition, Lewis and Ries state that their equation gives a better fit to the data of Bodenstein and Fink than does the equation proposed by those authors.

Uyehara and Watson[125] have analyzed the data of Lewis and Ries[84] on the assumption that one of the following four activated steps in the reaction was rate-controlling. The processes considered were: (a) activated adsorption of SO_2, (b) activated adsorption of O_2, (c) surface reaction between chemisorbed SO_2 and chemisorbed O_2, and (d) desorption of SO_3.

The experimental data were compared with rate equations calculated on the assumption that one of the four processes was rate-controlling. The possibility of the rate being limited by diffusional effects was not considered.

From this comparison it was concluded that the data best fitted the equation which was calculated on the assumption that a surface reaction between SO_2 and O_2, both chemisorbed on the catalyst, was the limiting step. However, the data do not permit a positive choice between this possibility and the possibility that the controlling step is the reaction of gas phase SO_2 with chemisorbed oxygen atoms as suggested by Bodenstein[17].

Shekhobalova *et al.*[115] have suggested that the following steps are involved in the oxidation:



$$Pt + O_2 \rightarrow Pt\!\!<\!\!\begin{array}{c}O\\|\\O\end{array}$$

$$Pt\!\!<\!\!\begin{array}{c}O\\|\\O\end{array} + SO_2 \rightarrow PtO + SO_3$$

$$PtO + SO_2 \rightarrow Pt + SO_3$$

Taylor and Lenher[122] studied the approach to equilibrium in the oxidation of SO_2 over a platinum surface using a hot-wire technique at 665°C. It was found that the rate of formation of SO_3 at any instant was proportional to the distance the reaction had to travel to equilibrium and inversely proportional to $[SO_3]^{1/2}$. The rate of decomposition of SO_3 was also found to be proportional to the distance from equilibrium, but was not retarded by the reaction products.

Pevnyi[99] measured the rates of adsorption and desorption of SO_3 on a number of catalysts including Pt on SiO_2, Pt on asbestos, and V_2O_5 promoted with either BaO or BaO plus Al_2O_3. It was found that the activity for oxidation of SO_2 paralleled the rate of desorption of SO_3 from the various catalysts.

Nakata *et al.*[93] have studied the oxidation of SO_2 over a platinum sponge catalyst using heavy oxygen. Below 400°C no exchange of O^{18} in the O_2 with the oxygen in the SO_2 was observed. Above this temperature exchange was found between the SO_3 and free oxygen. Above 600°C complete equilibration was obtained among the oxygen, SO_2 and SO_3.

Boreskov *et al.*[24, 26] have investigated the catalytic activity of various platinum catalysts (massive platinum in the form of wire or gauze, platinum sponge, platinized silica gel) with respect to the oxidation of sulfur dioxide.

It was found that the specific activity per unit surface area of platinum (as determined by measurements of hydrogen chemisorption) is approximately the same for all the catalysts studied and depends little on the size of the platinum crystals or on the temperature of preliminary heat treatment of the specimens. The activation energy of SO_2 oxidation on massive platinum and on platinized silica gel is 23.3 ± 0.6 kcal/mole. The catalytic activity of platinized silica gel per unit weight concentration of platinum remains approximately constant on changing the weight concentration of platinum from 0.001 to 0.5 per cent. The size of the platinum crystals in platinized silica gel is consequently independent of the platinum concentration and is determined only by the porous structure of the silica gel and the temperature of the preliminary heat treatment. Catalytic activities for the oxidation of SO_2 were measured for platinum, tungsten, palladium, gold, platinum-gold alloys, chromium, rhubidium and silver. Silver was found to be inactive; all of the others, except platinum, were of approximately equal activity, all less active than platinum.

Hurt[61] has used the concept of "height of an over-all reaction unit" to correlate data on the oxidation of SO_2 over platinum catalysts. The correlation covers a range from laboratory up to plant scale results, or for catalyst volumes from about 100 ml up to 100 cu. ft.

This concept is based on the realization that the over-all rate of a surface-catalyzed reaction is a function of both the surface reaction rate and the rate of mass transfer of reactant to the catalyst surface. The concept of H_T (height of a transfer unit) defined as "the height of packed bed which gives a change in partial pressure equal to the mean driving force across the gas film" is used as a measure of the diffusional resistance to reaction. In addition, two new concepts H_R (height of a reaction unit) and H_C (height of a catalytic unit) have been defined as H_R = depth of catalyst bed which gives a change in partial pressure of reactant equal to the mean over-all driving force of the reaction, and H_C = depth of catalyst bed which gives a change in partial pressure of reactant equal to the mean surface driving force of the reaction. Thus, the driving forces are $(y - y^*)$ for H_R, $(y - y_i)$ for H_T and $(y_i - y^*)$ for H_C, where

y = mole fraction of reactant in gas stream;
y_i = mole fraction of reactant at catalyst surface; and
y^* = equilibrium value of y at surface temperature.

It is shown that, for the simplified conditions of steady state, unpoisoned catalyst surface, first order reaction and equimolar counterdiffusion,

$$H_R = H_T + H_C$$

It is reported that for reactions in which the catalyst surface is poisoned by either the reactants or products, the fraction of the surface unpoisoned can be represented by the factor $1/[1 + k_1(P_p)]$ where: P_p = partial pressure of poison. Under these conditions H_R is given by

$$H_R = [1 + k_1(P_p)][H_T + H_C]$$

Values of H_T were obtained over a wide range of conditions by measurements of the humidification of air by wetted pellets, naphthalene vaporization into air or H_2, etc. A good correlation was found between

$$\frac{H_T}{(\mu/\rho D_v)^{2/3}} \text{ and Re}$$

where μ = viscosity of diffusing gases, ρ = density of diffusing gases, D_v = diffusivity, and Re = Reynolds number.

These techniques were applied to studies of SO_2 oxidation. Since the reaction is poisoned by SO_3, the pertinent equation is

$$H_R = (1 + k_1P_{SO_3})(H_T + H_C)$$

From observed values of H_R and H_T, values were calculated for k_1 and H_C over a wide range of conditions. From the plot of $\ln(k_1)$ vs. $1/T$ it was concluded that the activation energy for SO_3 adsorption is 12.1 kcal/mole, and from the plot of $\ln(H_C)$ vs. $1/T$ that the over-all activation energy for the SO_2 oxidation is 25.6 kcal/mole. At high temperatures (*ca.* 575°C) the over-all reaction rate is controlled largely by the mass transfer rate while at low temperatures (*ca.* 375°C) the surface reaction rate is the limiting factor.

Olson *et al.*[96] have studied the importance of diffusion in the oxidation of SO_2 using a 0.2 per cent Pt on Al_2O_3 catalyst in the form of ⅛-in. pellets. The catalyst bed was 1.5-in. in diameter and approximately ⅜-in. thick. The mass velocity of the feed was varied from 147 to 514 lb/(hr)(ft)^2 and the temperature from 350 to 480°C. By the use of a preconverter, it was possible to measure reaction rates under essentially differential conditions but at gas compositions corresponding to 4 to 70 per cent conversion of the SO_2 in the feed to the preconverter.

