Chapter 1

Determination of Mechanism in Heterogeneous Catalysis

Robert L. Burwell, Jr.

Ipatieff Laboratory, Department of Chemistry, Northwestern University,
Evanston, Illinois 60208, USA

Contents

J. R. Anderson et al. (eds.), *Catalysis*

1. Introduction

This chapter will discuss methods for the study of the mechanisms of heterogeneous catalytic reactions. The various examples of mechanistic studies have been chosen to illustrate techniques used in mechanistic studies and not to provide a general survey of the mechanisms which have been proposed for catalytic reactions. References have been chosen to be leading references rather than to indicate historical priority.

The beginning of modern catalytic mechanisms can be precisely dated to the 1915 paper of Langmuir [1]. It is necessary to consider this paper and the 1922 paper [2] in a little detail because all subsequent mechanistic work evolved from them. A survey of earlier mechanistic work is given in Ref. [3].

In these studies originally aimed at the tungsten filament light bulbs, Langmuir invented the concept of chemisorption, he proposed that oxygen and hydrogen were dissociatively chemisorbed on metal surfaces, he measured adsorption isotherms experimentally and he derived the Langmuir adsorption isotherm on the basis of kinetics. Langmuir also studied the kinetics of some chemisorptions and calculated the sticking coefficients. This work involved low pressure techniques. Thus, Langmuir 'invented' the area of surface chemical physics (surface science). The work just described led Langmuir to investigate heterogeneous catalytic reactions, in particular, the oxidations of hydrogen and of carbon monoxide on the surface of platinum.

The surface of a metal is capable of accepting another layer of metal atoms. Langmuir considered that the missing bonding made the surface of a metal necessarily chemically unsaturated or, to use a more modern term, coordinatively unsaturated. In this connection, it should be recalled that Langmuir along with

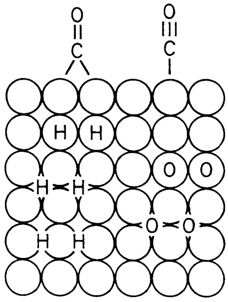


Figure 1. A(100) face of a face centered cubic metal showing linear and bridged forms of adsorbed carbon monoxide and possible locations for dissociatively adsorbed dihydrogen and dioxygen

G.N. Lewis was involved in developing the octet theory of the electronic structure of molecules. In 1913–14 the Braggs determined the atomic structures of a number of metals. Langmuir seized upon these results as providing specific structures for adsorption complexes on metals [4]. The octet theory led Langmuir to conclude that the carbon atom of carbon monoxide would become attached to surface atoms of metals like platinum as shown an Figure 1 for a (100) plane, Langmuir's "checkerboard plane." However, Langmuir specifically noted that he could not distinguish between the carbon atom becoming attached to one surface atom as shown at the right or to two atoms as shown at the left. Nothing definite could be said about this until the infrared adsorption studies of Eischens forty years later. Similarly, nothing could be said as to whether hydrogen atoms were attached above one atom or between two or four atoms as shown in Figure 1. The situation with respect to dissociatively adsorbed oxygen was similar. Approaches to answering this question were to come even later.

On this basis of kinetic measurements (the rate was first order in CO and minus first order in O_2) Langmuir proposed that the oxidation of carbon monoxide would occur by collisions between a molecule of carbon monoxide and an irreversibly adsorbed atom of oxygen in which the carbon monoxide molecule abstracted the atom of oxygen from the surface. He considered but rejected on the basis of his kinetic measurements a mechanism in which O_a and CO_a combined to produce carbon dioxide. Here O_a represents an adsorbed oxygen atom. Thus, Langmuir rejected what is sometimes erroneously [5] called a Langmuir–Hinshelwood mechanism in favor of what is sometimes erroneously called a Rideal–Eley mechanism. The reaction is more complicated than Langmuir imagined [6, 7], but the mechanistic gap between post-Langmuir and Langmuir is tiny compared to that between Langmuir and pre-Langmuir.

2. The Nature of Mechanism

Mechanisms occur in various levels. Sixty years ago, a physical chemist working in gas kinetics could consider that his mechanistic duty had been done when he could list the elementary processes involved in the reaction. For example, for the reaction:

$$A_2 + B_2 \rightarrow 2AB,$$

the elementary processes might be:

$$A_2 \rightarrow 2A$$

$$2A \rightarrow A_2$$

$$A + B_2 \rightarrow AB + B$$

$$B + A_2 \rightarrow AB + A$$

$$A + B \rightarrow AB$$

In general, the listing of all of the intermediates involved in a reaction is equivalent to giving the elementary processes involved in that reaction.

Today, for a simple elementary process, a chemical physicist might want to know something about the energy along the reaction coordinate. Given the translational energies of reactants and their rotational and vibrational quantum numbers, what are the corresponding quantities for the products?

The complications of surface chemistry have prevented much advance beyond the first level in the case of heterogeneous catalysis, but recently advances to higher levels of mechanism have been achieved for some simpler reactions, particularly for chemisorption on single crystal surfaces (see the accompanying article by Coulston and Haller).

Despite any phraseology in what is written above, one cannot rigorously deduce a mechanism from experimental facts. That is, a mechanism is a theory and, as such, cannot be rigorously proved. One can make rigorous experimental predictions from a theory but not the reverse. Thus, given a mechanism, one can deduce experimental predictions. If the experimental predictions disagree with what is in fact observed, the mechanism must be abandoned or modified. If the predictions accord with experimental data, the mechanism is not proved, it is simply not disproved. The next comparison of prediction and observation may invalidate the mechanism. In general the greater the number of accords between prediction and observation, that is, the greater the number and variety of experimental data which have been found to be correctly predicted, then the greater is the probable life of the mechanism. But even a mechanism which has lasted for many years and which seems very securely founded may become untenable. Thirty years ago all elementary physical chemistry textbooks gave the first order decomposition of N_2O_5 as the classic example of a unimolecular decomposition and the second order reaction:

$$H_2 + I_2 \rightarrow 2HI$$

as the classic example of a bimolecular reaction. Yet both mechanisms were shortly to be found to be incorrect. Thus, one cannot really "determine" a mechanism, but the expression is widely used and harmless if properly understood.

In principle, then, for a given reaction, one should list all conceivable mechanisms which do not violate some fundamental physical principle. All of these mechanisms will go at a finite rate [8], but some will be fast, some will be slow and most will be very slow, perhaps 1 molecule of product per m^2 of catalyst per megayear. The problem is to find which one in the list of mechanisms is the fastest. One would test as wide a variety of data as possible against the predictions of the mechanisms. This operation will eliminate most of the mechanisms as significant contributors to the rate of reaction. If two or more mechanisms survive this operation, one tries to design experiments which will distinguish among the residual mechanisms. Finally, one hopes to reduce the list of mechanisms which accord with the data to just one, "the mechanism."

What has just been described is an idealized situation which is unfortunately rarely found in this vale of tears and tribulations. First, two or more mechanisms may produce roughly equal rates. This, of course, seriously complicates the problem. Further, the accumulation of as much data as is needed to isolate "the mechanism" may take a very long time. In practice one must usually be content with partial mechanisms.

From what has been said above, there should be no mechanistic controversies. They are, however, lamentably common. Up to this point we have implicitly assumed that all of the experimental facts were correct and appropriate to the reaction on a particular catalyst. But, of course, experiments may have been defective and one author may have relied on one set of experiments and another author on another. More commonly, however, authors emphasize different sets of data and ignore other data. One should avoid becoming emotionally attached to a mechanism, but let him who is without sin cast the first stone.

3. Preliminaries to the Study of Mechanism

The descriptive chemistry of a catalytic reaction should be well worked out before starting mechanistic studies. That is, yields of products as functions of conversion should be known. There are some catalytic reactions like the hydrogenation of nitrogen and the oxidation of sulfur dioxide in which there is only one product and the question of selectivity does not arise. More commonly, however, there will be two or more products which are formed in series or in parallel. In particular, one needs to know whether intermediates are released to the gas phase and then are readsorbed to react further.
This is unlikely in the reaction:

$$H_2C{=}CH_2 + H_2 \rightarrow CH_3CH_3,$$

but in the hydrogenation of 1-butene on many metallic catalysts, some 2-butene appears in the gas phase at intermediate conversions and, on palladium catalysts, the rate of isomerization is as fast as that of hydrogenation [9]. The formation of 2-butene would of course be missed if one examined products only at 100% conversion to butane.

As another example, consider the hydrogenation of 2-butyne. On metallic catalysts one observes the formation of two intermediate products, *cis*- and *trans*-2-butene. At low conversions, *cis*-2-butene is the predominant product, but small

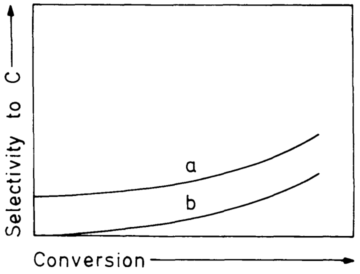


Figure 2. Selectivity for C in the reaction sequence given in the text. In curve **b**, C is formed only via B(g) and C is not an initial product. In curve **a**, some C is formed as an initial product (provided that there is no intrusion of mass transport effects)

amounts of *trans*-2-butene and butane may also be present. One then asks, are *trans*-2-butene and butane primary products or are they formed by further reaction of desorbed *cis*-2-butene? In principle, one can answer the question by measuring the selectivities to *trans*-2-butene and to butane as a function of conversion and extrapolating to zero conversion. If the selectivities to either or both have finite intercepts, then one or both are primary products, that is, some proportion or one or both is formed by a series of surface reactions which does not go through *cis*-2-butene (g). The situation is shown in Figure 2 for the simpler reaction:

$$A(g) \rightarrow B(g)$$
$$B(g) \rightarrow C(g)$$
$$A(g) \rightarrow C(g)$$

where all reactions proceed on the surface of a catalyst and the question is, whether the reaction, $A \rightarrow C$ has a significant rate. If selectivity to C (percentage of C in the product) vs. conversion follows curve b, then the rate of $A \rightarrow C$ is negligible. If curve a is followed, one might conclude that $A \rightarrow C$ has a significant rate and C is an initial product. However, before drawing this conclusion one must make sure that significant intrusion of the effects of mass transport are absent.

4. Effects of Mass and Heat Transport

A. Mass Transport

In the reaction just considered, if A is to diffuse from the external surface of a catalyst granule to the center of the granule, there must be a negative concentration gradient along this path, the distance along which will be denoted by z. If $-(d[A]/dz)/[A]$ (where [A] is the concentration of A in the pore space of the catalyst) is small enough, that is, if [A] in the gas phase of the pore volume at the center of a granule of catalyst is only a few percent smaller than that in the gas phase at the surface of the granule and if similar considerations apply to [B] and [C], then the effects of mass transport on the rate and selectivity of the reaction will be negligible. If, however, $-(d[A]/dz)/[A]$ is large, then [A] will decline rapidly as one penetrates into a pore, as shown in Figure 3. The interior of a granule is devoid of A and the rate of reaction of

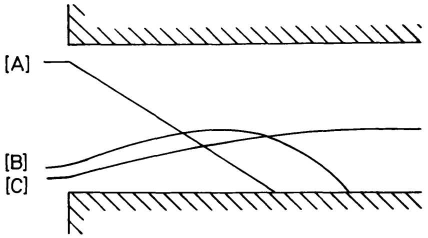


Figure 3. A case with serious concentration gradients in the catalyst pores for the reaction sequence given in the text. A pore which opens at the left is shown schematically. The concentrations are plotted vertically vs. distance into the pore

A is much below that which would be observed if all of the internal surface of the catalyst were exposed to A at [A] equal to the value at the external surface. In measuring kinetics for mechanistic purposes, one must avoid the situation shown in the Figure 3. Given certain parameters of the catalyst and the reaction rate, one can calculate an "effectiveness factor" which becomes unity as (d[A]/dz)/[A] approaches zero [10]. One can also test for the intrusion of serious effects of mass transport by measuring the rate of the reaction on several catalysts of varying granule size at otherwise fixed conditions. The deleterious effects of pore diffusion are absent in the range of granule sizes over which the rate is the same.

Serious concentration gradients in catalyst pores can lead to misleading rates and misleading dependence of rates on temperatures and concentrations of reactants. They can also distort selectivities as shown schematically in Figure 3 for conditions of extreme concentration gradients in which the center of the catalyst contains only C. Since [B] is much higher within the catalyst pores than at the external surface of the catalyst granules, the extent of formation of C is much larger than would be predicted from the measured external values of B. This will give the effect of C being a primary product (i.e., C follows curve a in Figure 2) when in fact C is not a primary product. If, in connection with measurements of rate, one has established that (d[A]/dz)/[A], etc. are negligible, then they will be negligible in so far as selectivities are concerned.

In general, other things being equal, catalysts with a large specific pore volume (ordinarily, then larger pore diameters) will exhibit less serious concentration gradients than catalysts with small pore volumes (and smaller pores). For a supported catalyst, it is better, for example, to use a wide pore silica gel (average pore diameter ~ 15 nm) then a narrow pore one (2.5 nm).

B. Heat Transport

Many catalysts, in particular, catalysts in which silica or alumina is the support, are poor conductors of heat and they are packed in a reactor under conditions such that thermal contact between granules is poor. Since the ratio of the enthalpy of reaction to the heat capacity of reactants plus products is usually large, adiabatic temperature rises at 100% reaction can amount to hundreds of degrees. Thus, the catalyst in gas phase flow reactors can have a temperature many degrees above the surrounding constant temperature bath. Such behavior can seriously distort kinetics [10]. One should have a thermocouple inside the catalyst bed and, in general, one should work under conditions which give very small temperature rises. One can usually achieve this situation by working at small conversions ($\sim 5\%$) and by using a small amount of catalyst diluted with an inert material, often the support for supported catalysts.

Over the years there have been a few claims that addition of "inert" support led to an exaltation of the rate of reaction which was ascribed to spillover of hydrogen onto the surface of the support and reaction there. It would appear that such an effect is very uncommon in practice and that the observed increases in rate were related to "spillover" of poisons from the catalyst to the support [11, 12].

5. Analogies

Mechanistic thinking in heterogeneous catalysis has often been influenced by mechanisms adopted in other areas of chemistry.

The first instance of this was the carbenium ion theory of catalytic cracking (*carbenium* is used for such species as $C_2H_5{}^+$) and alkylation [13]. This involved a relatively straightforward extension of the ideas of acidity and carbenium ion reactions developed in solution to reactions on solid strong acids. In recent years mechanistic ideas about reactions in the presence of superacids (carbonium ion reactions, for example, $C_2H_7{}^+$ is a carbonium ion) have also been extended to heterogeneous catalytic reactions [14].

Surface chemical physics (surface science) has also played an important role in providing analogies. To date, such analogies have involved only metallic catalysts. Contributions from studies on oxides are just beginning. Until recently, the contributions of surface chemical physics primarily dealt with chemisorption. Discoveries in this area have been stimulating, although to date there is no evidence that ordered chemisorption such as that often observed on single crystal planes by LEED ever occurs on the small metal particles of supported metal catalysts. In recent years, a number of chemical reactions, often at atmospheric pressures, have been studied on single crystal planes by the techniques of surface chemical physics. Results here are strongly influencing mechanistic thinking in heterogeneous catalysis on metals [7].

The extension of results from surface chemical physics to conventional heterogeneous catalysts involves two particular problems. The techniques of surface chemical physics involve a flux of electrons to or from the single crystal surface under investigation. This requires that the system be at a low pressure so that the mean free path of the electron is large. Thus, it is difficult to examine supported catalysts effectively, because the electrons cannot penetrate more than a few nm of the support. One cannot, then, examine a working catalyst at any normal pressure unlike the case with such techniques of surface physical chemistry as infrared absorption spectroscopy or electron paramagnetic resonance. A major advance has been the development of devices which permit enclosing the single crystal within a removable cup. With the cup removed, one examines the surface by such techniques of surface chemical physics as low-energy electron diffraction, electron energy loss spectroscopy (one of the mechanistically most useful tools of surface chemical physics), etc. After placement of the cup, one can run catalytic reactions under pressures of one atmosphere or above. One can, remove the cup and repeat the examination of the surface in vacuum. Useful as this technique has been, one still cannot examine the working catalyst.

This chapter will not consider in any detail the applications of surface chemical physics to the determination of mechanism in heterogeneous catalysis. Reference [7] can be referred to in this connection (see also Ref. [15]).

The other problem is extending results on a single crystal plane to the tiny particles of many supported catalysts. The degree to which one runs into trouble in extrapolating results from a 1-cm^2 crystal plane to the surface of a 1.5-nm metallic particle is not yet clear.

The final area which provides analogies is the organometallic chemistry of transition elements. The development of this area in the 1960s and 1970s stongly influenced catalytic thinking. Ideas and terminology, for example, π-complexed olefins and π-allyl, were taken directly into heterogenous catalysis. However, evidence for many of these species as surface species had been advanced well before they were discovered by organometallic chemists, for example, the surface alkyl (monoadsorbed alkane) of the Horiuti–Polanyi mechanism [16]. Once discovered, organometallic complexes were taken as models to interpret the infrared frequencies oberved for chemisorbed species, first done by Eischens in the case of linear and bridged carbonyls. Mechanistic ideas in organometallic chemistry have been applied directly to heterogeneous catalysis, for example, the concept of insertion reactions.

There has been some disagreement as to just how to apply organometallic analogies. One group [17] confines its analogies to mononuclear organometallic complexes and considers that the adsorbed species involved in a reaction on metals are all adsorbed on one surface atom. Another group tries to take its analogies from polynuclear organometallic compounds [18] and it does not restrict binding of intermediate species to just one metal atom. Most workers could probably be considered eclectic and to take ideas from both types of organometallic complexes. After all, both linear and bridged carbonyls are known on the surfaces of metals.

6. Basic Mechanistic Considerations

Consider a reaction which is first order in the gas phase. Mere physisorption of the reactant on the surface of a catalyst or in the pores of a zeolite would not change the rate of the reaction, since a characteristic of first order reactions is that the fraction which reacts per unit time is independent of concentration. However, in a second order reaction (rate $= k_2 C_A C_B$), the fraction of A reacting per unit time is proportional to C_B. Thus, mere adsorption on a surface or in pores would increase the rate of a reaction. This idea goes back to Faraday and Ostwald [3] and has been called the condensation mechanism of heterogeneous catalysis. One example of the condensation mechanism involves the second order Diels–Alder dimerization of butadiene catalyzed by NaY zeolite at 250°C, 1 atm. [19] in which the uncatalyzed reaction has a detectable rate under these conditions.

However, no evidence has been adduced that such mechanisms are common. Further, in the great majority of catalytic reactions, the ratio of the catalyzed rate to the uncatalyzed rate is much too large to be explained by the condensation mechanism. Thus, one is led to the view that ordinarily chemisorption is what leads to heterogeneous catalysis and that at least one of the reactants must be chemisorbed. In this case, the catalytic cycle for a porous catalyst must resemble the following:

a—Diffusion of reactants from the bulk fluid phase to the internal catalytic site of the catalyst
b—Chemisorption of reactants
c—Surface reaction among adsorbed species
d—Desorption of products
e—Diffusion of products to the bulk fluid phase.

In a reaction like the liquid phase hydrogenation of an olefin, where the hydrogen is in the gas phase and the catalyst is suspended in a liquid solution of the olefin, there is an additional complication, transport of hydrogen between the gas and the liquid phase. This step is slow unless the H_2(g)/liquid interface is made very large [20]. In most of the reported heterogeneous and homogeneous catalytic hydrogenations in the liquid phase, $[H_2]$ in solution must have been much below its value at saturation, rates were too slow, and mechanistically misleading results may have been obtained. In the rest of this chapter, we shall attempt to choose examples in which mass transport problems are absent.

There are two reaction schemes which are called mechanisms, but which really are schemes for just one elementary process in the overall catalytic cycle.

In a Langmuir–Hinshelwood mechanism, the reactants in the gas phase are in *preequilibrium* with the adsorbed reactants [5]. The rate determining step is the surface reaction among the adsorbed intermediates. For the reaction, $A + B \rightarrow C$, the Langmuir–Hinshelwood mechanism could involve:

$$A(g) + * \rightleftharpoons A*$$

$$B(g) + * \rightleftharpoons B*$$

$$A* + B* \rightarrow C* + * \quad \mathit{rdp}$$

$$C* \rightarrow C(g) + *$$

Here the * represents a surface site. However, if the last two steps were replaced by one step which was still a *rdp* (rate determining process):

$$A* + B* \rightarrow C(g) + 2*$$

this would also be a Langmuir–Hinshelwood mechanism.

Prequilibrium is a key requirement of the Langmuir–Hinshelwood mechanism, since, as will be seen, the rate of the *rdp*, $k\theta_A\theta_B$, can be converted to $k'f[P(H_A)P(H_B)]$ by the adsorption isotherms of A and B. Unfortunately a tendency has arisen in surface chemical physics to use the term, Langmuir–Hinshelwood mechanism, merely to mean that two adsorbed species react without consideration of preequilibrium.

The Rideal–Eley mechanism was originally applied to a mechanism for isotopic exchange between D_2 and H_2 in which:

$$D_2(g) + H* \rightarrow HD\ (g) + D*$$

Thus, one of the reactants does not pass through an adsorbed intermediate of minimum Gibbs Energy. D_2 and HD do interact with the surface in a transition state. The term Rideal-Eley mechanism or step was generalized in the literature to cover almost any kind of process in which one reactant was not chemisorbed in a minimum Gibbs energy intermediate. Thus, for example, the abstraction step:

$$*O + CO(g) \rightarrow CO_2(g) + *$$

of Langmuir's mechanism for the oxidation of CO might be called a Rideal–Eley mechanism. Since the term Rideal–Eley mechanism was being used in a variety of conflicting senses, IUPAC [5] recommended that the term be used only in its original sense, that is for the particular isotopic exchange reaction mentioned above. The recommendation appears to have had little effect.

A number of reactions have been proposed to involve "Rideal–Eley" mechanisms or steps in some loose sense. The first of these was Langmuir's abstraction step, but Langmuir, at least, did not call this a Rideal–Eley step. However, very few such mechanistic proposals have been widely accepted.

Heterogeneous catalysis is confronted with a mechanistic problem which, although not without parallel in other areas, is nevertheless particularly common in it: non-uniformity of catalytic sites.

A surface chemical physicist may run reactions on the [111] face of rhodium, but, even if the catalytic chemist works with rhodium on silica (probably the most "inert" of the commonly used supports), his catalytically active material consists of tiny particles of rhodium with a diameter in the vicinity of 12–50 Å. Two or more different crystal planes are apt to be present and also atoms at edges and vertices. That is, rhodium atoms will be present in more than one coordination number and with more than one arrangement of the surrounding metal atoms. Each kind of site might have a somewhat different activity and selectivity. To some degree one could say that a heterogeneous catalyst resembled a mixture of two or more homogeneous catalysts with differing activity and selectivity. Although this problem is always present, fortunately, as will become apparent, matters are often not so difficult as they may appear.

The same problem appears in studies of chemisorption. Because at least one of the reactants must become chemisorbed and probably all reactants become chemisorbed in most instances, study of mechanism will involve some study of chemisorption. However, from what has just been said, $A*$ can appear in more than one form; i.e. there are two or more "isomers" of $A*$.

The problem can be even more serious: only a fraction of the surface may be active for the reaction under investigation. For example, for a particular reaction on an oxide catalyst, the only catalytic sites might be coordinatively unsaturated surface (*cus*) cations of a particular degree of coordinative unsaturation. Thus, only some of the sites which adsorb A might be catalytically active and much adsorbed A might be catalytically dead. However, most techniques of studying chemisorption (measurement of amount of adsorption vs pressure, measurement of the rate of chemisorption, investigation of adsorbates by infrared or electron paramagnetic spectroscopies, etc.) look at the sum of the adsorbed species and not just at the adsorbed species responsible for the particular catalytic reaction. One must find a way to abstract the signal of the catalytically active adsorbates from the full signal. Particularly in reactions of hydrocarbons on metallic catalysts, much of the surface may become covered with slowly reacting hydrocarbon species with only a portion of the surface remaining active for the reaction in question. To abstract the signal of the catalytically active sites from the entire signal in any physical technique that examines the entire surface can be difficult. This usually requires correlation of the data from the physical technique with data from experiments which involve only the catalytic sites themselves such as the rate of the reaction as a function of operating conditions, isotopic tracer studies, kinetic isotope effects, and stereochemical results. However, this is not to say that studies of chemisorption have not been useful. Quite the contrary is true, but one must always keep in mind the problems described above One method for the direct determination of the amount of adsorbed species in the catalytic cycle is discussed in Sect. 9F.

7. Products and Their Proportions

The first prerequisite for mechanistic studies is of course the knowledge of the products and proportions and how they vary, if at all, with reaction conditions. Investigators are frequently tempted to propose mechanisms based solely upon these data. In general, such mechanistic proposals are not apt to have a very long life, although luck or intuition may provide a few exceptions.

In some instances, particularly of more complicated reactions, the nature and proportions of the products may alone provide a rather persuasive basis for mechanistic proposals. The original proposals for the carbenium ion mechanism for catalytic cracking on the solid strong acid, amorphous silica-alumina, fall into this category. The mechanism was taken directly from mechanisms in solution chemistry and applied to reactions on solid strong acids. The essence of the mechanism was:

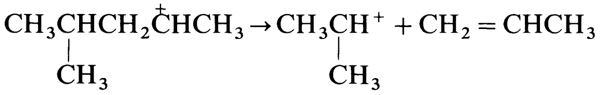
$$R^+ \rightarrow \text{a more branched chain } R^+, R'^+ \qquad (7.1)$$

$$R'^+ \rightarrow \text{olefin} + r^+ \tag{7.2}$$

$$r^+ + RH \rightarrow R^+ + rH \tag{7.3}$$

where a small amount of the carbenium ion R^+ (CH_3^+ is a carbenium ion) initially formed leads to many molecular events. Here, RH is a larger alkane and rH is an alkane formed by cleavage of R'^+. Equation (7.2) is the reverse of the alkylation of alkenes. Equation (7.2) is endothermic and requires higher temperatures to proceed as written. Since carbenium ion reactions in solution are often accompanied by structural rearrangements, one would expect that much of the cleaved alkane, rH, when C_4 or larger, would have a branched carbon skeleton as is indeed observed. Further, since in solution secondary and tertiary carbenium ions are much more stable than primary carbenium ions, one expects little formation of CH_4 and C_2 hydrocarbons, since that would require R^+ or r^+ to be primary carbenium ions. For example, the second of the equations below should be much favored over the first:

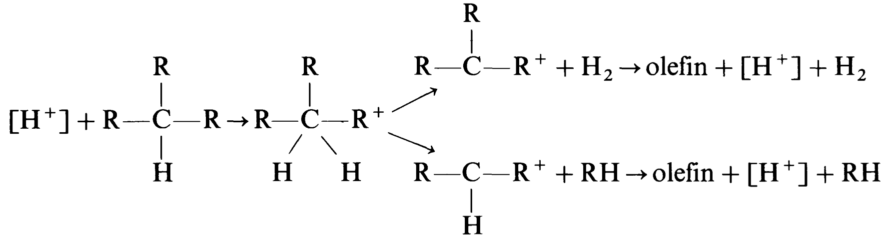
$$CH_3CH_2CH_2\overset{+}{C}HCH_3 \rightarrow CH_3CH_2^+ + CH_2=CHCH_3$$



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\overset{+}{C}HCH_3 \rightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H^+ + CH_2=CHCH_3$$

The carbenium ion mechanism does not provide for the formation of H_2 and, indeed, in normal catalytic cracking only very small amounts of H_2 are formed.

The modern zeolitic cracking catalysts behave in a fashion generally similar to the older silica-aluminas. In particular, HY with Si/Al = 3 was found to give products which corresponded to the carbenium ion mechanism [14]. However, dealuminized Y-zeolites with Si/Al = 10 [14] and Si/Al = 35 [21], behaved differently. With hexane and heptane they gave considerable amounts of C_1 and C_2 and accompanying C_{n-1} and C_{n-2} products and substantial amounts of hydrogen, products which do not accord with carbenium ion reactions and which were interpreted as occurring by the carbonium ion reactions of Olah (CH_5^+ is a carbonium ion):



In this mechanism, Eq. (7.2) is unimportant, and the carbenium ion, once formed, is involved in but one molecular event. In the lower reaction, unlike the situation in carbenium ion cracking, decomposition of the carbonium ion to give methane or ethane would not be disfavored.

However, even when the exact composition of the products affords considerable information, mechanistic decisions on product alone can be risky. To anticipate a result using isotopic tracers, it has been reported [22] that cracking of the nonane, $CH_3CH_2CH_2CH_2{}^{13}CH_2CH_2CH_2CH_2CH_3$, gives some propylene and isobutylene containing two atom of ^{13}C. This was interpreted as requiring that some of cracking of nonane proceeds by a process in which the nonane first forms a polymer (by, for example, alkylation of nonene by a nonane carbenium ion) which then undergoes cleavage by carbenium ion processes [22, 23].

In principle, one should resist the temptation to propose mechanisms on the basis of products alone. However, such speculation is harmless if the proposed mechanism is taken as very tentative. Further, such mechanistic speculation is often useful in leading to further experiments.

8. Classification of Mechanistic Probes

To some degree, the various mechanistic probes test different aspects of mechanism. Those labelled *direct* in Table 1 relate directly to the catalytic reaction at those sites which provide the bulk of the catalytic activity. In the cases of the two with a question mark, there may be some question as to whether the techniques are truly direct. On the other hand, those labeled indirect, refer to techniques which examine the total surface or the total catalyst. For example, in study of chemisorbed CO by infrared spectroscopy (IR) or by any of the techniques for measurement of amounts of adsorption, one "sees" all adsorbed CO. Perhaps all CO is adsorbed at the actual catalytic sites, but perhaps only some of the sites which adsorb CO are catalytic sites. Experiments are needed which endeavor to separate the sites for adsorption into those which are also catalytic sites and those which are not. In general, the *direct* probes test primarily those aspect of mechanism related to the structure of the adsorbate intermediates, but they are not usually very good tests of the nature of the catalytic site or of the bonding between adsorbate and the site. The last two aspects are better tested by the indirect probes.

