TECHNOLOGIES, INSTRUMENTATION AND MATERIALS FOR ENERGY AND ENVIRONMENT

Part 1.
CATALYSTS AND ADSORBENTS

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Prof. Guido Busca

For a larger discussion of this topic see:
G. Busca, Heterogeneous Catalytic Materials, Elsevier, 2014.

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1. Catalysis in the industry.

As first recognized by the Swedish chemist J.J. Berzelius in 1835, catalysis is a phenomenon allowing a chemical reaction occurring faster when a non-reactant species is present. In spite of the apparent limited interest of doing a reaction faster, catalysis gives rise to very relevant practical effects. In fact, the increase of the rate of a reaction can in practice result in many cases in its practical feasibility. The acceleration of a desirable chemical conversion in fact frequently allows it to be realized instead of other competitive reactions, less desirable, being definitely slower. Thus, finding an appropriate catalyst to make the desired reaction faster than the competitive ones, as well as allowing to perform it with high efficiency, is crucial in developing industrial processes. Thus since maybe 180 years (the contact process for sulphuric acid production was developed in 1831) heterogeneous catalysis is keystone in industrial chemistry. For this reasons, catalysts are also important products of the chemical industry itself and their industrial production represents a big business, like 13 billion dollars per year.

In practice, a large majority of industrial chemical processes (likely 85 %) are catalyzed and most of them are catalyzed by solids. The main reasons to use catalysts are synthetically the following:

1. The catalyst allows the desired reaction to become faster than competitive reactions thus allowing the desired reaction to be actually realized.
2. For exothermic equilibrium reactions: the catalyst allows the reaction to be performed also at lower temperature, where it would be kinetically hindered without it. Thus it allows the reaction to be realized in conditions where thermodynamics is more favourable.
3. For endothermic equilibrium reactions: the catalyst allows the reaction to be performed also at moderately high temperatures, where it would be kinetically hindered without it. Thus it allows the reaction to be realized in conditions where thermodynamics is already quite favourable with lower energy waste and allowing cheaper materials to be used for the reactor.
4. For exothermic non-equilibrium reactions: the catalyst allows reactions less favoured by thermodynamics and kinetics (without it) to be realized instead of more favoured and otherwise faster reactions.
5. A better catalyst allows reactions to be performed in smaller flow reactors with the same performances, or with better performances and lower recycles of un-converted reactants in the same reactor, or even with shorted times in batch reactors.

2. Heterogeneous catalysis in the industry

Solid catalysts are usually preferred in the industry with respect to liquid catalysts because of their easier separation from the reaction fluid. On the other hand, solid catalysts are frequently more environmentally friendly than liquid catalysts and their manipulation far safer. A typical example is that of acid catalysts for refinery and petrochemistry. Protonic zeolites substituted liquid acid catalysts in some important process. In practice, dangerous corrosive liquids characterized by unsafe manipulation procedures, difficult regeneration and unappropriate disposal, like sulphuric acid, and $AlCl_3$-based Friedel Crafts type liquid acid, and very toxic and volatile acids like hydrofluoric acid have been substituted by environmentally friendly silico-aluminates. Additionally, catalyst performances have also be improved.

Main types of industrial catalysis.

1. Homogeneous catalysis (the catalyst is dissolved in the liquid phase with the solvent (if any), the reactants and usually the products.
2. Liquid / liquid heterogeneous catalysis (reactants and products in one liquid phase, the catalyst in a second liquid phase).
3. Gas / solid heterogeneous catalysis (reactants and products in the gas phase, the catalyst in solid phase).
4. Liquid / solid heterogeneous catalysis (reactants and products in the liquid phase, the catalyst in solid phase).

Solid industrial catalytic materials

In Table 1 some examples of different kinds of catalysts actually used in the chemical industry are summarized.

Shaping of catalysts for industrial catalytic reactions.

Solid catalysts mostly consist of fine powders. Industrial catalytic rectors are either fixed bed or fluid/slurry bed. In all cases, the fine powder used as such could produce important drawbacks.

If packed in fixed bed reactors, powders tend to form high density layers opposing the reactants flow, causing high pressure drops. Also, fine particles could be transported out of the reactor by the effluent flow. On the other hand, a number of transport phenomena occur in fixed catalytic beds that can limit, and in any case may influence, the reaction rate. These phenomena, that can be taken into account in modelling of fixed bed reactors, are actually are influenced by particle or agglomerate size and shapes.

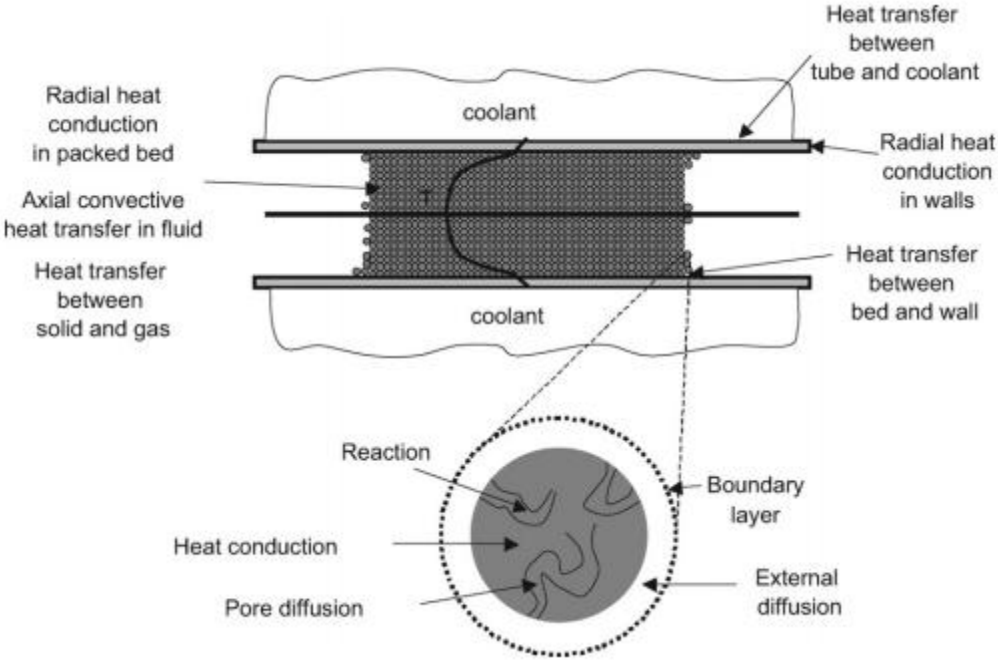
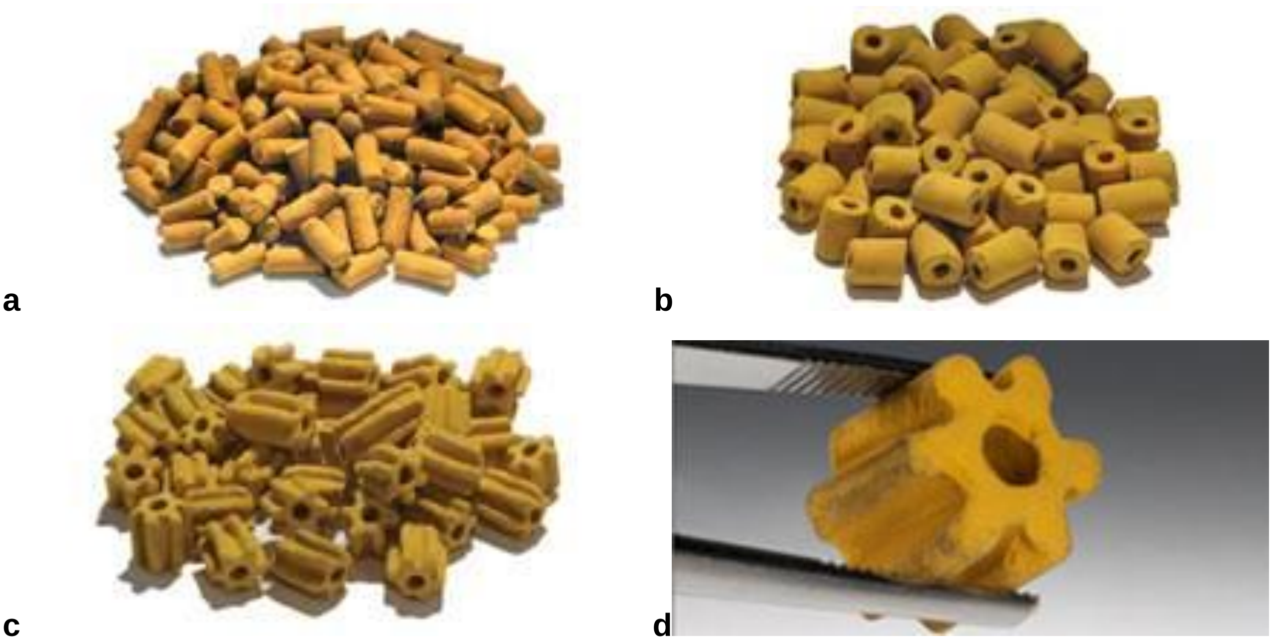


Table 1. Summary of some most relevant families of industrial catalysts.

Oxide catalysts			
Bulk single oxide	Alcohol dehydration to olefins	γ-Al_2O_3	Lewis acidic catalyst
Bulk mixed oxide	Aldol Condensation	MgO-Al_2O_3 - calcined hydrotalcite	Basic catalyst
	Propane to acrylonitrile	V/MoNb/Sb oxides	(Amm)oxidation
Oxide supported on oxide	o-xylene to phtahlic anhydride	V_2O_5-TiO_2	Selective oxidation
	Isobutane to isobutene	K_2O-Cr_2O_3/Al_2O_3	Dehydrogenation
Impregnated melt or liquid	SO_2 to SO_3	K_2SO_4-V_2O_5/SiO_2	Oxidation
	Olefin oligomerization	H_3PO_4/SiO_2 ("solid phosphoric acid")	Protonic acid catalyst
Zeolite catalysts			
Protonic zeolite	Benzene+ethylene to ethylbenzene	H-BEA	Protonic acid catalyst
Metal exchanged zeolite	N_2O decomposition/reduction	Fe-MFI	Redox catalyst
Metal catalysts			
Bulk metals	Ammonia synthesis	Fe (CaO, K_2O, Al_2O_3, SiO_2 promoters)	Hydrogenation
Metal gauzes	Ammonia oxidation to NO	Pt (Rh stabilizer)	Selective oxidation
Supported metal	Acetylene hydrogenation in ethylene	Pd/ Al_2O_3 (Ag promoter)	Preferential hydrogenation
	Car catalytic mufflers	Pt-Rh/ Al_2O_3-CeO_2-ZrO_2	Combustion + NO red
	Alcohols to aldehydes	Pt/Carbon	Liquid phase oxidation
	Aromatization of paraffins	Pt/K-L zeolite	Dehydrogenation
Sulphide catalysts			
Bulk sulphide	Bituminous sands to oil fractions	MoS_2	Hydrocracking
Supported sulphides	Gasoline treatment	NiS-MoS_2/γ-Al_2O_3	Hydrodesulphurization

Thus, to optimize flow and transport conditions, solid catalysts are shaped in pellets by extrusion procedures, producing “extrudates” which resist the reactant pressure and leave sufficient void fraction to limit pressure drops. Such extrudates and “miniliths” are formed by pushing a paste containing the cataltst through a die, followed by cutting, drying and calcining. In the figure the different shapes of commercial catalyst extrudates for SO_2 to SO_3 oxidation reactions are shown (MECS® Sulfuric Acid Catalyst Products).

Another important factor, occurring in particular when multitubular reactors/exchangers are used, is to favour the heat transfer between the gas phase and the tube surface. In fact, in heat exchange (either heating of the reactant mixture in the case of endothermic reactions, or cooling for exothermic reactions) occurs through the tube wall. The formation of a stationary gas film inside the tube wall, that reduces the rate of heat transfer, must be avoided. Using smaller catalyst particles reduces the thickness of the stationary gas film but increases pressure drops. Optimal behaviour is obtained designing an optical extrudate shape and size. In the following figure commercial extrudates of methane steam reforming catalysts and their disposition in the tubular reactor are shown (Johnson Matthey).



Sulfur dioxide oxidation catalysts: a) high pressure drop for low gas velocity converters; (b) medium pressure drop; (c and d) low pressure drop, MECS® Sulfuric Acid Catalyst Products**.**

Catalysts for moving or fluid bed reactors should resist the attrition due to the catalyst movement. To this purpose, particular agglomeration and extrusion procedures must be applied to form mechanically resistant microspheres.