In agreement with the data of Bodenstein and Fink[17] and that of Lewis and Ries[84], it was found that the presence of a small amount of SO_3 resulted in a marked retardation in the reaction rate.

Plots of reaction rate *vs.* mass velocity, at constant temperature and percentage conversion, showed an increase in rate with mass velocity approaching a constant value at high mass velocities. The effect was much more marked at the higher than at the lower temperatures. In order to obtain a quantitative measure of the extent to which the reaction is being diffusion-limited, the data were analyzed by the methods suggested by Hougen and Wilkie[57] and by Hurt[61].

Values of the partial pressures of SO_2, O_2 and SO_3 at the catalyst surface were evaluated using the mass-transfer correlations of Hougen and Wilkie[57]. Confirmation of the validity of this technique was obtained from the fact that when the reaction rate (at constant temperature) was plotted against the surface partial pressure of SO_3, all of the data for the different mass velocities fell on a single curve, whereas when the gas phase SO_3 partial pressures were used, different curves were obtained depending on mass velocity. Also, plots of the reaction rate *vs.* the partial pressure of SO_2 at the catalyst surface gave curves which were independent of mass velocity. This analysis of the data showed that at high temperatures, low mass velocities and low conversions, the pressure drop between the main gas and the catalyst surface for SO_2 was as much as 25 per cent of the partial pressure of SO_2 in the gas. At low temperatures and high mass velocities the pressure drop was negligible.

The technique proposed by Hurt[61] (see p. 336) for determining the effect of diffusion was also investigated. This method was found to be less satisfactory in that the calculated values for the resistance due to reaction at the catalyst surface (H_C, or H.C.U.*) were not independent of mass velocity.

Insufficient composition variables were studied to make a thorough study of the controlling mechanism at the catalyst surface. The data could not distinguish among the following possible rate-controlling steps:

1. adsorbed SO_2 + adsorbed O_2.
2. adsorbed SO_2 + gas phase molecular O_2.
3. adsorbed O_2 + gas phase molecular SO_2.

Both Damköhler[33] and Gabrielson[48] have developed equations for estimating the temperature rise in a catalyst pellet, above the gas stream temperature, during the oxidation of SO_2. Gabrielson's calculations lead to temperature rises of the order of 4°C for platinum on silica gel to about 20°C for the "Selden Co." V_2O_5 catalyst. However, Damköhler's estimates were substantially lower.

Davtyan and Ovchinnikova[34] adsorbed SO_2 and O_2 on a number of catalysts at room temperature. The total gas adsorption was determined by the increase in weight of each catalyst. The catalysts were then boiled in water and the amount of sulfuric acid present in the water was determined and taken as a measure of the amount of SO_3 formed on the catalyst surface. Since substantial amounts of sulfuric acid were found in all cases, it was concluded that the limiting step in the catalytic oxidation process at low temperatures was not the formation of chemisorbed SO_3 on the catalyst surface but rather its desorption into the gas phase.

* Height of a catalytic unit.

Summary of Kinetics and Proposed Mechanisms on Pt and V_2O_5 Catalysts

The foregoing data on the kinetics of the oxidation of SO_2 on various catalysts are summarized in Table 12. Most authors agree that in the presence of platinum catalysts, the rate is approximately proportional to the first power of the SO_2 concentration, inversely proportional to the square root of the SO_3 concentration and almost independent of the oxygen concentration. Boreskov[24] suggests that much of the data can be correlated by the equation:

TABLE 12. COMPARISON OF KINETICS ON PLATINUM AND VANADIUM CATALYSTS

Author and Ref.	Catalyst	Activation Energy (kcal/mole)	Observed Kinetics
Bodenstein[17]	Pt	~10 (static system)	$k(SO_2)/(SO_3)^{0.5}$
Lewis and Ries[84]	7% Pt on asbestos		$k(SO_2)$ or $k\,(SO_2)\left[\ln\left(\frac{SO_3}{SO_2}\right)_{eq.} - \ln\left(\frac{SO_3}{SO_2}\right)\right]$
Taylor and Lenher[122]	Pt (hot wire)		$\frac{k\ (\text{distance from equilibrium})}{(SO_3)^{0.5}}$
Boreskov[24, 26]	Pt (massive) or Pt on SiO_2	23.3 ± 0.6	
Hurt[61]	Commercial Pt	25.6	
Boreskov[23]	Pure V_2O_5	38	
Krichevskaya[77]	Pure V_2O_5	34	$\frac{k_1(SO_2)^{1/2}(O_2)^{1/2}}{(SO_3)} - k_2\frac{(SO_3)^{1/2}}{(SO_2)^{1/2}}$
Boreskov[23]	V_2O_5, K_2SO_4, SiO_2	27	
Boreskov[21]	Commercial V_2O_5	23	$\frac{k\ (SO_2)^{0.8}\ (O_2)}{(SO_3)^{0.8}}$
Calderbank[27]	Commercial V_2O_5	29–31	$k(SO_2)^{0.4}(O_2)^{0.8}$
Krichevskaya[77]	Commercial V_2O_5		$k(SO_2)^{0.5}(O_2)^{0.5}$
Baron *et al.*[13]	V_2O_5 on Alundum	21 (He) 15 (N_2) 9.5 (CO_2)	$k(SO_2)$

$$\frac{d(SO_3)}{dt} = \frac{k_1\,(SO_2)\;(O_2)^{0.25}}{(SO_3)^{0.5}} - \frac{k_2(SO_3)^{0.5}}{(O_2)^{0.25}}$$

where the first term represents the oxidation of SO_2 to SO_3 and the second the decomposition of SO_3. Activation energies (for k_1) in the range of 23 to 26 kcal/mole have been reported.

Whereas some authors believe that the limiting step is the reaction of chemisorbed O_2 with gaseous SO_2, others suggest that the rate-determining step is the reaction of chemisorbed O_2 with chemisorbed SO_2.

On the other hand, in the presence of vanadium catalysts the rate is strongly dependent on the oxygen partial pressure and perhaps somewhat less dependent on SO_2 concentration. The activation energy for the reaction on commercial V_2O_5 catalysts appears to be in the range of 23 to 30 kcal/mole, whereas for pure V_2O_5 it is somewhat higher, around 34 to 38 kcal/mole. Krichevskaya[77] has suggested that the limiting reaction is between chemisorbed SO_2 and chemisorbed O_2. However, on the basis of studies of both the kinetics of the reaction and rates of chemisorption of SO_2 and O_2 on the catalyst, Calderbank[27] has concluded that the rate-determining step is the reaction of chemisorbed SO_2 with gaseous O_2. Based on their observations of the effect of different "inert" gases on the reaction rate, Baron *et al.*[13] have concluded that the limiting step is the desorption of the SO_3.