In what follows we shall discuss first those probes which come under the heading, Direct. Except for kinetics, the exposition will rely heavily upon the use of examples.

Table 1. Mechanistic probes

Direct	Indirect
Detailed Product Analysis	
Kinetics	Rates and Amounts of Chemisorption
Structure Variation	Volumetric
Stereochemistry	Gravimetric
Isotopic Tracers	TPD
Kinetic Isotope Effects	UV-Visible Spectroscopy
Poisoning?	IR
Catalyst Alteration	EPR
Selective Feeding and	NMR
Selective Scavenging?	Mössbauer

9. Kinetics

Kinetics has probably been the most used probe in mechanistic studies. The present treatment of rates of catalytic reactions in terms of catalytic mechanisms is a development of that introduced by Langmuir [3]. Further treatments of heterogeneous catalytic kinetics are available in Refs. [10 and 24]. For purposes of presentation we shall define kinetics narrowly and as separate from the other items listed under *Direct* in Table 1. Thus, the kinetics of the hydrogenation of ethylene would include only the study of the rate of the reaction as a function of temperature and partial pressures. It would not include any study of the reaction between ethylene and deuterium (treated under isotopic tracers and kinetic isotope effects) or between propylene and hydrogen (treated under structure variation).

A. Ideal Adsorption

The original Langmuir treatment deals with *ideal* chemisorption, that is, chemisorption in which the surface has a fixed number of sites and ΔH of adsorption is independent of coverage. One could say that this corresponds to a surface with a fixed number of identical, noninteracting sites. Thus the adsorption can be written:

$$A(g) + * \rightleftharpoons A* \text{ at } P_A \tag{9.1}$$

where $*$ represents a surface site for adsorption and $\rightleftharpoons$ designates a reaction in equilibrium. Langmuir derived his adsorption isotherm on a kinetic basis in which he equated, at equilibrium, the rate of adsorption, r_{ads}, and the rate of desorption, r_{des}.

$$r_{\text{ads}} = k_{\text{ads}}(1-\theta)P_A \tag{9.2}$$

$$r_{\text{des}} = k_{\text{des}}\theta \tag{9.3}$$

$$r_{\text{ads}} = r_{\text{des}} = k_{\text{ads}}P_A(1-\theta) = k_{\text{des}}\theta$$

$$\theta/[P_A(1-\theta)] = K \tag{9.4}$$

$$\theta = KP_A/(1+KP_A) \tag{9.5}$$

Here, θ represents the *coverage*, the fraction of sites on which A is adsorbed, $(1-\theta)$ represents the fraction of free sites, and K is the equilibrium constant for Eq. (9.1). It is assumed that chemisorption occurs only consequent to collision between A(g) and a free site, $*$.

The Langmuir adsorption equation can also be derived thermodynamically. Equation (9.4) follows directly from Eq. (9.1) since:

$$K = [*A]/(P_A[*]) = \theta/(P_A(1-\theta))$$

Further, the equation:

$$\partial \ln K/\partial T = \Delta H/RT^2 \tag{9.6}$$

provides the enthalpy of adsorption which is independent of θ for ideal adsorption.

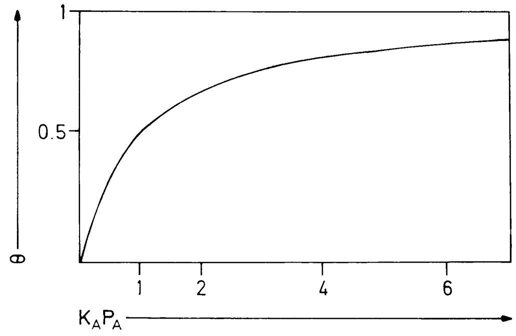


Figure 4. θ vs. K_AP_A according to the Langmuir Adsorption Isotherm

Figure 4 shows θ vs. K_AP_A according to the Langmuir adsorption isotherm. When $KP_A \ll 1$, Eq. (9.5) reduces to $\theta = KP_A$. This is called the Henry's law region. When KP_A becomes $\gg 1$, θ approaches unity and becomes independent of P_A. However, as may be seen from Figure 4, the approach to unity with increasing P_A is not very rapid. As may be seen from Eq. (9.4), $[*]$ and $1-\theta$ become proportional to $1/P_A$ when $KP_A \gg 1$. Thus, when $K_AP_A = 10$, $1-\theta$ is 0.1 and even when K_AP_A is 100, $1-\theta$ is still 0.01.

For equilibrium in dissociative chemisorption:

$$A_2(g) + 2* = 2A*$$

$$[A*]^2/[*]^2 = \theta^2/(1-\theta)^2 = KP_A \tag{9.7}$$

$$\theta = (KP_A)^{1/2}/(1+(KP_A)^{1/2}) \tag{9.8}$$

Consider the dissociative adsorption of isobutane on a metal surface in which the hydrogen-tertiary carbon bond is cleaved:

$$(CH_3)_3CH + 2* = (CH_3)_3C* + H*$$

Here, the adsorbed *t*-butyl group is large enough to block adsorption of other *t*-butyl groups at adjoining sites. In the previous cases, at monolayer coverage, all sites were bounded to the adsorbates. Here, however, in a monolayer of adsorbed isobutane not all sites would be bonded and matters become more complicated. Thus, after some isobutane has adsorbed, there are two kinds of free $*$, those available and those unavailable for bonding. This makes the calculation more complicated [25].

Suppose that we have two adsorptives which adsorb competitively in ideal adsorption such that there is no effect of adsorption at a site by occupation of adjoining sites:

$$\theta_A = \left[\frac{K_AP_A}{1+K_AP_A}\right](1-\theta_B); \qquad \theta_B = \left[\frac{K_BP_B}{1+K_BP_B}\right](1-\theta_A)$$

In the expression at the left, substitute for θ_B from the expression at the right and solve for θ_A:

$$\theta_A = K_AP_A/(1+K_AP_A+K_BP_B) \tag{9.9}$$

B. Reactors

In discussing the kinetics of any particular catalytic system, one needs to make some specification of the kind of reactor employed. Reactors for gas phase reactions may be classified as flow, batch, gradientless, and transient. Ignoring deactivation, in the flow reactor the concentrations of reactants and products are constant with time at any point in the catalyst bed, but they change as one moves through the bed. In a batch reactor, the concentrations are constant throughout the catalyst volume, but they change with time. In the grandientless reactor the concentrations are constant both in time and in space. Transient reactors involve rapid changes in concentrations with time. They will be considered in a later section. When flow reactors are used for mechanistic purposes, one usually operates in the differential mode since, at conversions of only a few percent, rates are directly proportional to conversion and the determination of the kinetic form from the rate data is simplified. In a flow reactor one can know that one is operating at steady state. In a batch reactor, the slopes of conversion vs. time gives rates. However, a catalyst may require a finite time to come to a steady with respect to the composition of the gas phase. It can be difficult to know whether the catalyst is keeping up with the rate of change of the gas phase composition in batch reactors. This problem is, in general, much more acute in transient reactors.

There can be cases in which confining the conversion of the pure reactants to a few percent can be inappropriate. For example, suppose one is studying the Fischer–Tropsch reaction ($\mathrm{CO} + \mathrm{H_2} \rightarrow \text{hydrocarbon} + \mathrm{H_2O}$) on an iron catalyst. The oxidation state of the surface of the catalyst might well be influenced by $[\mathrm{H_2O}]$ and the state of the surface at low conversions might well be quite different from that at normal conversions. One could, of course, add water to a mixture of $\mathrm{H_2}$ and CO and still operate differentially.

C. Langmuir Kinetics—Ideal Adsorption

Let us now consider a simple isomerization, $\mathrm{A(g)} \rightarrow \mathrm{B(g)}$, which involves a Langmuir–Hinshelwood step (preequilibrium in adsorbed reactant, the surface reaction is a *rate-determining process*, (*rdp*). That is:

$\mathrm{A(g)} + * \rightleftharpoons \mathrm{A}*$ step 1, preequilibrium
$\mathrm{A}* \mathrel{\rlap{\;\mathrm{A}}\longrightarrow} \mathrm{B}*$ step 2, *rdp*
$\mathrm{B}* \rightarrow \mathrm{B(g)}$ step 3

We consider first the case in which K_{eq} is so large that the rate of the reverse reaction is negligible. Since A(g) is in near equilibrium with A$*$, θ_{A} can be closely approximately by Eq. (9.9). Further, by the assumptions, the backward rate r_{b} is negligible and, thus, the rate r is equal the forward rate r_{f}. Since step 2 is an *rdp*:

$$r = r_{\mathrm{f}} = ak_2\,\theta_{\mathrm{A}}$$

Here, the rate constant has a variety of possible units. It could be in moles of A reacted per second per m^2 of catalyst surface. Or, k_2 could be a turnover frequency, molecules of A which react per sec per catalytic site. The quantity *a* represents the number of m^2 of surface, or of catalytic sites, etc. We shall ordinarily omit it from the equations. Substituting for θ_A from Eq. (9.9):

$$r = k_2K_AP_A/(1 + K_AP_A + K_BP_B) \tag{9.10}$$

Given that ΔG is large and negative, it is likely that A is adsorbed much more strongly than B. In this case A∗ is called the *mari*, the most abundant reaction intermediate [24]. Thus, $K_BP_B \ll 1$ and Eq. (9.10) reduces to:

$$r = k_2K_AP_A/(1 + K_AP_A) \tag{9.11}$$

In an intermediate region of P_A Eq. (9.11) must be employed, but still further simplification occurs at very low and very high P_A. At low enough P_A where $1 \gg K_AP_A$:

$$r = (ak_2K_A)P_A \qquad \text{first order in A} \tag{9.12}$$

At large enough P_A, where $K_AP_A \gg 1$:

$$r = ak_2 \qquad \text{zero order in A} \tag{9.13}$$

For an elementary step:

$$\partial \ln k/\partial T = E_a/RT^2 \tag{9.14}$$

where E_a is the activation energy of the elementary step. In the high pressure limit above, $\partial \ln ak_2/\partial T$ gives the true activation energy for step 2 since in the limit chosen, θ_A is independent of T. However, in the low pressure limit:

$$\partial \ln k/\partial T = \partial \ln ak_2K_A = E_a/RT^2 = E_a(2)/RT^2 + \Delta \mathrm{H}(1)/RT^2 \tag{9.15}$$

The measured rate constant k will be equal to ak_2K_A. In general, one cannot dissect the constant k into its components by kinetic measurements alone. Thus, the measured activation energy is a composite quantity called an *apparent* activation energy, which in this simple case is the sum of an activation energy for step 2 and the enthalpy of adsorption of A in step 1. In most cases of heterogeneous catalytic kinetics, calculated E_a's are rather complicated mixtures of activation energies of elementary steps and adsorption equilibrium constants.

The rate of decomposition of ammonia on clean Rh foil (cleanliness verified by Auger spectroscopy) as a function of temperature and $P(NH_3)$ provides a good example of the $r_f = ak_2\theta_A$ rate law [26]. In step 1, ammonia is adsorbed in pre-equilibrium. This is followed by the *rdp*, reaction of adsorbed ammonia to form a further intermediate. The subsequent reactions leading to H_2(g) and N_2(g) are fast. Data were collected at lower conversions and inhibition by hydrogen and nitrogen was ignored. Thus, the data were represented by Eqs. (9.11) plus (9.15) which has four adjustable constants, ΔH and ΔS for K_A, and E_a and a preexponential term for k_2. The data and the calculated rates are shown in Figure 5. Considering the wide range of rates covered, the agreement is impressive.

If data are extensive enough and cover a wide enough temperature range, one may be able to determine the ΔH for K_A and E_a for k_2. If the value of θ_B is not negligible, then the full Eq. (9.10) must be used. The rate of the reaction is now

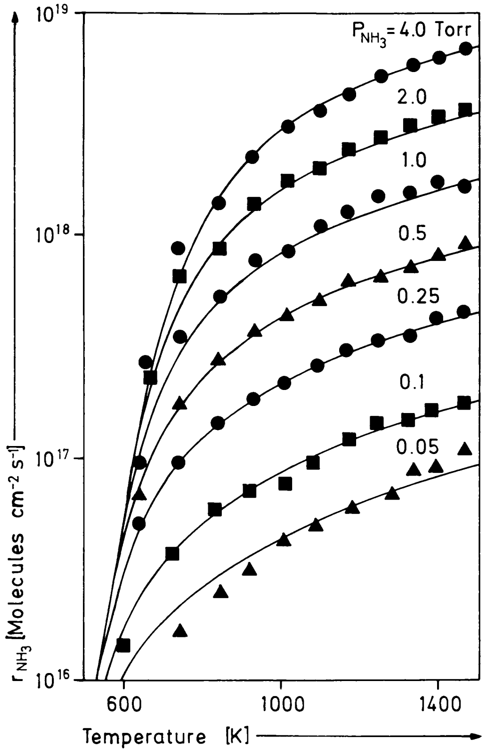


Figure 5. Rate of formation of dinitrogen in the decomposition of ammonia on rhodium foil, rate vs temperature at the various values of p_{NH^3} shown on the graph. The *solid lines* are plots of Eqs. (9.11) plus (9.15). Reproduced with permission from Hasenberg D, Schmidt LD (1985) J Catal 91: 116

inhibited by B, but not because B promotes the backwards reaction. Rather, B inhibits because its adsorption reduces the value of θ_A. If ΔG° for the reaction is not large and negative, the reverse reaction may become important and B reduces the rate by promoting the reverse reaction:

$$r = r_f - r_b = [k_2K_AP_A - k_{-2}K_BP_B]/(1 + K_AP_A + K_BP_B) \qquad (9.16)$$

However, for mechanistic purposes, one would ordinarily try to avoid measurements in the region in which a reaction is reversible.

Thus, even for the simplest reaction, A → B, a number of kinetic complications arise and we have considered only the case in which the reaction follows a Langmuir–Hinshelwood mechanism. Suppose that adsorption of A in step 1 is irreversible and that the adsorption is slow and activated. Suppose also that steps 2 and 3 are irreversible with values of k's such that θ_A and θ_B are small. Then:

$$r = k_1P_A \qquad (9.17)$$

Here, E_a would be the activation energy of adsorption of A. Notice that this mechanism could be said not to involve a rate determining process since there is no preequilibrium. Equation (9.17) often could not be distinguished by kinetics alone from Eq. (9.12) although the meaning of the rate constants would be different. Thus, two different mechanisms can give the same rate expression and other data may be needed to distinguish between them.

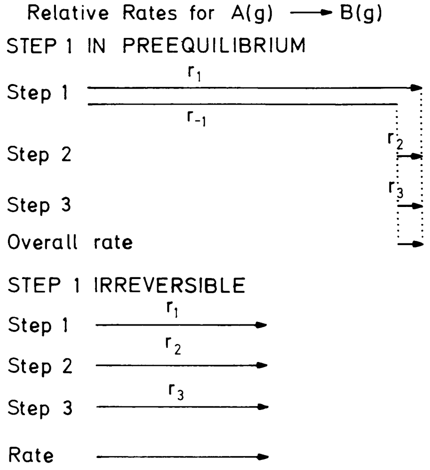


Figure 6. Relative rates of the various steps in the two mechanisms described in the text for the reaction A(g) → B(g)

Figure 6 is a representation of the two different mechanistic variants for $A(g) \rightarrow B(g)$, both of which involve:

(1) $A(g) + \ast \rightarrow A\ast$
(2) $A\ast \rightarrow B\ast$
(3) $B\ast \rightarrow B(g) + \ast$

In step 1 of the upper variant, the rates of adsorption and desorption of A are both large. Of course, r_1 must be larger than r_{-1} by the net rate of the reaction. A(g) is not precisely in equilibrium with $A\ast$, but calculating θ_A on the assumption of equilibrium is a good approximation if $r_1 \gg r_2$. Note that the net rate of each step must be the same as that of the overall reaction rate. In the lower mechanism, all steps are irreversible and all proceed at the same rate. The various *k*'s will, however, differ and therefore the values of θ_A and θ_B will not be the same. If step 2 is $A\ast + \ast \rightarrow B(\ast)_2$ and if step 2 is slow vs. step 1, then when two $\ast$'s are liberated by step 3, they will preferentially be seized by A. In consequence, $\theta_{A\ast}$ will become unity, step 2 will be blocked, and $A \rightarrow B$ will have zero rate. This is a kind of self-poisoned reaction.

Consider a somewhat more complicated reaction, $A(g) + B(g) \rightarrow C$, but again let us assume that conversions are such that r_b is negligible. If the adsorptions of A and B are in preequilibrium and the surface reaction of $A\ast$ and $B\ast$ is a *rdp*, then:

$A(g) + \ast \rightleftharpoons A\ast$ step 1, preequilibrium
$B(g) + \ast \rightleftharpoons B\ast$ step 2, preequilibrium
$A\ast + B\ast \mathrm{A}\!\!\!\!\!\longrightarrow C\ast + \ast$ step 3, *rdp*
$C\ast \rightarrow C(g) + \ast$ step 4

Equilibrium is nearly established in step 1 and the ratio $[A\ast]/[\ast]$ is proportional to P_A when $\theta_{A\ast}$ is small. Step 1 could be composite:

$A(g) + \ast \rightleftharpoons (A\ast)$ step 1a
$(A\ast) \rightleftharpoons A\ast$ step 1b

$(A\ast)$ could be physisorbed or weakly chemisorbed A (a *precursor* state), but more complicated cases could be imagined. Since overall, equilibrium is nearly established between A(g), $\ast$ and $A\ast$, the ratio $[A\ast]/[\ast]$ is the same function of P_A in both cases. Thus, kinetics can provide little or no detail as to the steps which precede a preequilibrium.

A particular step 4 is listed, but any steps beyond the *rdp* will not influence the rate of the reaction. Thus, steps 3 and the following steps could be:

$A\ast + B\ast \xrightarrow{\Lambda} X\ast + \ast$ step 3′, *rdp*
$X\ast \rightarrow C\ast$ step 4′
$C\ast \rightarrow C(g) + \ast$ step 5′

In both cases, if θ_X is small:

$$r = k_2K_AP_AK_BP_B/(1 + K_AP_A + K_BP_B + K_CP_C)^2$$

As before, if $K_CP_C \ll 1$, the equation simplifies somewhat. If, in addition, $K_AP_A \ll 1$ and $K_BP_B \ll 1$, then:

$$r = k_2K_AK_BP_AP_B \tag{9.19}$$

It is possible that at a temperature at which the rate of step 3 becomes measurable that θ_A and θ_B are small at all accessible values of the pressures.

Consider an alternative mechanism which involves an abstraction step. This type of mechanism is unfortunately frequently called a Rideal–Eley mechanism.

$A + \ast \rightleftharpoons A\ast$ step 1″, preequilibrium
$A\ast + B(g) \rightarrow C(g)$ step 2″, irreversible

In the second step, B abstracts A from the surface and is never present as a minimum Gibbs energy adsorbed intermediate. The rate of effective collisions in step 2″ will be:

$$r = k_2P_B\theta_A = k_2P_BK_AP_A/(1 + K_AP_A)$$

In the lower pressure limit:

$$r = k_2K_AP_AP_B \tag{9.20}$$

This equation cannot be distinguished by mere kinetic measurements from Eq. (9.19).

Despite the theoretical basis for Langmuir kinetics which has been discussed above, most of the kinetic data in the literature are presented in the form of a *power rate law*. That is the rate of the reaction:

$$A(g) + B(g) \rightarrow C(g)$$

is expressed in the form:

$$r = kP_A{}^aP_B{}^bP_C{}^c$$

where *a, b,* and *c* can have integral or fractional and positive or negative values. Some forms of the Langmuir adsorption isotherm like Eq. (9.8) can generate fractional exponents. As has been shown, at large and small extremes of pressure, a Langmuir isotherm reduces to θ = constant and θ = KP (or perhaps $\theta = K^{1/2}P^{1/2}$). Further, Langmuir adsorption isotherms can be approximated by a fractional power of P_i over some range of P_i. Consider some rate data which should precisely follow a Langmuir form. In practice, some level of experimental error will be associated with all of the data. Thus, the range of θ over which P_i^n would appear to fit the data depends upon the experimental error and upon the degree of agreement which one requires, but power rate laws have been applied over larger ranges of P_i than one would expect the approximation to work.

Some deactivation occurs during rate runs on many catalytic systems. Such declines in rate may result from deposition of carbonaceous residues, from loss in area of the catalytic ingredient, or from poisoning. Elimination of the first two causes of deactivation may be impossible and in some instances the elimination of poisoning may require extreme measures. If the rate of deactivation is not too severe, rates are often extrapolated to zero time, but inevitably some precision is lost in this operation.

In addition, if points are accumulated with fresh samples of catalyst even from the same batch, exact reproducibility is difficult. Thus, kinetic measurements in heterogeneous catalysis are apt to have more "noise" than those in homogeneous systems. It may be difficult to select just one possible kinetic form from rate data and, in particular, it may not be possible to distinguish between Langmuir and power rate law kinetics. Since even Langmuir kinetics may lead two or more different mechanisms to exhibit the same experimental form of the rate equations, it seems clear that one cannot expect, in general, to derive a complete mechanism from kinetics alone. In particular as noted above, if there is a rate limiting process, conventional kinetics does not provide information about steps following a *rdp* nor the details of steps preceeding a preequilibrium. There are additional complications. In reactions involving hydrocarbons, slowly reacting carbonaceous residues often form on catalysts and the areal concentration of these may depend upon pressures and temperatures. This can considerably complicate kinetics.

Most experiments with temperature-programmed desorption of adsorbed simple gases show that adsorption occurs in more than one state. This is true not only for conventional catalysts but also for single crystal planes. Reference [27] dealing with the adsorption of hydrogen provides a good example. The distinguishable adsorbed states may be rather different chemically. Ths simultaneous occurrence of linear and bridged carbon monoxide on metals is well known [28]. As evidenced by infrared absorption spectroscopy, the adsorption of NO on Pt/SiO_2 occurs in two forms, linear and bent [29]. Similar phenomena have been seen in the adsorption of NO on platinum foils and on Pt (110). In addition, on samples containing platinum in high dispersion, some dissociative adsorption leads to another band.

If the different forms of the adsorbed species occur on separate sites and if only one of the various forms is catalytically active, then Langmuir kinetics still could work correctly although θ would refer just to the restricted set of sites giving catalytic activity.

In sum, "noise" in kinetic measurements may be large enough to prevent the extraction of some of the potential information contained in the data. Furthermore, the kinetic data refer primarily to the *rdp* if one is present. Information on the *rdp* is sufficiently important for kinetics to have been widely studied and some examples follow. Of course, kinetics is rarely enough, nor is any other single mechanistic probe. In particular, kinetics is not apt to test more detailed aspects of mechanism, particularly those of more complicated molecules or reactions. For example, suppose that one has studied the kinetics of the hydrogenation of propylene on Pt/SiO_2.

$$C(1)H_2{=}C(2)H{-}C(3)H_3 + H_2 \rightarrow \text{propane}$$

During the course of the hydrogenation is a C(3)—H bond ever broken? Deuterium tracer experiments show that the bond is indeed broken, but one could hardly expect to test the possibility by mere kinetics.

On the other hand, fewer probes can be applied to simpler reactions like the oxidation of carbon monoxide than to reactions of more complicated molecules and the role of kinetics has been relatively more important in reactions of simpler molecules.

A more extensive and whole-hearted treatment of Langmuir kinetics (in the Hougen–Watson form) is provided in Ref. [30].

D. Nonideal Adsorption

Consider the simple reaction $A \rightarrow B$. Here, $r = k_2\theta_A$ and from this equation the Langmuir kinetics form, Eq. (9.10), follows. These equations are based on ideal adsorption (sites uniform and noninteracting, or ΔH_{ads} and E_a of adsorption independent of θ). If sites are nonuniform, θ_A will not be represented by a Langmuir adsorption isotherm and k_2 may vary with θ_A. Thus, Eq. (9.11) will not be valid.

Would one expect the sites of a supported metal catalyst to be uniform when more than one crystal plane could be exposed in the tiny crystallites of metal as well as varying proportions of edge and vertex atoms? Studies of single crystal planes by the techniques of surface chemical physics have shown that, in general, the energetics of adsorption differ from plane to plane and between terrace, edge and kink sites [15].

Most measurements of enthalpies of adsorption have indicated that $-\Delta H_{ads}$ decreases with coverage. In the case of chemisorptions which involve an activation energy, E_a usually increases with coverage. Thus, the rate of adsorption of A may not be simply proportional to $P_A\theta_*$. The E_a's of adsorption of simpler molecules on single crystal planes of metals are usually very small or zero and the sticking coefficients are usually near unity at $\theta = 0$. However, quite often the sticking coefficients do not decrease in proportion to $1 - \theta$ as θ increases [31].

Thus, the problem of nonuniform sites might seem almost inevitable with conventional catalysts both for reactions following Langmuir–Hinshelwood mechanisms and for those in which rate of adsorption is determining.

The problem of nonuniformity appeared in the 1930s in two improtant cases. One was the reaction:

$$H_2 + D_2 \rightarrow 2HD$$

on the surfaces of metals. Consider a mechanism which proceeds by dissociative adsorption of H_2 and D_2 followed by associative desorption of HD (the Bonhoeffer–Farkas mechanism). It was argued that this mechanism was impossible at low temperatures because the heat of adsorption of hydrogen which had been measured on metals was too high to permit desorption of HD at an adequate rate, since the activation energy for desorption of HD would have to be at least as large as $-\Delta H_{\mathrm{ads}}$. However, it later appeared that $-\Delta H_{\mathrm{ads}}$ became too small at large θ to permit the rejection of the B–H mechanism.

The other example arose in studies of the mechanism of ammonia synthesis on iron catalysts which began in the 1930s. The mechanism of this reaction is one of the most extensively explored of all reaction mechanisms. This subject is thoroughly covered by Ozaki and Aika [32].

Consider the following mechanism:

$$\begin{gathered} N_2 + 2* \xrightarrow{A} 2N* \\ N* + 3/2H_2 \rightleftharpoons NH_3 + * \end{gathered}$$

The dissociative adsorption of nitrogen is the *rdp*. (There may be a question as to whether this is a *rdp* since it does not involve a preequilibrium.) Thus, far on the $N_2 + H_2$ side of equilibrium (i.e., when the rate of reverse reaction can be ignored):

$$r = kP_{N_2}\theta_*{}^2 \tag{9.22}$$

That is, the rate is proportional to the rate at which molecules of N_2 strike empty pairs of sites. Nothing can be said from the kinetic measurements about the details by which equilibrium is established in the second step. Presumably, N$*$ would react with successive hydrogen atoms finally to give $NH_3(g)$:

$$N* \rightleftharpoons HN* \rightleftharpoons H_2N* \rightleftharpoons H_3N* \rightleftharpoons NH_3(g)$$

All of these steps would be fast in both directions compared with the rates of adsorption and desorption of nitrogen. Let us assume that N$*$ is the *mari*, that the concentrations of the H_xN* species are very small vs that of N$*$, and that the equilibrium constant for $N* + \frac{3}{2}H_2 \rightleftharpoons NH_3 + *$ is $1/K$. Thus:

$$(\theta_{N*}P_{H_2}^{3/2})/(P_{NH_3}\theta_*) = 1/K$$

$$\theta_* = (1 - \theta_N) = 1/[1 + (KP_{NH_3})/(P_{H_2})^{3/2}] \tag{9.23}$$

Whence:

$$r = kP_{N_2}(1 - \theta_N)^2 = \mathrm{k}P_{N_2}/[1 + (KP_{NH_3})/(P_{H_2})^{3/2}]^2 \tag{9.24}$$

Equation (9.24) can readily be converted to one which allows for the reverse reaction.

Such a mechanism would be supported by the fact that the adsorption of N_2 on iron is slow and activated and that the rate of formation of ammonia is roughly the same as the rate of adsorption of nitrogen on iron in the absence of H_2 and NH_3 and of isotopic exchange between $^{14}N_2$ and $^{15}N_2$. Further, since the isotopic exchange between H_2 and D_2 and the chemisorption of hydrogen are fast, the reaction $H_2 + 2* = 2H*$ is in preequilibrium and, since isotopic exchange between NH_3 and D_2 is fast, the adsorption of ammonia is in preequilibrium.

E. Kinetics with Nonideal Adsorption

However, the rate of the synthesis of ammonia did not appear to be adequately represented by Eq. (9.24). Temkin and Pyzhev proposed a mechanism similar to that just presented but which assumed a nonuniform distribution of sites. They used the Frumkin–Slygin isotherm which can be interpreted as resulting from a linear variation of $-\Delta H_{\text{ads}}$ with θ:

$$-\Delta H_{\text{ads}} = -\Delta H_{\text{ads}}(\theta = 0) - fRT\theta$$

and restriction to a particular range of P_{N_2}. Using an equation valid over a wider range of P_{N_2}, one gets:

$$r = kP_{N_2}/[1 + aKP_{NH_3}/(P_{H_2})^{3/2}]^d \tag{9.25}$$

Most of the earlier work gave a value of *d* of about unity, but from later work it seems to be near 1.5. Equations (9.24) and (9.25) do not differ very much and a few workers have preferred Eq. (9.24).

Most recent workers accept that a mechanism of the form just described applies to the synthesis of ammonia on iron catalysts under commercial conditions. There have, however, been proposals that the *mari* is $*$NH rather than $*$N.