Extrudates may actually be formed using mixtures of the real catalyst powder with additive powders such as binders (frequently alumina or silica based inorganics), lubricants, plasticizers, and compaction agents. Among the latter, organics such as stearic acid, oleic acid, naphthenic acid, oils, paraffins, stearates, polymers may be used. Additional inorganic components may also be present, as poison traps as well as graphite as a shaping agent. This is the case, e.g. of Fluid Catalytc Cracking catalysts where alumina powders are added to trap Ni arising from the feed impurities. These materials protect the catalyst from the formation of Ni metal that would cause unwanted dehydrogenations. Binders may have a relevant role in the catalytic phenomena and, in particular, in the diffusion of reactants and products in the bed. Interparticle mesoporosity may form between catalyst and binder particles, and sums to catalyst and binder intraparticle micro- or meso-porosity.

Shape of extrudate catalysts for methanne steam reforming and tjheir accomodation in the reator tube (Johnson Matthey).

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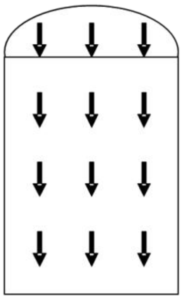
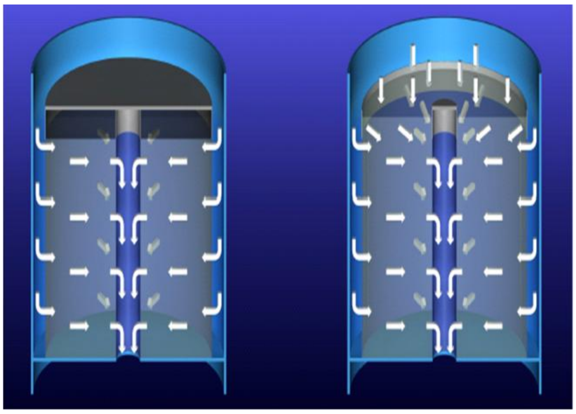
2.1 Industrial heterogeneous catalytic reactors.

Industrial catalytic reactors differ for several reasons: the catalyst bed may be fixed, stirred, ebullated, fluidized, transported, circulated. In the fixed beds the flow may be downwards or upwards, radial or axial. The reactor may be adiabatic, cooled or heated. The shape can be tubular, multi-tubular, tank, etc. In the following, a small summary of industrial reactor configurations is reported.

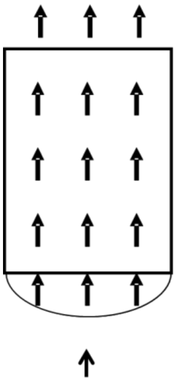


Axial down flow

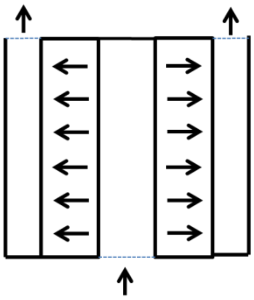


Radial flow

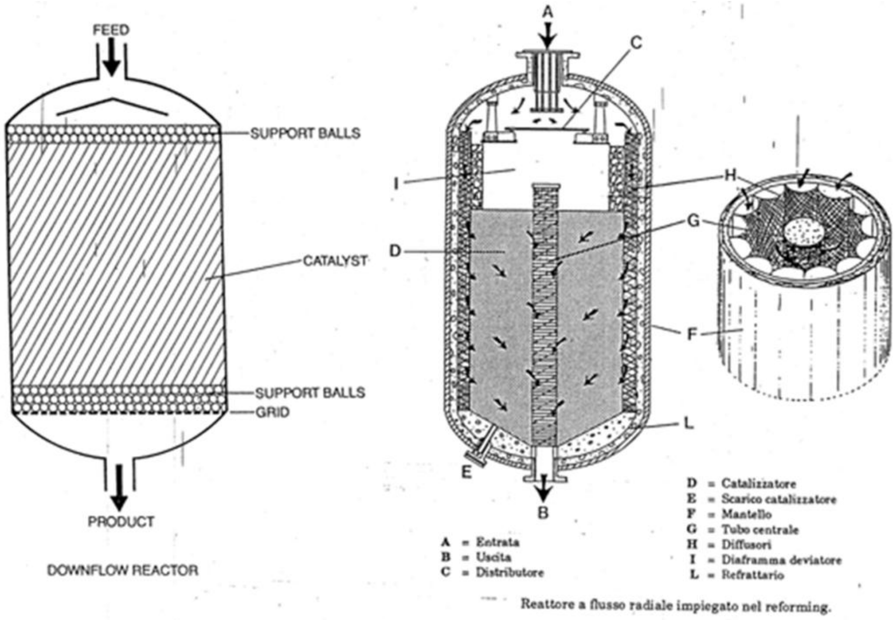
Axial-radial flow



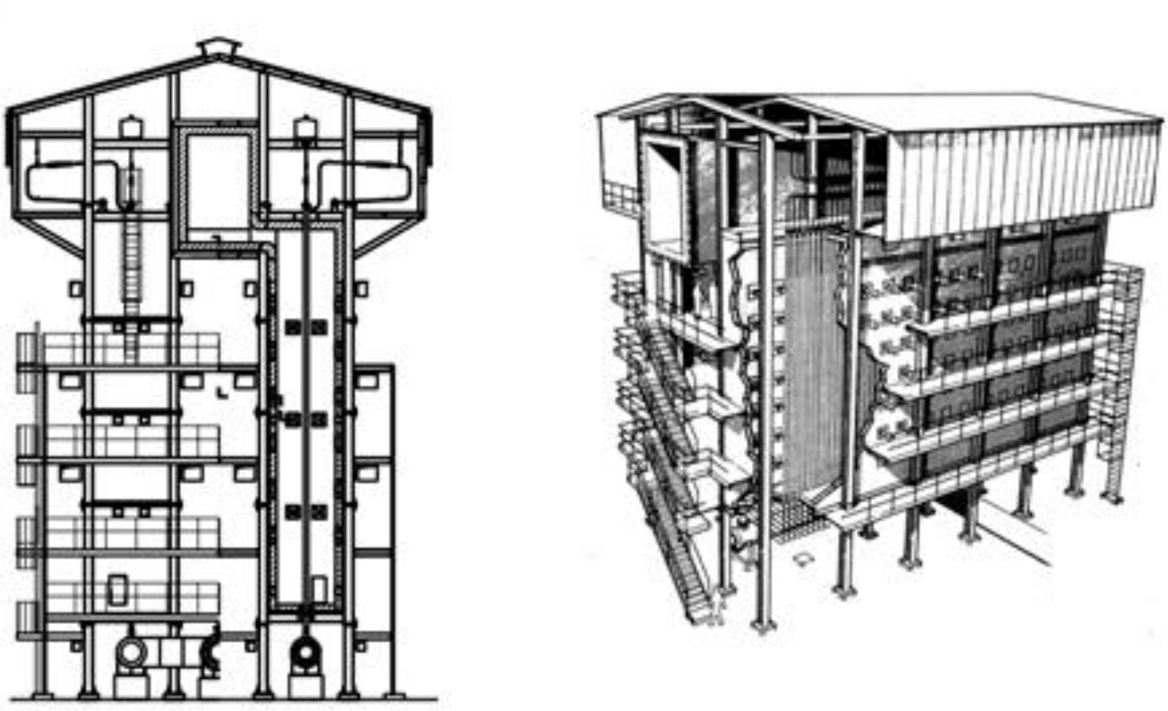
Axial up flow



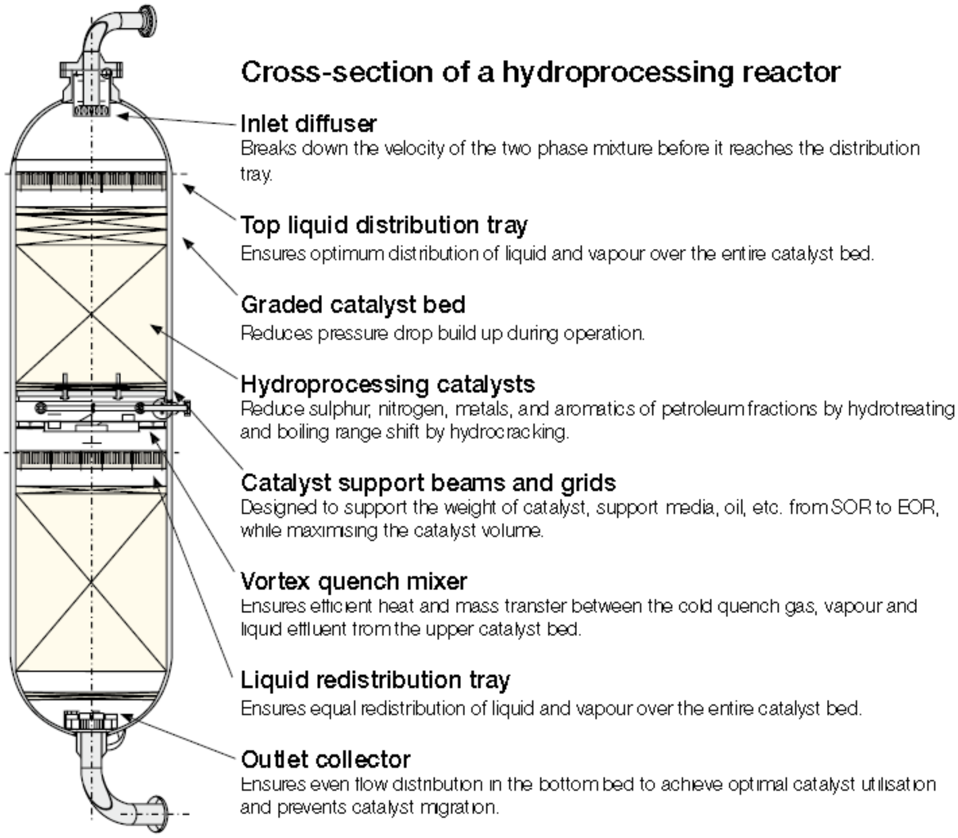
Radial up flow



Adiabatic, single fixed bed reactors, axial flow,left, and radial flow, right, for catalytic reforming.



Steam reforming furnace



Cross-section of a hydroprocessing reactor

Inlet diffuser
Breaks down the velocity of the two phase mixture before it reaches the distribution tray.

Top liquid distribution tray
Ensures optimum distribution of liquid and vapour over the entire catalyst bed.

Graded catalyst bed
Reduces pressure drop build up during operation.

Hydroprocessing catalysts
Reduce sulphur, nitrogen, metals, and aromatics of petroleum fractions by hydrotreating and boiling range shift by hydrocracking.

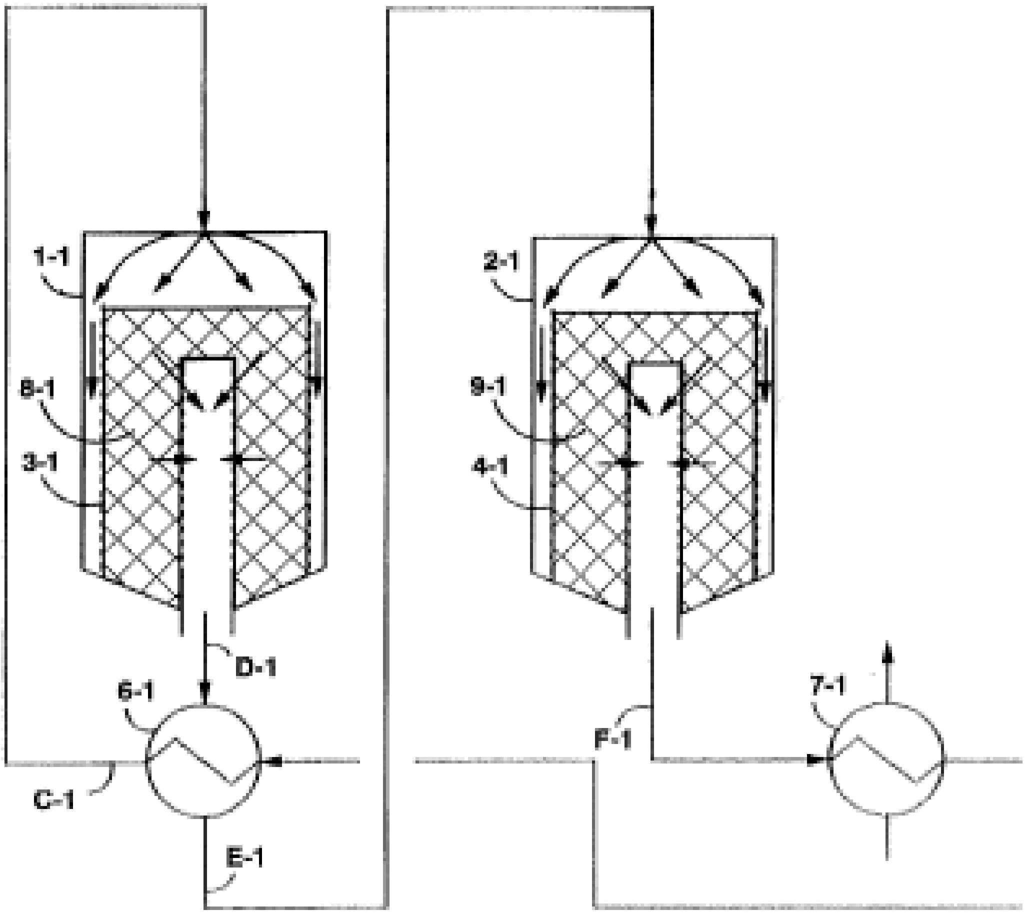
Catalyst support beams and grids
Designed to support the weight of catalyst, support media, oil, etc. from SOR to EOR, while maximising the catalyst volume.