Considering the data of Neumann[95], Kawaguchi[68] has pointed out that catalysts for the oxidation of SO_2 can be grouped roughly into two classes: high-temperature and low-temperature catalysts. The "low" temperature catalysts, which are active below about 500°C, include platinum, vanadates of potassium, sodium, barium, silver, copper, and tin and chromium-tin. The high-temperature catalysts include the oxides of tungsten, titanium, iron, vanadium, arsenic, tin and chromium. It is noted that, with the exception of chromium oxide, all of the high-temperature catalysts are *n*-type semiconductors. Further, it has been observed that the addition of oxides of Sn^{+4} and As^{+5}, which have a higher atomic valence than Fe^{+3}, to ferric oxide catalyst increases its catalytic activity. On the other hand, the addition of oxides of K^+ or Cu^{+2} results in a decrease in catalytic activity. These changes are in the direction to be expected if the catalytic activity is related to the number of semifree electrons in the semiconductor.

Based on these observations, Kawaguchi[68] suggests that the limiting step in the oxidation reaction on the "high" temperature catalysts is the chemisorption of oxygen with the transfer of an electron from the catalyst to the chemisorbed oxygen atom. The chemisorbed oxygen atoms are then supposed to undergo a rapid reaction with gaseous SO_2, producing SO_3 and restoring the catalyst to its original condition.

Studies of SO_2 Oxidation in Fluidized Beds

Goldman *et al.*[53] investigated the kinetics of the oxidation of sulfur dioxide over a commercial V_2O_5 catalyst in confined and fluidized beds under a variety of operating conditions. At mass velocities above a certain limiting value, the reaction rate was found to be independent of mass velocity indicating that under these conditions the rate is not limited by mass transfer effects.

Under these conditions, it was found that the data were in agreement with a kinetic scheme based on the assumption that the limiting step is the reaction of activatedly adsorbed SO_2 with activatedly adsorbed O_2. This is the mechanism suggested by Uyehara and Watson[125] for the interpretation of the data of Lewis and Ries[84] on a platinized asbestos catalyst. The data were then used to calculate values for the equilibrium constants for the adsorption of O_2, SO_2, and SO_3.

The data were correlated assuming that the adsorption equilibrium and the reaction velocity constants for both methods of gas-solid contact are the same. On this basis, the fluid-bed operation gave an effectiveness factor approximately 3 to 4 times greater than that for the confined bed operation.

Varlamov[128] studied the effect of particle size of a barium-promoted, vanadia on alumina catalyst on the rate of oxidation of SO_2 in a fluidized bed. An approximately 20 per cent increase in rate was observed on decreasing the particle size from 3 to 0.081 mm, indicating some diffusional resistance to the reaction on the larger particles.

Mertens[90] passed a finely divided (150μ) Pt on SiO_2 catalyst and a gaseous reaction mixture of SO_2 in air cocurrently through a long reaction chamber. The oxidation rate varied inversely with the flow rate through the reactor.

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CHAPTER 5

MECHANISM OF CATALYTIC OXIDATION

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Electronic Properties of Oxidation Catalysts

In recent years a better understanding of catalysis has been obtained as a result of the recognition that the behavior of a catalyst is related to the electronic structure of its lattice. The physics of the solid state provides background information necessary for consideration of the electronic behavior of catalysts. In a number of specific instances, notably in discussions of the oxidation of ammonia, xylene and carbon monoxide, some details of the connection between electronic properties and reaction mechanism have been presented. This subject has been treated in a number of excellent reviews since 1950 when Dowden[4] emphasized and summarized its status. The reader should consult a small monograph by Rees[11], "Chemistry of the Defect Solid State" which is concerned with the theoretical aspects of electronic structure, and this might be supplemented by reference to more recent papers of Hauffe, Stone and others[1, 3, 8, 10, 14, 9], the comprehensive treatise of Shockley on "Electrons and Holes in Semiconductors"[12], or the ACS Monograph "Semiconductors"[7a]. However, many readers might find it most advantageous to consult a recent review by Fensham[6] on "Semiconductivity and Catalysis" since it covers the subject in a brief and authoritative manner.

Electrical Properties of Nonstoichiometric Oxidation Catalysts

Many typical oxidation catalysts are metallic oxides or metals whose surfaces are covered with transient oxide layers. The catalytic properties of these oxides appear to be related to the electrical (conducting) properties of the oxide lattices in many cases and in turn the latter are often due to the nonstoichiometry of the metal and oxygen in the lattice. There are two general cases depending on whether there is an excess of metal or oxide. These are represented in Figure 1 (see Fensham[6], pp. 229–236). In the case of zinc oxide there is an excess of metal thus giving rise to an n-type (normal or excess) conductor in which electrical conductivity is due to mobility of quasi-free electrons as shown in Figure 1(a). Generally these n-type conductors are poor oxidation catalysts, although vanadium pentoxide is a notable exception.

Cuprous oxide represents the other type of oxide and conductor. Its conductivity is due to quasi-free positive holes in the lattice which arise because of a stoichiometric excess of oxygen, as shown in Figure 1(b).

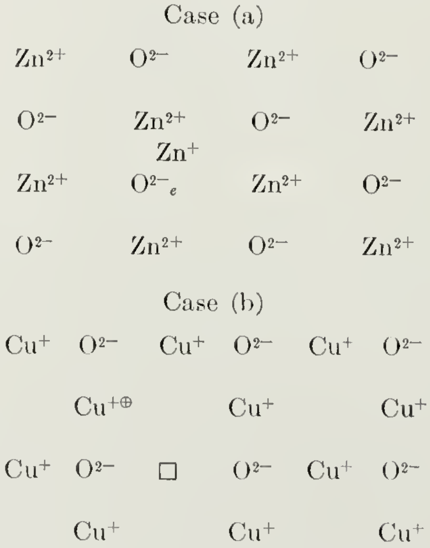

Figure 1. Lattices of n- and p-type oxide catalysts.[6] (Reprinted courtesy of *Quarterly Reviews*)

Generally, the p-type conductors such as cuprous oxide are good oxidation catalysts. Semiconductivity research provides experimental methods for determining the type of conduction involved for any oxide lattice (Fensham, p. 230–232 in Ref. 6). Reference should be made to the section on oxidation of carbon monoxide (p. 303) for further discussion of the correlation of electrical properties with catalytic behavior on a number of different oxide catalysts.

Since vanadium pentoxide is an excellent oxidation catalyst for SO_2, benzene, naphthalene and similar materials, reference should be made to the section on oxidation of *ortho*-xylene (p. 212) where the work of Clark and Berets on the system V_2O_6-O_2-xylene is discussed. It is shown that V_2O_5 and mixtures with V_2O_4 are n-type conductors. Quasi-free electrons in the lattice (see Figure 1a) which arise as a result of lattice oxygen defects convert oxygen gas to oxygen ions at the surface and thus initiate the chemical oxidation. This same section on xylene oxidation describes other structural aspects of the vanadium oxide system.