The likely difficulties with models based on ideal adsorption are widely recognized. Nevertheless, there have been few attempts to employ other models. It is not clear just what kind of nonuniformity of surfaces should be assumed, nor is it clear that kinetic data, in general, would permit a distinction among various possible models of nonuniformity. Boudart and Djéga–Mariadassou have presented arguments which led to the following conclusion [24, p. 141]. "..... a nonuniform surface behaves catalytically more like a uniform surface than suspected from a knowledge of its thermodynamic behavior. Rate equations are similar for a given mechanism on a uniform or a nonuniform surface. This result justifies the common practice of neglecting nonuniformity of catalytic surfaces in kinetic studies." Boudart has since argued [33] that Langmuir kinetics are exact for structure-insensitive reactions. He considers that nonuniformity in surface sites accounts for the decline in ΔH_{ads} at low coverages but that interadsorbate interactions account for the continuing decline at high coverages. He further considers that structure-sensitive reactions are characterized by large coverages and that, therefore, change in ΔH_{ads} does not result from site nonuniformity and Langmuir kinetics apply. Nevertheless, one may have a nagging worry as to whether Langmuir kinetics appropriately represents a given reaction or exactly what a given exponent in a power rate law really means.

F. Transient Kinetics

In transient reactors one changes the concentration of one or more reactants or of the temperature and one then follows the change in the gas phase composition with time. One may also monitor some other property of the system such as the infrared spectrum of the catalyst sample.

Pulse reactors are one kind of transient reactor. In another kind, one effects step changes in concentrations. As an example of the latter, suppose that A + H_2 has been passing over a catalyst at temperatures at which the rate of formation of B (AH_2) is rather slow and that the adsorption of A is irreversible under the conditions of the experiment. At $t = a$ one stops the flow of A. C_A in the gas phase would fall to zero

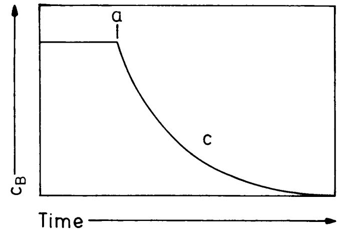


Figure 7. A transient kinetic experiment with the reaction A(g) + $H_2 \rightarrow$ B(g) under conditions where the reaction is rather slow. The adsorption of A is irreversible. The concentration of B is shown on the y-axis. To the left of point a, C_B is that for the reaction at steady state. At point a, the flow of A is interrupted but that of H_2 continues unchanged

rapidly. The evolution of C_B with time is shown in Figure 7. The area under the curve beyond 'a' gives the quantity of that adsorbed A during steady-state operation which is in the line of the catalytic cycle. The rate of reaction of adsorbed A can also be calculated from the data. If the catalyst is examined by IR during the process, one can determine which IR absorption bands are related to the reacting adsorbed A. The possibility of measuring the amount of adsorbed A on catalytic sites is a particular advantage of this procedure, since determination of this quantity is impossible by conventional kinetic procedures. However, for this measurement to be straightforward, the adsorption of A must be irreversible. Were it reversible, adsorbed A would desorb both as A and B. One might add the total amounts of A and B which desorbed beyond point a to get the amount of adsorbed A, but one cannot be sure that all reversibly adsorbed A is in the catalytic sequence. In general, one must operate under conditions where the steady state reaction is slow, since C_B cannot decline too rapidly after $t = a$ if good accuracy is to result. Refs. [34 and 35] consider possible results of such experiments and how to treat the data. However, various complications can arise [36].

As an example of a transient procedure consider the injection of a pulse of CO into hydrogen passing over a sample of Ru/Al_2O_3 at $T = 405\,K$ [37]. In this experiment the catalyst was monitored by IR diffuse reflectance spectrometry and the effluent stream, by a flame ionization detector to measure evolved methane. As the pulse of CO reached the catalyst an IR band due to linear CO appeared and methane appeared in the effluent beyond the catalyst. Water was formed at the same rate as methane. The intensity of the IR band decreased with time in concord with the signal from methane. If one assumes as is now usual that $OC* \rightarrow CH_X*$ ($x \geqslant 0$) $\rightarrow CH_4$, then the rate constant for the second step must be > 50 times larger than that of the first step. Further, linearly adsorbed CO appears to be the initial species.

Although the rate of reaction of adsorbed CO with hydrogen in the procedure just described is of interest, it is not unambiguously related to the rate of reaction of CO in the steady-state flow reaction. Such measurement may be effected by the procedure shown in Figure 8, in which one switches the feed from one isotopic form of a reactant to another at time a. Such a change should result in a negligible change in the areal steady-state concentrations of the surface reaction intermediates (ignoring isotopic effects). Let the change be from a flow of $H_2 + {}^{12}CO$ to one of $H_2 + {}^{13}CO$ passing over Ni/SiO_2 at $\sim 225°\,C$ [38]. Curve **c** represents the concentration of ${}^{12}CH_4$ with time and curve **b**, the concentration of ${}^{13}CH_4$ with time as determined by an inline mass spectrometer. The introduction of ${}^{13}CO$ into the vapor phase leads it frontally to displace ${}^{12}CO$ from the surface into the vapor

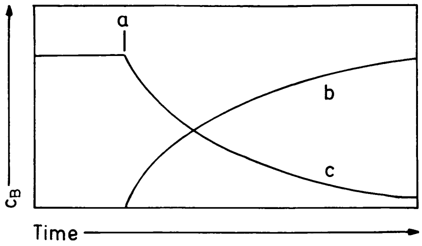


Figure 8. The hydrogenation of CO on Ni/SiO$_2$ at ~500 K. C_B, the concentration of CH$_4$ in the exit stream, is plotted vs. time. Initially, $H_2 + {}^{12}CO$ is fed and C_B to the left of time a represents the steady-state value of $^{12}CH_4$. At time a, the feed is switched abruptly to $^{13}CO + H_2$. Curve **c** represents the declining value of $^{12}CH_4$ and curve **b**, the rising value of $^{13}CH_4$

phase, i.e., to give the amount of adsorbed CO which reverts to CO(g). This amount corresponded approximately to a monolayer. The area under curve **c** from $t = a$ to $t = \infty$ gives the amount of adsorbed intermediates which cannot revert to ^{12}CO after the change to ^{13}CO. θ°_{12}, the coverage of irreversible reaction intermediates with ^{12}CO at steady state before point a, can be calculated from this. θ°_{12} was near 0.03. In the present case, θ_{12} for coverage by irreversible ^{12}C species is proportional to $^{12}CH_4(g)$ and thus to the rate of liberation of $^{12}CH_4$. The concentration of $^{12}CH_4$ declined exponentially with time and therefore so did θ_{12}:

$$d\theta_{12}/dt = k\theta_{12}dt \rightarrow \theta_{12} = \theta^\circ_{12}\exp(-kt)$$

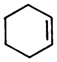
Since θ° for the sum of both isotopic CO species is constant, the rate of reaction of adsorbed CO could be calculated as well as θ° whereas conventional kinetics gives only the product of the two. Treating the Ni/SiO$_2$ with CO at $T \geqslant 300°C$ deposited unreactive carbon on the catalyst. The value of θ decreased, but that of k was unaffected. Thus, CO is adsorbed on the surface of nickel and not on the layer of 'hard' carbon. It is clear that these transient techniques are powerful ones. However, one must run the reactions at temperatures at which the reactions are slow and it is conceivable that the reaction mechanism might change in raising the temperature to that normally employed.

A general treatment of transient isotopic techniques has been provided by Happel et al. [39].

A final example of the application of transient kinetics concerns the hydrogenation of olefins on platinum. As originally found by Beeck [40], slowly reacting carbonaceous residues accumulate on metal surfaces during hydrogenations. In the view of Beeck, the residues were inactive and hydrogenation occurred on the residual metal surface. Over the years, however, there have been several proposals which invert Beeck's view and which consider the surface to become covered with a layer of residues which can pick up hydrogen atoms from *H formed at the metal surface by dissociative adsorption of hydrogen. Olefin adsorbs on the carbonaceous layer and abstracts the hydrogen atoms which had been transferred from the metal. In the most recent version of this idea, that of Zaera and Somorjai [41a], the catalytic carbonaceous residue is 1,1,1-triadsorbed ethane (adsorbed ethylidyne), $*{\equiv}C{-}CH_3$, although one of the authors has now advanced a substitute mechanism [41b]. As first shown by Somorjai and co-workers, the diadsorbed ethane which is formed by the adsorption of ethylene on Pt(111) below about 250 K reacts to form adsorbed ethylidyne at higher temperatures. In the presence of hydrogen, hydrogenation of $*\equiv C-CH_3$ to $*{=}C-CH_3$ is fast, but further hydrogenation of $*{=}CH-CH_3$ to ethane is slow. Similar behavior has been found on Pd, Rh, and Pt/Al_2O_3. The rate of reaction of $*\equiv C-CH_3$ with hydrogen is slow compared to that of the hydrogenation of ethylene. In Ref. [41a] Somorjai and co-workers proposed that the hydrogenation of ethylene involved the formation of a layer of adsorbed ethylidyne and that this species reacted with $H*$ on the surface of Pt to form $*{=}CH-CH_3$. Two such molecules transferred the added atoms of hydrogen to $H_2C{=}CH_2$ to form H_3C-CH_3 and $2*\equiv C-CH_3$. The latter were then rehydrogenated and the catalytic cycle continued.

A number of objections could be advanced against this mechanism. Just two will be mentioned here. The first comes under the heading of structure variation. The ethylidyne mechanism cannot apply to the hydrogenations of many olefins, for example, of:






Cyclopentene adsorbs on Pt(111) at room temperatures to form adsorbed cyclopentadienyl without cleavage of the ring [42] and, therefore, without forming any adsorbed alkylidyne. In general, it is not an attractive idea to have different mechanisms for hydrogenating ethylene and cyclopentene which phenomenologically appear to be very similar processes.

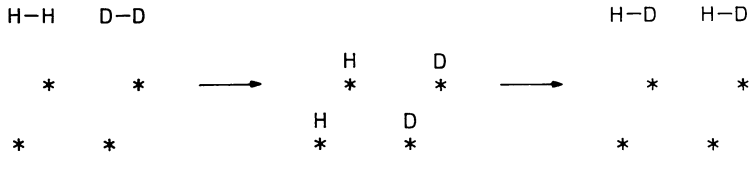
The other objection which applies to any mechanism in which the effective catalyst is a carbonaceous deposit arises from pulse experiments on Pt/SiO_2 catalysts at low temperatures [43]. Pulses of ethylene + hydrogen were injected into a rapid stream of hydrogen passing through a bed of catalyst. A temperature of $-31°C$ was required to keep conversions less than about 50%. The ratio, ethylene/Pt_s, per pulse was usually about 4. In some experiments, fresh catalyst had been pretreated in oxygen at 573 K, in hydrogen at 723 K, and cooled in hydrogen. In an 11-pulse sequence all conversions were the same. To within the experimental error, the total recovery of ethylene + ethane was 100% in all pulses. After 11 pulses the amount of residual carbon on the catalyst as measured by combustion corresponded to $C/Pt_s = 0.05$. The total amount of C_2 residues could not have exceeded 1 per 50 Pt_s after pulse 1. This material was released as ethane upon exposure to hydrogen at 298 K. The slowly hydrogenating residue may well have been $*\equiv C-CH_3$. Thus, if a carbonaceous residue was the catalyst, all catalytically active material was formed at the very beginning of pulse 1 and any residue formed later was catalytically inactive.

Experiments were also run with very high flow rates of H_2 at 195 K and ethylene/$Pt_s = 2$. At this temperature behavior was rather like that described above for Ref. [37] (CO on Ru/Al_2O_3). Ethylene adsorbed on Pt and on SiO_2. The ethylene on the latter desorbed as such within 10 s. Ethylene on Pt came off over a period of 60 s as ethane with an overall recovery of 100% to within experimental error. The recovered ethane corresponded to $(C_2H_4)_s/Pt_s$ being about 1/3 initially. Thus, in these pulse experiments, a monolayer of adsorbed ethylene is formed which then reacts with hdrogen to liberate ethane. It seems much simpler to assume that nearly the entire surface of platinum is catalytically active and that ethylene adsorbs on the platinum and reacts with hydrogen adsorbed on the platinum than to assume that the adsorbed ethylene must migrate to one of the few residue sites which would exist on the surface and to hydrogenate there. Strictly speaking these arguments are compelling only for low temperatures and low conversions. However, the initial rate of liberation of ethane at 195 K should have corresponded to the rate of formation of ethane in a gas phase reaction at 195 K and, indeed, the measured rate lay on the logarithm of rate vs 1/T of Ref. [11]. This agreement suggests that the conclusions derived for low temperatures can be extended to higher temperatures. In any case, hydrogenation of ethylene can occur at a normal rate on a surface which certainly contains no layer of carbonaceous residue.

Nevertheless, the role of carbonaceous residues remains unclear. Although the residues seemed merely to block surface in the experiments just described, there are reports that they can have more selective effects. An extreme form of transient kinetics is the replacement of one reactant by a different one. Thus, 1,1-dimethylcyclopropane was readily hydrogenolyzed at 318–373 K on Pt, Pd, and Rh catalysts [44]. However, if isobutylene was hydrogenated first, the subsequent hydrogenolysis of the cyclopropane was blocked although the catalyst was still active for the hydrogenation of isobutylene. The pair, 2,4-dimethyl-2-pentene and 1,1,2,2-tetramethylcyclopropane, behaved similarly. Would the cyclic olefins whose structures were given above inhibit hydrogenolysis?

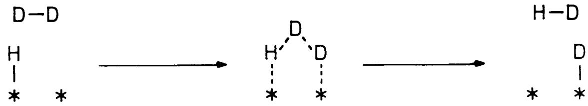
10. Use of Isotopes

The use of isotopes has been of major importance in mechanistic studies of heterogeneous catalysis, as important indeed as kinetic studies. Their use began when deuterium became available in the early 1930s and led to discoveries which were startling at the time: that H_2 and D_2 underwent isotopic exchange at near 100 K on Group VIII catalysts and on Cr_2O_3 and that the still supposedly inert alkanes exchanged with D_2 on nickel at ~ 473 K. These discoveries had mechanistic implications with respect to a number of catalytic reactions. Application of the data on isotopic exchange between H_2 and D_2, between D_2 and NH_3, and between isotopes of N_2 to the synthesis of ammonia was described in Sect. 9.D. However, the mechanism of the exchange reaction between H_2 and D_2 has not been easy to establish. Although most workers employ the Bonhoeffer-Farkas mechanism:



there are still supporters of the Rideal–Eley mechanism in which the bonding of the intermediate or transition state in nonclassical. The intermediate can be called a *quasisorbed* intermediate or transition state.

A form of the mechanism appears below:



Deciding between these mechanisms has been difficult because there are very few handles on the reaction; the reaction is too simple.

Since ^{13}C became available, it has played a major role along with deuterium. In recent years, stable isotopes have usually been preferred to radioactive ones except when the higher sensitivity of detection of the radioactive isotopes has been important. For a review of the use of radioactive isotopes, see Ref. [45]. In part, preference for stable isotopes arises from the nuisance of employing radioactive compounds, but primarily it arises from the larger amount of information which can often be obtained by using stable isotopes. For example, in the palladium-catalyzed hydrogenation of $CH_3—C{\equiv}C—CH_3$ with a hydrogen-tritium mixture, one would learn that on the average the *cis*-2-butene product contained the equivalent of two atoms of tritium, but it would be difficult to ascertain where they were or whether some molecules had one and other molecules had three. Using essentially pure deuterium rather than the H_2–T_2 mixture, mass spectroscopy coupled with NMR readily establishes that the *cis*-2-butene product is $CH_3—CD{=}CD—CH_3$.

A. Deuterium

Isotopic exchange between deuterium and surfaces containing hydrogen can assist in understanding the catalytic properties of such surfaces. Catalytic isotopic exchange between hydrogen-containing compounds and deuterium is of interest with respect to the mechanisms of a number of catalytic reactions. Reactions which involve the addition of deuterium have been used mainly to study hydrogenation and hydrogenolysis reactions. In some instances, stereochemical aspects of these reactions have been important. Studies of kinetic isotope effects with specifically deuterium labeled molecules have been used to identify *rdp*'s. Refs. [46, 47, and 48] review parts of this ares.

1. Exchange with the Surface

The data obtained in such studies are usually in the indirect category since the exchange reaction may involve surface species not involved in the catalytic cycle. Additional data will ordinarily be needed to provide a connection between the exchange reaction and some catalytic reaction.

There have been a number of studies of exchange between deuterium or D_2O and surface OH groups (σ-OH), most often of oxides like silica, alumina, and silica-alumina or catalysts consisting of metals supported on these oxides. Measurement of the amount of HD liberated when an oxide is exposed to D_2 gives the amount of σ-OH if it is shown, for example by infrared absorption spectroscopy, that exchange of σ-OH is complete. Chemical interaction between σ-OH and the added catalytic ingredient of supported catalysts is sometimes of major importance [49], particularly because $2\sigma\text{-OH} + 2e \rightarrow 2\sigma\text{-O}^- + H_2$ can oxidize many possible catalytic ingredients. In supported noble metals, however, it may be unimportant. For example, in the hydrogenation of ethylene, Pt/SiO_2 and evaported Pt films give nearly the same value of turnover frequency [11].

Gas chromatographic measurement of deuterium exchange has been employed to measure exchange with the surface. For example, a pulse of D_2 was injected into a stream of hydrogen passing over Ni/SiO_2 and the retention time for the appearance of HD was measured [50]. The retention time will depend upon the size of the hydrogen pool with which deuterium can exchange. It was found that at 298–393 K the retention volume was very small and corresponded to exchange with *H on Ni. At 393–473 K the retention volume was small and the exchange was assigned to adsorbed H_2O. At $T > 473$ K there was an increasing retention volume which resulted from exchange with σ-OH.

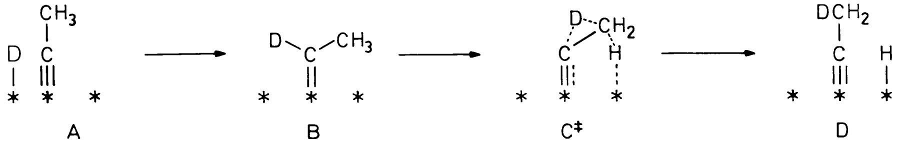
Exchange between deuterium and the zeolites H,CaY and Pt/H,CaY has been followed by measuring the infrared absorbance of the σ-OH band at $3640\,\text{cm}^{-1}$ [51]. The exchange with H,CaY was first order in unexchanged zeolite at 500–700 K, whereas the rate of exchange of Pt/H,CaY declined rapidly with time although the rate was intially 10^5 times greater than that of H, CaY. It was concluded that the σ-OH immediately adjacent to the particles of Pt exchanged rapidly whereas interchange between D^+ at Pt and H^+ at more distant σ-OH was slow. Similar observations have been made of exchange between D_2 and the σ-OH of Pt/Al_2O_3, but reaction was followed by NMR using selective RF pulses to invert nuclear spin moments [52]. At near room temperature, limited exchange occurred even on a millisecond time scale. Exchange averaged over the whole surface was very much slower. Here also, the fast exchange seems to be that of σ-OH immediately adjacent to the particles of metal.

In general, reactions involving hydrocarbons on supported metal catalysts lead to the deposition of slowly reacting carbonaceous residues. In reactions at $T \leqslant 298$ K, exposure to H_2 at a temperature about 25 K greater than that of the catalytic run converts the deposit to desorbed alkane with a structure equivalent to that of the reactant (e.g., propane after hydrogenation of propylene) [53]. After isotopic exchange reactions between D_2 and alkanes at about 343–373 K, similar release of hydrocarbon occurs upon elevating the temperature a relatively small amount, but in addition some methane is liberated at 573–673 K. In reactions of hydrocarbons at $T \geqslant 473$ K such as hydrogenolyses, the carbonaceous residue may be liberated only at higher temperatures and primarily as methane.

There have been many studies of carbonaceous residues but only a few have investigated isotopic exchange between deuterium and these residues at temperatures below that at which they are liberated from the surface by hydrogen.

The unevacuable residues formed on Pd/SiO_2 by exposure to 1-pentene were found to take up and lose H_2 reversibly at 293–353 K as determined by the IR absorptions bands due to $\text{—CH}_2\text{—}$ and —CH_3 [54]. The residues were not liberated from Pd during these operations. The residues underwent exchange with D_2 at 313 K and above with $E_a = 76\,kJ\,mol^{-1}$. H-residues underwent exchange with D_2 three times as fast as D-residues with H_2. This kinetic isotope effect indicates that the rate is influenced by the rate of cleavage of C—H bonds in the residues and not by the rate of dissociative adsorption of hydrogen.

The first carbonaceous residue to be identified on metallic surfaces was 1,1,1-triadsorbed ethane (adsorbed ethylidyne). On Rh(111) it does not react with D_2 (1 atm) to form ethane at 310 K, but the methyl group of $*{\equiv}C{-}CH_3$ does exchange slowly with D_2. The proposed mechanism of exchange was:



Scheme 10.A.1

As written, the mechanism violates the principle of microscopic reversibility (PMR), since the steps **A** → **B** and **B** → **D** are assumed to occur but not their reverses. It would become a nonforbidden mechanism if the reaction written above and its exact reverse occurred simultaneously and at the same rate (ignoring kinetic isotope effects) [8] A simpler, nonforbidden mechanism, however, would be the sequence **A** → **C** → **B** → **C** → **D** with the appropriate choice for the position of the deuterium atom and allowing rotation of the methyl group in **B**. PMR applies exactly only at equilibrium, but an isotopic exchange reaction must correspond very nearly to an equilibrium process.

2. Exchange Between Deuterium and Organic Compounds

An isolated study of exchange between butane and deuterium on Rh/MgO would not per se add to mechanistic knowledge. One could hardly get very far in unraveling the mechanism of the new reaction from the data. However, the steps involved in isotopic exchange of alkanes are likely to be related to those involved in hydrogenating unsaturated compounds. Two matters facilitate mechanistic studies of these exchange reactions. First, the isotopic distribution patterns, that is, the fractions of the isotopically exchanged molecules, $D_1, D_2, D_3, \ldots$ (where D_i is the fraction of the compound with i atoms of deuterium) provide a number of items of data for each experiment and the isotopic distribution patterns are often specific enough definitely to eliminate a number of conceivable mechanisms. Second, run in conjunction with structure variation, they have been effective in greatly narrowing the range of possible mechanisms, even though, of course, these studies cannot give "the mechanism."

The main tool for determining isotopic distribution patterns has been mass spectroscopy. But often, one would like to know where the deuterium atoms which have been introduced are located. Mass spectroscopy of the parent peak gives only the number of D atoms and not their location. Sometimes the istopic distributon pattern of fragment ions can provide this information, but often deuterium atoms are scrambled before fragmentation of the parent molecule ion. In such cases, D or H NMR, microwave spectroscopy, or infrared absorption have been successful.

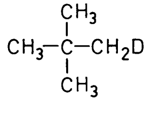
Hydrocarbons were the first organic compounds to be investigated and they have been by far the most extensively investigated group. With high probability one now can predict the general nature of the isotopic exchange pattern of most hydrocarbons on Pt, Pd, and Rh catalysts and on Cr_2O_3. Refs. [46–48, 55, and 56] provide further details on these reactions and their mechanistic implications. Some examples of this work are given below because the techniques have proved powerful in assessing the nature of the organic parts of the adsorption complexes which constitute reaction intermediates. On the other hand, the work has contributed much less to an understanding of the exact nature of the active sites and the nature of the bonding of the intermediates to the sites.

Ready interpretation of the isotopic distribution patterns requires that one work at low conversions so as to avoid significant contributions from molecules which have been adsorbed and exchanged twice and to avoid confusion of the pattern by dilution of the D_2 with HD.

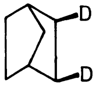
At temperatures of 273–373 K ethane exchanges on Pt, Pd, and Rh, supported or as films, to give a large D_6, propane gives a large D_8, neopentane exchanges to give a D_1 near unity and a small D_2, 3,3-dimethylpentane gives D_5 large and D_6–D_{16} equal to zero, norbornane gives only D_1 and D_2 with finite values, and adamantane gives only adamantane, singly substituted with deuterium either at a methylene or at a bridgehead. The D_1's given above are those of the initial products. The maximally exchanged species are shown below:

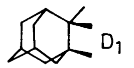
CD_3CD_3

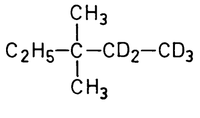
$CD_3CD_2CD_3$



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2D$$

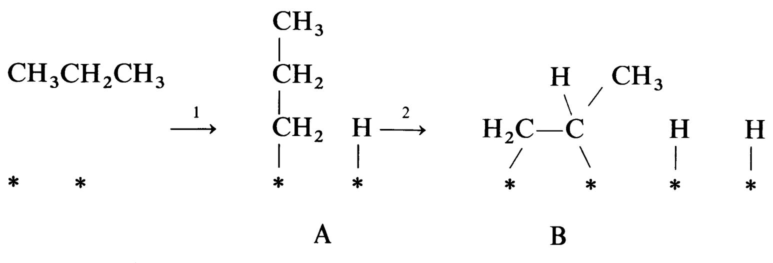






$$C_2H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CD_2-CD_3$$

The following model fits the data. An alkane adsorbs initially as a monoadsorbed alkane, R* + *H. Monoadsorbed alkane will then react where possible to form a 1,2-diadsorbed alkane (adsorbed olefin in the Horiuti-Polanyi mechanism). This reaction and its reverse are usually fast compared to desorption.



$$D_2 + {*}H \xrightarrow{3} HD + {*}D$$

Scheme 10.A.2

Alternation of reaction 2 and -2 will give ethane-d_6 and propane-d_8. Formation from monoadsorbed alkane of 1,1-diadsorbed alkanes (adsorbed alkylidene, $*=$CHR) and of 1,3-diadsorbed alkane is very slow at lower temperatures since only neopentane-d_1, adamantane-d_1, and no 3,3-dimethylpentane-d_6 are observed. 1,2-Diadsorbed alkane must have an eclipsed conformation since adamantane goes only to d_1 in one period of adsorption (all adjacent hydrogen atoms in adamantane are staggered) and norbornane exchanges a maximum of two hydrogen atoms in the ethylene unit (the adjoining bridgehead hydrogen atoms are staggered with respect to those in the ethylene unit). The mechanism of reaction 3 is not specified, but if probably proceeds by dissociative adsorption of D_2 followed by associative desorption of HD. These reactions put protium on the surface and reaction 3 replaces protium by deuterium. The ratio $D*/H*$ in the surface pool depends upon the relative rates of reactions 3, 2, and 1. (At steady state in isotopic exchange, $r_1 = r_{-1}, r_2 = r_{-2}$, and $r_3 = r_{-3}$). Suppose that in the exchange of propane, $r_2 \gg r_{-1}$ so that all eight atoms of hydrogen are exchanged with the surface pool and that r_1/r_3 is such that $D*/H*=1$. Then, as one may calculate from the binomial theorem [55], D_8 would be 0.004 and, even if $D*/H* = 3$, D_8 would be only 0.1. Since, in fact, $D_8 > D_7$, $D*/H*$ must be large, r_3 must be much larger than r_1, and in isotopic exchange between D_2 and alkanes on noble metals nearly every time a C—H bond is cleaved, a C—D bond results when the bond is reformed.

Alternation between the mono- and the diadsorbed species of pentane could exchange all 12 hydrogen atoms and, indeed, at ambient temperatures and above, the isotopic distribution pattern (D_i vs i) of pentane exhibits a maximum at D_{12}. It is curious, however, that the isotopic distribution patterns of pentane and other alkanes including ethane exhibit a deep minimum at about at half exchange, i = n/2. Kemball had proposed this to result from two different sets of surface sites with different values of r_2/r_{-1}, large and small. A different explanation has been proposed for the U-shaped curve obtained on platinum catalysts [57]. Two sets of sites [17], A and B are assumed. Ethane cannot adsorb on sites B but only on sites A for which r_2/r_{-1} is small. D_i, then, declines rather rapidly with increasing i in so far as the A sites alone are concerned. Some fraction of the intermediates on sites A transfer *irreversibly* to sites B on which r_2/r_1 is large and on which extensive multiple exchange occurs. Reaction of 1-monoadsorbed ethane with $*$H occurs on these sites to liberate ethane. The idea is ingenious, but modification is needed to avoid violating the principle of microscopic reversibility. The rates of adsorption of ethane and its microscopic reverse, desorption, on sites B must be equal, but the mechanism assumes that the rate of adsorption is zero. Transfer of intermediates occurs from sites A to sites B, but the microscopic reverse is forbidden.

On the basis of what has been said above, cyclopentane should exchange only to $C_5H_5D_5$ since there is no possible eclipsed diadsorbed species which could transfer the position of adsorption from one side of the ring to the other. In fact, at lower temperatures exchanged cyclopentane shows a large D_5 and small D_6–D_{10}. At higher temperatures, D_{10} also becomes large. Thus, there is at least one additional process which transfers the position of adsorption from one side of the ring to the other [55, 56, 58]. This isotopic exchange pattern of cyclopentane was originally discovered by Kemball who assumed that in $C_5H_5D_5$ the 5 atoms of deuterium were all on one side of the ring. This would seem very likely, but Kemball and colleagues [58a] have recently used deuterium NMR spectroscopy to prove that this assignment is indeed correct on Pt/SiO_2 and Ni/SiO_2. Although multiple exchange appears usually to involve a 1,2-process, this is impossible with neopentane. As shown by DMR, the neopentane-d_2 formed in low yield is $(CH_3)_3CCHD_2$ rather than $(CH_3)_2C(CH_2D)_2$. However, with propane and isobutane at higher temperatures, isotopic distribution patterns plus determination of deuterium location by DMR seem to require slow formation of the 1,3-diadsorbed species as evidenced by formation of $CHD_2—CH(CH_3)—CH_2D$.