Vortex quench mixer
Ensures efficient heat and mass transfer between the cold quench gas, vapour and liquid effluent from the upper catalyst bed.

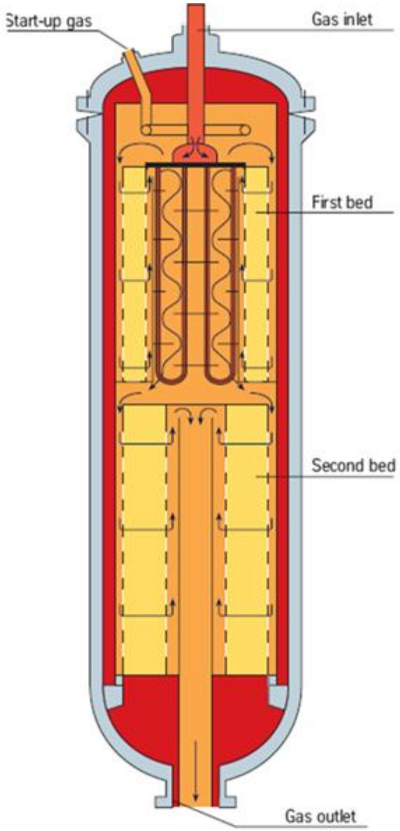
Liquid redistribution tray
Ensures equal redistribution of liquid and vapour over the entire catalyst bed.

Outlet collector
Ensures even flow distribution in the bottom bed to achieve optimal catalyst utilisation and prevents catalyst migration.

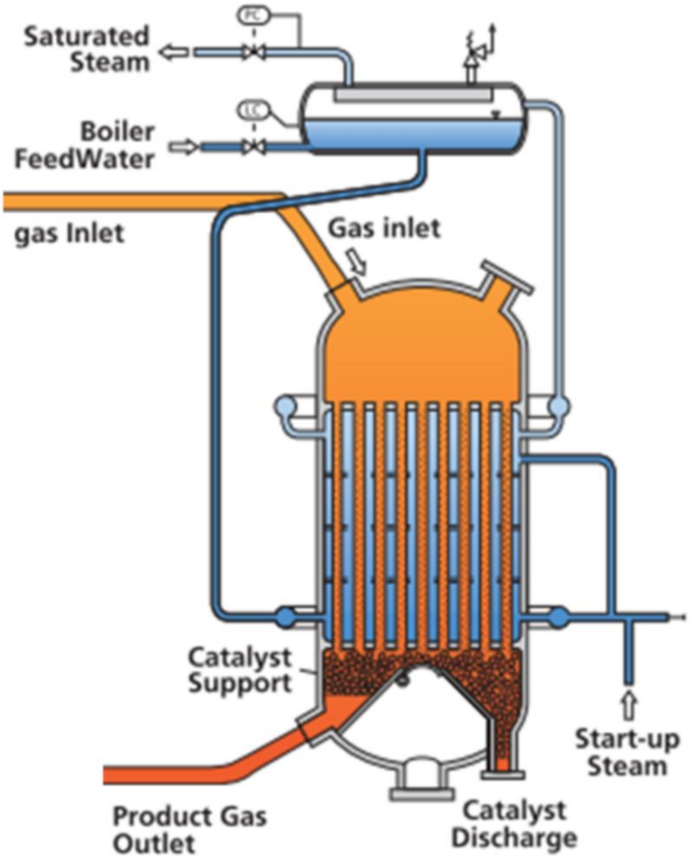
Double fixed bed reactor cooled by quenching



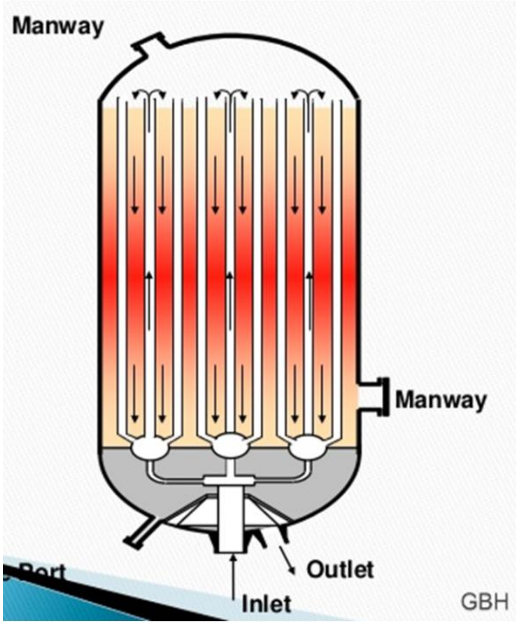
Two radial fixed bed reactors with interbed cooling by heat exchange.

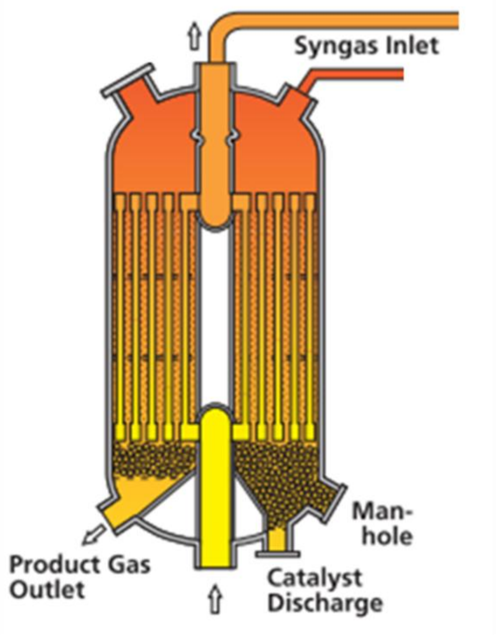


Double fixed bed reactor with interbed heat exchange by gas cooling for ammonia synthesis

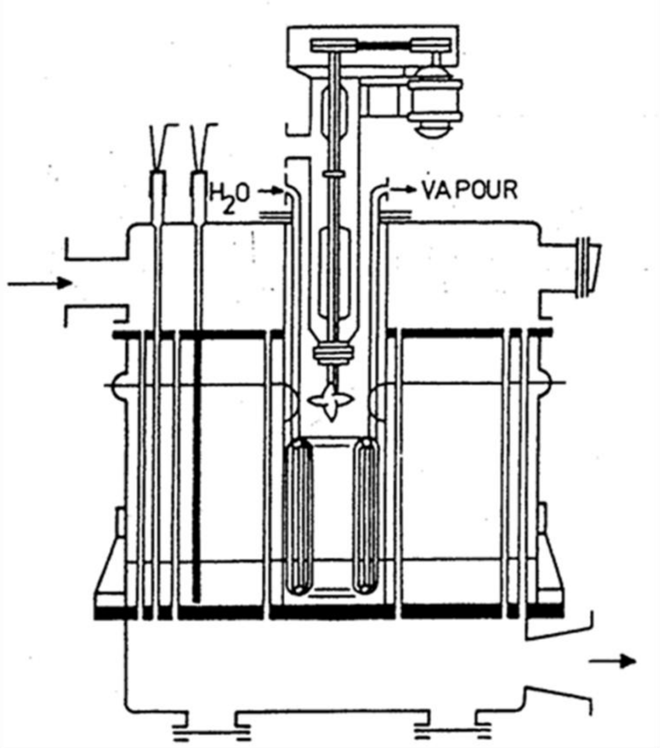


Water cooled (steam rising) multitubular reactor for methanol synthesis

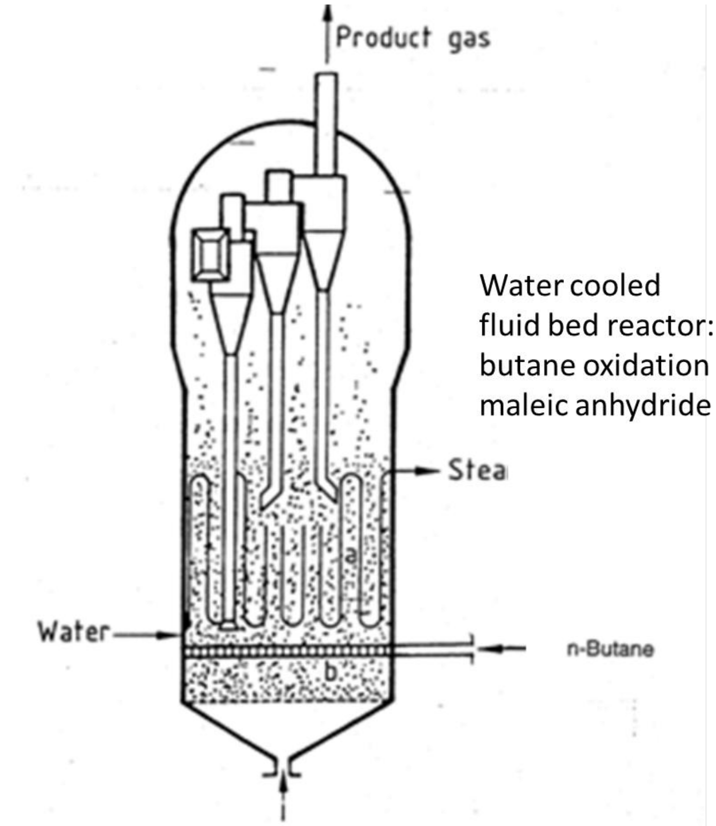




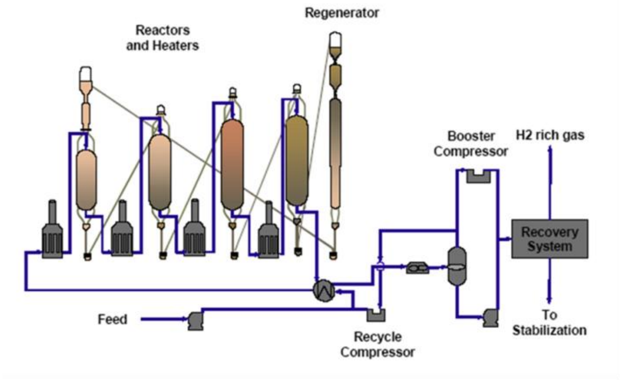
Gas cooled reactors : methanol synthesis

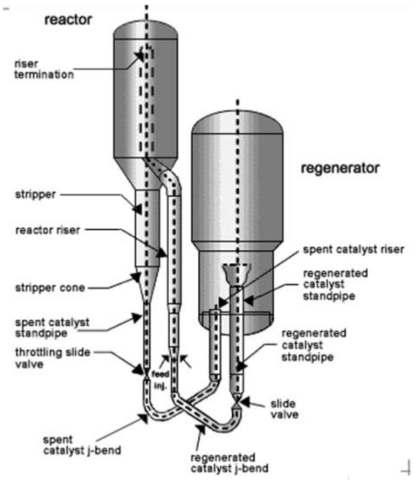


Multitubular reactor (10000-30000 tubes) cooled by gasoils or eutectic salts: o-xylene oxidation to phthalic anhydride