Lattice Defects Due to Foreign Ions

The above description of a nonstoichiometric catalyst lattice involves only the metal and oxygen which make up the metal oxide catalysts. One may also obtain lattice defects as a result of the presence of foreign ions in the lattice structure. This is especially important where the foreign impurities are of a different valence from the main constituents of the lattice. The valences of these foreign atoms, their size, and their ionization potentials are often factors governing the way they affect the properties of the solid under consideration, as emphasized by Dowden[4] and others[1, 3, 8, 9, 11, 14].

Case (a)

$O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$

V^{+5} $O^{=}$ V^{+5} $O^{=}$ V^{+5}

$O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$

ⓔ

V^{+5} $O^{=}$ W^{+6} $O^{=}$ V^{-5}

ⓔ = quasi-free electron

Case (b)

$O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$

V^{+5} $O^{=}$ $V^{+5\oplus}$ $O^{=}$ V^{+5}

$O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$

V^{+5} $O^{=}$ Ti^{+4} $O^{=}$ V^{+5}

$\oplus$ = quasi-free positive hole

Figure 2. Lattice defect arising from a foreign ion in vanadium oxide.[6] (Reprinted courtesy of *Quarterly Reviews*)

It is of interest to illustrate by means of hypothetical example how lattice defects are produced in semiconductors by addition of impurities—e.g., by addition of titanium or tungsten to a vanadium oxide lattice (see Figure 2 and Ref. 6, p. 234). The vanadium atoms in a vanadium oxide lattice have a valency requirement of five. When a tungsten atom is substituted into the lattice as the impurity, there is an extra valence electron left over, since tungsten has six valence electrons (Case a, Figure 2). The sixth electron, however, is not very tightly bound to the tungsten atom when present in the lattice, and, as a result, it may migrate by thermal vibrations through the vanadium oxide lattice as an electrical current carrier, or may influence adsorption of oxygen at the surface. The electrical neutrality of the crystal is maintained because the excess positive charge on the tungsten atom neutralizes the excess electron that has been contributed to the crystal. However, the electron can migrate through the lattice and carry electric current, while the positive charge must remain localized at the point where the tungsten atom is located. The net result is that the tungsten contributes conduction electrons to the solid.

In contrast, when a titanium atom is substituted into the vanadium pentoxide lattice (Case b, Figure 2), this impurity contributes only four valence electrons. The fifth electron necessary for the valence structure of the crystal is accepted from another vanadium atom in the lattice, thus forming in effect a so-called positive hole in the solid. In this case, the current carried in electrical conduction takes place by means of movement of these positive holes. The reviews referred to in the introduction of this section describe in some detail (1) the quantitative laws governing the rate of movement of electrical charge carriers, and (2) the energy factors governing their movement from one position in the lattice to another. Lattice defects, whether due to nonstoichiometry or to foreign impurities, are capable of and responsible for transfer of electrons from a solid to an adsorbed molecule or, conversely, accepting electrons from an adsorbed molecule. Likewise, the movement of electrons or positive holes in the solid are of importance in catalytic behavior, for they may account for the rapid creation of defects where an adsorbed molecule is about to strike the surface. It is also recognized that the defects are not localized as pictured in Figures 1 and 2, but extend over a relatively large number of atoms. The presentation given in this section is oversimplified but will serve to guide the reader in a qualitative manner until the more authoritative reviews listed in Ref. 4, 6 and 12 are consulted.

In the oxidation of naphthalene to phthalic anhydride, the patent and other literature is full of descriptions of special V_2O_5 catalysts containing other oxides, impurities, etc. Although the claims made may be valid for industrial applications, there is not much basis for claims of any great improvement by addition of impurities based on the experience of the authors in a number of instances, notably for oxidation of naphthalene. This suggests that the combination of V_2O_4 and V_2O_5 which exists in the operating catalyst represents the best combination of valences for many oxidations, the V^{+4} acting as an impurity in the V^{+5}, or vice versa. In effect, therefore, it might have been preferred to use V^{+4} as the impurity in the Case (b) of Figure 2 in place of Ti^{+4}.

Due to the defect structure of the oxide lattice, oxygen may be converted to O^- or O^{2-} ions at the surface, as in the *n*-type oxide, V_2O_5, for xylene oxidation, or for the *p*-type oxide, Cu_2O for CO oxidation. (See pp. 212, 307.) The oxide ion may then diffuse into the lattice through a small number of surface layers or throughout the entire catalyst lattice. Simard, Steger, Arnott and Siegel[13] have presented a description of oxygen diffusion in V-O lattices, and similarly an analogous process is shown for oxygen diffusion in NiO as presented in Figure 8, p. 307. It is evident that the kinetic picture is complicated by the fact that reaction involves (1) adsorption of O_2 (gas) to form an ion which involves only electron transfer, and no oxygen in diffusion, and (2) a combination of this *with oxygen with diffusion*. All combinations of these may be involved and this complicates kinetic and mechanistic studies.

Studies of the electrical conductivity properties of solids have provided evidence indicating why their surfaces are active in catalysis (see Ref. 6, pp. 236–238). In certain cases, the conditions existing at the surface and not those involved in the interior of the crystal may determine the observed electrical properties and the catalytic behavior of the solid. Experimental methods are becoming available for determining the electronic properties at the surface as well as in the bulk phase, and undoubtedly as studies on catalysis progress, the large amount of work being performed on the physics of the solid state will be useful in studies of catalysis. It should be emphasized that the electrical and catalytic properties should be measured simultaneously for reasons pointed out by Clark and Berets[2] for the oxidation of xylene (p. 212).

Chemisorption and Electron Transfer at the Catalyst Surface

The following qualitative discussion is given to emphasize certain current ideas regarding the effects of electron transfer to and from the solid to the adsorbed reactants at the catalyst surface. Although this description may be oversimplified, it will emphasize the matters which are being stressed at this point.

The heterogeneous catalysis of a vapor phase reaction can frequently be described by the following five consecutive steps:

1. Adsorption of the reactants on the surface of the solid catalyst.
2. Diffusion of the adsorbed reactants over the surface to a catalytically active site.
3. Formation of an activated complex from the reactants.
4. Rearrangement of the activated complex into the products.
5. Desorption of the products into the gas phase.

In considering the electron transfers which occur at the surface we are most interested in those which involve the formation of the activated complex. That is, we assume that step (3) is the rate-determining process. In many catalytic oxidations, it is suggested that the activation of the adsorbed reactants occurs as a result of transfer of electrons between the catalyst and the reactants. The transfer of electrons can occur when the electronic free energy level of the solid differs from that of the reactant. Thus a correlation between energy levels of the electrons in the solid and the catalytic activity may be realized.