Although the isotopic exchange experiments have been informative as to the identity of surface intermediates, they do not provide much information about the nature of the binding of the adsorbate to the catalyst. Thus, the 1,2-diadsorbed intermediate has been represented above as a disubstituted alkane. However, a π-complexed olefin with the four substituents at the double bond bent back as in molecular π-complexes would have almost the same geometry and some have preferred it. The author of this chapter does not believe that it is possible to distinguish between the two representations by isotopic exchange experiments [55].

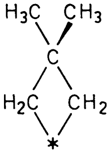
Structure variation can yield other kinds of information. For example, on alumina [58b] (and also, as previously found, on Cr_2O_3) the predominant initial product is alkane-d_1. Primary hydrogen atoms exchange more rapidly than secondary. For example, with butane the hydrogen atoms of CH_3 exchange 60 times as fast as those of CH_2. The faster exchange of primary hydrogen atoms indicates that the carbon atom acquires some carbanion character in the transition state leading to exchange. This conclusion depends upon the results of organic mechanistic work, i.e., carbanions at primary positions are favored over those at secondary positions.

Finally, isotopic exchange studies can still reveal surprizing reactions which may have mechanistic utility. Thus, gold is one of the least catalytic of metals, a very poor catalyst for olefin hydrogenation, isotopic exchange between D_2 and alkanes, and between D_2 and H_2. Nevertheless, an evaporated gold film very rapidly catalyzes exchange between CH_3SiH_3 and CH_3SiD_3 at 195 K [59]. Thus, it is not that one cannot have a surface Au—H bond. Rather, the bond energy is too small to permit breaking the H—H bond (435 kJ mol^{-1}), whereas the surface Au—Si and Au—H bonds are strong enough to permit the rapid cleavage of the Si—H bond.

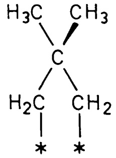
3. *Addition of Deuterium*

Since the hydrogenolysis of cyclopropane on metallic catalysts is very likely to involve 1-monoadsorbed propane as the terminal intermediate, a study of the reaction by use of deuterium is apt not to be very informative. The monoadsorbed propane will undergo isotopic exchange as discussed earlier for propane. Indeed, extensively exchanged propane is the product and one learns nothing about the initial activation. However, one does learn that little formation of exchanged cyclopropane accompanies hydrogenolysis. On chromia, however, exchange of cyclopropane is fast vs hydrogenolysis and one can learn little about hydrogenolysis because cyclopropane is exchanged before it is hydrogenated.

Study of the hydrogenolysis on metals of 1,1-dimethylcyclopropane obviates the problem of exchange after adsorption. As described in the previous section, a *gem*-dimethyl group blocks the propagation of isotopic exchange and permits one to observe the consequences of the initial activation of the cyclopropane. Since on Pd and Rh the product of hydrogenolysis is $CH_2D—C(CH_3)_2—CH_2D$ [60], it appears very likely that hydrogenolysis commences on Pd and Rh not by C—H dissociative adsorption bt by C—C dissociative adsorption to form either:



or



Deuterium converts the 1,3-diadsorbed propane shown above to neopentane-d_2, but the deuterium distribution provides no information as to whether the addition of two atoms of deuterium is concerted or sequential. However, if, as is likely, addition proceeds via an intermediate monoadsorbed neopentane-d_1, conversion of the diadsorbed to this monoadsorbed neopentane must reverse at a negligible rate (otherwise D_3 would not be zero) in accord with results of isotopic exchange of neopentane. Thus, cyclopropane readily forms a 1,3-diadsorbed propane at 273 K, whereas in deuterium exchange of propane this species is formed slowly at 333 K. However, with cyclopropane one starts higher in energy since cyclopropane has a strain energy of about $42\,\mathrm{kJ\,mol^{-1}}$. An important aspect of the hydrogenolysis of 1,1-dimethylcylopropane with deuterium is the absence of isotopic exchange reactions which would lower D*/H* and confuse the isotopic distribution pattern.

Many investigations of reactions between deuterium and olefins on metals have been reported. In general, they suffer from the complication that D*/H* is small, often in the vicinity of unity. This results from a coupling of slow desorption of HD with two kinds of exchange reactions, that forming alkane-d_3, -d_4, etc. and that forming exchanged olefin. Thus, adsorption of propene would form species B in Scheme 10.2. Alternation between A and B would equilibrate many positions with the surface D*/H* pool, but unless D*/H* is very large, reforming a carbon–hydrogen bond will often lead to the introduction of protium rather than deuterium. We shall represent by F a position which has been equilibrated with the surface D/H pool. In the propane product there will be a distribution $C_3H_6F_2$, $C_3H_5F_3, \ldots$. C_3F_8. F_0 and F_1 are necessarily zero since the two atoms added to the olefin will have been equilibrated with the surface D/H pool. D*/H* can be calculated from d_{av} in the alkane and the ratio, alkane/deuterium, in the feed. From D*/H* and the distribution in D_i's, one can calculate the distribution in F_i's which, for mechanistic purposes, is what one wants to know rather than the D_i's [47].

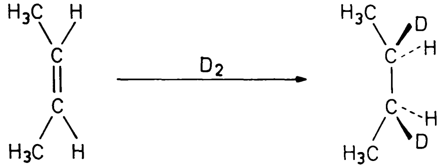
In Pt/Al_2O_3-catalyzed liquid phase hydrogenation with deuterium of cyclopentene, neat or in a solvent like an alkane or tetrahydrofuran, d_{av} for cyclopentane is ~ 1.3 at low conversions. Some exchanged cyclopentene is also formed [47]. One might expect to see $D_5 \gg D_6$ in analogy to results of isotopic exchange between deuterium and cyclopentane. However, because of the low value of D*/H*, D_5 and

D_6 are both very small and no clear break separates them. If CH_3COOD is used as the solvent, exchange between the solvent and $*H$ occurs and $D*/H*$ is raised to about 5; d_{av} is raised considerably, and a clear break follows D_5; i.e., the pattern becomes close to that observed in isotopic exchange between cyclopentane and deuterium. These results support the view that isotopic exchange and hydrogenation have steps in common.

If there should be two groups of sites each with a different value of $D*/H*$, there are insufficient data to calculate the distribution in F_i. It was indeed observed that the distribution pattern in D_i's could not be accommodated by the same value of $D*/H*$ both for large d_i and for small d_i [47]. Thus, clearly, the reaction involved two different kinds sites. The addition of deuterium to olefins and the isotopic exchange of alkanes have provided powerful evidence for the existence of more than one set of sites for these reactions.

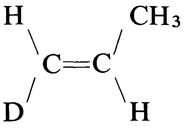
Hydrogenations are simpler on some oxides, for example chromia [61], where alkanes-d_2 are the primary products of reaction with deuterium. Thus, $D*/H*$ remains high.

Whether H_2 adds *cis* or *trans* during hydrogenation is an important mechanistic datum. Suppose that one wished to determine whether H_2 added *cis* or *trans* to *cis*-2-butene on Pt. One might hope to answer the question by hydrogenation with deuterium, but the wide distribution of D in the product and the low value of $D*/H*$ during hydrogenation would defeat the attempt. On chromia, however, one can show that the two atoms of D add *cis* to generate *meso*-2,3-dideuterobutane as nearly the only product [61]:

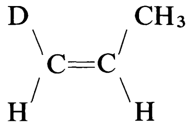


In this case the hyperfine distribution of the atoms of D was measured by IR absorption spectroscopy, since the *meso*- and the *d,l*-2,3-dideuterobutane have distinguishable spectra.

Microwave spectra result from molecular rotational transitions, the frequencies of which depend upon the moments of inertia of the molecules. This phenomenon permits one to measure the hyperfine distributions (relative concentrations) of all of the possible isomers of propene-d_1, since each has a different moment:



trans-1-d_1



cis-1-d_1

$H_2C{=}CD{-}CH_3$

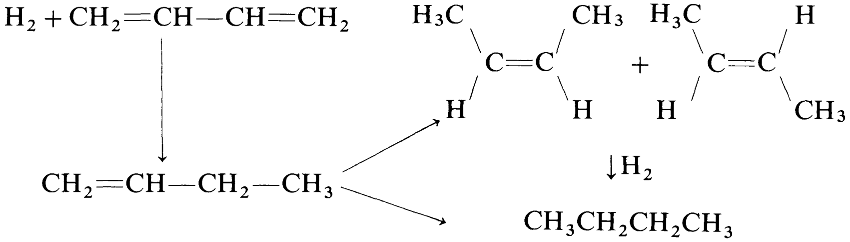
2-d_1

$H_2C{=}CH{-}CH_2D$

3-d_1

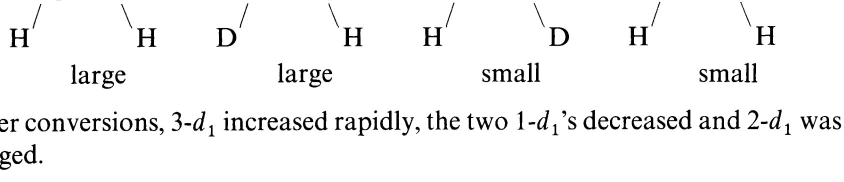
Similar analysis of butenes is also possible.

Determination of hyperfine distributions may permit some conclusions about mechanism even when D*/H* is low. For example, one knows that 1-butene is almost the only initial product of the hydrogenation of 1,3-butadiene on copper powder at about 323 K [62]. The 1-butene isomerizes slowly to *cis*- and *trans*-2-butene until the butadiene disappears. Isomerization then becomes very fast and hydrogenation to butane becomes measurable but slow.



One learns several things by substituting deuterium for hydrogen. Isotopic exchange to form butadiene-d_1 and a little -d_2 is rapid. Negligible HD appears in the vapor phase as is also true when a mixture of H_2 and D_2 is employed. Thus, adsorption of hydrogen is irreversible, D*/H* must be small and, even though deuterium is being employed, D_0 for 1-butene is 80% and D_1 only 20% at low conversions. As determined by microwave spectroscopy, 2-d_1 ($CH_2CH_2CD{=}CH_3$) was absent and 85% of the butene-d_1's were 3-*d* and 4-*d*. Thus, adsorbed butadiene adds two atoms of (H, D), symbolized F, to give $CH_2F{-}CHF{-}CH{=}CH_2$. This species may be further exchanged, but the low value of *D/H* would have prevented this from being seen. Finally, the rate of hydrogenation with hydrogen was five times that with deuterium. This kinetic isotope effect arises from the larger zero point energy of the H—H bond and the consequent larger bond dissociation energy of D_2 than H_2. It therefore appears that the adsorption of hydrogen is rate limiting.

As is usual in hydrogenations with deuterium on Group VIII catalysts, the initial reaction between D_2 and propene on Pd/SiO_2 was found to involve the formation of both propane and exchanged propene [63]. Temperatures well below 273 K were required to secure low conversions and to avoid mass transport problems. Interpretation was complicated by D*/H* being only about unity. The kinetic orders and activation energies of the hydrogenation and of the exchange of propene were identical. In the exchanged propene, D_1 was large and D_2 was small, but if D*/H* was near unity for exchange as well as hydrogenation, F_1 for exchanged propene would have been twice as large as the observed D_1 and F_2 would have been relatively even larger. The hyperfine distribution at very low conversions follows.

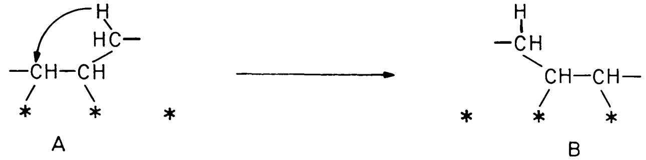


At higher conversions, 3-d_1 increased rapidly, the two 1-d_1's decreased and 2-d_1 was unchanged.

Accordingly the authors investigated the reaction of propene-1-d_1 with hydrogen. The two isomers of propene-1-d_1 reacted rapidly to form propene-3-d_1 with this from being seen. Finally, the rate of hydrogenation with hydrogen was five little loss of deuterium. In the absence of data for reaction between propene and D_2 at very low conversions, it would have appeared that 3-d_1 rather than 1-d_1 was the major initial exchanged propene and one would have concluded that exchange mainly occurred via an allyl intermediate:

$$\begin{aligned} CH_3{-}CH{=}CH_2 &\rightarrow {*}CH_2{-}CH{=}CH_2 \quad (\text{or } \pi\text{-allyl}{*}) \\ &\rightarrow CH_2D{-}CH{=}CH_3 \end{aligned}$$

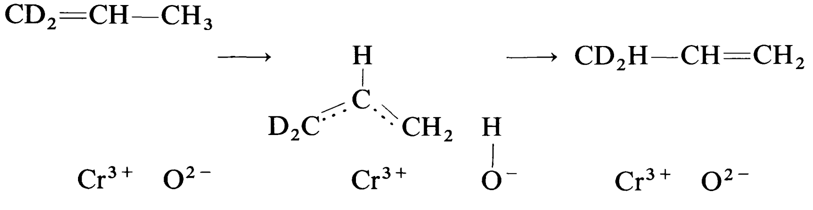
Another mechanism for isomerization of 1-d_1 to 3-d_1 is that of Smith and Swoap [64] in which a hydrogen atom at position 3 of **A** jumps to position 1 to produce the intermediate **B**:



A B

However, in an interesting example of the application of structure variation, Siegel [65] notes that a certain cholestenol cannot be hydrogenated on palladium catalysts in neutral solution. The double bond in this molecule is tetrasubstituted and such species are difficult to hydrogenate. However, a double bond shift by the Smith and Swoap mechanism would convert the cholestenol to an isomer with a trisubstituted double bond which should be hydrogenatable. This, then, argues against the Smith and Swoap mechanism, but it argues equally against any mechanism of double bond migration in neutral conditions. The cholestenol may be too specialized a molecule for the purpose.

A similar application of microwave spectroscopy has involved the isomerization of $CD_2{=}CH{-}CH_3$ on amorphous Cr_2O_3 in the absence of hydrogen gas [66]. When the propene-d_2 was passed over chromia at ~ 283 K, 80% of the product was isomeric propene-d_2's, mainly $CD_2H{-}CH{=}CH_2$. There was also about 10% each of propene-d_1 and propene-d_3. There was no D on the central carbon atom of propene in any product. The observed products are compatible with a carbenium ion reaction, the addition of a proton to form a *sec*-propyl carbenium ion followed by loss of a proton. However, this mechanism was eliminated because the rate of double bond isomerization without loss of deuterium in $CD_2{=}C(CH_3)_2$ was nearly the same as that in $CD_2{=}CH{-}CH_3$. One would expect a process forming the tertiary carbenium ion, $(CH_3)_3C^+$, to be much faster than that forming $(CH_3)_2CH^+$. The authors then proposed that the reaction proceeded via initial heterolytic, dissociative adsorption of propene to form adsorbed allyl:



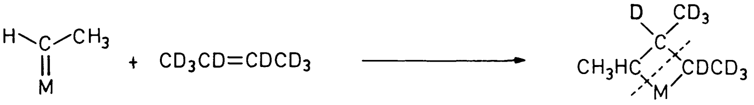
$$\begin{array}{ccc} CD_2{=}CH{-}CH_3 & \longrightarrow \quad D_2C\overset{\overset{H}{|}}{\cdots C \cdots}CH_2 \quad \overset{H}{\underset{O^-}{|}} & \longrightarrow \quad CD_2H{-}CH{=}CH_2 \\ Cr^{3+} \quad O^{2-} & Cr^{3+} & Cr^{3+} \quad O^{2-} \end{array}$$

The dissociative adsorption of propene is called heterolytic because the hydrogen atom is transferred to O^{2-} as an H^+ whereas the allyl ion is formally negative.

4. *Tracing*

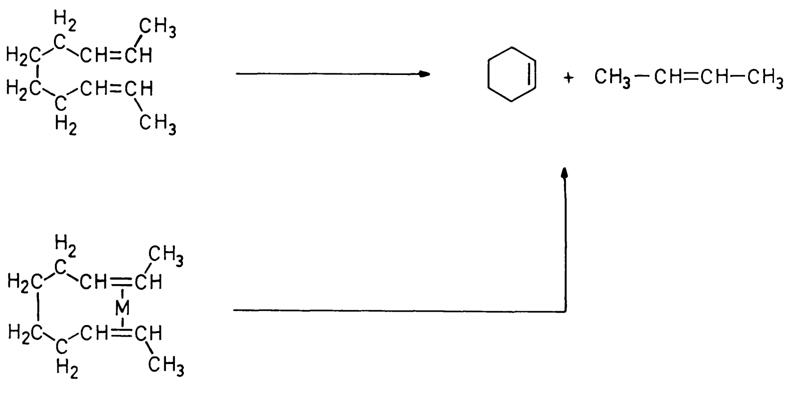
In organic reactions, deuterium labeling is sometimes used to determine which carbon atoms end up where or whether a reaction is inter- or intramolecular. We shall exemplify this procedure by two examples from olefin metathesis.

At 263–298 K metathesis of an equimolar mixture of *cis*—CD_3—$CD{=}CD$—CD_3 and *cis*=CH_3—$CH{=}CH$—CH_3 on reduced MoO_3 rapidly formed CD_3—$CD{=}CH$—CH_3 (60% *cis* and 40% *trans*) and *trans*-d_0 and *trans*-d_8 [67]. Thus, the rapid *cis–trans* isomerization occurs by metathesis and not by one of the more usual mechanisms of olefin isomerization. Further, the metathesis involves the cleavage of $C{=}C$ bonds and interchange of $R_2C{=}$ groups between different molecules. C—H bonds are not cleaved in the process and stereochemistry has some tendency to be preserved during metathesis. The products are consistent with the Hérisson–Chauvin mechanism, where M represents a metal ion site:



If the metallocyclobutane at the right cleaves as shown, $CH_3CH{=}CDCD_3$ and $M{=}CDCD_3$ result. Continuation of the sequence forms 2-butene-d_0, -d_4, and d_8 in random proportions, 1:2:1. However, various other mechanisms could lead to the same results.

A similar metathesis of an equimolar mixture of 2,8-decadiene and $CD_3CH{=}CHCH_2CH_2CH_2CH_2CH{=}CHCD_3$ was examined on reduced MoO_3, CoO/Al_2O_3 [68]. The products were cyclohexene and butene-d_0, -d_3, and d_6 in the random proportions, 1:2:1, expected from the Hérisson–Chauvin mechanism. This result requires that the $CH_3CH{=}$ units assembled into 2-butene come from different molecules and it suggests that the concerted, one step mechanism shown at the bottom below does not occur:



since it would give no butene-d_3, but even the added complications which would result from decomposition of the species at the lower left only as far as M-π-olefin cannot lead to proportions in which d_3 becomes as high as 2(69). Thus, only some kind of a chain reaction in which only one olefin unit appears in the transition state appears to be compatible with these results.

B. Isotopes of Carbon and Oxygen

Isotopes of carbon and oxygen have most commonly been used in ways which may be classified as isotopic tracing. Often the isotopic studies were accompanied by other mechanistic probes, but here we shall usually give just the conclusions derivable from the isotopic experiments. One application of the use of ^{13}C has already appeared at the end of Sect. 7 [22]. A classic example of the use of ^{14}C arose from mechanistic consideration of the oxidation of propylene to acrolein on bismuth molybdate [70]. What is the nature of the initial attack on propylene? $^{14}CH_2{=}CH{-}CH_3$ and $CH_2{=}CH{-}{}^{14}CH_3$ were oxidized and the acrolein was degraded photolytically:

$$CH_2{=}CH{-}CHO \rightarrow CH_2{=}CH_2 + CO$$

Ethylene and carbon monoxide were then counted. Both initial propylenes led to acrolein in which 1/2 of the ^{14}C was in the ethylene and 1/2, in the CO. This result accords with initial removal of H from CH_3 to form an allylic species, either the symmetric π-complex or a pair of rapidly equilibrating σ-complexes.

^{13}C and ^{18}O have been frequently employed in studies of the hydrogenation of CO. One example was given in Sect. (9.F) [38]. Another concerns the mechanism of hydrogenation of CO to methanol on Rh/TiO_2 [71]. The products of hydrogenation of a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ were $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ with very little of the other isotopic methanols. Thus, under the conditions of the experiments (423 K, 1 atm total pressure), the C—O bond appears to remain intact during hydrogenation and all reactions which might equilibrate the isotopic species (such as isotopic exchange between the two isotopic species of CO) are slow relative to hydrogenation.

Isotopic labeling can, in suitable cases, help to resolve the question as to which of two molecules reacts more rapidly or whether a conceivable intermediate is an actual one. Thus, in the commercial production of methanol, a mixture of CO + CO_2 rather than just CO is usually employed. Which of the two is hydrogenated more rapidly? Is CO an intermediate in the hydrogenation of CO_2? On a Cu/Zn oxide catalyst at 493 K, 17 atm, $C^{18}O_2/C^{16}O = 0.2$–0.5, CO_2 hydrogenates more rapidly than CO as judged by the relative rates of formation of $CH_3{}^{18}OH$ and $CH_3{}^{16}OH$ [72]. Thus, reactions leading to the equilibration of the two isotopic species of oxygen were slow relative to the rate of hydrogenation of CO_2. Further, CO_2 was reduced without much formation of gas phase CO.

A somewhat similar question arises in the hydrogenation of mixtures of ethylene and acetylene. The question has attracted considerable interest because small amounts of acetylene must be removed from the ethylene to be used to manufacture polyethylene. Under suitable conditions on a palladium catalyst, the acetylene can be removed with little conversion of ethylene to ethane.

In experiments on a palladium black catalyst, it was found that selectivities varied considerably with pretreatment conditions [73]. Hydrogenation of a mixture of $H^{14}C{\equiv}CH$ and ordinary ethylene showed that, in the steady state, the main route of hydrogenation of acetylene at low pressure of acetylene was the formation of C_2H_6, C_2H_4, and C_4 hydrocarbons. Above a certain partial pressure of acetylene, the hydrogenation of ethylene was completely inhibited, as was shown by the hydrogenation of a mixture of C_2H_2 and $H_2{}^{14}C{=}CH_2$.

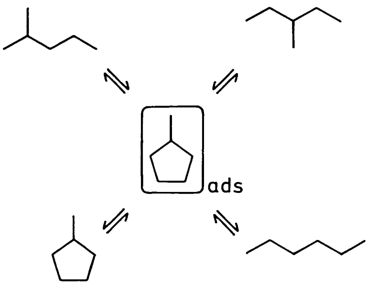
Similar initial transient behavior was observed on Ni/SiO_2 at 293 K [74]. $H^{14}C{\equiv}CH$, initially adsorbed on the catalyst in the absence of hydrogen, was not removed when flow of $H_2 + C_2H_2$ was started. The hydrogenation of mixtures of $H^{14}C{\equiv}CH$ and C_2H_4 showed that hydrogenation of acetylene to ethane proceeded as a surface reaction and not via desorbed ethylene. The surface of the nickel became heavily covered with slowly reacting carbonaceous residues. The adsorption of ^{14}CO on the used catalyst was only 4% that on fresh catalyst. The authors concluded that separate sites are involved in the hydrogenation of ethylene and acetylene and, since they adhere to the view that hydrogenation involves transfer of hydrogen from the carbonaceous overlayer to the unsaturated hydrocarbons, they did not believe that hydrogenation occurred on the 4% of metal surface detected by adsorption of ^{14}CO.

In organic heterogeneous catalysis, ^{14}C and ^{13}C have frequently been employed to determine where a particular carbon atom in the reactant appears in the product. A classic example from the work of Pines is provided by the dehydrocyclization of heptane-1-^{14}C to toluene at ~ 773 K on Cr_2O_3/Al_2O_3 [75]. If the reaction goes by a 1,6-ring closure, one-half of the toluene formed would be labeled in the ring and one-half in the methyl group. To ascertain the location of the labeled carbon atom, the toluene was oxidized and decarboxylated. Both the benzene and the carbon dioxide were counted:

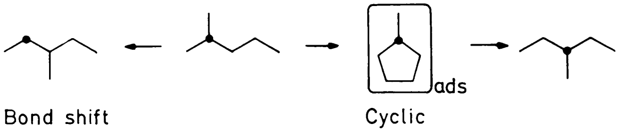
$$\begin{aligned} {}^{14}CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 &\rightarrow C_6H_5{-}CH_3 \\ &\rightarrow C_6H_5{-}COOH \\ &\rightarrow C_6H_6 + CO_2 \end{aligned}$$

It was found that about 75% of the label was in the ring rather than just 50%. This by itself does not provide a mechanism, but it does eliminate mere 1,6-ring closure as a mechanism.

A large and important amount of work using ^{13}C as a tracer was done by Gault and his collaborators, particularly with respect to the isomerization of alkanes on metal catalysts (for a review, see Ref. [76]). At about 540 K in the presence of hydrogen, platinum catalysts can lead to equilibrium in the system, hexane, 2-methylpentane, 3-methylpentane, and methycyclopentane. Thus, it was a plausible hypothesis that the reaction proceeded by some kind of an adsorbed intermediate (or cluster of interconverting adsorbed intermediates) equivalent to an adsorbed methylcyclopentane. It is assumed that hydrogenolysis can cleave any ring C—C bond in the adsorbed methylcyclopentane:



However, under the same conditions, neopentane isomerises to isopentane. This cannot proceed by a cyclopentane intermediate, rather it appears to involve simple migration of a methyl group. The first process has been called cyclic, the second bond shift. Consider the isomerization of 2-methylpentane to 3-methylpentane. This might be imagined to proceed by either process, cyclic or bond shift. How can one determine the fraction by each process? This was investigated by labeling the 2-methylpentane (● represents ^{13}C) and locating the label in the product 3-methylpentane by mass spectrometry. The reaction was run on a series of Pt/Al_2O_3 catalysts with D (fractions exposed) varying from 0.04 to 1.0.



It was found that the cyclic mechanism accounted for 20% of the mechanism for D=0.04 to 0.5. With further increase of D the fraction proceeding by the cyclic process rose and reached 80% at D=1.0. There is no other way in which such information could be obtained.

As would be expected, ^{18}O is particularly useful in studies of the mechanism of oxidation reactions.

One example involves the oxidation of ethylene to ethylene oxide on metallic silver. It was generally accepted for some years that molecularly adsorbed O_2, O_2^{n-}(ads), reacted with ethylene to form ethylene oxide and O^-(ads) and that the latter species led to complete combustion to give CO_2. However, if one preadsorbs ^{16}O atoms on silver and then passes a mixture of $^{18}O_2$ and ethylene over the catalyst, the product is $C_2H_4{}^{16}O$[77]. Thus, it appears that atomically adsorbed oxygen is the reactant or less likely that two atoms of adsorbed oxygen react to form some O_2(ads) species just before reaction.

Another example is concerned with the mechanism of the oxidation of propylene to acrolein on bismuth molybdate [78]. A mixture of C_3H_6, $^{16}O_2$, and He (1:1:8) was passed over γ-Bi_2MoO_6 at 623–673 K. This gave about 90% acrolein and 10% CO_2. After several hours the $^{16}O_2$ was changed to $^{18}O_2$. The acrolein and the CO_2 were then analyzed vs. time for their isotopic composition by an in-line mass spectrometer. One could then sum the ^{16}O which appeared in the products. Initially the products primarily contained ^{16}O. Its concentration decreased slowly with time.

It could be calculated that 282 layers of oxygen atoms in the Bi_2Mo_6 reacted at 723 K and 126, at 673 K. No $^{16}O\,^{18}O$ appeared in the gas phase. Thus, as reported at the beginning of this section, propylene is probably initially adsorbed heterolytically as H^+ and allyl$^-$ and in succeeding steps it abstracts an O^{2-} from the lattice. The O vacancy is replaced by oxygen from the gas phase at a later stage. Since clearly the rate of migration of O^{2-} in the lattice is large compared to the rate of oxidation, the oxygen which is returned to the lattice is likely to enter at a location remote from that from which it was abstracted. In such oxidation mechanisms, called redox mechanisms, the hydrocarbon molecules are oxidized by metal ions in the catalyst and these ions are subsequently reoxidized by oxygen. O_2 is not the proximate oxidant although it is the oxidant in the stoichiometric equation.

11. Kinetic Isotope Effect

We shall consider only the kinetic isotope effect [79] between hydrogen and deuterium. Consider first the simple case of HCl vs. DCl. Figure 9 shows the potential energy as a function of the separation *r* of the two nuclei. Possible vibrational energies for HCl are restricted to the vibrational quantum numbers $(n + 1/2)h\nu$. The lowest possible energy for HCl is at $1/2\,h\nu$ as shown in Figure 9. This is the zero point energy. Since the mass of D is greater than that of H, the DCl vibrational frequency is less than that of HCl and, $1/2\,h\nu$ being smaller, the lowest possible energy of DCl is less than that of HCl. The bond dissociation energy of HCl, the difference in energy $E_{HCl}—E_H—E_{Cl}$, is the vertical line at the left, the corresponding bond dissociation energy for DCl is the vertical line at the right. In more complicated cases like C_6H_6 vs C_6H_5D, the total zero point energy will be the sum of the zero point energies of all vibrations. If a reaction mechanism involves the complete cleavage of a C—H bond as the *rdp*, then the C—D compound will react more slowly than the C—H one. Ordinarily, however, in heterogeneous catalysis the hydrogen atom is bound both in the reactant and in a surface intermediate. The transition state separating these two species will itself have a zero point energy and the zero point energies of the H and D forms will be different. Thus, the relative rates of reaction of RH and RD will involve the differences between the zero point energies in transition state and reactant for RH and RD:

$$[\Sigma\, 1/2\, h\nu_i(\text{transition state}) — \Sigma\, 1/2\, h\nu_i(\text{reactants})]_H$$
$$- [\Sigma\, 1/2\, h\nu_i(\text{transition state}) — \Sigma\, 1/2\, h\nu_i(\text{reactants})]_D$$

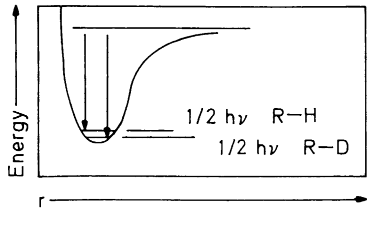


Figure 9. Zero point energies in the stretching vibrations of HCl and DCl, energy vs. *r*, the internuclear distance

The matter is of some complexity and can be put more precisely in terms of the various partition functions [79]. It is possible to have an inverse isotope effect, RD reacting more rapidly than RH, but one can ordinarily assume that an RH bond will react more rapidly than an RD one.