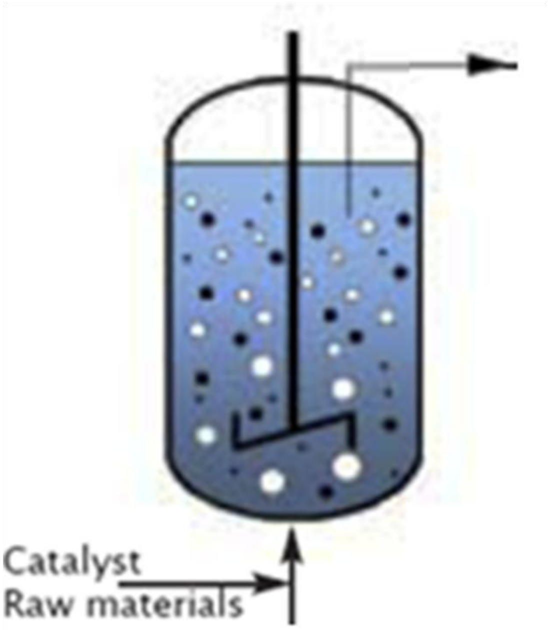


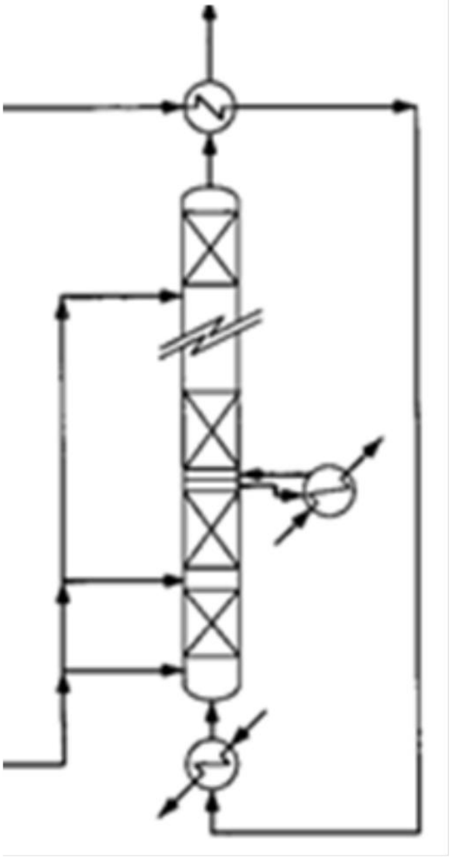
Water cooled
fluid bed reactor:
butane oxidation to
maleic anhydride



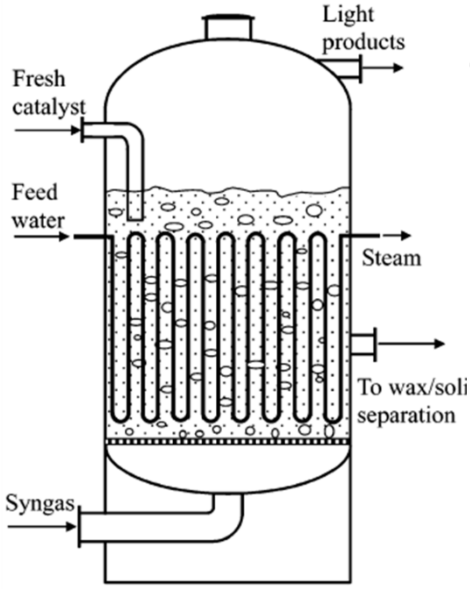


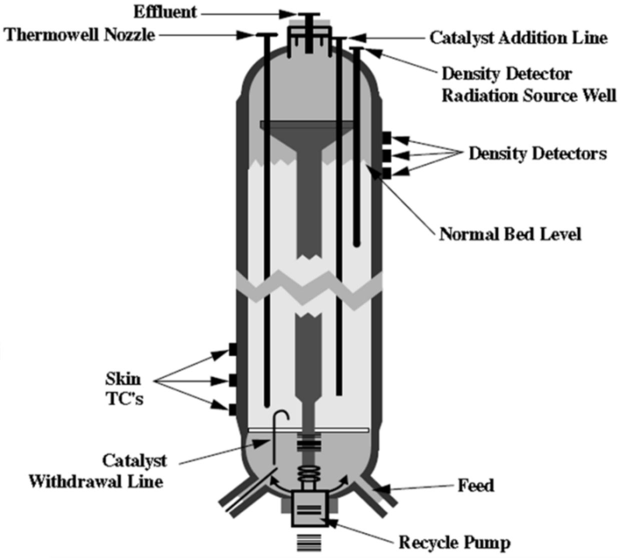
Moving (transport) bed reactors (bove, catalytic reforming) and moving fluidized bed reactors (fluid catalytic cracking raiser and regenerator)





Liquid/solid catalytic reactors:
slurry tank reactor (Ziegler-Natta ethylene polymerization, left) and multibed quench reactor (benzene alkylation by ethylene to ethylbenzene, right)





Liquid/solid catalytic reactors:
slurry fluid bed (left, Fischer Tropsch) and ebullated bed (right, hydrocracking).

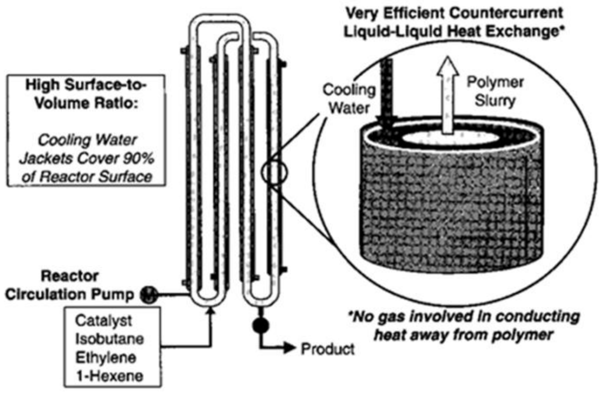
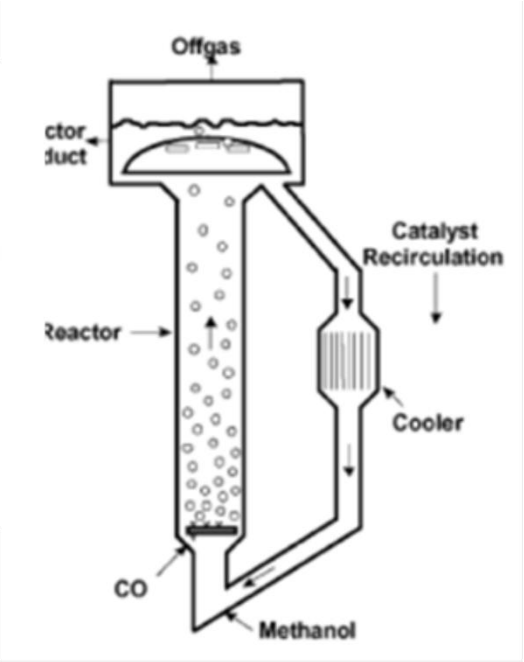


FIGURE 14.3.5 CPChem slurry-pipe-loop reactor has high heat-removal capacity.



Liquid/solid catalytic reactors:
loop slurry reactor (left) and slurry bubble columne recirculation (right)

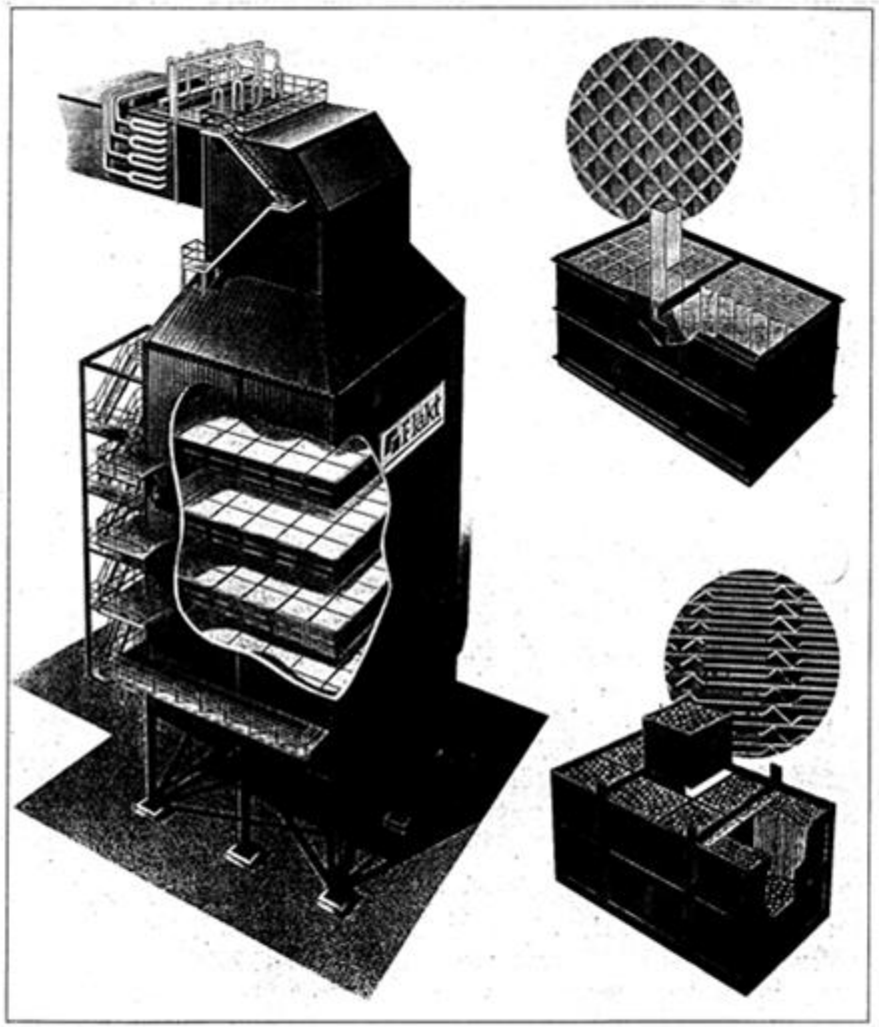
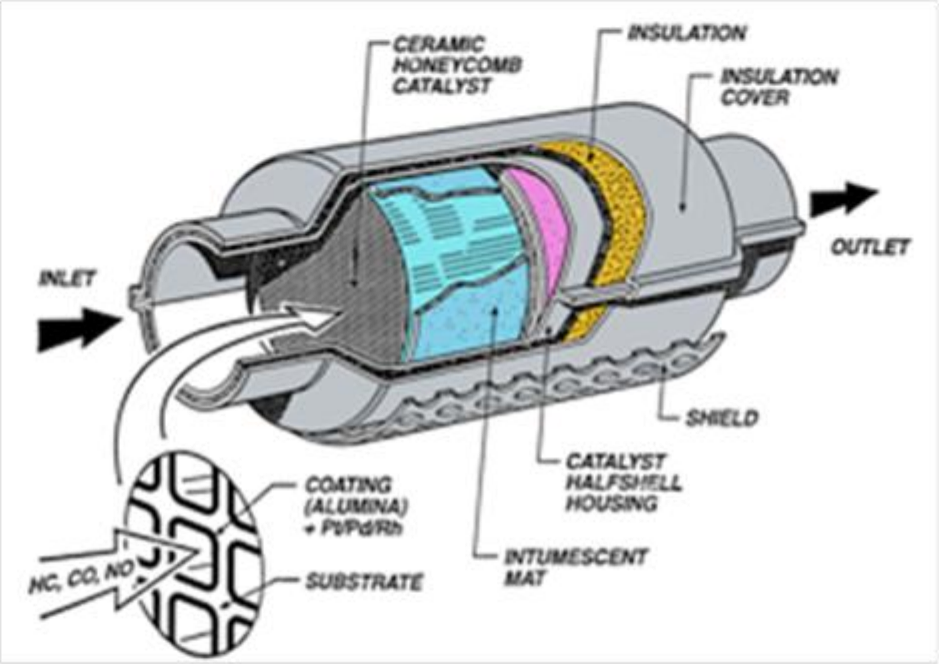


Fig. 3. SCR reactor with four catalyst layers. Catalyst elements are either of extruded type (top) or plate type (bottom).



Monolytic reactors:
SCR-DeNOx reactors (left) and
catalytic mufflers (right).

Temperature control in catalytic reactors.

In the most common case, the chemical reactor is fed with the reactant mixture previously pre-heated to allow the reaction rate be sufficiently high in all points of the reactor. The temperature limits (lower and higher) forecasted to be obtained in a working catalyst bed are determined either from the behaviour of the catalytic material itself, or by thermodynamics. The lowest temperature to which the bed is designed to work is that at which the minimum useful reaction rate is obtained. The highest temperature forecasted for the bed is frequently determined, to care of the thermal stability of the catalyst in the entire bed; in fact catalytic materials tend to lose progressively catalytic activity above an high temperature limit, due to starting of solid state phenomena, such as surface area loss by sintering, phase transitions, volatilization of some constituent, etc.. For exothermic reactions, the high temperature limit may also be determined by thermodynamics, that can become too un-favoured above a temperature limit.