Depending on the direction of the transfer of electrons, the catalyst is either a *donor* or *acceptor*. In a donor-catalyzed reaction, the free energy of the electrons in the solid at the active sites is higher than the free-energy levels of the electrons in the adsorbed reactant. Consequently electrons will tend to move from the catalyst into the reactant until the free-energy gradient between the two is zero and equilibrium is reached. The increase in negative charge aids the adsorbed reactant in the formation of the activated complex. Decomposition of the complex occurs into the products and the desorption of the products then occurs readily. In oxidation of hydrocarbons, for example, there is transfer of electrons from catalyst to oxygen. In acceptor-type catalysis, the free energy of electrons in the active site in the lattice is lower than that in the adsorbed gas, and the flow of electrons is from the adsorbed reactants into the catalyst surface. The net positive charge on the adsorbed molecules now induces formation of the activated complex and the complex decomposes into the product in order to complete the reaction.

When oxygen is adsorbed on a metallic oxide, an electron may be transferred from the lattice to the adsorbed oxygen which is probably present as an oxygen atom. The electron which is provided to the oxygen atom may be made available by a variety of processes taking place in the lattice. As soon as the oxygen ion is formed, it may diffuse into the lattice. For example, it might move interstitially through the lattice and thus there would be an excess of oxygen, thus creating a lattice defect at the point where the extra oxygen ion is located. Adsorption of appreciable amounts of oxygen on a vanadium pentoxide lattice would result in the formation of negatively charged oxygen ions which might remain on the surface and thus might lead to a positive charge in the lattice as a result of the withdrawal of the electrons to the adsorbed oxygen layer. This positive charge might then prevent further adsorption of oxygen due to electrostatic forces.

If oxygen is adsorbed on a lattice which contains both vanadium pentoxide and vanadium tetroxide, the formation of a monatomic oxygen ion by adsorption of oxygen gas would lead to an oxygen ion which might then move through the lattice to the point where the quadrivalent vanadium is located. The oxygen ion would, therefore, change the lattice at this point by converting quadrivalent vanadium to pentavalent vanadium. The movement of this oxygen ion through the lattice might be through the interstitial spaces between the oxygen and metal ions in the lattice, or it might occur by a so-called hopping or pushing mechanism in which the oxygen ion would push all of the oxygen atoms in the lattice ahead of it toward the vacancy or defect where the quadrivalent vanadium is located. Simard *et al.*[13] have discussed the ready movement of oxygen in vanadium oxide in a pictorial way.

In what has just been said, an attempt has been made to emphasize that an adsorbed gas can take up or give to the surface an electron. This electron may come from the lattice at a point not necessarily adjacent to the point at which the adsorption takes place. The movement of the electron or an atom through the lattice may take place interstitially or by other methods. No attempt is made herein to describe in any detail how these movements take place. These processes usually require activation energies, and in many cases the quantitative laws governing the movement of diffusion of either the electrons or the atoms through the lattice are probably similar in nature to those that have been used in catalysis theory in connection with kinetic and activated adsorption processes[15].

If a metal oxide is at equilibrium with oxygen, the thermodynamic equilibrium constant for the formation of the metal oxide from its components will give the composition of the solid as a function of the partial pressure of oxygen in the gas phase. When the oxide is formed from a metal cation in its highest valence state—for example, V_2O_5—the stoichiometric oxide is attained under a high pressure of oxygen. Similarly, when the metal cation is in a lower valence state—for example, V_2O_4—stoichiometry is attained at a lower oxygen pressure. If an oxide involved with the metal cation is in its highest valence state, then the equilibrium at ordinary pressures involves loss of oxygen from the stoichiometric compound. Excess oxygen is first desorbed from the surface. This creates a lattice defect which then migrates into or through the crystal as described previously. These defects so created then move into the solid until the equilibrium concentration is reached throughout the bulk of the lattice. Thus, by changing the partial pressure of oxygen over the solid, the composition may be varied reversibly. Since the defects must originate at the surface, the process of equilibration may be a fairly slow one, although in the case of the vanadium oxide the migration seems to be rapid. It is also evident that the desorption of oxygen creates a large number of lattice defects of one form or another. This may account for the fact that certain oxides often appear to be catalytically active because of alternate oxidation and reduction. The oxidation-reduction mechanism proposed might actually be synonymous with the idea that such mixed lattices do contain a large number of defects, or the whole lattice might be considered as an enormously large defect.

It might be well to define certain nomenclature which appears in the literature on catalysis, or certainly that which is used in descriptions of semiconductors.

Where the direction of electron flow is from the solid to the adsorbed phase, the process is called *anionic* chemisorption. When the solid is an excess electron semiconductor (n-type), a decrease in the number of free electrons in the surface region of the solid and thus in electrical conductivity will occur. When the solid is a "hole" conductor (p-type), the adsorption with electron transfer from the semiconductor to the adsorbed phase will increase the number of positive holes, and an increase in conductivity will be observed. On the other hand, donation of electrons from the adsorbate to the solid accompanies *cationic* chemisorption. The increase in electron concentration of the solid will lead to increased conductivity in an n-type conductor and decreased conductivity in a p-type semiconductor.

If the charge carrier type is known for a semiconductor, measurement of the electrical conductivity will reveal the direction of the electron transfer between adsorbent and adsorbate. When oxygen is adsorbed on n-type oxides such as V_2O_5, ZnO, CdO, or TiO_2, the conductivity is decreased, indicating that anionic chemisorption is involved. Since the conductivity is increased during the adsorption of oxygen on the p-type semiconductors (Cu_2O, NiO, and FeO), anionic chemisorption is occurring. In contrast, cationic chemisorption occurs when CO is adsorbed on the same oxides, and in both cases affects the conductivity in a manner opposite to oxygen. Thus, we see that the direction of electron flow depends not only on the type of semiconductor but also involves the particular gas being adsorbed. The electron flow will always be in the direction to minimize the free energy of the system. That is, both the direction and amount of electron flow will thus depend on the electronic structures of the solid and the gas. Dowden[4] recognized this dependence, and reached some conclusions regarding the relative ease with which positive or negative adsorbate ions would be formed on the surface of a metal. He proposed for example that the work function of the metal should be small if a negative adsorbate ion is to be formed, the work function measuring the work necessary to remove an electron from the surface of a metal into the gas phase. Thus, a metal with a low work function will donate an electron to the adsorbed phase with relative ease. By analogy, the metal should have a large work function to favor the formation of a positive adsorbate ion.

When a gas is adsorbed on a solid surface, the chemisorption may result in transfer of electrons from the surface to the adsorbed gas as mentioned above. Adsorption may become extensive enough so that the charge built up in the surface may limit further transfer of electrons across the surface boundary, and thus adsorption will cease. This is apparently the situation with vanadium oxide where the amount of oxygen adsorption is relatively small *in the absence of other adsorbed gases.*

Activated States at the Surface of the Solid

In the next few paragraphs some qualitative statements will be made which are consistent with studies of the electrical conductivity properties of solid lattices in order to emphasize the peculiar activity of the surface.