Two examples of the kinetic isotope effect have already been given, isotopic exchange between $H_2(D_2)$ and surface carbonaceous residues, Sect. 10.A.1, Ref. [53], and the much larger rate of hydrogenation of butadiene with H_2 than with D_2, Sect. 10.A.3, Ref. [62].

An important early example of the application of the kinetic isotope effect involved the oxidation of propylene on bismuth molybdate at 723 K. Variously deuterated propylenes were oxidized and the rates measured [80]. The results were:

	obs. rate	calc. rate
$CH_3{-}CH{=}CH_2$	1.00	(1.00)
$CH_2D{-}CH{=}CH_2$	$0.85 \pm .02$	0.83
$CH_3{-}CH{=}CHD$	0.98 ± 0.02	1.00
$CD_3{-}CD{=}CD_2$	0.55	0.50

It is apparent that D in the methyl group slows the reaction, whereas D in the methylene group is without effect. Thus, initial activation of propylene involves cleavage of a H—C bond in methyl to form an allylic species and this reaction is rate determining. This result and those at the beginning and at the end of Sect. 10.B clearly considerably restrict the choice of possible mechanisms for the oxidation of propylene to acrolein on bismuth molybdate. Other data would be needed to test for whether the proximate oxidizing agent is Mo(VI) or Bi(III), how and when a second hydrogen atom is removed and how and when the oxygen atom is transferred from the lattice, etc.

Suppose that a reaction involves the following steps:

(1) $H_2 + 2{*} \rightleftharpoons 2H{*}$
(2) $A + {*} \rightleftharpoons A{*}$
(3) $H{*} + A{*} \mathrel{-\!\!\!\!\!\Lambda\!\!\!\!\rightarrow} HA{*} + {*}$ *rdp*

An equilibrium isotope effect would be involved in step 1 since D_2 and H_2 will not have the same adsorption equilibrium constant. A kinetic isotope effect would be involved in step 3. Thus, the rate of reaction would be influenced both by an equilibrium and by a kinetic isotope effect.

Suppose that both steps 1 and 2 are irreversible. Run the hydrogenation with a mixture of H_2 and D_2. In view of the irreversibility of step 1, the ratio, (D added to A)/(H added to A), in the competition between H∗ and D∗ in step 3, will be simply the ratio of the rates of adsorption of D_2 and H_2 in step 1. A factor in this ratio should be equal to the ratio of the rates at which D_2 and H_2 strike the active sites, $1/\sqrt{2}$ [81]. The ratio, (D added)/(H added), has been called the incorporation isotope effect. In Sect. 9.3. in connection with the reaction $A \rightarrow B$, it was noted that difficulties could arise with an irreversible step. Here we assume that both steps 1 and 2 are irreversible. If H_2 and A both adsorb on the same sites and if adsorption of H_2 and A are uninfluenced by the occupancy of adjoining sites, then the mechanism is impossible. As free sites are formed at the end of the catalytic cycle, the more rapidly adsorbing species, A or H_2, will get most of the sites and after a few catalytic cycles the more rapidly adsorbing species will cover the surface, its rate of desorption is negligible, and so the reaction will become clogged and stop. The mechanism is possible if H_2 and A adsorb on separate sites. If the catalyst is a metal and A is rather bulky, a more likely possibility is that a monolayer of A will inevitably leave isolated site pairs accessible to the small hydrogen molecule but not to A.

An interesting example of isotope effects is provided by a study of the conversion of methanol to methyl formate on copper at 473 K, 0.3–1.0 atm [82]:

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2$$

The relative rates of reaction of CH_3OH, CH_3OD, CD_3OH, and CD_3OD were 8:4:2:1. The ratio of 8 for CH_3OH/CD_3OD is unusually large for an isotope effect. The authors concluded that it was the product of a factor of 2 for an equilibrium isotope effect, CH_3OH vs CH_3OD, in the initial step:

$$CH_3OH \rightleftharpoons CH_3O(ads) + H(ads)$$

and a factor of 4 for a kinetic isotope effect, CH_3 vs CD_3, in the *rdp*:

$$CH_3O(ads) \xrightarrow{A} CH_2O(ads) + H(ads) \quad rdp$$

For a statistical mechanical analysis of the situation see Ref. [82]. The proposed mechanism is also consistent with a number of other data on this reaction.

Rates of reaction of the following systems were measured at 358 K on Pt/Al_2O_3 and Ni/SiO_2, $H_2 + C_6H_6$, $D_2 + C_6H_6$, $H_2 + C_6D_6$, and $D_2 + C_6D_6$ [83]. The rate of hydrogenation was the same for all four isotopic combinations on Pt/Al_2O_3, but on Ni/SiO_2 the rate was slightly faster with D_2 and slightly slower with C_6D_6. Isotopic exchange occurred at a rate roughly equal to that of hydrogenation, but the kinetic forms of the two reactions were different. Further, the C—H bond exchanged 6.5 times faster than the C—D bond. This would be consistent with a rate determining dissociative chemisorption in the isotope exchange reaction:

$$C_6H_5{-}H + 2* \rightarrow C_6H_5* + *H$$

However, the authors gave no definite explanation for the absence or near absence of an isotope effect on hydrogenation. It is not clear why the kinetic isotope effect in the hydrogenation of benzene on Pt should be so different from that in the hydrogenation of butadiene on Cu [62]. The explanation of isotope effects is not always simple.

12. Applications of Stereochemistry

The compass of stereochemistry will be taken as rather large and applications to the determination of mechanism will be considered under the headings:

(1) Stereoisomerism. Work in this area primarily provides information as to what happens at asymmetric centers when some reaction occurs there or might occur there.

(2) Stereochemistry of addition to multiple bonds or elimination reactions forming them. Here the stereochemical data provide important information against which to test possible mechanisms of these reactions.
(3) Adsorbate-surface interactions. These studies provide almost the only way directly to probe the steric nature of catalytic sites without confusion with sites for adsorption which are not catalytic sites.

Most stereochemical experiments do not provide a large information content; either the product is *cis* or *trans*, either one finds racemization, retention, or inversion of configuration. However, often stereochemical data are powerful and direct in eliminating mechanisms without detailed argument.

Inevitably, molecules which would provide interesting stereochemical data are apt to be of some complexity and not many workers in heterogeneous catalysis have chosen to work with such molecules. Those who have so chosen usually have had a background in organic chemistry. Such workers are unfortunately less common than would be desirable for progress in heterogeneous catalysis.

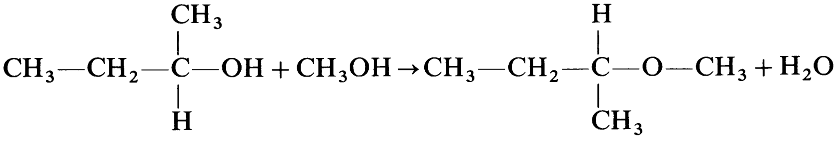
One caveat must be given with respect to data in the literature dealing with stereochemistry in heterogenous catalysis. Much of the data involves hydrogenations in solution. Unfortunately, in the bulk of this work, no attempt was made to establish the absence of poisoning and the absence of mass transport limitations, particularly of hydrogen. Much of the work was likely to have involved hydrogen fugacities in solution much below those in the gas phase and fugacities in the catalyst pores were probably distinctly lower than in solution. Further, judging from reported rates, many reported hydrogenations must have been seriously poisoned. Unless techniques equivalent to those developed by Hussey [84] were employed to establish the absence of poisoning and mass transport limitations, one cannot really know the exact conditions to which the data apply.

The application of stereochemical data to mechanism has been reviewed [85] and there is much related to mechanism in the invaluable encyclopedic compendium on stereochemistry in heterogenous catalysis on metals prepared by a consortium at Szeged [86].

A. Stereoisomers

1. Optical Activity

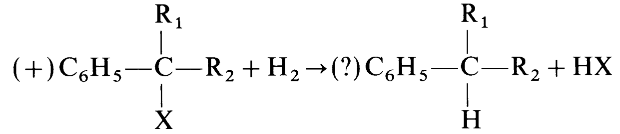
Although studies of chiral compounds have been applied to mechanistic studies in heterogeneous catalysis in the past, few such studies have been reported in recent years. These studies provide information as to what happens to an optical center during a reaction. For example, in the reaction on alumina of optically active 2-butanol with methanol to form *s*-butyl methyl ether:



$$CH_3—CH_2—\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH + CH_3OH \rightarrow CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—O—CH_3 + H_2O$$

the ether formed has a configuration inverted from that of the alcohol [87]. Thus, it is likely that the oxygen atom of the ether comes from the methanol, the oxygen atom of which displaces the oxygen atom of the butanol by something like an S_N2 reaction with inversion of configuration. The steric data alone do not test whether the 2-butanol first forms a surface alkoxide.

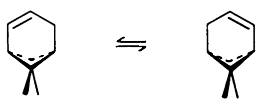
A number of studies have been made of the hydrogenolysis of optically active benzyl compounds on metal catalysts. Unlike the case just discussed, one must employ compounds with a tertiary carbon atom of the type, $C_6H_5R^1R^2CX$, where X is Br, Cl, SCH_3, OCH_3 and the like:



$$(+)C_6H_5-\overset{\displaystyle R_1}{\underset{\displaystyle X}{C}}-R_2 + H_2 \rightarrow (?)C_6H_5-\overset{\displaystyle R_1}{\underset{\displaystyle H}{C}}-R_2 + HX$$

[Ref. [86], pp. 310 and 526]. Otherwise the product would be $C_6H_5RCH_2$ which is necessarily optically inactive.

Optical activity can be used as a tracer is suitable cases. The hydrogenation of an olefin is often accompanied by double bond migration. One could examine the hydrogenation of 1-butene and measure the amounts of butane, 1-butene, and *cis*- and *trans*-2-butene as functions of time. Here, however the matter might be somewhat complicated by the differing energies of the three butenes. An ingenious application of optical activity avoids this [88]. Consider the hydrogenation of (+) apopinene, an optically active *gem*-dimethylbicycloheptene. There is only one possible migration of the double bond because one cannot form a double bond at the bridgehead positions. As may be seen the two forms of apopinene are mirror images:

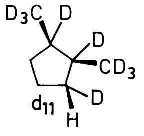


Further, the bulky *gem*-dimethyl group insures that the olefin will so adsorb that the least hindered side of the double bond becomes attached to the surface. The ratio of the rates, isomerization/hydrogenation, was found to vary rather widely over a series of palladium catalysts. Following the Siegel hypothesis [17], Sect. 5, isomerization was assumed to be possible at terrace sites (atoms on high density planes like [111] and [100] of FCC), but hydrogenation was assumed to require more coordinatively unsaturated atoms like those at edges or vertices. The variation in the ratio of rates can be interpreted using these assumptions, but that is not the only possibility.

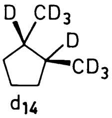
2. *Epimerization*

The occurrence or nonoccurrence of epimerization in reactions of diastereomers can provide much the same kind of information as that discussed in the preceding section.

In Sect. 10.A.2 it was noted that all of the hydrogen atoms in one of the two sets of 5 hydrogen atoms on each side of the cyclopentane ring can readily exchange during the period of adsorption. There is, however, a barrier to the transfer of the position of adsorption from one side of the ring to another and the nature of the transfer process has received much discussion [55, 56]. Epimerization accompanies the exchange between D_2 and *cis*-1,2-dimethylcyclopentane on Pd/Al_2O_3 [55]. The *trans*-dimethylcyclopentane so formed is highly exchanged and much of it is completely exchanged whereas the maximally exchanged *cis*-cyclopentane is d_{11}, a degree of exchange which can result from simple alternation between mono- and diadsorbed intermediates. Thus, epimerization and the switch of adsorption from one side of the ring to another are correlated.



Cis



Trans

This fact puts a substantial constraint on any mechanism for switching from one side of a cyclopentane ring to another on Pd. For example, if the switch in *cis*-dimethylcyclopentane were effected by an intermediate which was α,α-diadsorbed on an unsubstituted ring carbon atom, there should be no correlation with epimerization and some *cis*-d_{14} should be formed at lower conversions. None is observed.

B. Stereochemistry Related to Multiple Bonds

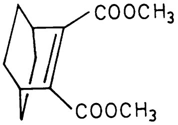
1. *Hydrogenation of Carbon–Carbon Multiple Bonds*

The result of the hydrogenation of a carbon–carbon double bond might be the addition of two atoms of hydrogen from one side of the plane of the double bond (*cis*-addition) or the addition of one atom of hydrogen from each side (*trans*-addition) (Sect. 10.A.3). In the 1930s, analysis of much preparative data led to the conclusion that *cis*-addition prevailed in heterogeneous catalytic hydrogenation on metallic catalysts [85, 86]. Later work showed that the hydrogen atoms inserted between the olefin and the surface [85]. These stereochemical data put substantial restrictions upon the choice of the mechanism of olefin hydrogenation on metals.

It is not easy to test directly whether hydrogenation is *cis* or *trans* because for this one needs to hydrogenate a compound with a tetrasubstituted double bond. For example, would the hydrogenation of 1,2-dimethylcyclopentene with hydrogen give the *cis*- or the *trans*-cyclopentane shown at the end of the last section. Hydrogenation of such compounds is very slow and isomerization to compounds with three substituents on the double bond (2,3-dimethylcyclopentene in the example) is often fast. These trisubstituted species hydrogenate fast relative to the tetrasubstituted precursor, fast enough, indeed, that it is difficult to detect the presence of the trisubstituted intermediate. Since the product of hydrogenation of the trisubstituted species is a mixture of *cis* and *trans*, one could erroneously conclude that hydrogenation of tetrasubstituted species gave *cis–trans* mixtures [85, 86].

One could imagine reducing the complexity of the required olefin by hydrogenating a secondary olefin with deuterium. As noted in Sect. 10.A.3, such experiments demonstrate that addition is *cis* on chromia, but experiments with metals fail because isotopic exchange which accompanies the addition of deuterium obscures the stereochemical location of the two added atoms of D.

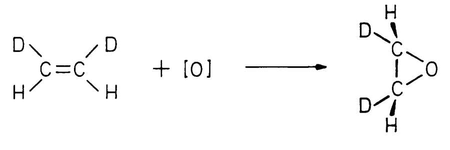
However, the addition of hydrogen to a C=C bond is not invariably *cis*. It is true that the product of the liquid phase hydrogenation on Pd of the bicyclooctene derivative:



in heptane or methanol is the result of 99% *cis* (or suprafacial) addition of 2 hydrogen atoms [89]. Thus, this is one of the rare cases in which *cis*-addition can be seen directly on metal catalysts. However, when the solvent was 0.02 M CF_3COOH in MeOH, 36% of the product resulted from *trans* (antarafacial) addition. In the bicyclooctene derivative, migration of the double bond is impossible because it would be necessary to form a double bond at a bridgehead which is forbidden for smaller rings. When the system, $H_2 + CH_3OD + CF_3COOD$ was employed, d_{av} for the *cis* product was 0.78, whereas that for the *trans* was 1.37. Thus, it appears that *trans*-addition resulted from the addition of a hydride ion to the face of the double bond towards the catalyst and of a proton from the solution side.

The stereochemistry of the hydrogenation of acetylenes on metals is simpler because the olefin which is formed desorbs and then reacts very slowly as long as unreacted acetylene remains. The primary product of hydrogenation is the *cis*-olefin. Selectivity to this product is particularly high on palladium. It is the major product in the hydrogenation of di-*tert*-butylacetylene even though the *cis*-di-*tert*-butylethylene has a strain energy of 36 kJ mol^{-1} with respect to the *trans* because of the strong interference between the two *tert*-butyl groups [90]. This is an example of stereochemical results which strongly limit possible mechanisms.

One might expect that the epoxidation of ethylene on silver catalysts would proceed with *cis*-addition of an atom of oxygen. The reaction has been investigated using *cis*- and *trans*-1,2-dideuteroethylene. *Cis*-addition to the *cis*-ethylene would proceed as follows:

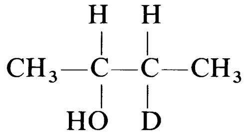


However, although *cis*-addition is favored, stereoselectivity is low [91, 86 p. 188]. No formation of gas phase $C_2H_2D_2$ isomers occurs. Finding low stereoselectivity might be less significant than finding high stereoselectivity. Low stereoselectivity might result from the sequence of elementary processes on the main line leading to epoxide. For example, there might be two simultaneous catalytic cycles leading to epoxide which give opposite stereochemistry. However, the observation that the selectivity is independent of temperature over a rather wide range makes this explanation somewhat improbable. Of course the low steroselectivity might result from a side shoot to the main catalytic cycle. Although any mechanism of epoxidation must accord with these data, their exact significance is probably not yet clear, see the references.

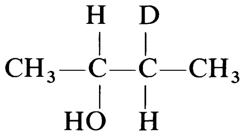
2. *Formation of Double Bonds*

There are few examples in this category, but an interesting one concerns the dehydration of secondary alcohols [92]. The dehydration on alumina and hydroxyapatite at 473 K of the two isomers of 3-deutero-2-butanol:

A



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ CH_3 & - & C & - & C & - & CH_3 \\ & & | & & | & & \\ & & HO & & D & & \end{array}$$



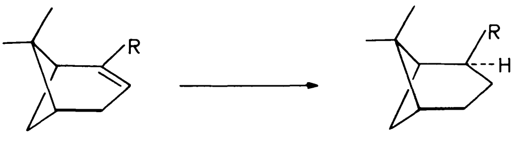
$$\begin{array}{ccccccc} & & H & & D & & \\ & & | & & | & & \\ CH_3 & - & C & - & C & - & CH_3 \\ & & | & & | & & \\ & & HO & & H & & \end{array}$$

B

was investigated. *Cis*-2-butene produced by *cis* elimination of H_2O from **A** would be devoid of deuterium whereas the *trans*-2-butene would contain an atom of deuterium. The reverse would be true of **B**. It was found that *trans*-elimination dominated over *cis* by 4 to 1 on alumina, but *cis*-elimination dominated on hydroxy apatite. These results are important to the mechanism of dehydrations on these materials and they probably result from the detailed geometry of acid and basic sites on the surface.

C. Steric Interactions Between Adsorbate and Surface

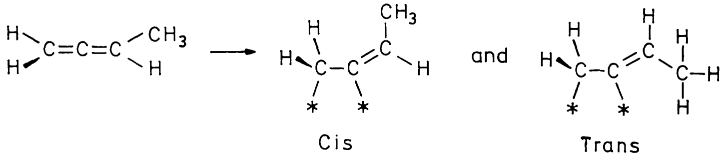
There are many experimental indications of the reality of interactions between an adsorbate and the surface and of steric interaction in transition complexes leading to adsorption. Two rather extreme cases are provided below. The first involves the hydrogenation of derivatives of α-pinene on platinum catalysts which proceeds with rather high stereoselectivity as shown below:



The bulk of the gem dimethyl groups causes the molecule to approach the surface of the catalyst with the gem dimethyl group away from the catalyst surface even though this leads to the formation of the thermodynamically less stable product [86, p. 133].

In those cases in which hydrogenation can form two stereiosomers, one can usually predict which stereoisomer will predominate with platinum catalysts by placing the olefin on the catalyst with the face which produces the least steric hindrance toward the catalyst surface.

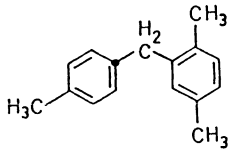
A particularly clear case of adsorbate-surface hindrance appears in the hydrogenation of methylallene on Pd/Al_2O_3 [86, p. 75]. In methylallene, the plane of the CH_2 group is perpendicular to that of the $CH(CH_3)$ group. Thus, there are two forms of the allene adsorbed at the terminal double bond:



The hydrogenation of methylallene leads initially to three products, 1-butene derived from a surface species adsorbed at the central double bond, *cis*-2-butene derived from the central species above and *trans*-2-butene derived from the form at the right. Although the *trans*/*cis* ratio in the gas phase at equilibrium is 3, the 2-butene formed by hydrogenation is very heavily *cis*. Except perhaps for adsorption at edge atoms, in the allene adsorbed in the *trans* form, there is at least one hydrogen atom of the methyl group which would be closer to the palladium surface than the two carbon atoms bonded to the surface. Since there is clearly much less adsorbate-surface strain in the *cis* than in the *trans* form, predominant formation of *cis*-2-butene is to be expected.

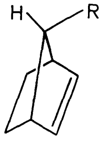
If one replaces the $—CH_3$ group in methylallene by $—CH_2OH$, one increases the bulk of this group, but one increases the yield of the *trans* product in hydrogenations on $Pd/BaSO_4$ [86, p. 78]. This has been interpreted as indicating that the haptophilic (attractive) interaction between OH and the metal surface nearly outweighs the effects of steric hindrance. The *cis*/*trans* ratio in such cases offers the possibility of evaluating interactions between surfaces and adsorbates which are not ordinarily considered in heterogeneous catalysis.

Some zeolites have small pores, for example, A-zeolite, mordenite and ZSM-5, which are in the range of 0.4–0.7 nm. Not surprizingly, the small pore size results in some clear effects on chemical reactions called shape selectivity [93, 94]. Some usual reactant molecules may be too large to enter the pores of the zeolite and some usual products may be unable to diffuse out. From a mechanistic point of view, the most interesting feature is steric constraint on transition states in which reactants and products are not restricted, but some reactions of the reactants are inhibited because the needed transition state is too large for the pores. For example, the acid catalyzed isomerization of xylenes (1,2-$\rightleftharpoons$1,3-$\rightleftharpoons$1,4-) is accompanied by disproportionation to form toluene and trimethylbenzenes. The transalkylation has usually been interpreted as involving a diphenylmethane intermediate:



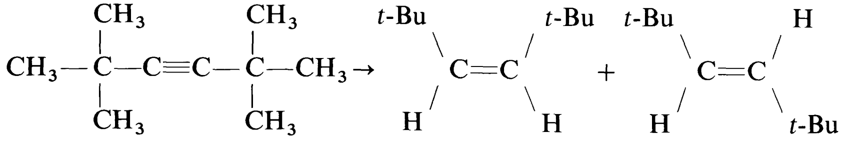
Protonation of this intermediate at the position marked with the black disk would result in final formation of toluene and 1,2,4-trimethylbenzene. The pore diameter of ZSM-5 is about 0.55 nm. The zeolite readily catalyzes the isomerization of xylenes, but it does not give disproportionation. The diphenylmethane would be too large to fit into the pores whereas the intermediate for isomerization contains but one benzene ring. Thus, the absence of diproportionation in ZSM-5 accords with the usual mechanism for disproportionation.

Let us suppose that R∗ is an intermediate in some reaction. Until this section, discussion has almost entirely concerned the structure of R. But one would like to know as much as possible about the nature of the catalytic site∗ and its interaction with R. One aspect of adsorbate-surface strain provides data relating to the geometry of the catalytic site and the region surrounding it. For example, at the beginning of this section, we discussed the question of the ratio of the addition of hydrogen to the two sides of the plane of the double bond in certain cyclic molecules. A suitably rigid molecule with suitable substituents would form a kind of template which one could test for fit against various surface morphologies. It would be useful systematically to measure the ratio for a catalyst set with wide variation in percentage exposed. One would learn how some aspect of surface roughness varies with particle size for that catalyst set. Steroids tend to be rigid and might provide suitable test molecules. A structure could be designed which would block the approach of a double bond to the surface of a large, flat plane of (100) or (111) in FCC but not to edges. Alternatively, some compound like the following bicycloheptene might be suitable:



Ordinarily, a bicycloheptene adds hydrogen to the face of the double bond towards the methylene bridge, the *exo* face, although the reason for this is not entirely clear [95]. Varying the size of R would vary the hindrance to addition to the *exo* side of the double bond and provide a template to test an aspect of the surface morphology of catalysts.

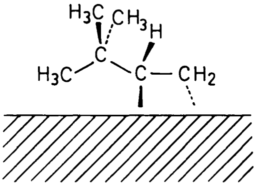
One related system has been examined, the hydrogenation of di-*t*-butylacetylene on Pd:



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3} \rightarrow \begin{matrix} t\text{-Bu} & & t\text{-Bu} \\ & \mathrm{C{=}C} & \\ \mathrm{H} & & \mathrm{H} \end{matrix} + \begin{matrix} t\text{-Bu} & & \mathrm{H} \\ & \mathrm{C{=}C} & \\ \mathrm{H} & & t\text{-Bu} \end{matrix}$$

The triple bond is surrounded by the bulky *t*-butyl groups which one would think would hold the triple bond away from the surface and prevent its hydrogenation on the densely packed (100) or (111) planes. However, adsorption of the triple bond at edge atoms should be possible. Hydrogenation was investigated on a series of Pt/SiO_2 catalysts with average percentages exposed from 6 to 60% [90]. One expects to find a much higher proportion of edge atoms on the smaller particles of platinum. Nevertheless, the turnover frequency of hydrogenation on a series of Pt/SiO_2 catalysts was nearly independent of percentage exposed. There was, however, a very real steric effect and an effect of particle size. In competitive hydrogenation between the acetylene and cyclopentene, the cyclopentene won, whereas normally an acetylene heavily dominates in competition with an olefin. Further, the rate ratio, acetylene/olefin, in competitive hydrogenation, although always below unity, was much larger on the Pt particles of smaller size. Thus, the rate of hydrogenation is structure insensitive, but the selectivity in competitive hydrogenation is very structure sensitive. Further, if as usually claimed, the largest particle had considerable exposure of (111) and (100) faces, then the rate of hydrogenation on these faces must be as large as at the edge atoms of the small crystallites.

A similar phenomenon appears in isotopic exchange between deuterium and neohexane of Pt/SiO_2 and Pd/SiO_2. One would expect the *t*-butyl group to inhibit multiple exchange in the ethyl side chain since this would require alternation of 4-monoadsorbed 2,2-dimethylbutane and 3-monoadsorbed 2,2-dimethylbutane with the 3,4-diadsorbed species which we might call α,β-diadsorbed *t*-butylethane:



Here, the C-atoms bonded to the surface are taken to be sp^3 hybrids, but a similar geometry results if the binding is taken to be that of a π-complex. Let us assume that the surface is a perfect (111) or (100) plane of FCC. It is clear that, no matter how the *t*-butyl group is rotated, there must be one or two non-bonded hydrogen atoms of one of the methyl groups which are closer to the surface than the bonded carbon atoms. On the common idea that the metal crystallites of supported metal catalysts are bonded by perfect crystal planes [96], the ratio multiple/single exchange in the ethyl group should be much larger on small crystallites than on large ones, because the diadsorbed species could form with little or no steric hindrance at edge atoms. The problem is similar to that in the hydrogenation of di-*t*-butylacetylene.

Isotopic exchange between neohexane and deuterium has been investigated on a set of Pt/SiO_2 and a set of Pd/SiO_2 catalysts [53]. Exchange into methylene group is much slower than in the case of the unhindered methylene groups of cyclopentane. However, the expected dependence of multiple exchange upon the particle size of the metal was not found. Indeed, the isotopic distribution in the ethyl group varied little with percentage exposed.

The most likely explanation for the failure to find the expected effect of particle size in the case of di-*t*-butylacetylene and neohexane is that the bounding planes of metal crystallites are defective rather than perfect and that they provide many more sites for formation of the critical adsorbed intermediates than one would expect if the bounding planes were smooth. This view is tentative because the question is one which has excited little interest and few data are available to test the matter.

13. Catalyst Alteration

A wide variety of variations in the composition, preparation, pretreatment, etc. of particular catalysts has been made and studied for mechanistic purposes. Two quite different examples follow.

How many surface atoms constitute a catalytic site or assembly? One approach to the matter is the following. Consider a catalyst consisting of a solid solution of two components, an active component and an inactive one. Several such catalysts are prepared with different ratios of the active to the inactive component. One measures the rate of a reaction per m^2 of catalyst area and plots this vs. the concentration of active ingredient. As an example, take the active ingredient to be platinum and the inactive ingredient to be gold. If the rate is linear in the concentration of platinum, one would conclude that the effective catalytic site is just one atom of Pt, if the rate is proportional to the square of the concentration, the assembly size is two, etc.

In one set of Pt-Au alloys in the form of low area powders [97], the concentration of platinum was 14% or less. The rate of dehydrogenation of propane in the presence of a large excess of hydrogen was measured at 633 K. Conversions were kept very low. The areal rate (rate per unit area) was proportional to the first power of the bulk concentration of Pt, whereas, in the isomerization at 663 K of hexane to 2-methylpentane, the rate was proportional to the cube of the concentration.

The authors concluded that the dehydrogenation proceeded on a single atom of Pt as, for example, in hydrogenation of olefins by mononuclear organometallic complexes. However, in the isomerization of hexane, the assembly size was near three.

A number of problems with this procedure are discussed in Ref. [97]. The areal concentrations of the active ingredient must be known or it must be shown to be proportional to the bulk concentration. The distribution of the atoms of the active ingredient must be random. Were the active ingredient to form islands on the surface, the rate would be proportional to concentration no matter what was the assembly size. The rate of isomerization being proportional to the cube of the concentration argues against islands in the present case. The activity of an assembly needs to be independent of bulk concentrations. This is more likely when the bulk concentration of the active ingredient is low.