Gas/solid and liquid/solid fixed bed reactors.

In the perhaps most simple case, heterogeneous catalysts are stored in one or more fixed beds in a tubular or multitubular reactor, the fluid reactant mixture being fed either axial downflow, axial upflow, radial and radial/axial. Normally, the axial flow causes more pressure losses while the he radial flow can give rise to preferential paths and may not allow the appropriate use of the first part of the catalytic bed . The reactor configuration strongly depends on the type of the reaction, with particular relation to the thermal and equilibrium behaviour and the optimal time of contact with the catalyst bed.

Adiabatic fixed-bed catalytic reactors.

Adiabatic reactors, i.e. fixed beds tubular reactors without any heating or cooling, are used for reactions having a small ΔH; in this case the actual temperatures in the bed does not bypasses the lower or the higher acceptable temperatures, for endothermic and exothermic reactions reactions, respectively, even without heat exchange. Heating and cooling can be performed before or after the adiabatic reactor. Several adiabatic reactors can be used in series with heating or cooling steps in between, to perform endothermic and exothermic reactions, respectively, and fulfilling both temperature limits in the beds and contact time requirements.

Heated fixed-bed reactors for gas / solid endothermic reactions.

For typical endothermic reactions, tubular reactors filled with the catalyst may be heated from outside in the radiant section of a combustion oven, such as the reformer furnace, where the tubes are located in a furnace with wall burners. Alternatively, the tubes may be heated by hot fluids, such as combustion gases in the convective section of a combustion oven. The tube diameter is thin, to limit temperature gradients, thus several tubes (sometimes hundreds) are needed for high productivities reactors.

Cooled fixed-bed reactors for gas/solid exothermic reactions.

Exothermic equilibrium reactions must be carried out at the lowest temperature made possible by the activity of the catalyst, because these are the conditions in which the equilibrium is more favourable. On the other hand the occurrence of the reaction causes the heating of the bed, thus heat must be subtracted to limit temperature raise. Also for exothermic non-equilibrium reactions sometimes cooling is needed to protect the catalyst from deactivation phenomena. Cooling may be performed within the reactor with several different configurations.

Heat exchangers can be placed between the beds, using cooling fluids such as water or using the cooler reactants allowing their needed preheating. In the case of radial flow reactors, inter-bed heat exchangers can be coaxial within the beds. Sometimes the heat exchangers are placed outside of the structure of the reactor, with the reactant mixture coming in and out the reactor each bed. Alternatively, direct cooling between the beds can be performed directly, by quenching with cooler reactant flows.

Another configuration is that of exchanger reactors. Gas cooled reactors, GCR , are denoted those reactor/heat exchangers where a coolant gas flows in tubes internal into the catalyst bed.

Water cooled reactors, WCR, also denotes as boiling water reactor, BWR, are those where the tubes containing the catalyst are in a bath containing flowing water converting into steam. So-called "isothermal" reactors have been recently developed by Linde, with the heat exchanger inside the bed made by helical coils, and by Casale with cooling elements in perforated vertical plates.

Exchangers/reactors usually denoted as “multitubular” reactors, are used for highly exothermic partial oxidation reactions where an impressively high number of very thin tubes (up to 30000, 1 inch diameter, tubes) are in contact with a bath where gasoils or inorganic liquid eutectics cool them.

Cooled fixed-bed reactors for liquid/solid exothermic reactions.

Exothermic equilibrium reactions can also be performed in the liquid phase. To perform liquid phase exothermic reactions fixed bed reactors can be used. Also in this case, cooling can be performed by inter-bed heat exchange with cooling fluids such as water, or by inter-bed quenching with cool reactants. Alternatively, multitubular exchanger - reactors can be applied.

Catalytic distillation reactors.

Catalytic distillation reactors are distillation towers one section of that is packed with the catalyst. Reactants are fed to the tower and products, formed in the catalytic section, are separated simultaneously each other or from reactants by distillation. Among other advantages, this may allow to remove thermodynamic limitations in several equilibrium reactions.

Monolithic reactors.

Monolithic reactors are used when minimum pressure drops and high reactant flow rates are needed. The catalyst is deposed as a thin layer on the surface of solid structures such as ceramic filters made of cordierite, such as in most cases catalytic converters for cars and Diesel oxidation catalysts, honeycomb monoliths made of TiO_2, metal plates over which an oxide layer is deposed or formed chemically or electrochemically. Over these systems both exothermal and endothermal reactions can be performed, reaction temperature being controlled by controlling the feed flow rate. Catalytic burners are usually monolytic, in this case strongly exothermic reaction occurs. Similarly, metal monoliths such as metal gauze pads are used as the catalyst bed for some highly exothermic reactions.

Catalytic membrane reactors.

As for catalytic distillation, also catalytic membrane reactors combine a catalytic reaction with separation, thus allowing to remove thermodynamic constraints in equilibrium reactions. In fact, selective membranes allow one of the products to come out from the reactor thus subtracting itself from equilibrium. A typical application is that of dehydrogenation reaction, using membranes allowing the separation of hydrogen. Otherwise, the evolution of oxygen, when it is a reaction product, allows improvements e.g. in N_2O decomposition reaction.

Another interesting application is the use of “dense oxygen permeable membrane reactor” where an oxygen permeable membrane allows to feed a tuned amount of oxygen, coming from air, in the reaction chamber to feed partial oxidation reaction.

Gas/solid fluidized and transported bed reactors.

Powder beds can become “fluidized” when a fluid flow passes through it with a sufficiently high flow rate to expand it and powder grains move in a dynamic fluid-like state.

Fluid bed reactors are applied to some exothermal selective oxidation reactions, such as the maleic anhydride synthesis from n-butane air oxidation, where air or oxygen are fed from below to a large reservoir containing the catalyst powder. These reactors are cooled internally by serpentines. The resulting temperature gradients are small and there are basically not hot-spots, thus allowing an excellent temperature control. Additionally charge of the catalysts to the reactor is easy, thus time for catalyst change is fast. However, there is a great remixing and back-diffusion of reaction products which largely cancels the advantage of the better temperature control. On the other hand, since the fluid bed provides a barrier to the flame, it is possible to operate with higher concentrations of the substrate, thus entering safely in the region of explosiveness addressing faster reaction rate conditions. Gas-phase low-pressure bulk polymerization of ethylene and propylene is commonly performed in gas phase reactors, but in this case the polymer grows on the catalyst particles and the catalyst is consumed with the product thus being continuously fed.

Raiser reactors, Circulating Fluidized Bed (CFB) and loop reactors

Fluidized catalyst beds can be transported along cyclic reactor systems, usually called Circulating Fluidized Bed (CFB) reactors. In most cases the reaction occurs in columns, said “raisers”, which are “transport bed” reactors i.e. tubes where the catalyst moves up-flow pushed by and together the fluid feed. In the upper part of the riser there is a cyclone which allows the separation of the catalyst from the fluid products. The catalyst, usually deactivated, moves then in a regenerator reactor to be later fed again to the raiser. This continuous circulating system is used for fluid catalytic cracking as well as for paraffins dehydrogenation: in this case the catalyst is deactivated by coking in the riser and is regenerated by coke combustion in a fluid bed regenerator. From the regenerator the cleaned catalyst moves back to the base of the raiser. A similar system has been developed for partial oxidation: the catalyst reacts in the raiser with the substrate, and oxidizes it becoming reduced. The catalyst is reoxidized by oxygen in the regenerator and comes back to the raiser.

Similar systems can also be applied in solid-liquid slurry conditions. This is the case of slurry loop polymerization reactors, using Ziegler-Natta or Phillips-type solid catalysts, where reaction occurs, in different conditions, in the raiser but also in the downer.

Slurry liquid/solid and gas/liquid/solid reactors.

Besides the cited loop reactors, a number of different reactors can be applied to liquid/solid and gas/liquid/solid slurries such as e.g. those can be applied to the Fischer Tropsch synthesis. The most common reactors for slurry reaction conditions are the Continuously Stirred Tank Reactors (CSTR) whose temperature may be controlled by external jackets or internal coils, or even by evaporation or boiling /re-condensation of the most volatile components or finally with external cycling to heat exchangers. Analogous batch tank reactors may be used.

Fluid bed or ebullating bed reactors can also be used, where fluidization or ebullition is provided by the liquid feed entering the reaction from the bottom.

2.2 Deactivation and regeneration of heterogeneous catalysts.

Conditioning and deactivation of catalysts

In few cases, catalyst may increase their activity at the beginning of their use. This is sometimes called “conditioning”. More frequently, instead, catalysts tend to lose activity with time on stream, down to a limit where their prolonged use is antieconomic.

There are several reasons for deactivation. In some cases the catalyst can be regenerated (reversible deactivation), in other cases deactivation is irreversible. .

Poisoning.

Deactivation is sometimes due to the deposition (usually from the feed) of contaminants that modify the structure of the catalyst converting the active phase in an inactive form. Sulphur poisoning is a typical deactivation phenomenon for metal hydrogenation catalysts such as those based on Ni and noble metals. Metal catalysts are also poisoned by chlorine compounds, nitrogen compounds or oxygen compounds including water. Similarly, acid catalysts (ex. zeolites) are deactivated by adsorption of basic compounds (amines, nitriles), but can be regenerated by desorption or washing.

Irreversible poisoning occurs when the contaminant cannot be practically removed. This is the case, e.g. for lead coming from gasoline poisoning platinum present in catalytic converters, because of the formation of inert Pt-Pb alloy.

Coking.

The thermodynamic instability of hydrocarbons in reducing environment is the cause of one of the most common deactivation phenomenon occurring with solid catalysts: coking.

Due to the negative ΔS_{form}, the hydrocarbons (except acetylene) become less stable, with respect to the elements, i.e. hydrogen and carbon, above a certain temperature limit. Coking may be considered as the reverse reaction of the formation of hydrocarbons, and is consequently thermodynamically favored at T > 200 °C for all hydrocarbons except methane. Thus, carbonaceous materials, denoted sometimes roughly as “coke”, may form on the surface of catalysts upon high temperature contact with hydrocarbons. This phenomenon results in catalyst deactivation. Most of solid acid-catalyzed processes for hydrocarbon conversion are influenced by the occurrence of catalyst coking and the need of frequent catalyst regeneration.

In some cases particular forms of carbon are produced, such as carbon nanotubes (whiskers) produced on Ni catalysts. In this case, before real deactivation phenomena, filling of void volume by carbon whiskers results in enhancement of pressure drop.

Sintering.

Deactivation may come from the loss of the active surface area resulting from sintering of the active phase. Typically, supported metal nanoparticles can coalesce thus producing larger particles with smaller surface areas as well as smaller adensity of defects (corners edges) that can act as active sites.

Phase transitions and solid state reactions.

Phase transitions of the components may also be the cause of deactivation. Typically, the phase transitions of anatase to rutile is a main cause of deactivation of V_2O_5-TiO_2 oxidation catalysts, while the volatilization of MoO_3 is a main cause of deactivation of metal molybdates or MoO_3-containing catalysts. The formation of the $CuAl_2O_4$ spinel is a main deactivation cause of Cu/Al_2O_3 hydrogenation and dehydrogenation catalysts.

Breaking of extrudates.

As said, catalysts are shaped in the form of extrudates to limit pressure drop and to improve heat transfer. Catalysts for use in fluidized beds are also formed to produce fluidizable powders. In the case of fixed bed, under use (sometimes under pressure and high temperature), the extrudates can progressively crunch, thus reproducing fine powders. This matter tend to obstacle the reactants flow, plugging it, thus resulting in increased pressure drop. This phenomenon can progressively grow finally coming to unacceptable pressure drops.

Fluidized bed matter can also undergo erosion, also producing fine powders that will finally be transported out from the reactor.

Erosion or breaking of monoliths.

Monolitic catalysts can be submitted to flows containing powder matter, such as soot from Diesel engines and ash from coal combustion or gasification. The catalyst layer can be damaged, the active phase being lost.

Regeneration of reversibly deactivated catalysts

Deactivation by solid state reaction, phase transition, volatilization, breaking and pulverization of the extrudates, erosion, cannot generally be contrasted. After the catalyst activity slowed down to a given extent, the catalyst must be replaced. In contrast, coking and poisoning can usually be contrasted, submitting the deactivated catalyst to some regeneration procedure.