In certain semiconductors—for example, vanadium pentoxide which is a typical oxidation catalyst—it has been demonstrated that the nature of the surface is such that it tends to trap or concentrate conduction electrons near the surface. In some cases it has been found that the energy levels of the electrons in the surface may arise or be influenced by the presence of foreign atoms in the surface phase. Thus, impurities tend to concentrate in the less orderly boundary phase rather than disturb the orderly array of the crystal lattice. Therefore, studies of solids have indicated that the surface has properties considerably different from those of the bulk phase. This is in accord with previous conceptions in catalysis: namely, that the surface of the solid is peculiar or active in catalytic reactions. Furthermore, the accumulation of lattice defects at the surface which are thought to be responsible for catalytic action are consistent with a great deal of information in the literature on catalysis. When a molecule or atom is adsorbed at the surface of the solid, the adsorbed material may induce electronic energy levels at the surface which are different from those in the solid catalyst, and thus provide donor or acceptor electronic levels required for the creation of electron defects or movement of electrons and atoms within the lattice which otherwise would not take place. In the case of oxygen it appears that oxygen provides the necessary acceptor level to permit transfer of electrons through the lattice to the oxygen atom, thus creating an oxygen ion.

Generalized Mechanism for Oxidation Processes

The catalysis of a hypothetical bimolecular reaction by an oxide semiconductor may be used to illustrate the generalized theory just described (see below). For our purpose, it is assumed that the catalyst is a donor for one reactant (B), and is an acceptor of an electron for another reactant (A), and there is a total transfer of one electron in each case.

Reaction Scheme Involving Electron Transfer

A = reactant S = active site on catalyst
B = reactant (e) = electron

$$\text{(e)} + S \rightarrow S\cdot\text{(e)}$$
$$B\text{(adsorbed)} + S\cdot\text{(e)} \rightarrow B^{-}\text{(ads.)} + S$$
$$A\text{(adsorbed)} \rightarrow A^{+}\text{(ads.)} + \text{(e)}$$
$$A^{+}\text{(ads.)} + B^{-}\text{(ads.)} \rightarrow AB\text{(ads.)} \rightarrow AB\text{ (gas)}$$

The degree of electron transfer may vary from one reactant to another, and it is imagined that all that is necessary is a partial charge transfer between the active site on the catalyst and one reactant. Based on these simple assumptions, the action is as follows: first, a conduction electron diffuses through the solid and is finally trapped at an active site, *S*. Reactant *B* is adsorbed somewhere on the surface, and diffuses to the active site *S*. The free energy of the electrons at the active site is higher than the free energy of the adsorbed molecules, *B*. Electron flow will then be from the catalyst into the reactant *B* in the adsorbed layer until the free energies of the electrons are the same in the phases *B* and *S*. Meanwhile, chemisorption of *A* on another part of the surface results in the formation of a donor level with respect to the solid. Therefore, electrons will tend to move from *A* into the catalyst until the free energies are equalized. The reactant *A* which now holds a positive charge diffuses to the active site where *B* is located and an an activated complex $A{\cdot}B{\cdot}S$ is formed. The molecular and atomic orbitals in the activated complex rearrange to form the product *A*-*B*. In the final step *A*-*B* leaves the active site and is desorbed. The electron released by *A* during adsorption is transferred or diffuses through the lattice by some mechanism to the site where the electron was liberated for transfer from the active site to *B*. Thus the catalyst is restored to its original state and the process may be repeated.

For a reaction which occurs through this general mechanism, three general requirements become necessary for a solid to act as a catalyst. (1) In the solid there must be available electrons which can migrate to the active site. These may be conduction electrons. (2) A difference in the free energy of the electrons in the crystal and the free energy of the electrons in the adsorbed reactants exists in order to induce the electron charge flow in the correct direction. (3) The stereochemistry of the adsorbed reactants at the active site must be such that a sufficient distortion of the activated complex into the desired product is possible.

An energy of activation may be necessary for an electron to move through a solid lattice. As the temperature is lowered, the rate of diffusion decreases. Finally, at low temperatures the electron defect may be completely immobilized and the diffusion to the equilibrium positions in the solid may not occur within sensible time. However, diffusion often takes place more readily in the surface phase than in the bulk. In this case, then equilibrium will still be obtained in the surface at temperatures where the defects within the crystal have been frozen. Thus, with the changing temperature, either complete equilibrium in the system, or equilibrium only in the surface, or total nonequilibrium is possible in the defect structure of a solid.

The above description refers to the effects of electron transfer through the lattice, and back and forth between the surface and adsorbed molecules as an important part of a catalytic oxidation. It is emphasized, however, that the electron transfer from the surface to adsorbed oxygen might create an adsorbed oxygen ion. The entity which reacts or diffuses through the lattice might actually be an oxygen ion rather than an electron. It is suggested that if this is the case, the general qualitative and schematic picture which has been given on p. 355 and described in the text will be essentially the same with appropriate changes. In connection with the chapters on *o*-xylene oxidation and on carbon monoxide oxidation, references are made to the fact that the oxygen transfer through the lattice either as an ion, as a molecule, or as an atom might be possible with a very high rate of diffusion. In order to obtain any considerable understanding of the details of what goes on in the lattice during catalytic oxidation, considerably more work on the physics of the solid state of these oxidation catalysts under special conditions will have to be carried out in order to determine the correct detailed mechanism. It is also likely that in some instances the adsorption of oxygen or the material being oxidized at the surface may create its own "defect" at the surface as a result of a very rapid transfer of electrons or other materials through the lattice as the adsorbed gas approaches the surface[16].

Correlation of Catalyst Properties and Catalytic Performance

The performance of a number of oxidation catalysts for a variety of reactions is described in preceding chapters. It seems desirable to assemble and tabulate in this section the catalytic properties of typical metal and metal oxides as oxidation catalysts. In some instances the properties of these catalysts will be correlated with their performance in certain typical catalytic oxidations.

Table 1 summarizes certain properties of the metallic oxides. The first column gives the formula of the oxide. Column 2 shows the so-called semiconductor type. In an *n*-type, conduction is by electrons arising from lattice defects of several kinds, whereas in the *p*-type, it is by positive holes (lack of electrons). Within the class tabulated as insulators, conduction is due to electrons, after their activation from the valence band levels to the conducting bands. The third column shows the element which is in nonstoichiometric excess in the crystal lattice, thus creating the defects which are responsible for conduction. Column 4 describes the qualitative nature of oxygen adsorption. For the *p*-type semiconductors, the surface of the oxide has a high surface coverage. Many electrons are available from the electron valence bands for transfer to the adsorbed oxygen to create oxygen to create oxygen ions, O^- or $O^=$. The *n*-type oxides have low surface coverage by oxygen and there are few electrons available from the so-called impurity levels below the conduction band for transfer to form O^- or $O^=$. The number of electrons transferred depends not only on the number available but also on the energy relationships involved in the transfer.