The original reforming catalyst was platinum on acidic alumina, that is, on alumina containing chloride. It was proposed that reforming reactions required two kinds of sites, acidic and metallic. A classic case of catalyst alteration was concerned with the mechanism of reactions on such dual functional catalysts [98]. Platinum on silica-alumina was an active catalyst for the conversion of heptane to isoheptanes in the presence of hydrogen at 743 K, $P_{H_2} = 20$ atm, but Pt/SiO_2 and SiO_2-Al_2O_3 were inactive. When the last two catalysts were ground, mixed, and pelleted, the resulting material was an active catalyst for the isomerization. This result was consistent with the proposal that the platinum catalyzed the reaction:

$$n\text{-heptane} \rightleftharpoons n\text{-heptene} + H_2$$

The heptene then migrated to acidic sites where it reacted with $[H^+]$ to form a secondary heptyl carbenium ion which underwent skeletal isomerization. The branched chain carbenium ion lost a proton and the resulting isoheptene migrated to platinum where it underwent hydrogenation to form isoheptanes. Clearly migration of olefin could occur via the gas phase. However, the equilibrium pressure of olefin was very low and one needed to worry about diffusional resistance. In fact, as one would expect, the rate of isomerization increased as the particle size of the two materials which were pelleted to make the final catalyst decreased. When 10 μm particles were employed, the rate on the mixed catalyst was very nearly equal to that of the Pt/SiO_2-Al_2O_3 catalyst.

14. Selective Feeding and Selective Scavenging

Suppose that Q is suspected to be an intermediate for a particular reaction. One can imagine two related procedures to test such an hypothesis, in both of which one adds some compound to the reaction mixture. In selective feeding, one adds compound M which one believes will adsorb to form the suspected intermediate and one determines whether the added compound is indeed converted to the expected product. In scavenging, one adds compound X which should react with the intermediate to form compound Y which is not a normal product. Thus, at least to some degree, the catalytic reaction is diverted from the formation of its normal products to the formation of compound V. Of course, experiments might well be found to combine features of both selective feeding and selective scavenging.

A. Selective Feeding

One needs to be sure that compound M adsorbs rapidly to form the suspected intermediate under reaction conditions. In the pioneering work of Emmett, feeding was employed in the study of reactions with complicated pathways leading to multiple products such as catalytic cracking and the Fischer–Tropsch reaction. Feeding still appears to be particularly appropriate for such reactions. It will often be useful to make compound M in some radioactive form so as to facilitate determining exactly where it is found in the products.

An example from the hydrogenation of carbon monoxide involves passage of $CO + H_2$ over three different catalysts, Ru/SiO_2 (a catalyst for the synthesis of higher hydrocarbons), Rh/SiO_2 (a catalyst with an unusually large selectivity for C_2 oxygenates) and Pd/SiO_2 (a catalyst with high selectivity for methanol). Small amounts of ethylene or of ethanol were added to $CO + H_2$ passing over each of the catalyst at 573 K, 10 atm [99].

In the absence of ethylene and ethanol, Ru/SiO_2 gave 77% CH_4 and 2.4% oxygenates. Added ethanol reacted to distribute itself in almost the same proportions throughout the products except for an extra 1% appearing as acetaldehyde. Added ethylene went predominantly to ethane (97%), but 3% reacted to form higher hydrocarbons and oxygenates.

Rh/SiO_2 gave 41% CH_4, 8.2% higher hydrocarbons, 1.4% MeOH, and 49% higher oxygenates. Added ethanol reacted selectively to give oxygenates and, in particular, substantial ethyl acetate, the concentration of which was low in the absence of added ethanol. Added ethylene went to oxygenates (23%) and ethane (76%).

Pd/SiO_2 gave methanol with high selectivity, 97%. Added ethanol went to acetaldehyde (88%), hydrocarbons (8%), and oxygenates (4%). Added ethylene went almost entirely (99.5%) to ethane.

These experiments provide useful information about relative rates of various reactions on these catalysts: that insertion of CO appears to be favored on Rh/SiO_2, that insertion of CH_X is favored on Ru/SiO_2, and that insertion of neither is favored on Pd/SiO_2.

Let us suppose that a particular intermediate is suspected to be involved in a reaction. In an extreme case, one might form the intermediate on the surface and then compare its rate of reaction with the rate of the catalytic reaction in question. For example, decomposition of ethanol on Ni (111) forms CH_3* which is hydrogenated to produce CH_4 about 10^6 times more rapidly than CH_4 is formed from $CO + H_2$ [100]. This suggests that the hydrogenation of CH_3 comes after a step which gives the rate of the formation of methane from H_2 and CO.

B. Selective Scavenging

This technique has been used more often in homogeneous than in heterogeneous reactions. Isotopically labeled scavengers are not usually needed since the product of reaction between a scavenger and an intermediate is a compound not formed in the absence of the scavenger. Such compounds should be detectable by normal analytical procedures.

An interesting example of scavenging occurred during the addition of cyclohexene or *cis*-2-butene to $CO + H_2$ passing over a Ru/SiO_2 catalyst [101]. The temperature was about 500 K, the pressure, 1 atm, and the mole fraction of the added olefin was $\sim 1\%$. The great majority of the cyclohexene which reacted appeared as cyclohexane, but about 1/300 as much norcarane was also formed. This substituted cyclopropane could result from the addition of methylene to the double bond of cyclohexene. *Cis*-2-butene reacted similarly to give mostly butane but also small amounts of *cis*- and *trans*-dimethylcyclopropane. Thus, these results accord with the view that hydrocarbon chains on this catalyst grow by insertion of methylene.

However, the fraction of the added olefin which reacted to form cyclopropanes was so small that one might worry that the formation of cyclopropanes occurred on minority sites outside of the main catalytic cycle.

In a study of the synthesis of methanol on supported palladium, after a period of methanol synthesis, various compounds were added to test for intermediates on the catalyst surface [102]. In favorable circumstances, it was possible to detect 10^{11} molecules cm^{-2}. The following reactions were observed:

$*CHO + CH_3I(g) \rightarrow CH_3CHO(g) + [*I]$
$*OCH_3 + H_2O(g) \rightarrow CH_3OH(g) + [*OH]$
$*O_2CH + (CH_3)_2SO_4 \rightarrow CH_3O_2CH$ (methyl formate)

There was a good correlation between the surface concentrations of formyl and methoxy species on Pd/MgO, SiO_2 and the rate of formation of methanol, but only traces of formate were detected.

In Table 1, Selective Feeding and Selective Scavenging are followed by a question mark to indicate that the information provided by these experiments may not be straightforwardly direct. Suppose that there are two channels leading to a particular product. One channel may be fast, the other might have a bottleneck such that very little product is formed via that channel. One adds compound M, finds that it is converted to the usual product, and concludes that the reaction involves the intermediate which M should form upon adsorption. However, M might be entering the slow channel after the bottleneck and the usual fast channel might not involve the suspected intermediate at all. The additional information provided in the work just discussed, that the activity for formation of methanol was proportional to the surface concentrations of methoxy and formyl, indicates that the added compounds entered the channel normally leading to methanol. Similarly, in selective scavenging, the added compound might react with a surface species on the reactant side of a bottleneck. Again, one could reach an incorrect conclusion.

Comparison of the rate of formation of methyl isopropyl amine from $CO + H_2$ + isopropyl amine and from $CH_3OH + H_2$ + isopropyl amine on Cu/ZnO under methanol synthesis conditions established that methyl isopropyl amine was formed from a precussor of CH_3OH and not from poduct methanol [103]. Further, hydrogenation of the formamide, $HCONEt_2$, gave $MeNEt_2$ as a primary product but at a rate too slow to permit the formamide to be an intermediate in the reaction between CO, H_2, and amine. These observations are compatible with the presence on the catalyst of some type of an aldehydic intermediate which is scavenged by amines.

15. Poisoning

As in scavenging and feeding, so in poisoning one adds some foreign compound to the catalyst-reactant system. Instead of reacting to form volatile compounds as in scavenging and feeding, the added compound (poison) adsorbs on the catalytically active sites and blocks reaction. The poisoning effect is detected by measurement of the rate of a catalytic reaction in the absence and then in the presence of a poison. In suitable cases, poisoning studies provide two kinds of information about the catalytically active sites, an upper limit to their number and information about their chemical nature.

A number of problems appear in poisoning studies. These are critically discussed in Knözinger's review on the poisoning of catalytic reactions on oxides [104]. One will usually want a poison which is adsorbed irreversibly at the temperature of the catalytic reaction in question. In some cases one may want to saturate the catalyst with poison. This usually causes no trouble since one may inject pulses of poison into the reactants flowing over the catalyst until the rate of the reaction is zero and pulses of poison pass through the catalyst without loss. However, and particularly with oxides, the catalyst surface may present several different kinds of sites two or more of which will adsorb the poison and yet only one of which is a catalytic site for the reaction in question. In this case one will wish to add the poison gradually and uniformly over the surface of the catalyst. However, if the poison is adsorbed strongly and irreversibly, it is vey likely to be adsorbed rapidly. Thus, if one introduces a series of small pulses of poison at the entrance to a catalyst bed in a flow reactor, the poison will adsorb nonselectively with each pulse being adsorbed in a later layer of the catalyst bed. A plot of rate against amount of catalyst will then resemble curve **a** in Figure 10. On the other hand, if the poison could be adsorbed successively on the strongest to the weakest sites, the curve would resemble **b** provided that those sites which adsorb the poison most strongly are the catalytic sites and those sites which adsorb more weakly are catalytically inactive. The reverse, of course, is also possible. The intercept of curve **b** with the x-axis gives an upper limit to the number of sites for the reaction which can be expressed as moles of catalytic sites per m^2 of catalyst surface or nm^2 per site, etc. These values will represent an upper limit to the number of catalytic sites since it will not be known that the poison adsorbed exclusively on catalytic sites. There is unfortunately no general procedure for starting with zero coverage by poison and increasing the coverage gradually. One can, however, measure the rate of the catalytic reaction at a temperature T_1, saturate the catalyst with poison at some temperature T_2, measure the rate of reaction at T_1, evacuate or flush with an inert gas at $T > T_1$, measure the amount of poison desorbed, and then remeasure the rate of the catalytic reaction at T_1. This sequence is then repeated with T_2 at successively higher temperatures. One can calculate the amount of the poison adsorbed for each temperature of desorption and construct a graph like Figure 10, curve **b**.

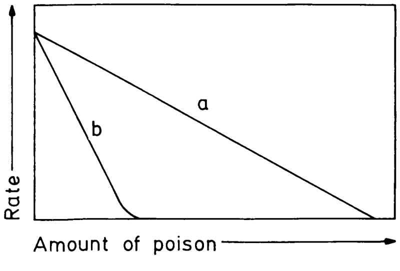


Figure 10. The rate of a reaction as a function of the amount of poison added. In **a**, the poisoning is nonselective, in **b**, selective

What is a poison for one catalyst may not be for another. Thus, water is not a strong poison for platinum (one can hydrogenate maleic acid in aqueous solution), but water is a strong poison for the synthesis of ammonia on iron catalysts (water oxidizes the surface of iron). Water is also a strong poison for many reactions on oxides (acting as Lewis base, H_2O adsorbs on *cus* cations like Cr^{3+} acting as a Lewis acid). The relative degree of poisoning exerted for a particular reaction on a particular catalyst provides information about the chemical nature of the catalytic sites. Thus, the relative degree of poisoning by the soft base, H_2S, vs. that by the hard base, H_2O, should provide qualitative information about whether the catalytic site is a hard acid or a soft acid provided adsorption occurs as $M^{n+}\ OH_2$ and $M^{n+}SH_2$. Application of the theory of soft and strong acids and bases is reviewed in Ref. [104].

A particular application of considerable utility has been the detection of the contribution of acidic sites to catalytic reactions by using bases as probes, a procedure pioneered by H. Pines. Of course, the mere observation that rate is reduced by addition of a volatile base does not reveal whether the acid site is a Brønsted acid or a Lewis acid. If one uses pyridine as the basic probe, infrared examination of the catalyst can distinguish between pyridine adsorbed at a Lewis acid site and one adsorbed at a proton acid site [28]. Thus, if catalytic activity paralleled the areal concentration of Brønsted sites, one could conclude that the catalytically active sites were Brønsted acids, but one could not conclude that all of the measured Brøsites were catalytically active.

Alumina has been subjected to a particularly large number of poisoning studies. They have been useful in outlining some of the factors involved in alumina acting as a catalyst. However, there is a great deal of divergence in the literature as to the catalytic activity of alumina, for example, its hydrogenative capacity. Some of this probably results from variation in structure (γ-, δ-, θ-, etc.), in the relative proportions of 4- and 6- coordinate Al^{3+} exposed at the surface, in the degree of dehydroxylation as fixed by the temperature of pretreatment (this leads to various areal concentrations of Al^{3+} (*cus*) and O^{2-} (*cus*)), in content in such impurities as Fe, Si, Na^+, and $SO_4{}^{2-}$, and in the texture of the alumina. Thus, the precise nature and origin of the catalytic activity of alumina is as yet by no means clear. A few examples of poisoning studies on alumina follow.

As judged by temperature-programmed desorption [105], NH_3 adsorbed in two forms on alumina. Adsorption at 298 K led to a rather weakly adsorbed form (perhaps $Al^{3+}NH_3$), whereas adsorption at 523 K was strong and it was not the result of the mere Lewis basicity of ammonia. Judging from infrared evidence, it involved the adsorption of NH_3 as $NH_2{}^-$ and H^+ on Lewis acid–Lewis base pair sites, probably:

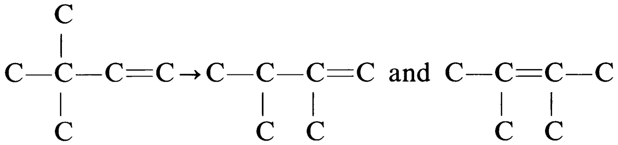
$$NH_3 + Al^{3+}(cus) + O^{2-}(cus) \rightarrow Al^{3+}NH_2{}^- + OH^-$$

The isomerization of 1-butene at 293 K was blocked by the strongly adsorbed ammonia, but only slightly inhibited by the weakly adsorbed ammonia.

Carbon dioxide is a particularly interesting poison for some reactions on alumina: isotopic exchange between σ-OH (surface OH) and CD_4, between CD_4 and CH_4, between alkenes and D_2 at 298 K, and between H_2 and D_2 at 195 K [106, 104]. Carbon dioxide is a hard Lewis acid and should be particularly inclined to form carbonates by reaction with O^{2-}(*cus*) or bicarbonates with OH^-(*cus*). One of the most interesting results of the studies of poisoning by CO_2 has been the discovery that only a very small fraction of the alumina surface is catalytically active for the isotopic exchange reactions, $\sim 5 \times 10^{12}$ sites per cm^2 or 1 site in 20 nm^2. This value was determined by measuring the rate of a reaction at 298 K, saturating the catalyst with CO_2 at 298 K, and then progressively removing measured quantities of poison by elevating the temperature. It was necessary to evacuate at 300°C before the rate of the isotopic exchange reactions again became significant at 25°C.

The adsorption of CO_2 on alumina is complicated. In an infrared spectroscopic study of the effect of the temperature of dehydroxylation upon the adsorption of carbon dioxide, 5 forms of adsorbed carbonate and bicarbonate were observed at room temperature [107]. Most of these were removed by evacuation at temperatures lower than 523 K. It appeared probable that the adsorbed CO_2 which blocked the isotopic exchange reactions was a bicarbonate with an IR band at 3770 cm^{-1} that was formed by the interaction of CO_2 with σ-OH.

There must also be strong acid sites on some aluminas. Thus, skeletal isomerization of 3,3-dimethyl-1-butene has been observed at 353 K [108].



$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}C{=}C \rightarrow C{-}\underset{\underset{C}{|}}{C}{-}\underset{\underset{C}{|}}{C}{=}C \text{ and } C{-}\underset{\underset{C}{|}}{C}{=}\underset{\underset{C}{|}}{C}{-}C}$$

In addition, the hydrogen atoms attached to the double bond exchanged with D_2 or C_2D_4 at 352 K. This reaction was poisoned by CO_2 but the skeletal isomerization was not. Double bond migration in 1-butene was not poisoned by CO_2, but it was poisoned by H_2S although rather a lot was required, one H_2S per 2 nm^2. Double bond migration was believed to proceed via an allylic intermediate. As shown by temperature-programmed desorption, H_2S adsorbs at 298 K in two forms, one desorbing at about 393 K and the other at about 548 K [109]. Only the latter poisons the isomerization of 1-butene. Infrared examination of the OH stretch region suggests that the higher temperature form results from the heterolytic dissociative adsorption of H_2S at Al^{3+}(*cus*) O^{2-}(*cus*) pair sites. Thus, the poisoning activity of NH_3 just discussed (Ref. [105]) and that of H_2S are similar. This might seem surprizing on the theory of soft and hard acids and bases [104]. However, the heterolytic bond dissociation energies of NH_3 and H_2S (and H_2O when it is adsorbed) will also be involved as well as the strength of Lewis acid–Lewis base combinations.

Thus, poisoning studies can provide useful information about the areal concentration of a catalytic site even though the resulting datum is only an upper limit. Information which can be used to test hypotheses about the chemical nature of the catalytic sites can also obtained from poisoning studies, but interpretation of such results without other data is apt to be difficult. Further, although poisoning studies depend upon measuring rates of catalytic reactions, they are only semidirect since further information is needed to ensure that the poison had adsorbed exclusively on catalytic sites.

16. Indirect Mechanistic Probes

The detector in the use of the mechanistic probes so far considered has been the catalytic reaction itself. The indirect probes (see Table 1) primarily involve studies of chemisorption either by chemical or by spectroscopic means. These are called "indirect" because they examine all sites for adsorption rather than just the catalytic sites and because the application of the probe does not itself involve catalysis. This would occasion no problem if the sites for adsorption and the catalytic sites were uniform and identical, but this situation is probably not very common. Reference to this matter has appeared near the ends of Sects. 6 and 9.C. Even on the simplest supported metal catalyst such as Pt/SiO_2, the particles of Pt can expose atoms in different crystal faces, edge atoms, and vertex atoms. The surfaces of oxides may be even more complex as illustrated by alumina in the preceding section.

Thus, in general, two or more sites for adsorption will respond to the indirect probes and one must try to ascertain which site or sites are also catalytic sites. Ordinarily one tries to correlate the results of the indirect probe with catalytic rate for a series of related catalysts and thus to discover which adsorbed species correlate with rate. For example, the reaction, $A \rightarrow$ products, acquires a significant rate at 373 K on alumina. An infrared absorption study of the adsorption of A on alumina reveals the apparent existence of three different chemisorbed forms of A. One compares the rates of the reaction on a variety of aluminas (different temperatures of dehydroxylation, different crystallographic forms, etc.) with the IR spectra of A on the same aluminas and attempts to find which of the three chemisorbed forms corresponds to the catalytically active one. Unfortunately, it might eventually turn out that the true catalytically active form was invisible in IR because its adsorption fell in a region of wavelength where alumina was strongly adsorbing. However, one must try, *per aspera ad astra.*

Another approach is to apply one of the spectroscopic probes to a catalyst while a catalytic reaction is in progress. Observation of the IR spectrum during a transient kinetic experiment can be particularly fruitful. An example appears in Sect. 9.F. Ref. [37]. If a reaction should happen to proceed by a Langmuir–Hinshelwood mechanism, then there is a reasonable chance that the areal concentrations of the adsorbed intermediate(s) in preequilibrium will be large enough to detect. However, it must be recognized a priori that some surface intermediates may be present at too small an areal concentration to be visible using a particular spectroscopic technique or, indeed, using any spectroscopic technique. As one example, consider a reaction in which the rate of a reaction is the rate of adsorption of A and that A, once adsorbed, reacts rapidly. One could hardly hope to detect adsorbed A by spectroscopic techniques but one might by selective scavenging. Nor could one expect to see $*NH$ in the synthesis of ammonia on iron catalysts if $*N$ is indeed the *mari* (Sect. 9.E).

In some cases, observation during a catalytic reaction may prove essential. For example, study of the adsorption of olefins on the surfaces of clean metals may be of considerable interest to the area of chemisorption, but it may not prove very informative with respect to the mechanism of catalytic hydrogenation. Extensive dissociation of C—H bonds may occur in the absence of hydrogen but not in the presence of hydrogen. For example, on Pd/SiO_2 [110], during the hydrogenation of ethylene at $H_2/C_2H_4 > 1$, no ethylidyne, $*{\equiv}C{-}CH_3$ was formed, but ethylidyne developed with time when $H_2/C_2H_4 < 1$. Precovering the catalyst with ethylidyne did not affect the rate of reaction. Thus, it was concluded that ethylidyne was not in the catalytic cycle but on an unproductive sideshoot. One worry about this work is that the turnover frequency for the hydrogenation of ethylene, $0.004\,s^{-1}$ at 292 K, appears to be unduly low.

Most results with direct probes provide information about the identity of intermediates and perhaps about the structure of the adsorbate, but in most cases they give little information about the identity and structure of the surface site nor about the nature of the adsorbate-surface bond. Subject to a solution of the problems given above, in appropriate cases spectroscopic probes may provide information relating to some aspect or aspects of the adsorption complex of one or more intermediates including information about the nature of the site and its binding to the adsorbate. The use of indirect probes is thus essential to progress in mechanism. However, problems may be difficult. One cannot remove the adsorption complex from the surface, crystallize it, and determine its structure by X-ray diffraction. Thus, despite considerable work, there is as yet no consensus as to whether Pd(0) or Pd^{+1} is the catalytic site for the synthesis of methanol or whether Cr^{+2} or Cr^{+3} is the site for the polymerization of ethylene in the Phillips process.

Techniques and theoretical considerations are important features of the application of most of the indirect probes. It will not be practical to cover indirect probes in the detail which has been employed for direct probes. Furthermore, there are good reviews which cover individual probes. Reference will be made to these for detail. In particular, one book [111] may be referenced which treats the application to catalysis of the following spectroscopies: infrared, diffuse reflectance, Raman, Mössbauer, electron paramagnetic resonance, NMR, and X-ray photoelectron spectroscopy.

Many studies involving the spectroscopic techniques of Table 1 are aimed at catalyst structure rather than at the mechanism of any particular catalytic reaction. In a sense, any elucidation of catalyst structure may contribute to mechanistic studies of any reaction on that catalyst. Also, determination of structure of adsorbed species can be useful to mechanism in general even when such species have not yet been experimentally connected to catalysis. Such structures can suggest possible structures of intermediates which can be considered in attempts to devise mechanisms. However, in what follows we shall take a relatively restricted view and consider only cases in which there is some correlation between studies employing indirect probes and heterogeneous catalysis.

17. Chemisorption by Chemical Techniques

On the basic hypothesis of mechanism that at least one reactant must be chemisorbed, it is clearly necessary to study chemisorption. Such studies were very helpful at the beginning of mechanistic thinking in the 1930s. An example has been given in connection with the mechanism of the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (end of

Sect. 9.D.). The measured rates of adsorption of N_2 and H_2 and the rates of adsorption and desorption of NH_3 measured by isotopic exchange with D_2 were consistent with $N* + 3/2H_2(g) \rightleftharpoons NH_3(g)$ being in preequilibrium and with the *rlp* being the adsorption–desorption of nitrogen. In cases like this, semiquantitative data may suffice to answer the question, is the measured rate of adsorption of a reactant fast enough to accord with some particular mechanism? If the answer is no, one is spared worrying about whether adsorption occurred only on catalytic sites.

What might one like to learn from studies of adsorption? For example, consider the hydrogenation of carbon monoxide on metal M. On a large wish list one might like to know the number of different forms of adsorption of H_2 and CO, the site concentrations for each form, rates of adsorption and desorption, enthalpies of adsorption, and activation energies of adsorption and desorption. One might also like to know the rates and energies as functions of coverage and at temperatures as close as possible to the temperature at which H_2 and CO react. One would also like to know what fraction of the molecules of CO adsorbed in each form are dissociated. This is both a large order and inadequate since no allowance has been made for possible interactions of CO and H_2 during adsorption. Measurement of adsorbed CO during reaction by the transient kinetic techniques of Sect. 9.F, Ref. [38] would probably provide information at least as useful as studies of the adsorption of CO alone.

This section will be divided into several categories, adsorption, desorption, and thermodynamic data. Ref. [112] provides two general references to chemisorption.

A. Adsorption

One experimental problem in chemisorption is the measurement either volumetrically or by use of a vacuum microbalance of the rate of chemisorption as a function of temperature, pressure, catalyst pretreatment, and perhaps of catalyst alteration. Some rates of adsorption are too fast to measure even at 123 K like the adsorption of H_2 on clean Pt. On the other hand, chromia adsorbs H_2 in two activated forms readily observable by measurements of the rates of adsorption at about 323 K and 453 K [113].

For quantitative purposes, the most useful rates of adsorption are those giving the rate vs. amount adsorbed (or θ) at constant pressure. If the temperature dependence of the rate is given by $e^{-E_a/RT}$, measurement of amount adsorbed vs θ at several temperatures permits one to calculate the activation energies $E_a(\theta)$ at various values of θ:

$$\ln(r_2/r_1)_\theta = E_a(1/RT_1 - 1/RT_2)$$

That is, the rates r_2 and r_1 are measured at the two temperatures T_2 and T_1 but at the same value of θ. It is most commonly found that E_a increases with increasing θ. One may wish also to determine the pressure dependence of the rate of adsorption.

Another problem is the measurement of the equilibrium amount adsorbed vs. pressure of adsorptive at constant temperature. The classic method of measurement is volumetric. One introduces successive portions of a gaseous reactant into a closed system and measure the pressure after equilibrium has been attained after each addition. Then knowing the dead space in the system, the pressure and the quantities injected, an isotherm can be constructed of amount adsorbed vs. the pressure of the adsorptive. Unfortunately, there can be troubles. If the adsorption is strong, a problem like that in poisoning arises. The adsorbate may not be uniformly distributed throughout the catalyst but rather may be concentrated near the point of admission of the adsorptive. If adsorption has a significant activation energy, the attainment of equilibrium at lower temperatures may require impracticably long times. For θ vs P properly to be called an isotherm, equilibrium must exist at all coverages and one should obtain the same values of coverage in reducing the pressure as in increasing it. However, in many so-called isotherms, the system was not in equilibrium or in equilibrium only over a certain range of θ. If desorption does not lead to the initial adsorptive, it is difficult or impossible to measure equilibrium adsorption. Such a situation is not extremely rare. As one example, much of the oxygen chemisorbed onto carbons can be removed upon heating and evacuating only as oxides of carbon.

The vacuum microbalance may also be used for measurement of the rate of adsorption and the quantity adsorbed. Its use is convenient, but it does have one disadvantage. Since the sample is suspended in the adsorptive, it is in poor thermal contact with any temperature-controlled object. Thus, dissipation of the heat of adsorption is slow and attainment of equilibrium in adsorption can be slow. Also, sensitivity in the measurement of the adsorption of hydrogen is likely to be inadequate.

Conventional pulse techniques can be used to measure the total amount adsorbed provided adsorption is fast. If adsorption is slow, a pulse containing a known amount of adsorptive can be trapped in the catalyst container, held for any desired period and then released as a pulse for measurement by reestablishing the flow of carrier gas. It is often difficult to decompose measurements of adsorption into amounts adsorbed on sites having different rates or different enthalpies of adsorption. In such cases, it is impossible to compare the adsorptive properties of the various set of sites with the rate or selectivity of one particular reaction. However, this can be accomplished when the difference between the activation energies of adsorption or the enthalpies of adsorption of two adsorption states is sufficiently large. Thus, in a system in which the author has been interested for several years, hydrogen adsorbs on chromia in two activated forms which can be conveniently measured at about 453 K and 323 K [113]. At the higher temperature, the form with the lower activation energy is almost immediately in equilibrium and correction may be made for it in measuring the rate of adsorption into the form with the higher energy of activation. At temperatures below 273 K, a third chemisorbed form appears with still lower enthalpy of adsorption and activation energy. Since chromia rather rapidly catalyzes the hydrogenation of ethylene at 195 K [61], neither of the two higher temperature forms of adsorption can be involved in the hydrogenation. Presumably, then, it is the lowest temperature form which is involved although one cannot exclude the possibility that hydrogen from the gas phase reacts in a concerted process with Cr-alkyl.

A different problem appears in the application of chemisorption studies to hydrogenation on metals. Hydrogen adsorbs rapidly and dissociatively on transition metals and in most cases at about 298 K to $H/M_s = 1$. Further, H is quite mobile on the surface at 298 K. However, ethylene adsorbs strongly on transition metals and it is not clear how much of the data measured in the adsorption of H_2 alone can be carried over to the system H_2 + ethylene. One needs to measure the amount of hydrogen adsorbed during an actual hydrogenation.

Provided that adsorption equilibrium is established rapidly, one can also measure adsorption isotherms by chromatographic techniques [114].

B. Desorption

In desorption, one first saturates a catalyst with some adsorptive at a suitable temperature. One then measures the amount removed by evacuation or by a flow of inert gas like helium as the temperature is raised. This is most often done by temperature-programmed desorption (TPD), sometimes called thermal desorption. In this, a flow of inert carrier like helium is maintained over a fixed bed of catalyst at a suitable low temperature, the adsorptive is introduced and, after saturation, the catalyst is flushed with helium. The temperature is now elevated at some constant rate to some chosen final temperature and the concentration of the desorbed adsorptive in the helium is measured as a function of time and therefore of temperature. A thermal conductivity cell is usually employed as a detector, but use of a mass spectrometer permits one more securely to know what actually desorbs. If there is only one adsorbed form, the concentration of the desorbed adsorptive in the carrier will rise to a maximum at some temperature. In the simplest case, the shape of the peak will depend upon the kinetic order of desorption and the degree of nonuniformity of the energetics of desorption. If there are two different adsorbed forms with sufficiently different rates of desorption, there will be two peaks in the TPD graph and so on. Complicated peaks can be deconvoluted, but as Disraeli is reported to have said, "There are three kinds of liars: liars, damned liars, and deconvoluters." In principle, one can determine the kinetic order of the desorption from the shape of the peak, for example, desorption of $*CO$ should be first order in $[*CO]$, whereas desorption of H_2 from $*H$ should be second order if $H*$ is mobile. On certain assumptions, one can also determine the activation energy of desorption.