Burning of coke.

Coked catalysts can be usually regenerated by burning coke. Sometimes, trace amount of noble metals are introduced into the catalyst just to favour coke burning. Sometimes burning of coke can also be used to provide reaction heat just by heating the catalyst, like it occurs in the Fluid Catalytic Cracking process, thus converting the process from endothermic to autothermic. In this case, however, a non- negligible fraction of organic reactants is lost, being converted into coke first and carbon oxides later.

Hydrogenation.

Hydrogenation of carbonaceous materials is sometimes used to regenerate catalyst. However, most frequently hydrogenation is used to limit coking. For this reasons, some acid-catalyzed reaction are performed under hydrogen in the presence of trace amounts of noble metals. In this conditions, coke precursors are hydrogenated.

Washing or rejuvenation.

Some catalysts can be regenerated or rejuvenated by washing. This is the case, e.g. of solid catalysts for isobutane/isobutene alkylation, which are washed by liquid isobutane/hydrogen to remove carbonaceous matter. Similarly, polymeric catalysts such as sulphonic acid resins, used mostly in liquid phase reactions, are frequently poisoned by basic organic molecules as well as by metal cationic species coming with the feed. Rejuvenation can be obtained by washing with opportune solvents.

Steaming.

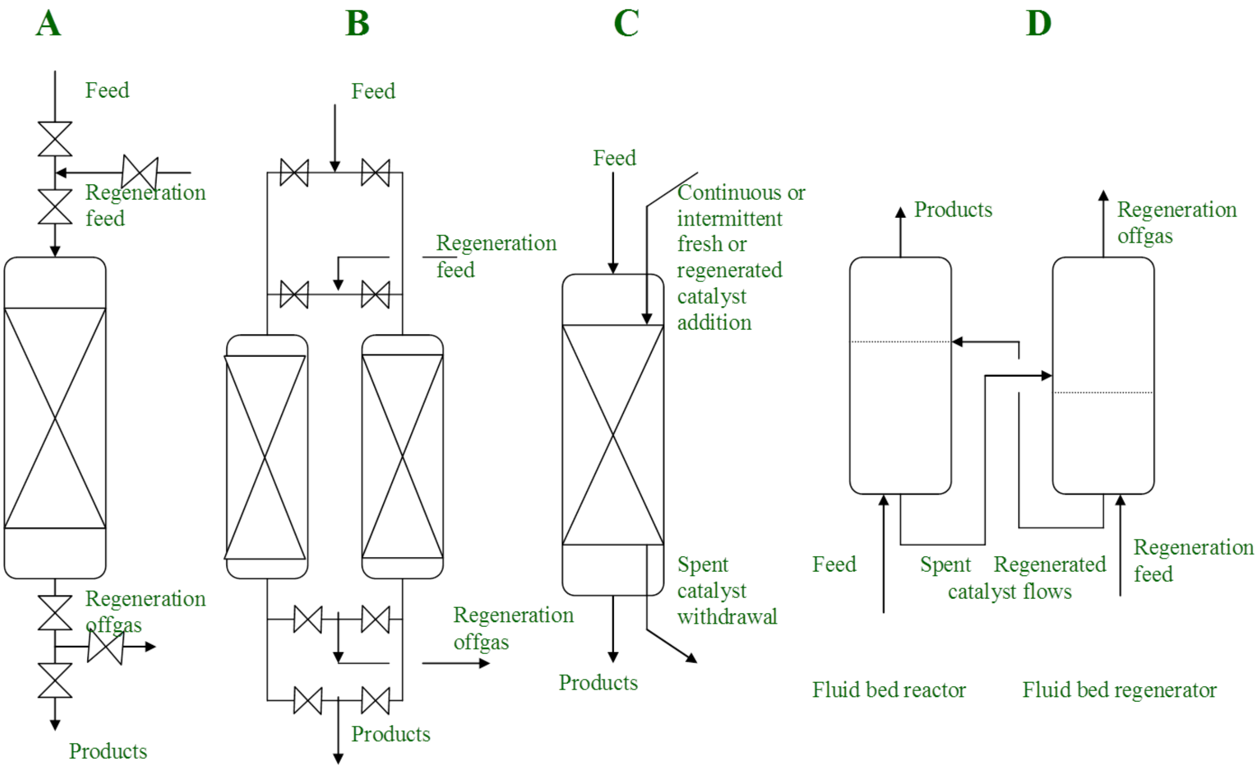
Steaming is a possible regeneration procedure, used e.g. to reduce sulphur poisoning of nickel steam reforming catalysts. This treatment also possibly allows restructuring of nichel with recovery of activity also reduced by sintering.

Regeneration of catalysts and the reactors.

Different reactivation procedures are possible, depending on the rate of catalyst deactivation. The schematics of the plants, depending on the different regeneration procedures, are reported in the figure. When deactivation occurs in years, reactivation might not be necessary at all. The catalyst might be substituted after his cycle life or regenerated *in situ*, during a normal switch off of the plant for maintenace, can be performed. Alternatively, during maintenance times, the catalyst may be removed, reactivated *ex situ* elsewhere and reloaded in the reactor.

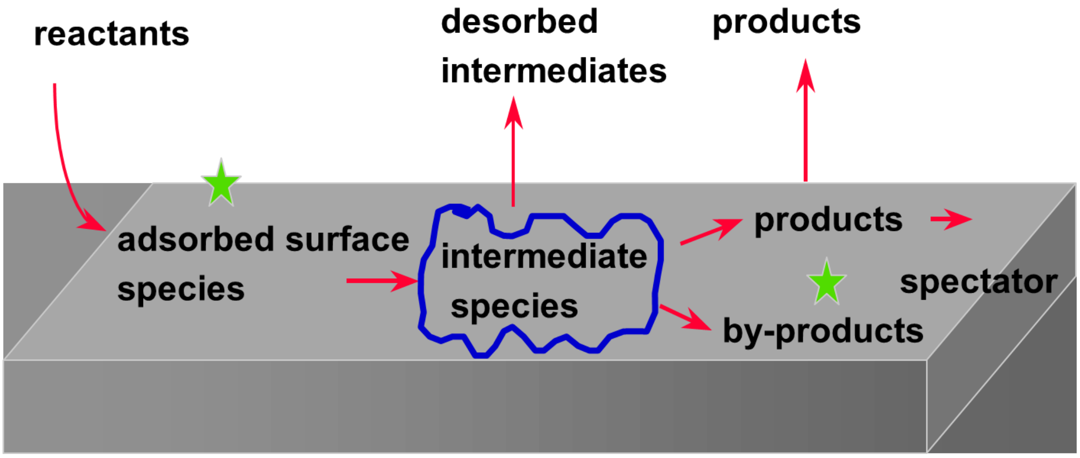
When deactivation occurs in mounths or weeks, swing-type regeneration may be performed. An additional reactor may be used (two instead of one or five instead of four) and the reactor beds may be regenerated alternatively, allowing a continuous operation of the plant. This is applied, e.g., in the cyclic catalytic reforming process, as well as in several gas-phase acid-catalyzed processes. When deactivation is even fast, moving bed reactors with intermittent or continuous addition of active catalyst and withdrawal of deactivated catalyst may be applied. This is applied in the moving bed continuous regeneration catalytic reforming processes as well as in hydrocracking in slurry ebullated beds.

In the case of very fast deactivation by coking, occurring in minutes, continuously circulating fluid beds are used. The fluid bed catalyst may recycle from the reactor to the regeneration vessel where coke burning occurs heating strongly the catalyst itself, and in this way it may provide the heat of reaction. This system has been developed for Fluid Catalytic Cracking processes (FCC) and has also been used in the paraffin dehydrogenation.



2.3 General mechanisms in heterogeneous catalysis.

As said, a catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules (in the case of heterogeneous catalysis, by adsorption), such that they are “activated”. They can thus react to produce a particular product, which detaches itself from the catalyst (i.e. desorption), and leaves the catalyst unaltered so that it is ready to interact with the next set of molecules. In fact, we can describe the catalytic reaction as a cyclic (turnover) event in which the catalyst participates and is recovered in its original form at the end of the cycle.



Catalytic materials can be roughly divided into two families:

a) Bulk catalytic materials.

b) Supported catalytic materials.

Supported catalysts are mostly defined those where a pre-synthesized carrier materials is used to depose on it a thin layer or the “active phase, or nanoparticles or even, some times, isolated complexes or clusters or atoms. Supported catalysts are usually intended as those the nature of the support influences the morphological properties and, frequently, also the chemical properties of the supported phase, thus participating to the generation of the catalytic properties of the pverall catalyst.

However, in the practical industrial work low-surface area ceramic supports (such as corundum powders, carborundum powders, cordierite monolyts) are sometimes used to support a bulk catalyst. In this case, where big particles or porous thick layers of a “bulk” catalyst are physically deposed on ceramic supports, the support plays a determinant role in heat transfer and flow-dynamics of the system, without exerting a definite role in the chemical - catalytic behaviour of the material. Thus, the term “support” is somehow ambiguous.

Preparation procedures of catalyst powders may differ significantly between supported and unsupported bulk catalysts. However, for most sophisticated materials several components can be included in catalyst formulations using techniques typical for both supported and bulk materials preparation.

In fact, in a typical catalytic materials a number of components can be included. They are:

a) The active phase, supposed to be that responsible for the rate determinant catalytic act.

b) The support, if needed to produce optimal activity of the active phase and optimal morphology and surface area, with optimization sometimes also of heat transfer and flow-dynamics aspects.

c) Promoters, that can further improve the catalytic activity.

d) Stabilizers, which stabilize the catalyst from a number of possible deactivation phenomena, such as stabilizers from sintering, from phase transformation, from coke deposits formation, from active phase volatilization, etc.

3. **Acid Catalysts in the Industrial Chemistry.**

Definitions of acidity and basicity

1884, S.A., Arrhenius, Nobel prize for Chemistry in 1903,

$HA \rightarrow H^+ + A^-$ acid: release of a proton

$BOH \rightarrow B^+ + OH^-$ base: release of an hydroxide ion

1923, J.M. Brønsted and T.M. Lowry

$HA + B = A^- + HB^+$ acid-base: exchange of protons

acid: release of a proton

base: bonds with a proton

1923, G.N. Lewis

$B: + A = {}^{\delta+}B \rightarrow A^{\delta-}$ acid: available empty orbital

base: available doublet of electrons

The so called Brønsted acids and also the so called Lewis acids catalyse many reactions of industrial relevance, as bases also do.

Reactant activation and acid-base catalysis in diluted water solutions.

Acid and bases may act as catalysts when they perturb reactant molecules thus offering to a reactant species a different way to evolve towards products associated to a lower activation energy. In this case, the reaction may occur faster. Many reactions involving polar molecules may be performed in water solutions and may be catalyzed by acids or by bases or by both. It is well known that, in several cases, polar molecules (which present both a negatively charged and a positively charged pole) can be activated both by bases (by interaction with the positively charged pole) and by acids (by interaction with the negatively charged pole. In the industry, the cheaper acids and bases are obviously preferred as catalysts, sulphuric acid and caustic soda being the most commonly used.

Activation of weak basic molecules by acids.

Typical basic species have electron pairs in non-bonding (n-) orbitals. These “doublets” can be used to produce a dative bond with species having empty orbitals, such as protons or coordinatively unsaturated cations. They are consequently denoted as n-bases. Such a n-type basic molecules can be activated by protic acids, mostly used in water solution, or by Lewis acids, which can be used in both water solutions and in non protic solvents. The protonation of the coordination of lone pairs perturbs the nearest bonds inducing, e.g. nucleophylic attacks by other reactant species. This is, e.g., the case of rections such as etherifications and esterifications, where both Bronsted and Lewis acid catalysts can be use to attack the most basic oxygen atoms of the reactants.