Columns 5, 6 and 7 describe the degree of activity of an oxide in (1) the decomposition of N_2O to $N_2 + O_2$, (2) the oxidation of propylene to CO_2 and (3) the oxidation of CO to CO_2. Tables 2 through 6 give additional information on the oxidation of CO, propylene, NH_3, methanol, and C_4 hydrocarbons. The reader is referred to the appropriate sections for more detailed discussions of the oxidation of each of these compounds.

TABLE 1. SUMMARY OF CATALYST PROPERTIES AND ACTIVITY

Oxide	Type	Excess Element in Lattice	Adsorption of Oxygen gas	Activity		
				N_2O Decomposition	Oxidation of Propylene	Oxidation of CO
Cu_2O	*p*	Oxygen	High surface coverage	high	high	high
NiO	*p*	"	High surface coverage	"	"	"
CoO	*p*	"	High surface coverage	"	"	"
MnO_2			Many electrons available for transfer to O			
CuO	ins	none		medium		medium
MgO	"	"		"		
Al_2O_3	"	"		"		low
PtO_2	"					
Ag_2O	"					low
Cr_2O_3	"					
ZnO	*n*	Zn	Low surface coverage	low		low
TiO_2	*n*	Ti				low
V_2O_5-*x*	*n*	V	Low number of electrons available for transfer		low	low
MoO_3-*x*	*n*	Mo			"	
WO_3-*x*		W			"	
Fe_2O_3	*n*	Fe	Low number of electrons available for transfer			medium

At the 1956 International Congress on Catalysis, Dowden, Mackenzie and Trapnell[5] summarized the present situation on the correlation of semiconductivity behavior of oxides and their catalytic activity during oxidation of carbon monoxide[7]. Table 2 presents the activity of the oxides in their order of activity. It is noted that (except for cuprous ion) the first oxides contain metallic ions in which there are unpaired *d* electrons. Chromium oxide, which is inactive in this oxidation also possesses unpaired *d* electrons. The cuprous ion in cuprous oxide is thought to possess its unique high activity because the *d* electron shell is unstable. In general the *p*-type oxides are more active than the *n*-type oxides and the latter are more active than the insulators. Dowden *et al.*, expressed the opinion that in the carbon monoxide oxidation, semiconductivity properties of the oxide are of more importance than the electronic configurations, because oxygen adsorption is likely to involve simple formation of negative ions by transfer of an electron from the catalyst to the oxygen. This is governed by boundary layer considerations and conductive properties. A correlation of catalytic activity with electron configuration is not in fact as successful as one with semiconductivity.

TABLE 2. CARBON MONOXIDE OXIDATION CATALYSTS

1. Active Below 150°C:
   CoO Cu_2O NiO MnO_2
2. Active between 150 and 400°C:
   CuO Fe_2O_3 ZnO CeO_2 TiO_2 Cr_2O_3 ThO_2

TABLE 3. PROPYLENE OXIDATION ON METALLIC OXIDE CATALYSTS

Catalyst Oxide	Acrolein Yield (%)	% CO	Remarks
Cu	40–70	Small	
Fe	10–20	High	
Co	10–20	"	
Ni	10–20	"	
Mn	10–20	"	
Ce	10–20	"	
Cr	10–20	"	
V	Low	"	Some aldehydes
W	"	"	Aldehydes low
Mo	"	"	" "
U	"	"	" "

TABLE 4. AMMONIA OXIDATION TO N_2O ON METALLIC OXIDES

Catalyst Oxide	Temp. for Activity (°C)	Type	Activity	Surface Oxygen	Excess Element in Lattice
Fe-Bi	200	*p*	High		—
Mn		*p*	"	High	O
Co		*p*	"		O
Ni		*p*	"		O
Fe		*p*	"		Fe
Pr	375	*n*	Low	Low	Pr
Bi	475	?	"		—
Cu	500	ins.	"	—	none

Dowden *et al.* studied the hydrogen-deuterium exchange on oxide catalysts in order to correlate the activity with the electronic and semiconductivity properties of the oxides. The results obtained are not similar to those encountered with the oxidation of carbon monoxide, and nitrous oxide decomposition. As a result of this they conclude that catalysis induced by oxides is too complex to be interpreted in terms of a single electronic factor. This same conclusion may well apply to the carbon monoxide oxidation since Table 2 shows that there are some outstanding exceptions to the correlations between semiconducting properties or electronic configurations and catalytic activity. As stated by Dowden *et al.*, further data are needed on the activity of the different oxides in other reactions in order to build up additional rules for predicting the relationship between catalyst activity and structure of the oxide. Undoubtedly, the work of Dowden and other investigators of this subject, along with the work on carbon monoxide oxidation and nitrous oxide decomposition, will provide the preliminary basis for further understanding of catalyst behavior.

TABLE 5. OXIDATION OF METHYL ALCOHOL ON METALLIC OXIDES

Reactant	Product	Temp. (°C)	Catalyst Composition	Type
MeOH	CH_2O	525	Cu	*p*
		525	Ag	Insulator
		525	Au	
"	CO_2	400	Fe_2O_3	*n*
"	CH_2O	400	MoO_3	*n*
"	"	400	50 Fe_2O_3-50 MoO_3	—
"	"	250	10 Fe_2O_3-90 MoO_3	—
"	"	300	V_2O_5	*n*
"	"	300	WO_3:MoO_3	—

TABLE 6. OXIDATION OF FOUR-CARBON HYDROCARBONS

Catalyst Oxide	Temp. Range (°C)	Products
Ag	150–260	CO_2
V_2O_5	300–425	See Section on C_4 Hydrocarbons Maleic Anhydride, etc.
MoO_3		Maleic Anhydride

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CHAPTER 6

MISCELLANEOUS CATALYTIC OXIDATIONS

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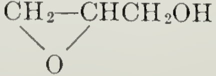
Many of the references found during the preparation of this chapter did not lead to important information on reaction kinetics or the mechanism of action of the catalyst. A number were obtained, however, that may be of general interest and are easily cataloged. These references are assembled in Table 1. The table is broken down into sections, each section containing references to papers which describe products of a similar nature.

It was of interest to condense further the results of the references shown in Table 1. Such a condensation is shown in Table 2. It is evident that the principal metallic constituents of oxidation catalysts are silver, vanadium, platinum and copper. Copper behaves a great deal like silver in catalytic oxidations and in some cases appears to work as well as silver. In general one may say that silver catalysts used in catalytic oxidations operate in the temperature range from 200 to 300°C whereas the vanadium oxide catalysts are used most successfully in the range from 400 to 500°C. For both of these types of catalysts it is likely that during oxidation the catalyst may consist of several valence forms of the metal. In the case of silver, one probably deals with silver oxide and silver, whereas in the case of vanadium one probably has a mixture of vanadium oxides in the 4 and 5 valence states.