As applied to desorption from a filament or from a single crystal face into high vacuum, the procedure is straightforward,. Since any molecule which desorbs has a negligible chance of being readsorbed, the procedure measures a true rate of desorption. Matters may be different for a bed of catalyst granules. The question is what determines the rate of desorption? At one extreme, all molecules which desorb diffuse through the catalyst pores into the helium stream and are carried away. The rate of appearance of adsorptive in the helium is thus the rate of desorption and the system is equivalent to that in high vacuum. At the other extreme, equilibrium between adsorptive and adsorbate is established in the interior of the granules and the rate of appearance of adsorptive in the helium is that at which the adsorptive diffuses into the helium stream. Or, perhaps, the situation is intermediate. This matter is considered in Refs. [115 and 116].

In sum, if due precautions are taken, TPD is a useful technique. In general, the existence of various different adsorbed forms and their amounts are observed more readily than in adsorption studies.

C. Thermodynamic Data

Enthalpies of adsorption have been measured calorimetrically [112, 117] or from adsorption isotherms [112]. Several different heats of adsorption can be defined and measured [112]. That derived from adsorption isotherms is usually the isosteric heat of adsorption. The following is a somewhat artificial derivation, but it should make the nature of *isosteric* clear. Consider the reaction:

$$* + \mathrm{A} \rightleftharpoons *\mathrm{A}$$

that is, reaction of 1 mole of A(g) at P_{A} with 1 mole of sites to form 1 mole of $*$A with $*$ and $*$A both at some fixed value of θ, i.e., the size of the system if very large. (But, of course, one could economize and take a millimole system, transfer a nanomole and multiply the result by 10^9.) To the ideal gas approximation and ignoring the very small effect of P upon condensed phases:

$$\Delta G = \mu_{*\mathrm{A}}(T,\theta) - \mu_{*}(T,\theta) - (\mu_{\mathrm{A}}{}^{\circ}(\mathrm{g})(T) + RT\ln P)$$

$$\Delta H = h_{*\mathrm{A}}(T,\theta) - h_{*}(T,\theta) - h_{\mathrm{A}}{}^{\circ}(\mathrm{g})(T)$$

where h represents the molar enthalpy. At equilibrium, $\Delta G = 0$. Consider $T$and P to change at constant θ so as to maintain equilibrium ($\Delta G = 0$). Since by a fundamental thermodynamic formula equivalent to $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$,

$$\mathrm{d}(G/T) = -(H/T^2)\mathrm{d}T + (V/T)\mathrm{d}P$$

Then:

$$\mathrm{d}(\Delta G(T,P)_\theta/T) = -(\Delta H_\theta/T^2)\mathrm{d}T + (\Delta V/T)\mathrm{d}P = 0$$

Since $\Delta V$is very nearly just minus the volume of one mole of gaseous A:

$$\Delta V = -RT/P$$

$$(\partial \ln P/\partial T)_\theta = -\Delta H_\theta/RT^2$$

and integrating:

$$\ln(P_2/P_1)_\theta = \Delta H_\theta(1/RT_2 - 1/RT_1)$$

The molar enthalpy of adsorption, ΔH_θ, is negative. Thus, the pressure of the adsorptive must increase as the temperature is increased to maintain the coverage constant. One can consider ΔH_θ as equal to the enthalpy change when 1 mole of A at pressure P is adsorbed on an infinite amount of adsorbent at a coverage θ.

Figure 11 shows two isotherms for the adsorption of some adsorptive at two temperatures where $T_1 > T_2$. The two values of pressure, a and b, at a fixed value of

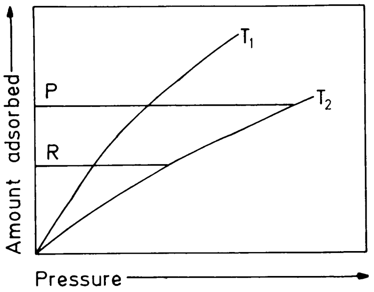


Figure 11. Adsorption isotherms for the adsorption of a gas at two temperatures T_2 and a higher temperature T_1. The adsorption is not ideal. P and R are particular values of θ

θ when substituted into the previous equation give the isosteric ΔH of adsorption. For ideal adsorption, all values of θ will lead to the same value of ΔH, but in non-ideal cases ΔH will decrease as θ increases.

Clearly, the isotherms of Figure 11 must be equilibrium isotherms or ΔG will not be zero and the calculation will be invalid.

It is also possible to measure an enthalpy of adsorption by calorimetric means [112, 117, 118]. The resulting ΔH is some kind of an integral enthalpy of adsorption. In principle, the adsorption need not be reversible. However, a problem much like that in poisoning studies appears in calorimetric studies of chemisorption. One would like to add successive increments of the adsorptive to the adsorbent and to measure each successive ΔH. However, for this to be meaningful each successive addition would always need to add to the sites giving the largest $-\Delta H_{\mathrm{ads}}$ (more correctly, the largest $-\Delta G_{\mathrm{ads}}$). This poses experimental problems. If a molecule is adsorbed very strongly and with a large sticking coefficient, uniform distribution of adsorptive on the surface is difficult, particularly for adsorbent in the form of a porous powder. If one admitted such an adsorptive to one end of a bed of adsorbent, the adsorptive would adsorb on successive layers of adsorbent. Even though $-\Delta H$ might decrease substantially as θ increased, the measured liberation of heat vs θ would appear to be constant and to indicate that ΔH was independent of θ. It is easier to avoid such problems on evaporated metal films than on porous powders, but even here, in extreme cases, the adsorptive will adsorb on the exterior surface first and then in the pores.

It would be very desirable to have more thermodynamic data relating to elementary processes in heterogeneous catalysis. It would be particularly desirable to have data which have clearly been shown to relate to the operative catalytic sites.

18. Infrared Spectroscopy

A. General

Transmission infrared spectroscopy has been by far the most used and the most useful of the spectroscopic techniques applied to heterogeneous catalysis. Refs. [28, 111, and 119] review various aspects of the area.

The study of chemisorption or other surface reactions is an eminently respectable branch of science and one may apply infrared spectroscopy or other spectroscopies to such study with no obligation to attempt to apply the work to heterogeneous catalysis. However, this chapter will consider only those applications of IR spectroscopy which have some clear relation with the mechanisms of particular reactions. This considerably restricts the area to be covered.

Simultaneous rate and IR measurements provide a powerful technique as exemplified by hydrogenation of pulses of CO on Ru/Al_2O_3 which was discussed in Sect. 9.6 [37]. For other examples, see Ref. [119]. Simultaneous measurement is not always easy, but cells have been designed for this purpose, see Refs. [119 and 120]. For problems and accomplishments in simultaneous measurement, see Ref. [28], Sect. 4.E. IR absorption, thermal desorption, and catalytic rate can also be correlated as exemplified by the poisoning of reactions on alumina by ammonia and hydrogen sulfide given in Sect. 15 [103, 107]. This work led to substantial information about the nature of the catalytic sites.

Either Fourier transform or computerized dispersive instruments are capable of excellent work [28, Sect. 3.D]. Unfortunately, at least at present, neither delivers IR absorption spectra in which the physical origin of each absorption band is printed on the chart. This poses problems. For the most part, band assignments have been derived by analogy with organometallic complexes. Thus, the assignment of bands with wave numbers above 2000 cm^{-1} to linearly adsorbed CO and of those below 2000 cm^{-1}, to bridging C0 (see Figure 1) was based upon mononuclear carbonyls vs. dinuclear carbonyls with bridging carbonyl ligands [111, Sect. 2.3]. Similarly the assignment of a band to $*{\equiv}C{-}CH_3$ was based on the IR spectrum of a triangular Os_3 carbonyl complex in which $CH_3{-}C$ is bonded to all three Os atoms.

Inevitably, disagreements arise as to interpretations of bands. Wherever possible, band assignments should be confirmed by the use of isotopic labeling. Suppose that one has a band which is thought to represent an OH stretch. If this assignment is correct, isotopic exchange to form OD would shift the band to lower frequencies by a factor of about $\sqrt{2}$. If substitution of ^{13}CO for ^{12}CO results in no shift in the position of a band, then the band does not represent a CO stretching vibration. The assignment of σ-OH bands, for example on γ-alumina, can be more difficult because molecular analogies are not available.

In favorable cases, IR spectroscopy can provide information about the following items: the identity of M^{n+} (*cus*) sites, the amount, nature and acidity of various σ-OH, structure and binding of chemisorbed species, and the identity of intermediates in catalyzed reactions. Restrictions on the wavelength regions which can be used constitute the major limitation on transmission infrared spectroscopy. Most catalysts involve oxide supports which become opaque at wave numbers smaller than ca. 1100 cm^{-1}. One can observe stretching vibrations involving $C{=}O$ (adsorbed CO, carbonates, and bicarbonates, for example), $C{=}C$ and $C{-}H$, but not $C{-}C$, $C{-}Cl$ nor, in general, can one observe bending vibrations. In suitable cases, such vibrations can be observed by Raman spectroscopy or diffuse reflectance IR spectroscopy [119]. On the other hand, IR has two important advantages, IR photons are of low energy and are nondestructive. Further, IR studies do not require UHV, in fact, one can use high pressures.

B. The Identity of M^{n+} (*cus*) Sites

Adsorbed CO or NO on oxides, for example, on Cr_2O_3, or on supported oxides like Cr_2O_3/Al_2O_3, can provide useful systems for IR absorption spectroscopy. Each CO or NO will ordinarily be bound to just one metal ion. In general, CO binds to M^{n+} (*cus*) ions and since CO is soft and M^{n+} becomes increasingly hard as n increases, the strength of binding will usually decrease as n increases. Further, the frequency of the CO stretch will increase as n increases. Although there is no absolute way to deduce the value of n in M^{n+} from the frequency of the CO stretch, there are empirical correlations which can be used [28, Sect. 4.3.4.]. NO is also a useful adsorptive and it gives frequency shifts which are usually larger than those of CO [28, Sect. 4.4.5]. M^{n+} (*cus*) is coordinatively usaturated, but how much.? Let CO be adsorbed on Cr^{2+}/SiO_2. One sees a CO band, but it will not be clear whether this results from the adsorption of one or two CO at the Cr^{2+} site. Suppose now that one adsorbs a mixture of ^{12}CO and ^{13}CO. If only one CO is adsorbed at each Cr^{2+}, then one will observe two bands in the CO stretch region, one from $Cr^{2+}(^{12}CO)$ and one from $Cr^{2+}(^{13}CO)$. However, if each Cr^{2+} can bind two CO, there will be three species and three bands, $Cr^{2+}(^{12}CO)_2$, $Cr^{2+}(^{12}CO)(^{13}CO)$, and $Cr^{2+}(^{13}CO)_2$, as was indeed observed on some sites for adsorption [121].

C. The Acidity of Sites and σ-OH Sites

Pyridine can adsorb at sufficiently acidic σ-OH to form $\sigma\text{-}O^-$ pyH^+, and at M^{n+}(*cus*) to form M^{n+}:py. IR can distinguish between these two forms of adsorption and thus between strong proton sites and Lewis sites [28].

Study of the IR absorption of oxides at varying levels of dehydroxylation have been rather frequent and useful. There have been a number of studies of isotopic exchange between D_2 and σ-OH on various catalysts and supports. An example appears in Sect. 10.1.1 [51].

The appearance or disappearance of particular σ-OH bands consequent to adsorption on oxides has proved useful particularly for the identification of heterolytic dissociative adsorption at acid-base pair sites [28, Sect. 4.2.]. Adsorption of ammonia on alumina, Sect. 15 [105] exemplifies such adsorption. A classic case was the work of Kokes which showed that the adsorption of H_2 on ZnO formed $Zn^{2+}H^-$ OH^-.

D. Chemisorbed Species

IR has been useful in identifying such species as linear and bridged CO, linear and bent NO [29], various carbonate and bicarbonate species on oxides, and formyl. The recent identification of $*{\equiv}C{-}CH_3$ on metal surfaces is one of the few reasonably clear identifications of adsorbed hydrocarbon species on metals.

E. Catalytic Intermediates

The early success of Kokes and his group in identifying catalytic intermediates in the reactions between olefins and hydrogen on ZnO has not been followed by many similar successes probably, at least in part, because ZnO is unusually transparent in the IR and because it is a rather inactive catalyst which gives one a chance to see the intermediates. This work is still a model in careful assignment of adsorption bands (Ref. [28], Sect. 4.E.; Ref. [111], Sect. 2.7.C).

Sometimes even the most careful comparison of IR spectra and catalytic activity fails to develop correlations. The IR absorption of adsorbed CO was measured on Pd/SiO_2 catalysts of different preparations and a wide range of percentage metal exposed [122]. The rate of methanol synthesis was also measured on these catalysts at 33 atm., 548 K. The addition of a few percent of LiOH to the catalysts increased activities by a factor of up to 6. Different catalysts exhibited different intensities of the various infrared absorption bands, in particular the linear and bridged bands, but no correlation of band intensities with rate could be detected. Despite a careful search, no bands attributable to CO adsorbed on Pd^{+1} could be detected. The authors suggested that the key difference among the various Pd/SiO_2 catalyst might lie in their ability to dissociate H_2 in a particular fashion. It is unlikely that the catalytic sites for the adsorption of CO were present in such small areal concentrations as to have been invisible in IR, but perhaps this possibility cannot be completely excluded. However, the infrared observations were not made in situ under operating conditions and one cannot exclude the possibility that some interaction between adsorbed H_2 and CO may be involved. It might have been more satisfying to have found rate to be linearly correlated with the intensity of some one CO band, but the absence of any such correlation and the absence of any band assignable to Pd^{+1} are important mechanistic criteria.

IR has not been particularly helpful in mechanistic studies of reactions of hydrocarbons on metals. Such reactions are extreme examples of the difficulty in trying to find the spectrum of a catalytic intermediate in the presence of much adsorbate not in the catalytic sequence.

The pulse hydrogenation of CO on Ru/Al_2O_3 (Sect. 9.F [37]) is an example of the application of transient techniques to a combined study of rate and the IR spectrum (see also Ref. [111], Sect. 2.7.D). It appears that transient techniques provide excellent opportunities for such combined studies now that modern fast spectrometers make them practicable [119].

19. Raman Spectroscopy

Like infrared absorption spectroscopy, Raman spectroscopy signals vibrations in molecules or in solids. Whereas in IR, radiation of the frequency of the vibration is absorbed, in Raman, a photon of light, usually one in the visible region of the spectrum, reacts with the vibrating system to gain or lose an amount of energy corresponding to one quantum of the vibration, $h\nu$, or to be scattered without change in energy. Most of the incident radiation is scattered at its incident frequency. One examines the scattered beam spectroscopically, detects the light of lowered frequency and measures the intensity and the wave numbers of the various lines. For details, see Ref. [111]. As in IR, problems are likely to arise about the assignment of lines.

The selection rules of Raman differ from those of IR. In IR only those absorptions occur in which the dipole moment changes during the vibration; in Raman it is the polarizability which must change. Thus, the IR absorption of such substantially ionic oxides as silica, alumina, and magnesia is very strong over substantial ranges of IR wavelengths, whereas Raman scattering of these materials is weak.

Unfortunately, there are problems. The intensity of inelastic Raman scattering is very small. Although the use of laser light has helped matters considerably, the signal is still small. Because the Raman intensity is so low, it it usually necessary to use a rather wide slit opening in the spectrometer. This makes the recorded Raman lines rather wide and hurts resolution. To increase the strength of the signal and get a useful signal to noise ratio, one uses an intense beam of laser light. If the sample absorbs much of this incident radiation it gets very hot and surface damage is likely to occur. One can reduce this problem by rotating the sample and thus greatly reducing the power absorbed by any spot on the sample. However, this induces complications, particularly if one must precisely control the atmosphere surrounding the cell and if one is trying to study the Raman absorption of an operating catalyst.

In IR, the frequencies of vibrations which can be detected for that large group of catalysts which consist of metals or oxides supported on silica, alumina or magnesia is restricted to larger values and many vibrational frequencies which one would like to examine are inaccessible. However, since these supports do not absorb in the visible, there is no restriction on what wavelengths are accessible in Raman. Further, as mentioned above, the supports themselves give very little Raman scattering. Thus, although the situation would appear to be ideal for studying supported catalysts by Raman spectroscopy, few successful studies in this area have been published. The problem is that the supports fluoresce so badly in the exciting beam that the weak Raman lines are completely obscured. At least in some cases, the fluorescence can be reduced by calcining a catalyst at about 773 K. In such cases the origin of the fluorescence is probably carbonaceous material adsorbed on the support.

Thus, although Raman spectroscopy offers some attractive features, practical problems have hindered is application to catalytic studies.

There are, however, reports of the application of Raman spectroscopy to catalytic problems and an example follows of an in situ study of the hydrogenation of CO on an iron catalyst [123]. $Fe_3O_4 + K_2O\,(1\%) + Al_2O_3\,(3\%)$ was reduced with H_2 at 723 K and $H_2 + CO\,(5{:}1)$ was passed over the catalyst for 3 h at 473 K and the Raman spectrum was then accumulated over 4 h. Twelve bands were present in the interval 1556 to 2175 cm^{-1}. It was impossible rigorously to assign most of the bands nor could they be directly correlated with rates or products of the hydrogenation reaction. However, there were arguments for assigning two of the bands to H_a, one cluster of bands to a formate-like species and eight to adsorbed CO. Perhaps the most interesting item was the assignment of some of the lines to CO adsorbed at Fe^{2+} and Fe^{3+} as well as Fe(0). The authors concluded that all of these iron species were present at the surface of the operating catalyst and that oxygen-containing products were made at the oxidized Fe sites.

20. Electron Paramagnetic Resonance (EPR)

Electron spin resonance (ESR) is an equivalent term. Theory, instrumentation and some examples of applications to heterogenous catalysis are given in Refs [111 and 124]. A review of the EPR of *cus* transition-metal ions at surfaces appears in Ref. [125].

Atoms or molecules with one or more unpaired electrons will have a magnetic moment associated with electron spin and, if present, with orbital magnetic moments. These moments interact with an applied external magnetic field to produce various energy levels. Any nuclear magnetic moments will also be involved in the interactions. In an EPR spectrometer the sample region is flooded with microwave power and the externally applied magnetic field is varied. At certain magnetic fields, the $h\nu$ of the microwave frequency will correspond to transitions between two of the various energy levels and resonance absorption of power will be detected. The spectra can be complicated in detail, but, of course, the more complicated, the larger is apt to be the potential information content. Error-free extraction of the information content requires that the extractor have a thorough understanding of the theory of EPR spectra. Thus, to go beyond the mere observation of whether paramagnetic species are present, one needs to study EPR theory carefully. In this, EPR resembles NMR.

EPR is not generally applicable to metallic catalysts. Its contributions, and they have been substantial, have come from studies on oxides.

Among the advantages of EPR are that the radiation employed is low energy and nondestructive, that UHV is not needed; indeed, most gases can be present at rather high pressure without interferring with measurements, and that EPR can provide a substantial amount of structural information about catalytic sites and their interaction with adsorbates.

There are limitations, most obviously that there must be paramagnetism somewhere. However, although one or more unpaired electrons is a necessary condition for the observation of an EPR spectrum, it is not a sufficient condition. At 298 K, an EPR line may be so broad as to be undetectable. One may be able to observe the signal by going to a lower temperature. Operation at 77–600 K is routine, but operations at 4 K or below is possible. However, EPR spectra obtained at such temperatures would provide data under conditions rather far from catalytic ones, although this would not necessarily be fatal.

If two paramagnetic ions are sufficiently close, magnetic coupling between the two ions will broaden the signal even to the point of making it undetectable. Thus, one might observe only the more isolated fraction of a particular paramagnetic species [124, p. 48].

EPR is a bulk technique. In principle, the EPR signal from M^{n+} (*cus*) is different from that of Mn^{n+} in bulk, but, even though EPR can be one of the most sensitive techniques, the signal from a surface ion can be overwhelmed by those from bulk ions. Thus, low area oxides may not be suitable for EPR studies, but high area oxides or supported oxides like Cr_2O_3/Al_2O_3 can be appropriate. On such materials, if the system is not too complicated, one can generally recognize a surface ion by admitting a suitable ligand like water or ammonia to the system. The ligand will adsorb at M^{n+} (*cus*) and change its spectrum.

In favorable cases, the oxidation state of the ion giving the signal, its concentration, and its coordination environment (for example, square planar) can be determined from the EPR spectrum of a high area or a supported oxide containing paramagnetic ions. Of course, the sample may contain some ions of the same oxidation state as the observed paramagnetic ions but which are present in sites of a symmetry such that one cannot detect the signals or which have disappeared because of magnetic coupling. Or, the dominant cation present may not be paramagnetic. All of this can cause trouble. It is human nature to want return from effort and one may be tempted to detect a correlation between the signal one can see and catalytic activity when indeed there is none. Cr^{2+} is EPR inactive and Cr^{3+}, because of its very broad EPR line, is not easy to detect in smaller concentrations. Cr^{5+}, onthe other hand, has a narrow line and even small quantities lead to a good signal. Thus, in earlier days, it was almost inevitable that a correlation would be discovered between the intensity of the Cr^{5+} signal and the activity of the Phillips chromia/silica catalyst for the polymerization of ethylene. In fact, none exists.

Where sites are nonuniform, the effect of the adsorption of such ligands as H_2O or CO on the EPR spectrum in conjunction with studies of adsorption or desorption can help in assigning the nature of different chemisorption forms as determined, for example, by TPD. However, catalysts, not being single crystals, will present the EPR-active species in all orientations. The spectra from such random samples are much more difficult to interpret than those from single crystals. Also, if there are too many different kinds of surface sites involving one M^{n+} ion, signal overlap will be so serious that the effects of adsorption will be hard to detect [124, p. 48].

Rather than the site for adsorption being paramagnetic, the adsorptive or the adsorbate might have an odd electron. There are not so many potential adsorptives with an odd electron, but NO is one and its adsorption has been extensively investigated particularly on nontransition metal oxides like alumina and magnesia.

Finally, EPR has been important is characterizing adsorbed forms of oxygen. Three of these, not counting physisorbed O_2 are paramagnetic, O^-, O^{2-} (the superoxide ion), and O^{3-} (the ozonide ion). The O^- ion is extremely reactive, reacting at 100 K with hydrogen and methane. The surface O^- ion is reviewed in Ref. [126].

Overall, the great bulk of the literature on EPR studies of surfaces is concerned primarily with catalyst structure and chemisorption. Not many studies provide direct links to heterogeneous catalysis. Even so, the results of general EPR studies have provided some notion of what kinds of catalytic sites one can expect and what kinds of structures chemisorbed species are likely to have. Such information is useful even if not conclusive for a particular catalytic reaction.

There are some investigations which directly link EPR data and catalytic data. A straightforward example is related to the isomerization of 1-butene on alumina. In Sect. 15 [107] it was noted that H_2S poisoned the isomerization. Adsorption of H_2S also poisoned the adsorption of NO as measured by EPR. Both [rate (poisoned)/rate (unpoisoned)] and [EPR intensity (poisoned)/EPR intensity (unpoisoned)] fell along the same line when plotted vs. amount of H_2S adsorbed as in Figure 15.1 [111, p. 185]. In this, EPR is used merely as a tool to measure the amount of NO adsorbed. However, the spectra also provided structural information. The observed hyperfine structure which resulted from interaction with the nuclear moment of $^{27}Al^{3+}$ (*cus*) demonstrated that the NO radical was bonded to Al^{3+} (*cus*).

In another example which employs more of the unique features of EPR, C_2H_6 and N_2O were found to react on MoO_3/SiO_2 to form C_2H_4 and CH_3CHO [127]. It was shown by EPR that N_2O reacted with Mo^{5+} to form O^-.

$$\mathrm{Mo(V)} + N_2O \rightarrow \mathrm{Mo(VI)}\,O^- + N^2$$

The O^- centers reacted with ethane at 154 K, but no ethyl radicals became detectable, probably because the ethyl radicals reacted to form ethoxide. Adsorbed ethyl radicals could be made photolytically at 77 K. These species were readily detected by EPR, but they disappeared at about 113 K. The initial reaction at low temperatures is very likely to be:

$$\mathrm{Mo(VI)}\,O^- + HC_2H_5 \rightarrow C_2H_5\cdot + \mathrm{Mo(VI)}\,OH^-$$

Yet it appeared that the same radicals were formed in reaction at 823 K because when a mixture of $C_2H_6 + N_2O + Ar + H_2O$ was passed over the catalyst at 823 K and the products were condensed on a sapphire rod at 12 K, the presence of the ethyl radical was detected by EPR. As usual, these data alone do not permit one to select the exact mechanism but they do eliminate many conceivable mechanisms.

21. Visible-Ultraviolet Spectroscopy

When a beam of light traveling through a phase of lower refractive index hits an object with a higher refractive index, some of the beam is reflected and some penetrates the object. Consider a wafer used in infrared transmission spectroscopy which is made by compressing a powdered catalyst. Transmission of infrared radiation at $1500\,cm^{-1}$ is rather good (unless there is an absorption band at that frequency), but as the frequency of the radiation rises the fraction of the beam which is scattered rises and the fraction transmitted to the detector accordingly falls. In most cases, beyond about $5000\,cm^{-1}$ too little radiation passes through the wafer for transmission spectroscopy to be practicable. Refractive index discontinuities which are small compared to the wavelength of the radiation do not scatter light. Thus, porous glass of a pore diameter of 5 nm appears transparent in the visible, a disk of silica aerogel is transparent, and γ-alumina of a conventional texture can be prepared as a film which is transparent from about $1200\,\mathrm{cm}^{-1}$ well into the ultraviolet [128]. In some cases, one could prepare catalysts on such supports and determine their UV-visible spectra by conventional methods. A catalyst powder can be made transparent by replacing the air with a liquid whose index of refraction is the same as that of the support, for example, heptane with catalysts supported on silica gel. Spectra of high quality can be obtained in such systems but the technique will rarely be convenient.

In general then, if one wishes to study the UV-visible spectrum of a catalyst one must use diffuse reflectance spectroscopy. The article by Kellerman in Ref. [111] is good introduction to the technique.

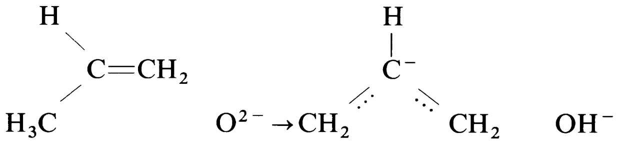
The technique is primarily of interest for the study of transition-metal compounds or complexes supported on oxides. What can one hope to learn here? In terms of ligand field theory, the electronic absorption spectrum results from transitions between two electronic states and the energy difference between these depends upon the ligands involved and upon the symmetry of the coordination environment surrounding the transition-metal ion. There are problems which may impede the extraction of the information about the symmetry and the identity of the ligands at the surface sites. As in other cases, spectroscopy looks at the entire wafer and signals come from bulk as well as from surface. Presumably the catalytic site will involve transition-metal ions, M^{n+} (*cus*). One may hope to locate the signal from these ions by adding a ligand (adsorptive) like H_2O or NH_3. The absorption bands which shift are those which come from the surface sites. However, if the surface/bulk ratio is small, absorption by surface sites may be obscured. Thus, the technique is likely to work best on supported catalysts with a large percentage exposed of the active ingredient. Even here, if there are several sites with different environments, it may be difficult to disentangle the spectrum. Transition-metal ions in zeolites are particularly appropriate systems for study. All ions are on the 'surface' and there are a restricted number of possible environments for an ion.

Both from the point of view of determining diffuse reflectance spectra and from that of interpreting the spectra, one needs a good grasp of the theory involved if one is to get the maximum information from the work and to avoid errors of interpretation.

The results of diffuse reflectance spectroscopy relate directly to catalyst structure. Refs. [125 and 121] are reviews of this subject. The first reference reviews diffuse reflectance spectroscopy and EPR, the second, IR, Raman, and UV-visible spectroscopies. Catalyst structure is an important subject and mechanism must in some way be connected with it. However, the connection is rarely simple and rather few efforts have been made to make this connection in the domain of diffuse reflectance spectroscopy.

Cr^{n+} on Cr_2O_3, Cr_2O_3/SiO_2, and Cr_2O_3/Al_2O_3 are among the systems which have been most extensively investigated by diffuse reflectance spectroscopy. For example, the spectrum of Cr_2O_3/Al_2O_3 shows absorptions assigned to bulk Cr^{3+} in octahedral coordination and Cr^{3+} (*cus*) in square pyramidal coordination. Adsorption of ammonia or methanol shifts the absorption of the latter species to higher frequencies with the formation of surface complexes with distorted octahedral coordination [125]. However, despite the rather large amount of work on this subject, Ref. [121] says that "no complete agreement exists on the coordination state of Cr^{II} and Cr^{III} ions."