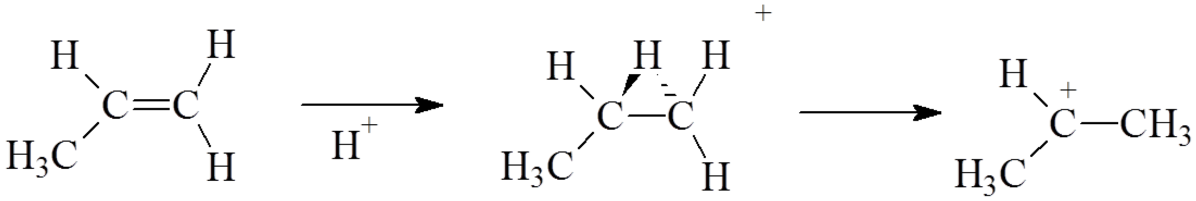
However, Brønsted and Lewis acid catalysis also occurs with molecules not containing non-bonding orbitals such as hydrocarbons. The ability of hydrocarbons (which do not have n-orbitals) to interact with protic acids has been recognized long ago. In fact, paraffins give rise to weak hydrogen bonding interactions with hydroxyls having some acidity, such as those of alcohols, carboxuylic acids and also surface silanols of silica. At higher temperature or in the presence of very strong acidity these interactions can produce a true proton transfer, thus hydrocarbons acting as Brønsted bases. In the Table the proton affinity scale of some hydrocarbons is reported. The proton affinity is the measure of the heat evolved by interaction with H^+ in the gas phase and is currently used as a measure of vthe absolute basicity of molecules.

Proton affinities (kJ/mol) of hydrocarbons and of ammonia for comparison
(from NIST database).

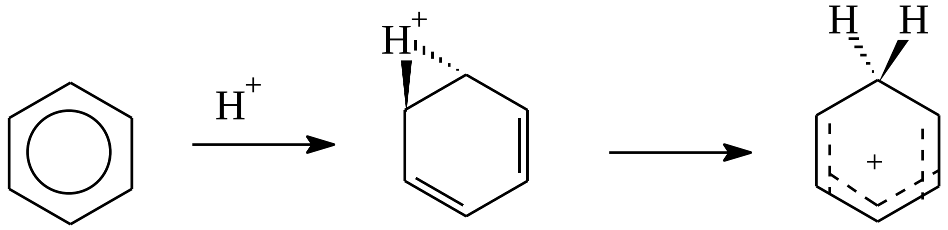
Ammonia	846.0	n-bases
Isobutylene	802.1	π - bases
Toluene	784.0	
1,3-butadiene	783,4	
Propylene	751.6	
Benzene	750.4	
Ethylene	680.5	
Isobutane	677,8	σ– bases
Propane	625,7	
Ethane	596,3	
Methane	543,5	

The PA data follow the trend: π-orbital containing compounds (olefins and aromatics) > isoalkanes > n-alkanes > methane.

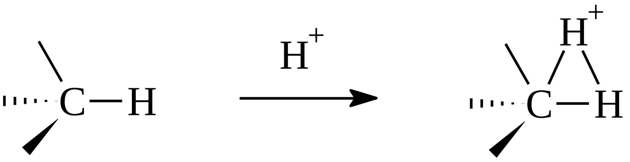
Olefins can react with protic acids and can produce the so-called trivalent “classical” carbocations (carbenium ions) as intermediates of electrophylic addition reactions. The history of carbocations, which are intermediates also in nucleophylic sostitution reactions (SN_1) and in elimination reactions (E_1), begins at the end of the XIX century, and involves very distinguished organic chemists such as Meerwein, Ingold, Whitmore, and many others. The reactivity of olefins, through their π-type orbitals, towards protons is evidence of the so-called π-basicity of these compounds, probably first proposed by M.J. Dewar in 1946. The result of this interaction, with the intermediacy of protonated π-bonded transition state, is the formation of carbenium ions, where the π-type orbitals disappear and one of carbon atoms rehybridizes from sp_2 to sp_3, the hydrogen becoming covalently bonded to the carbon atom via a σ-bond. The carbenium ions are more stable and more easily formed on tertiary carbon atoms, while their formation on primary carbon atoms is very difficult. This is associated to the electron-donating properties of alkyl groups that allow the cationic charge to be delocalized, thus stabilizing the cation.

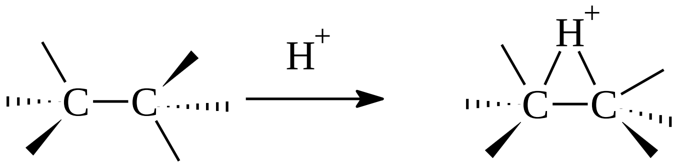


The π-basicity of aromatic hydrocarbons was also observed long ago and the existence of quite stable protonated forms of benzenes and the methyl substituent effects on them was determined. Protonation of aromatic rings generates arenium ions whose cationic charge is delocalized on the ring and in particular in the ortho and para position with respect to the position where the attack of the electrophile (the proton in this case) occurred.



More recently, in 1967, George Olah (Nobel prize for Chemistry in 1994) and Hogeveen et al. for the first time observed the protonation of alkanes by superacids, thus suggesting that alkanes may behave as σ-bases.





The basicity scale for σ-bonds of hydrocarbons is reported to be tert-C-H > C-C > sec-C-H > prim-C-H > CH_4, although this depends also on the protonating agent and the steric hindrance of the hydrocarbons. In fact, protonation at C-C bond may be significantly affected by steric hindrance. Protonation of alkanes generates the so called “non-classical” pentacoordinated carbonium ions, which contain five-coordinated (or higher) carbon atoms.

The carbocations, which may be stabilized by solvation, are more o less stable species and may act as intermediate species or as transition states in the conversion of hydrocarbons. In this case the acid is regenerated after the completion of the reaction and acts consequently as a catalyst. Many of the hydrocarbon conversion industrial processes are acid catalysed and the formation of carbenium and carbonium ions is one of the steps in the reaction mechanism, both over liquid and over solid acid catalysts.

Liquid phase Brønsted acid catalysts in the industry.

A very large number of liquids and solutions have been tested as acid catalysts for hydrocarbon conversion in the academic research. Clearly, only few of them found a real industrial application, due to their superior properties as well as for economic reasons. Liquid acid catalysts may offer some advantages with respect solid acids, such as high activity and selectivity at low temperature, low investment costs and better flexibility.

Eventual drawbacks are related to difficult and expensive product/catalyst separation, loss of the catalyst, as well as safety and environmental concerns.

Sulphuric acid

Sulphuric acid is a strong diprotic acid in diluted water solutions ($K_{a1} \sim 10^2$, $K_{a2} = 1.2\ 10^{-2}$). H_2SO_4 is an intermediate compound in the SO_3-H_2O system. This system presents a maximum azeotrope boiling at 339 °C with composition 98.3 % wt H_2SO_4 : 1.7 % H_2O. Pure H_2SO_4 is a dense liquid (d = 1.8356) reported to boil at 279,6 °C. SO_3 is soluble in H_2SO_4 producing "oleum", the solutions of SO_3 in H_2SO_4. By reaction of SO_3 with H_2SO_4 disulfuric acid $H_2S_2O_7$ is formed, which corresponds to 44.9 % wt oleum, and is a superacid, with H_0 of –15.

Industrial processes for hydrocarbon conversion may employ highly concentrated H_2SO_4 solutions (> 40 % wt) up to azeotropic or pure H_2SO_4. Oleums are mostly used for sulphonations. Concentrated sulphuric acid, with compositions generally close to the azeotrope or a little less (90-99 %), is a stable solution with high density (d ~ 1.8 depending on the concentration and temperature) and low volatility (vapour pressure 10^{-1}-10^{-3} mbar, mostly due to water vapour). While for some reactions, the processes based on sulphuric acid have been substituted by more performant and environmentally friendly processes based on other catalysts several processes based on sulphuric acid are still used worldwide.

A main drawback of the use of concentrated sulphuric acid is related to the difficulty in its regeneration, purification and concentration. For this reason, spent acid may be disposed and stored in spent acid tanks: its consumption can be as high as 70-100 kg of acid/ton of alkylates in the case of isobutane / butylenes alkylation. Reconcentration of sulphuric acid is very demanding Additional difficulties are associated to the corrosive behaviour of sulphuric acid, which imposes the use of lead, tantalum and Al alloys for reactors and distillation towers, as well as the potentially unsafe disposal of the spent acid .

Hydrofluoric acid

Hydrofluoric acid is a weak acid in water solution ($K_{aq} = 2 - 7\ 10^{-4}$). Its acidity increases as a function of its concentration because of the increased stabilization of the F^- anion when its surroundings become more ionic. The HF-water system presents a maximum azeotrope at 38.26 % vol of HF. The solution has a maximum density around 70 % HF (d ~ 1.27 at 0°C). At increasing HF concentration, density decreases and vapour pressure increases. Pure anhydrous hydrofluoric acid HF, characterized by a density of 0,97, condensates at 1 atm at 19.5 °C forming H-bonded "polymeric" chains $(HF)_n$. The extent of H-bonding at the liquid-vapor equilibrium at 1 atm is limited to n = 3,75 corresponding to a molecular mass of 74.9. As a pure liquid it is a superacid, its acidity being only slightly lower in presence of traces of water.

The acidity of HF is further enhanced by its combination with Lewis acids such as SbF_5. The system HF/SbF_5 is considered to be strongest known. In this system the formation of solvated H_2F^+ ions ($H_2F^+(HF)_n$) and of solvated anions such as $Sb_2F_{11}^-$ and $Sb_3F_{15}^-$ tend to increase the acidity.

Characteristics of some industrial conversion processes involving sulfuric acid catalysts.

Products / Process	Protonated species	H_2SO_4 conc.	T	P	Reactor type
cellulose hydrolysis to glucose “diluted acid process”	cellulose	0.5 %	150-250 °C	1 MPa	continuous reactors
ethylene glicol synthesis	ethylene oxide	1 %	50-70 °C	0.1 MPa	tank reactor
phenol and acetone synthesis	cumene hydroperoxide	Few %			backmixed reactor
i-butylene hydration to tert-butanol	i-butylene	50 %	50 °C	0.4-0.5 MPa	wash towers
propylene indirect hydration to 2-propanol	propylene	60 %	75-85 °C	0.6-1 MPa	wash towers
i-butylene oligomerization	i-butylene	60-65 %	20-25 °C		
cellulose hydrolysis to glucose “concentrated acid process”	cellulose	72 %	30-55 °C		batch reactors
benzene alkylation to cumene	propylene	90%	35-40 °C	1,15 MPa	stirred tank
methyl acetate synthesis	acetic acid	> 90 %	55-100°C	0.1 MPa	reactive distillation tower
ethylene indirect hydration to ethanol	ethylene	94-98 %	65-85 °C	1-3.5 MPa	wash towers
i-butane / butylene alkylation	i-butylene	90-98 %	20-40 °C	0.3-0.5 MPa	orizontal stirred tank contactor or cascade reactor
Linear alkylbenzenes	linear higher olefins	96-98%	10-30 °C		stirred tank-type

.

Since decades HF is largely used in the refinery industry as the catalyst of the isobutane/butylene alkylation process and in the petrochemical industry for benzene alkylation processes such as the synthesis of LABs (linear alkylbenzenes) and of cumene. For the synthesis of LABs, the liquid feed contains about 79 % HF. The reaction temperature is very low, 0-10 °C, at ambient pressure with a large excess of benzene (4-10 mol benzene/olefin). For isobutane / butylene alkylation with the ConocoPhillips process, the reaction temperature is 25 °C, molar isobutane / alkene ratios are about 14–15, and acid concentrations of 86–92 wt%. After reaction, occurring in a riser, the HF fase is separated from the hydrocarbon phase in a settler, cooled by heat exchange with water, and recycled to the reactor. However, Acid Soluble Oils are formed and dilute the catalyst. A strong advantage of HF with respect to H_2SO_4 is its easy separation and purification by distillation, due to its very high volatility. Accordingly the acid loss is very small.

The main drawback in its use is related to safety concerns, due to its toxicity coupled with its volatility, with the possible formation of toxic aerosol clouds. A strategy to limit this drawback consists in the use of a vapor suppression additive. HF makes less volatile complexes with n-donor bases, such as the pyridinium poly(hydrogen fluoride) reagent. ConocoPhillips together with Mobil developed an HF modified technology named ReVape. The additive is most likely based on sulfones.

Friedel - Crafts type catalysts.