It is difficult to determine the exact nature of the products formed from a number of the literature references and, furthermore, the yields may not be reliable in many cases where the references are to patents.

One should also note that the effects of addition of minor constituents are described. A notable example is the addition of selenium during the oxidation of olefins on copper catalysts in which unsaturated aldehydes are formed. It will also be observed that the effects of dilution by water, traces

Table 1. Miscellaneous Catalytic Oxidations

Products	Reactants	Catalyst	Conditions	Ref.
A. Maleic and Succinic Acid				
Maleic acid	Crotonaldehyde	V-Mo-P	Dilution with H_2O	6
" "	Halogenated hydrocarbons	V, Mo, W, Cr, V	4–8 C atoms in hydrocarbon	17
" and succinic acids	Butyrolactone	V_2O_5, CuO	225–250°C	26
"	Halogenated hydrocarbons	V_2O_5	425°C; C_4 and C_5 hydrocarbon	16
"	Succinic acid	V or Mo	250–600°C	14
"	Branched-chain dienes	V or Mo	C_6 diolefins as reactants	33
Maleic anhydride, acids	*cis*-Butene	V or Mo + Na_2SO_4	350°C	4
Maleic anhydride	Crotonaldehyde	V, Mo, P on Al_2O_3	340–425°C	8
" "	Succinic acid		300–600°C	13
" "	2-Butene,-1,4-diol			39
" "	Pentenes, hexenes, etc.			19
Maleic acid	Furfuraldehyde	V_2O_5 plus Mo, P_2O_5, etc.	Effects of promoters on V_2O_5	45
" "	Furane	" " " " "	" " "	25
" "	Benzene	V_2O_5 plus MoO_3	Effect of Mo on V_2O_5	44
B. Ketones, Aldehydes and Acids from Alcohols				
Methacrolein	Methallyl alcohol	Cu	300–350°C	11
Aldehydes	Alcohols	Mo + CaO_2	MeOH, CH_2O	9
"	"	Ag	Effect of traces of S	36
CH_2O	MeOH + O_2	Ag	540–580°C; effect of additives, H_2O	47
CH_2O	$CH_4 + O_2$		Effect of traces of NO_2	41
Formaldehyde cyanohydrin	MeOH + NH_3 + O_2	Mo, Mo + P + Fe, Mn, Cd	Ferric molybdate catalyst, 300–600°C	28
Dicarboxylic acids, aldehydes	Glycols, alkylene glycols	Ag, Cu, Cu-Si-Mn	225–400°C	30
Acrolein	Allyl alcohol	Ag	200–240°C	48
Methyl vinyl ketone	Methyl vinyl carbinol	ZnO + CuO	250–360°C	27
Acids, MeOH, etc.	CH_4	Cu, Ag, Zn, Ni, Monel	High pressure; gauge catalyst	7
Acrolein,  $CH_2\text{—}CHCH_2OH$ (O)	Allyl alcohol	Ag	150–300°C	49
Diketone with adjacent C═O groups	4-Carbon ketone	Cu_2O on SiC	4 or more C atoms in ketone	23
Acetaldehyde	Ethyl alcohol	Cu	Reaction in presence of deficiency of O_2	3

Methylal, $CH_2(OCH_3)_2$	Methanol	Cu on silica	Effect of HCl addition to air	21
Acetone	Isopropyl alcohol	Cu	Reaction in presence of deficiency of O_2	2
Acrolein	Allyl alcohol	Ag	200–400°C	1
Hexylmethyl acetone	Hexylmethyl carbinol	V_2O_5	350°C	35
D-Et Me CHCHO	D-Et Me $CHCH_2OH$	Ag	480–520°C	10
		C. Olefin Oxides etc. from Olefins		
Acids	Olefins	V_2O_5	350–500°C. Effect of C chain length	18
Olefin oxides	"	Ag	Effect of acetylene compounds	20
Miscellaneous	"	Ag, Pt, Ni, Au, etc.	Fluid catalyst	42
" (ethylene oxide)	" (ethylene)	Ag	" "	43
Propylene oxide	Propylene	Cu, Ag + Se	" "	22
Aldehyde	2-Cyclopentene-1-ethanol	Ag	400°C	34
Acetaldehyde	Ethyl alcohol	Ag, Cu on clays		24
		D. Nitriles		
Acrylonitrile	Methallylamine, etc.	Ag	500–525°C; 1:1 ratio amine to O_2	29
Pyridine nitrile	Alkyl pyridine + NH_3 + O_2	V-Mo-P	425°C	38
Aromatic nitrile	Cyclopentane; cyclohexane + NH_3	V + Mo + P	475°C	15
Alkylaryl nitrile	Alkylbenzene + NH_3 + O_2	V + Mo + P	450°C	12
		E. Sulfides		
$(t\text{-Bu})_2S + (t\text{-Bu})_2S_3$	Tertiary BuSH + O_2	Bauxite	275–350°C; Fe in bauxite 2–8%	31
t-Alkyl sulfides	*t*-Alkylmercaptan + O_2	Al_2O_3 + Ce + V + Fe	"	32
		F. Phthalic Anhydride		
Phthalic anhyd.; naphthoquinone	Naphthalene, xylene, etc.	V_2O_5	Fluid bed catalyst	5
Phthalic anhyd.	Xylene (*ortho*)	"	Effect of SO_2 on oxidation	46
Phthalic acid, etc.	Naphthalene, etc.	V_2O_5 or $TiO(VO_3)_2$	Catalyst with TiO sinters less	37
		G. Dibasic Long Chain Fatty Acids		
Long chain dibasic fatty acids	Unsaturated long chain fatty acids	V, Fe, Os	Oleic gives suberic and azelaic acids	40

of sulfur and NO_2 etc., are mentioned in Table 1. It is not intended that the literature shown in Table 1 be complete, but it does serve to cover the use of a number of oxidation catalysts in certain reactions which have been studied rather intensively on an industrial scale.

TABLE 2. SUMMARY OF CATALYSTS FOR OXIDATION OF CERTAIN ORGANIC COMPOUNDS WITH OXYGEN

Reactant	Principal Oxidation Products (other than CO_2)	Main Metallic Catalyst Constituent
Olefins	Aldehydes	Ag
Alkyl groups + NH_3	Nitriles	V
Amines	Nitriles	Ag
Hydrocarbons + NH_3	HCN	Pt
Unsaturated acids	Dibasic acids	V
4-Carbon ketones	Diketones	Cu
Aldehydes, etc.	Maleic anhydride	V
Alcohols	Ketones, aldehydes, acids	Ag, Cu
Olefins	Olefin oxides, etc.	Ag, Cu
Mercaptans	Sulfides	Al_2O_3 (active)

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