A particularly interesting application of UV diffuse reflectance spectroscopy is provided by microcrystalline MgO [121]. Three excitonic bands were observed at energies below the bulk excitonic transitions [129]. One was assigned to O^{2-} (*cus*) in the cube face of a crystal and the other two to O^{2-} (*cus*) in 4 and 3-fold coordination. The latter two are thought to occur at steps, edges, and kinks. The adsorption of propylene on MgO which had been treated in vacuo at 1073 K led to two new bands at 26,000 and 34,000 cm^{-1} while simultaneously the surface excitonic bands were reduced in intensity [130]. The new bands were assigned to the allyl carbanion which was proposed to result from heterolytic dissociative adsorption at basic *cus* anions.



Although correlations between band intensities and catalytic activities were not attempted, the reasonable if necessarily tentative proposal was made that the observed formation of carbanions was correlated with the double bond migration of olefins on MgO and CaO by an apparent allyl carbanion mechanism.

Overall, then, diffuse reflectance spectroscopy has provided data relating to catalyst structure and surface (*cus*) sites and some data relating to chemisorption at these sites, but direct correlation of these results with catalytic activity and selectivity have rarely been made. However, experiments of such a nature would appear to be possible.

22. Nuclear Magnetic Resonance

Reference [131] provides a clear, nonmathematical introduction to solid-state NMR. However, as with EPR, IR absorption spectroscopy, and UV-visible spectroscopy, a good grounding in the theory of NMR is needed if one is to run the best experiments and correctly to extract the most information from the experimental data. Chapter 7 of Ref. [111] can serve as an introduction to this matter and Refs. [132 and 133] provide detailed treatments.

In an applied magnetic field, the nuclear spins of the atoms of a molecule (^{1}H, ^{2}H, ^{13}C, ^{15}N, ^{17}O but not ^{12}C nor ^{16}O which have nuclear spins of zero) interact with the field to form various energy states. In NMR spectroscopy, transitions between states are observed by the resonant absorption of radiofrequency radiation. NMR spectroscopy does not require that the sample be in vacuum, rather, the sample can be exposed to any gas with which it does not interact chemically. Another advantage of NMR is the low energy, nondestructive nature of the radiation. However, this means that the energy levels are separated by very small energies and one item which influences the absorbance in any spectroscopy is the excess of the concentration of molecules in the ground state over that in the excited state. The excess is only of the order of one ppm for NMR states. Thus, the sensitivity of NMR spectroscopy tends to be rather low. However, this problem can be ameliorated by measurement at low temperatures, often that of liquid nitrogen, which augments the concentration excess, and by use of powerful magnets since the signal strength tends to increase with about the 3/2 power of the magnetic field. Fourier transform techniques also help in this regard.

The nuclear magnetic moments of identical adjacent nuclei with nuclear spin interact strongly. When such nuclei are in molecules dissolved in less viscous solvents, the rapid tumbling motion of the molecules averages these *dipolar* interactions to zero and permits weaker and more interesting interactions to become visible. Since such motion cannot occur in solids or in chemisorbed species, the application of conventional NMR techniques to catalysts leads to very broad lines. In consequence, for many years, contributions of NMR to surface studies of possible catalytic interest were restricted to relaxation data relating to the rate of motion of protons in zeolites or on oxide surfaces. In recent years several developments have increased the possible utility of NMR in heterogeneous catalysis, particularly with respect to ^{13}C NMR which involves the nucleus which is likely to be of the greatest interest to mechanism in catalysis. Pulse NMR techniques, spin echo techniques, cross polarization, and proton decoupling have had favorable effects upon signal sharpness or relaxation times. Magic angle spinning (MAS) has been of major importance in solid-state NMR. In this technique, the sample is spun very rapidly about an axis which make an angle α to the applied magnetic field where α is such that $(1 - 3\cos^2\alpha)$ is zero, 54° 44′ (the magic angle). This sharpens lines considerably by reducing dipolar broadening, quadrupole broadening and chemical shift anisotropy. For most purposes, it is necessary to maintain the concentration of paramagnetic ions like the ubiquitous Fe^{3+} ion at very low levels in order to obtain sharp lines.

To date the contributions of NMR to catalysis and, in particular, to mechanism have been minor. However, it would appear likely that 'minor' will change to 'major.' In suitable cases, bond distances and angles can be extracted as well as what is bonded to what. The in situ application of NMR has been very useful in studies of homogeneous catalysis, but in situ studies of heterogeneous catalysis in spun samples is not so easy.

Of the applications of solid-state NMR to catalysis, most have been structural. One of the most important has been the application of ^{29}Si and ^{27}Al NMR to the structure of zeolites, silica, and alumina. The oxide ions of γ-Al_2O_3 are ordered in a face-centered cubic array. Some of the Al^{3+} ions are in octahedral and some in tetrahedral sites. With MAS, ^{27}Al NMR can distinguish between the two since the Al^{3+} chemical shifts are different. However, NMR looks at the entire sample and it has not been possible to see the surface Al^{3+} ions in the presence of Al^{3+} ions in bulk [131].

Nevertheless, the surface *cus* ions can be seen by adsorbing ^{15}N-pyridine on them [135]. ^{15}N-pyridine is used rather than ^{14}N-pyridine because ^{15}N has a nuclear spin of 1/2 whereas the nuclear spin of ^{14}N is larger with consequent added complications. Thus, with MAS ^{15}N NMR and a coverage of one molecule of pyridine per nm^2 on partially dehydroxylated γ-Al_2O_3, one can discern two ^{15}N resonances, one of which corresponds to pyridine bonded to Al^{3+} in octa-hedral coordination and one in tetrahedral. Using MAS, cross polarization, rotationally synchronized spin echo refocusing, and high power proton decoupling (explanations of which are left to the references), it was shown that none of the pyridine nitrogen atoms were bonded to protons, i.e., the σ-OH groups of alumina are too weakly acidic for this. These experiments were run on γ-Al_2O_3 with three degrees of dehydroxylation. The relative proportions of tetrahedral and octahedral species are compatible with equal exposures of (111) and (110) planes. None of these investigations involved correlation of the NMR data with catalytic rates or selectivities, but it should be possible to effect such experiments. It would be important to ascertain which Al^{3+} (*cus*) are involved in the catalytic reactions discussed in Sect. 15. However, the areal site concentrations for some reactions are so small that this may be difficult.

One instance of the few correlations between rate and NMR is provided by experiments on the hydrogenation of CO on Ru/SiO_2 and Ru powder [136]. In this, transient catalytic runs at 443–463 K involved switching between H_2 and D_2 and ^{13}CO and ^{12}CO (Sect. 9.6, [38]). At appropriate times the catalysts were quenched and examined by NMR at 298 K. The NMR techniques involved pulse sequences rather than MAS. To obtain adequate signal to noise ratios, 10,000 to 64,000 pulse sequences were accumulated for each spectrum.

Four forms of carbon could be seen on the surface after a methanation run to steady state, C_α, $C_{\beta 1}$, $C_{\beta 2}$, and unreactive carbon. C_α is the reactive carbon formed from CO which reacts to from hydrocarbon. The C_β's are adsorbed hydrocarbon species with different reactivities and motional properties. They are formed from C_α. If the catalyst is exposed to hydrogen after reaction so as to remove all reactive forms of carbon (C_α and the C_β's) the unreactive carbon which remains exhibits a broadened chemical shift powder pattern resembling turbostratic graphite. $C_{\beta 2}$ may be the origin of the unreactive carbon.

Adsorption and reaction of ethylene and acetylene on supported platinum catalysts in the absence of H_2 (g) provides one of the most advanced applications of pulse techniques to ^{13}C NMR so far reported [137]. The C—C distance in adsorbed ethylene was measured to be 1.49 ± 0.02 Å, near that of a C—C single bond. Spin echo double resonance experiments showed that one-half of the carbon atoms were attached to hydrogen atoms and the other half were not. It was thus concluded that adsorbed ethylene was $*\equiv C—CH_3$ in which the methyl group rotated rapidly. The hydrogen atoms attached to the carbon atoms of adsorbed acetylene were counted by two and three quantum coherence experiments. These data indicated that 75% of the adsorbed acetylene was adsorbed $C{=}CH_2$ and 25%, HC—CH. If C_2H_4/Pt was heated to 690 K and then cooled back to 77 K, at which temperatures measurements were made, atomic carbon immobile at 77 K, was detected. The C atoms became mobile at 350 K with $E_a \approx 30\,kJ\,mol^{-1}$. This is perhaps a surprizingly low temperature. The conclusion that carbon atoms moved from one Pt cluster to another at 430 K is certainly surprizing. No direct correlations were made between NMR and catalytic runs on these catalysts, but it should be possible to carry out such experiments in some cases as in the previous paper [136]. However, except in special cases, NMR observations during actual catalytic runs are likely to be difficult.

It would appear that solid-state NMR offers substantial possibilities for progress in mechanistic studies in heterogeneous catalysis. However, because of the complications of solid-state NMR, such research will probably best be effected by collaborative research involving a catalysis expert and a NMR expert as in the work just cited [137].

23. Mössbauer Spectroscopy

Mössbauer spectroscopy observes transitions from the ground to an excited state of atomic nuclei. The energies of these states are influenced by, among other things, the electronic structure of the atom, its coordination number and symmetry, ligand field effects, and any magnetic fields present at the nucleus (for example, in ferromagnetic materials). These perturbations are very small, but they can be seen and measured because the resolution of Mössbauer spectroscopy is extraordinarily high. For ^{57}Fe the ratio of the line half width to the energy of the excitation is $\sim 10^{-13}$. Chapter 5 in Ref. [111] and Refs. [138 and 139] provide an introduction to Mössbauer spectroscopy and its application to catalysis.

Mössbauer spectroscopy can provide detailed structural information related to the factors mention in the preceding paragraph. Since the γ-rays (14.4 keV in the case of 57Fe) can penetrate gases, UHV is not necessary. Cells with beryllium windows permit operation in controlled atmospheres. In principle, in situ experiments are possible. There are, however, a number of restrictions on the application of Mössbauer spectroscopy to catalytic mechanisms. First, although ^{57}Fe is nearly an ideal Mössbauer nucleus, it is one of the few species useful in heterogeneous catalysis. One problem in Mössbauer spectroscopy is that absorption of a photon by a nucleus will be accompanied by its recoil with consequent displacement of the absorption frequency and elimination of the marvelously high resolution of Mössbauer spectroscopy. Depending upon various factors, in a certain fraction of photon absorptions, the recoil energy is transferred to the entire solid and the change in frequency is negligible. This "recoil-free fraction" increases as the temperature is lowered and for a number of Mössbauer nuclei operation at 4 K or lower is needed to get an adequate recoil-free fraction. However, use of ^{57}Fe is often possible for some purposes at temperatures well above room temperature, but, since the recoil-free fraction of surface atoms is apt to be smaller than that of atoms in bulk, Mössbauer studies related to surface sites or chemisorption are likely to require studies at room temperatures or at liquid nitrogen temperatures.

Since Mössbauer spectroscopy is a bulk technique and not a surface technique, one is unlikely to be able to study surface sites or adsorbed species if the ratio Fe_s/Fe_{total} is too small. Thus, much of the data of catalytic interest so far reported are primarily structural. Mössbauer spectroscopy has been very useful in identifying the phases present in iron Fisher-Tropsch catalysts: Fe, various Fe carbides, Fe oxides and hydroxyoxides [140]. "Pure" iron compounds are not required. For example considerable structural and chemical information has been obtained for supported Pt-Fe and Pd-Fe catalysts [138, Sect. 3.3.1].

In working with a supported catalyst one may be able to have the Fe-containing species in a more dispersed state with a larger ratio, Fe_s/Fe_{total}. An extreme of this consists of Fe^{n+} ion exchanged into zeolites. A study of iron exchanged Y-zeolite has provided a good example of correlation of Mössbauer and catalytic studies [141]. This work involved a series of iron exchanged Y-zeolite in which Si/Al varied from 2.5 to 8.9. Mössbauer studies were performed at ~ 300 K and measurements of the rate of decomposition of N_2O, at 800 K. As Si/Al increased over the range investigated, the turnover frequency per atom of Fe increased by a factor of 100. This could be correlated with the location of the iron ion in the zeolite lattice, more exposed locations being favored by a high ratio, Si/Al. In this work it was also possible to observe the effect of adsorption of CO and H_2O.

Overall, then, the use of Mössbauer spectroscopy in studies of the mechanism of heterogeneous catalysis is restricted, but where it can be employed it is capable of supplying information which is often difficult to obtain by any other technique.

24. Other Probes

There are other probes which have possible application to mechanistic investigations such as XPS (x-ray photoelectron spectroscopy), neutron inelastic scattering spectroscopy, and EXAFS. However, the applications of these techniques to mechanistic studies on conventional catalysts have not yet been extensive enough to require consideration here.

This chapter will close with a final caution. If such catalysts as metal foils, wires, or powders are being investigated, the catalysts should always be examined by x-ray photoelectron spectroscopy or Auger spectroscopy to make sure that the surfaces are free of contaminants. Noble metals are usually about 99.99% pure, but segregation of impurities to the surface is apt to occur at higher temperatures and there may well be enough impurity in bulk samples to lead to substantial contamination of the surface. Thus, several different groups had observed that oxygen reacted with platinum single crystals at $T > 770$ K to form a thermally stable oxide which could not be reduced with hydrogen at high temperatures. It was concluded that platinum formed a hitherto unknown oxide of extraordinary stability. It turned out, however, that silicon had diffused to the surface at the temperature at which the ultrastable oxide formed and that the ultrastable oxide was silicon dioxide.

Unfortunately there is no technique which can straightforwardly diagnose the cleanliness of the metal particles of supported catalysts. However, the problem of contaminants in the metal is a much less serious problem for supported catalysts than for bulk metals. About 50% of the metal atoms of a 2-nm particle of platinum are on the surface. The content in impurity atoms in such a particle is such that, even if all segregate to the surface, only a small coverage by impurity can result.

Unfortunately, there is no direct technique to determine whether species derived from the support or from some contaminant in the support have migrated onto the surface. The problem here is exemplified by the so-called strong metal support interaction which occurs when Pt/TiO_2 is heated in hydrogen at 770 K and which is thought at present to result from migration of TiO_x (x being less than 2) onto the surface. Accord between percentages exposed measured by hydrogen or carbon monoxide chemisorption and particle sizes measured by transmission electron microscopy or by line profile analysis in x-ray diffraction provides some assurance that the metal surface of supported catalysts is not grossly contaminated.

25. References

1. Langmuir I (1915) J Amer Chem Soc 37: 1139
2. Langmuir I (1922) Trans Faraday Soc 17: 621
3. Burwell RL, Jr (1987) CHEMTECH 17: 586
4. Gaines GL, Jr, Wise G (1983) in: Heterogeneous catalysis, selected American Histories, Davis BH, Hettinger WP, Jr (eds) American Chemical Society, Washington DC ACS Symp Ser 222, p 13
5. IUPAC, Manual of symbols and terminology for physicochemical quantities and units-Appendix II, Definitions, terminology and symbols in colloid and surface chemistry. Part II. Heterogeneous Catalysis (1977) Adv Catal 26: 351
6. For leading references see: Cant NW, Angove DE (1986), J Catal 97: 36, Akhter S, White JM (1986) Surf Sci 171: 527
7. Haller GL, Delgass WN (1986) in: Techniques of chemistry, vol 6, pt 1, 4th ed, Bernasconi CF (ed) Wiley Interscience, New York, p 951
8. Burwell RL, Jr, Pearson RG (1966) J Phys Chem 70: 300
9. Hussey AS, Nowack GP (1969) J Org Chem 34: 439
10. Butt JB (1980) Reaction kinetics and reactor design, Englewood Cliffs, New Jersey, Prentice-Hall
11. Schlatter JC, Boudart M (1972) J Catal 24: 482
12. Fortin T, Burwell RL, Jr, Butt JB, Barbier J (1986) Actas del X Simposio Iberoamericano de Catálisis p 1199
13. Pines H (1981) The chemistry of catalytic hydrocarbon conversion, New York, Academic Press
14. Haag WO, Dessau RM (1984) Proc 8th Int Congr Catal, vol 2, Verlag Chemie, Weinheim p 305
15. Koel BE, Somorjai GA in: Catalysis—science and technology, Anderson JR, Boudart M (eds) (1985) vol 7, Springer Verlag, Berlin, p 159
16. Horiuti J, Polanyi M (1934) Trans Faraday Soc 30: 1164
17. Siegel S (1973) J Catal 30: 139, Rooney JJ (1985) J Mol Catal 31: 147
18. Muetterties EL, Rhodin TN, Band E, Brucker CF, Pretzer WR (1979) Chem Revs 79: 91
19. Dessau RM (1986) J Chem Soc Chem Commun 1167
20. Kung HH, Pellet RJ, Burwell RL, Jr (1976) J Amer Chem Soc 98: 5603
21. Giannetto G, Sansare S, Guisnet M (1986) J Chem Soc Chem Commun 1302
22. Weeks TJ, Jr, Ladd IR, Bolton AP (1980) J Chem Soc Faraday Trans 1 76: 84
23. Fajula F (1985) Stud Surf Sci Catal 20 (Catal. Acids Bases) 361
24. Boudart M, Djéga-Mariadassou G (1984) Kinetics of heterogeneous catalytic reactions, Princeton Univ Press, Princeton, NJ
25. Langmuir I (1940) J Chem Soc (London) 511
26. Hasenberg D, Schmidt LD (1985) J Catal 91: 116
27. Knor Z (1982) Chemisorption of dihydrogen. in: Catalysis—science and technology, Anderson JR, Boudart M (eds), vol 3, Berlin, Sringer Verlag, p 231
28. Peri JB (1984) Infrared spectroscopy in catalytic research. in: Catalysis—science and technology, Anderson JR, Boudart M (eds), vol 5, Berlin, Springer Verlag p 171
29. Morrow BA, Chevrier JP, Moran LE (1985) J Catal 91: 208
30. Froment GF, Hosten LH (1981) Catalytic reactions modeling. in: Catalysis—science and technology, Anderson JR, Boudart M (eds), vol 2, Berlin, Springer Verlag, p 97
31. Ertl G (1983) Kinetics of chemical process on well-defined surfaces. in: Catalysis—science and technology, Anderson JR, Boudart M (eds) vol 4, Springer Verlag, Berlin, p 210

32. Ozaki A, Aika K (1981) Catalytic activation of dinitrogen. in: Catalysis—science and technology, Anderson JR, Boudart M (eds), vol 1, Springer-Verlag, Berlin, p 87
33. Boudart M (1986) Ind Eng Chem Fundam 25: 656
34. Kobayashi H Kobayashi M (1974) Catal Rev-Sci Eng 10: 139
35. Kobayashi M (1982) Chem Eng Sci 37: 393
36. Jain AK, Li C, Silveston PL, Hudgins RR (1985) Chem Eng Sci 40: 1029
37. Mori T, Miyamoto A, Niizuma H, Takahashi N, Hattori T, Murakami Y (1986) J Phys Chem 90: 109
38. Yang C-H, Soong Y, Biloen P (1984) Proc 8th Int Congr Catal, vol 2, Verlag Chemie, Weinheim, p 3
39. Happel J, Walter E, Lecourtier Y (1986) Ind Eng Chem Fundam 25: 704
40. Beeck O (1945) Rev Mod Physics 17: 61
41a. Zaera F, Somorjai GA (1984) J Amer Chem Soc 106: 2288
41b. Somorjai GA (1989) 198th Meeting of the American Chemical Society, Sept 12, Division of Inorganic Chemistry, paper 79
42. Avery NR (1984) Surf Sci 137, L 109
43. Hattori T, Burwell RL, Jr (1979) J Phys Chem 83: 241
44. Pálinkó I, Notheisz F, Bartók M (1988) Catal Lett 1: 127
45. Berndt GF (1983) Catalysis (London) 6: 144
46. Kemball C (1984) Chem Soc Rev 13: 375
47. Burwell RL, Jr (1972) Catal Rev 7: 25
48. Ozaki A (1977) Isotopic studies of heterogeneous catalysis, Kodansha Tokyo
49. Burwell RL, Jr (1986) Langmuir 2: 2
50. Scott KF, Phillips CSG (1978) J Catal 51: 131
51. Dalla Betta RA, Boudart M (1976) J Chem Soc Faraday Trans 1, 72: 1723
52. Root TW, Duncan TM (1986) Paper 217, Div Colloid & Surf Chem, National Meeting, Amer Chem Soc, Anaheim CA, Sept 7–12
53. Eskinazi V, Burwell RL, Jr (1983) J Catal 79: 118
54. Avery NR (1972) J Catal 24: 92
55. Burwell RL, Jr (1969) Accts Chem Res 2: 289
56. Clarke JKA, Rooney JJ (1976) Adv Catal 25: 125
57. Hegarty BF, Rooney JJ (1989) J Chem Soc Faraday Trans 1, 85: 1861
58a. Brown R, Kemball C, Oliver JA, Sadler IA (1985) J Chem Res Synop 274; Brown R, Kemball C (1987) J Catal 104: 480
58b. Robertson PJ, Scurrell MS, Kemball C (1975) J Chem Soc Faraday Trans 1, 71: 903
59. Bradshaw DI, Moyes RB, Wells PB (1975) J Chem Soc Chem Commun 137
60. Chevreau T, Gault FG (1977) J Catal 50: 124
61. Burwell RL, Jr, Littlewood AB, Cardew M, Pass G, Stoddart CTH (1960) J Amer Chem Soc 82: 6272
62. Nishimura E, Inoue Y, Yasumori I (1975) Bull Chem Soc Jpn 48: 803
63. Naito S, Tanimoto M (1986) J Catal 102: 377
64. Smith GV, Swoap JR (1966) J Org Chem 31: 3904
65. Siegel S (1986) J Catal 102: 475
66. Haller GL, John CS, Tyler JK (1980) Proc 7th Int Congr Catal, Kodansha, Tokyo, p 965
67. Tanaka K, Tanaka K-I, Miyahara K (1980) J Chem Soc Chem Commun 666
68. Grubbs RH, Swetnick S (1980) J Mol Catal 8: 25
69. Grubbs RH, Hoppin CR (1979) J Am Chem Soc 101: 1499
70. Sachtler WMH (1970) Catal Rev 4: 27
71. Takeuchi A, Katzer JR (1981) J Phys Chem 85: 937
72. Liu G. Willcox D, Garland M, Kung HH (1985) J Catal 96: 251
73. Margitfalvi J, Guczi L, Weiss AH (1981) J Catal 72: 185
74. Berndt GF, Thomson SJ, Webb G (1983) J Chem Soc Faraday Trans 1 79: 195
75. Pines H, Chen C-T (1961) J Org Chem 26: 1057; Pines H, Goetschel CT (1965) ibid 30: 3530
76. Gault FG, Gazz Chim Ital 109: 255 (1979) See Also, Maire G, Garin (1984) Metal catalysed skeletal reactions of hydrocarbons on metal catalysts. In: Catalysis—science and technology, Anderson JR, Boudart M (eds) vol. 6, Springer-Verlag, Berlin, p 161
77. Van Santen RA, de Groot CPM (1986) J Catal 98: 530
78. Krenzke LD, Keulks GW (1980) J Catal 61: 316
79. Bell RP (1974) Chem Soc Rev 3: 513; Melander L, Sauder WH, Jr (1980) Reaction rates of isotopic molecules, Wiley, New York
80. Adams CR, Jennings TJ (1964) J Catal 3: 549
81. Meyer EF, Burwell RL, Jr (1963) J Amer Chem Soc 85: 2877
82. Cant NW, Tonner SP, Trimm DL, Wainwright MS (1985) J Catal 91: 197

83. van Meerten RZC, Morales A, Barbier J, Maurel R (1979) J Catal 58: 43
84. Hussey AS, Baker RH, Keulks GW (1968) J Catal 10: 258
85. Siegel S (1966) Adv Catal 16: 124; Burwell RL, Jr (1972) Intra-Science Chem Rept 6: 135; Clarke JKA, Rooney JJ (1976) Adv Catal 25: 125
86. Bartók M, Czombos J, Felföldi K, Gera L, Göndös G, Molnár Á, Notheisz F, Pálinkó I, Wittmann G, Zsigmond AG (1985) Stereochemistry of heterogeneous metal catalysis, John Wiley Sons, Chichester
87. Kannan SV, Pillai CN (1968) Curr Sci 37: 665
88. Smith GV, Molnár A, Khan MM, Ostgard D, Yoshida N (1986) J Catal 98: 502
89. van Rantwijk F, van Vliet A, van Bekkum H (1980) J Mol Catal 9: 283
90. Kung HH, Pellet RJ, Burwell RL, Jr (1976) J Amer Chem Soc 98, 5603; See also Siegel S, Hawkins JA (1986) J Org Chem 51: 1638
91. Imachi M, Egashira M, Kuczkowski RL, Cant NW (1981) J Catal 70: 177
92. Kibby CL, Lande SS, Hall WK (1972) J Amer Chem Soc 94: 214
93. Csicsery SM (1986) Pure Appl Chem 58: 841, Zeolites 4: 202 (1984)
94. Derouane EG (1984) Studies in surface science and catalysis, 19 (Catalysis on the Energy Scene), Elsevier, Amsterdam, p 1
95. Huisgen R, Ooms PHJ, Mingin M, Allinger NL (1980) J Amer Chem Soc 102: 3951
96. van Hardeveld R, Hartog F (1969) Surf Sci 15: 189
97. Biloen P, Dautzenberg FM, Sachtler WMH (1977) J Catal 50: 77
98. Weisz PB (1962) Adv Catal 13: 137
99. Chuang SC, Tian YH, Goodwin JG, Jr, Wender I (1985) J Catal 96: 396
100. Yates JT, Jr, Gates SM, Russell JN, Jr (1985) Surf Sci 164: L839
101. Baker JA, Bell AT (1982) J Catal 78: 165
102. Deluzarche A, Hindermann J-P, Kiennemann A, Kieffer R (1985) J Mol Catal 31: 225, Kiennemann A, Hindermann J-P, Chakor-Alami A (1985) Bull Soc Chim Fr 399
103. Vedage GA, Herman RG, Klier K (1985) J Catal 95: 423
104. Knözinger H (1976) Adv Catal 25: 184
105. Amenomiya Y (1977) J Catal 46: 326
106. Larson JG, Hall WK (1965) J Phys Chem 69: 3080
107. Morterra C, Zecchina A, Coluccia S, Chiorino A (1977) J Chem Soc Faraday Trans 1 73: 1544
108. John CS, Kemball C, Rajadhyaksha RA (1979) J Catal 57: 264
109. Okamoto Y, Oh-Hara M, Maezawa A, Imanaka T, Teranishi S (1986) J Phys Chem 90: 2396
110. Beebe TP, Jr, Yates JT, Jr (1986) J Amer Chem Soc 108: 663
111. Delgass WN, Haller GL, Kellerman R, Lunsford JH (1979) Spectroscopy in heterogeneous catalysis, Academic Press, New York
112. Wedler G (1976) Chemisorption: an experimental approach, Butterworths, Boston, Hayward DO, Trapnell BMW (1964) Chemisorption, 2nd ed, Butterworths, Washington
113. Burwell RL, Jr, Taylor HS (1936) J Amer Chem Soc 58: 697; Burwell RL, Jr, Stec KS (1977) J Coll Interface Sci 58: 54
114. Lyne PM, Scott KF (1981) J Chromatogr Sci 19: 599; Parcher JF, Hyver KJ (1984) J Chromatogr 302: 195
115. Demmin RA, Gorte RJ (1984) J Catal 90: 32
116. Rieck JS, Bell AT (1984) J Catal 85: 143
117. Gravelle PC (1977) Catal Rev-Sci Eng 16: 37
118. Chou P, Vannice MA (1987) J Catal 104: 1
119. Bell AT (1984) in: Chemistry and physics of solid surfaces V, Springer Series in Chemical Physics 35, Springer-Verlag, Berlin, p 2
120. Nagai M, Lucietto LL, Li Y-E, Gonzalez RD (1986) J Catal 101: 522
121. Zecchina A, Garrone E, Guglielminotti E (1983) Catalysis (London) 6: 90
122. Deligianni H, Mieville RL, Peri JB (1985) J Catal 95: 465
123. Zhang H-B, Schrader GL (1985) J Catal 95: 325
124. Howe RF (1984) Chemistry and physics of solid surfaces V, Springer Series in Chemical Physics 35, Springer-Verlag, Berlin, p 39
125. Shvets VA (1986) Russ Chem Revs 55: 200
126. Che M, Tench AJ (1982) Adv Catal 31: 77
127. Mendelovici L, Lunsford JH (1985) J Catal 94: 37
128. Laniecki M, Burwell RL, Jr (1980) J Coll Interface Sci 75: 95
129. Garrone E, Zecchina A, Stone FS (1980) Philos Mag B 42: 683
130. Garrone E, Zecchina A, Stone FS (1980) J Catal 62: 396
131. Clague ADH (1985) Catalysis (London), 7: 75

132. Mehring M (1983) Principles of high resolution NMR in solids, Springer-Verlag, New York
133. Slichter CP (1978) Principles of magnetic resonance, 2nd ed, Springer, New York
134. McMillan M, Brinen JS, Haller GL (1986) J Catal 97: 243
135. Majors PD, Ellis PD (1987) J Am Chem Soc 109: 1648
136. Duncan TM, Winslow P, Bell AT (1985) J Catal 93: 1
137. Wang P-K, Ansermet J-P, Rudaz SL, Wang Z, Shore S, Slichter CP, Sinfelt JH (1986) Science 234: 35
138. Berry FJ (1984) in: Mössbauer spectroscopy applied to inorganic chemisty, Long GJ (ed), Plenum Press, New York, p 391
139. Tatarchuk BJ, Dumesic JA (1984) Springer Ser Chem Phys 35: (Chem Phys Solid Surf 5), 65
140. Amelse JA, Grynkewich G, Butt JB, Schwartz LH (1981) J Phys Chem 85: 2484
141. Aparicio LM, Dumesic JA, Fang S-M, Long MA, Ulla MA, Millman WS, Hall WK (1987) J Catal 104: 381