Aluminum trichloride, $AlCl_3$, has been proposed as a catalyst for aromatic alkylation and acylation reactions by C. Friedel and J.M. Crafts at the end of the XIX century. It melts at 193 °C, producing a typical molecular liquid mostly composed by the dimer Al_2Cl_6 although higher polymers may also exist. It also produces several low temperature eutectics with other metal chlorides and gives rise to liquid complexes with hydrocarbons and ionic liquids with organohalide precursors. In the solutions, ionic species such as $AlCl_4^-$, $Al_2Cl_7^-$ or $Al_3Cl_{10}^-$ are formed. $AlCl_3$ is considered to be a very typical Lewis acid, according to the coordinative unsaturation of Al in the formal $AlCl_3$ monomeric molecule, which is saturated in the polymeric anions by very weak nucleophyle, the Cl^- anion. When additivated with proton donor species, such as water or HCl, or its precursors such as alkyl halides, alkyl amine salts, imidazolium halides, pyridinium halides, or phosphonium halides, $AlCl_3$ gives rise to the formation of ionic liquids with very strong Brønsted superacidity, whose strength evaluated to be similar to that of dry HF. These are very active as aromatic alkylation catalysts. The strong Brønsted acidity of this system, which allows olefins protonation, can be cooperatively enhanced by the Lewis acidity of $AlCl_3$, able to interact with and activate aromatic rings. The electrophilic character of the carbenium ion is enhanced by complexation of the halide to a Lewis acid such as Al_2Cl_6, allowing it to leave as a less nucleophilic anion such as $Al_2Cl_7^-$.

Systems based on $AlCl_3$ and HCl have been used since the forty's in the industry for liquid phase aromatic alkylations such as ethylbenzene synthesis from ethylene and benzene, several plants being still in operation. In the original process, the reaction temperature is 130 °C, pressure 2-4 bar. An improved process has been commercialised from Monsanto in the seventies: slight increase in reaction pressure (up tp 10 bar) and temperature (160 °C) and a careful drying of the reactants allows the use of less catalyst and improves the process in terms of energy and acid consumptions

With the same catalyst, cumene and linear higher alkylbenzenes (LAB) for the detergents industry may be produced through benzene alkylation by propene (110 °C) and by linear higher olefins (55- 60 °C). Several other reactions are catalysed by similar systems such as e.g. the Gattermann-Koch carbonylation of toluene producing para-tolualdehyde (Mitsubishi process) using either HF/BF_3 or an aluminum halide alkyl pyridinium halide ionic liquid catalyst. The system HF/BF_3 is also used in the Mitsubishi process for the separation of m-xylene from C8 aromatic mixture. The acid forms the complex preferentially with the more basic m-xylene isomer.

Main problems to these processes are represented by the requirement of reactors made in anti-corrosion materials (ceramics, enamels. glasses), corrosion of piping, non regenerability of the catalysts and problems on disposal of the spent catalyst. Classical Friedel Crafts catalysts present problems in their separation from the products.

Solid acid catalysts.

Solids may present, at their surface, both Brønsted acidity (active protons) and Lewis acidity (coordinatively unsaturated cationic centers) and basicity as well (active oxide anions or other electron rich species).

Strength, amount, and distribution of surface acid sites on the ideal surface of a solid.

In heterogeneous catalysis, the catalytic activity (reaction rate) depends on the amount of active sites (e.g. of acid sites having the appropriate strength) present on the catalyst as a whole. This means that the “density” of active sites (amount of sites per gram of the solid or per unit surface area), is an important parameter. On solids, amount and strength of acid or basic sites are quite independent parameters, so both of them must be analysed independently for a complete characterisation. Additionally, several different families of acid sites may occur in the same solid surface, so their “distribution” (density of sites of any site family) must be characterised.

Additionally, both acidic and basic sites can be present in different position (but frequently near each other) on the same solid surface, and can work synergistically. This provides evidence for the significant complexity of acid-base characterisation of solids.

Surface of solid catalysts.

The surface of solid catalysts is formed by the extended surfaces, defects, edges, corners. It is likely that in most cases the most reactive and active sites are just the most defective.

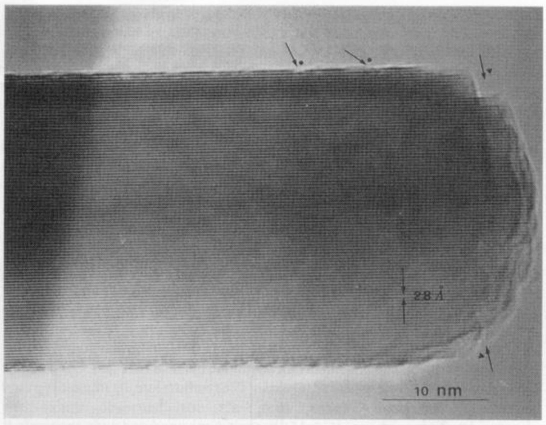
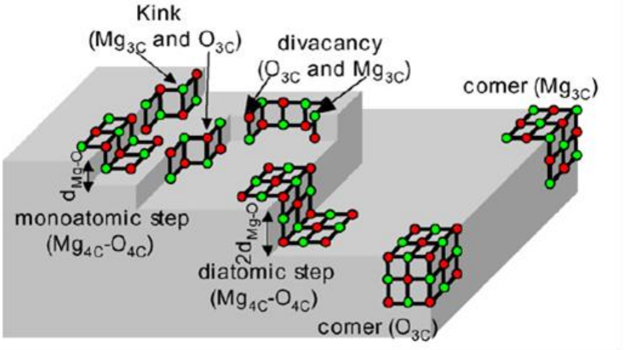


FIG. 14. HRTEM image of a ZnO microcrystal, where $(10\bar{1}0)$ planes are evident. The arrows show the presence of terraces and steps along the prismatic direction and many small facets (having the same symmetry as the predominant one) at the prism terminations [reproduced from Scarano *et al.* (*394*) with permission of Elsevier Science Publishers].



Metal oxides as typical acido-basic catalysts.

Metal and semimetal oxides are among the most used materials in catalysis, as catalysts as well as catalysts supports. One of the reasons is that oxygen is the most electronegative element besides fluorine. Thus, the metal-oxygen bond is the most ionic bond between e metal and a non metal element. Ionici of the bond results in Lewis acidity ofv the cations and basicity of the anion. The balance between Lewis acidity and basicity mostly depends on the size (the radius, r) and charge (C) of the cation, i.e. in its polarizing power (either C/r or C/r^2). The smaller and the more charged the cation, the more its polarizing power, i.e. its electronwithdrawing power and, consequently, its Lewis acidty. As a results, the surface Lewis acidity increases and the surface basicity decreases. In contrast, the larger and the less charged the cation, the weaker is its lewis acidity and, consequently, the stronger the basicity of the oxide anions which are less bonded to the cations.

The semimetal elements (such as B, Si) or the non-metal elements (e.g. P) give rise to non-ionic bonds with oxygen being their electronegativity higher with respect to metals. In other words, cations that they “formally” form are very small and very highly polarizing, so polarizing that they bond with oxygen becomes covalent. Thus the Lewis acidity and basicity disappear. This also occurs with metallic elements in very high oxidation state, such as Os^{VIII+}, Mn^{VII+}, Re^{VII+}, Cr^{VI+}, Mo^{VI+}, W^{VI+}, V^{V+}, Nb^{V+} and Ta^{V+}. These ions give rise to essentially covalent bonds with oxygen. In these cases however, the cations have variable coordination state and Lewis acidity can also be present.

Typical solid acids used in the industry

	Furmula/example	Acid group / Catalytic active species	Reaction (ex.)	Phase	Typical T range °C	Deactivation	Reactivation
Alumina (silicated)	Al_2O_3 $Al_{2-x}Si_xO_{3+x/2}$	AlOH or Al-OH-Al (SiOH) Al^{3+}	Olefin skeletal isom. Alcohol dehydration	Gas /solid	> 400	coking	burning
Silicalite-1	SiO_2	SiOH	Beckmann rearrangment of cyclohexanone-oxime	Gas/solid	300	Coking/tar formation	burning
Chlorided Alumina	$Al_2O_{3-x}Cl_{2x}$	Cl_xAlOH Al^{3+}	Paraffin isomerization Aliphatic alkylation	Gas/solid Liquid/solid	120-200	Chlorine loss Coking Coking/poisoning	difficult washing
Acid-treated montmorillonite clays	$Na_x[Al_{2-x}Mg_xSi_4O_{10}(OH)_2]$. n H_2O	SiOH Al^{3+}	Cracking	Gas/solid (Liquid/solid)	200-550	Coking Structural damage	burning
Silica-alumina / aluminated silica	$H_ySi_{1-x}Al_xO_{2-x/2+2y}$	SiOH	Cracking Dehydrochlorination Alkylation	Gas/solid Liquid/solid	200-550 200	Coking	burning
Zeolites	$H_xSi_{1-x}Al_xO_2$	Si-OH-Al	Aromatics alkylation Paraffin and olefin isomerization, Cracking Aromatics alkylation	Gas/solid Liquid/solid	200-550 150-250	Coking Structural collapse Poisoning	Burning, hydrogenation Burning
SAPO	$H_{x-y}Si_{1-x-y}P_yAl_xO_2$	Si-OH-Al	Methanol to olefins	Gas/solid	400-450	Coking	Burning
Sulphated zirconia	H_2SO_4-ZrO_2	SOH	Paraffin isomerization	Gas/solid	170-230	Coking	difficult
Tungstated zirconia	WO_3-ZrO_2	WOH	Paraffin isomerization	Gas/solid	200-270	Coking	Burning
Solid phosphoric acid	H_3PO_4/SiO_2 (kiselghur)	POH $[H(H_2O)_n]^+$	Olefin oligomerization and hydration Aromatics alkulation	Gas/solid	150-300	Leaching coking	difficult
Heteropolyacid	$Cs_xH_{3-x}PW_{12}O_{40}$.	W-OH-W $[H(H_2O)_n]^+$	Ethylacetate synthesis	Gas/solid Liquid/solid	140-250 60		difficult
Niobic acid	Nb_2O_5 . n H_2O	NbOH $[H(H_2O)_n]^+$	Ethylene hydration Fructose dehydration	Gas/solid Water/solid	200 100	Coking	burning
Sulphonated polystyrene-polydivinylbenzene resins		$-SO_3H$ $[H(H_2O)_n]^+$ $[H(ROH)]^+$	Ether synthesis Olefin oligomerization	Liquid/solid	40-100	Poisoning	Washing

Summary of the acid-base properties of binary metal oxides

Element	Oxidation state	Cation size (radius, Å)	Polarizing power range		M-O bond nature	% ionicity	Acidity type	Acidity strength	Basicity,	Examples
			C/r	C/r^2					Nucleophilicity	
Semi-metal	≥ +5	Very small ≤ 0.2	> 25	> 60	Covalent molecular	< 30	Brønsted	Medium-strong	None	P_2O_5 (SO_3)
	+3, +4	Small ≤ 0.4	> 10	25-60	Covalent network			Medium-weak		SiO_2, GeO_2 (B_2O_3)
Metal	High +5 - +7	Small to medium 0.3-0.7	> 8	12-35	Largely covalent Network → layered → polymeric		Brønsted Lewis	Medium to strong		WO_3, MoO_3, CrO_3, Ta_2O_5, Nb_2O_5, V_2O_5
	Medium +3 - +4	Small 0.35-0.5	6-8	12-20	Ionic network	> 30	Lewis	Strong	Weak	γ-Al_2O_3, β-Ga_2O_3,
		Medium 0.5-0.6	5-6	7-12				Medium	Medium-weak	TiO_2, Fe_2O_3, Cr_2O_3,
		Large 0.7-1.2	3.5-5	2-7				Medium-weak	Medium-strong	La_2O_3, SnO_2, ZrO_2, CeO_2, ThO_2
	Low +1 - +2	Large 0.7-1.0	2-3.5					Medium to	Strong	MgO, CoO, NiO, CuO, ZnO, (Cu_2O)
		Very large > 1.0	<2	< 2				very weak	very strong	CaO, SrO, BaO, Na_2O, K_2O, Cs_2O

Metal oxides with almost covalent bond with oxygen (thus non-metal oxides as well as oxides of metals in very high oxidation states) can give rise to Brønsted acidity, because the (MO)-H bond becomes more ionic. .

Except for the fluorides, which can have strong basicity, but are much less stable and more volatile compounds, the bonds of metals with other non-metal elemnts is more covalent with respect to oxides, thus giving rise to weaker iconicity and acido-basicity. Actually, metal halides have interesting Lewis acidic properties.

Pauling electronegativity of non metal elements		**binary compounds**
F	3.98	fluorides
O	3.44	oxides
Cl	3.16	chlorides
N	3.04	nitrides
Br	2.96	bromides
I	2.66	iodides
S	2.58	sulphides
C	2.55	carbides
Se	2.55	selenides
P	2.19	phosphides

The Silicas

Silica forms many different crystalline structures, which have thermodynamic stability in different pressure and temperature conditions. All the structures which are formed at ambient pressure present tetrahedrally coordinated silicon atom and the structure is associated to a covalent network. On the other hand, silica is also the best known glass forming material, i.e. it has very stable amorphous states, that also consist of a tetrahedral covalent network structure, although disordered.

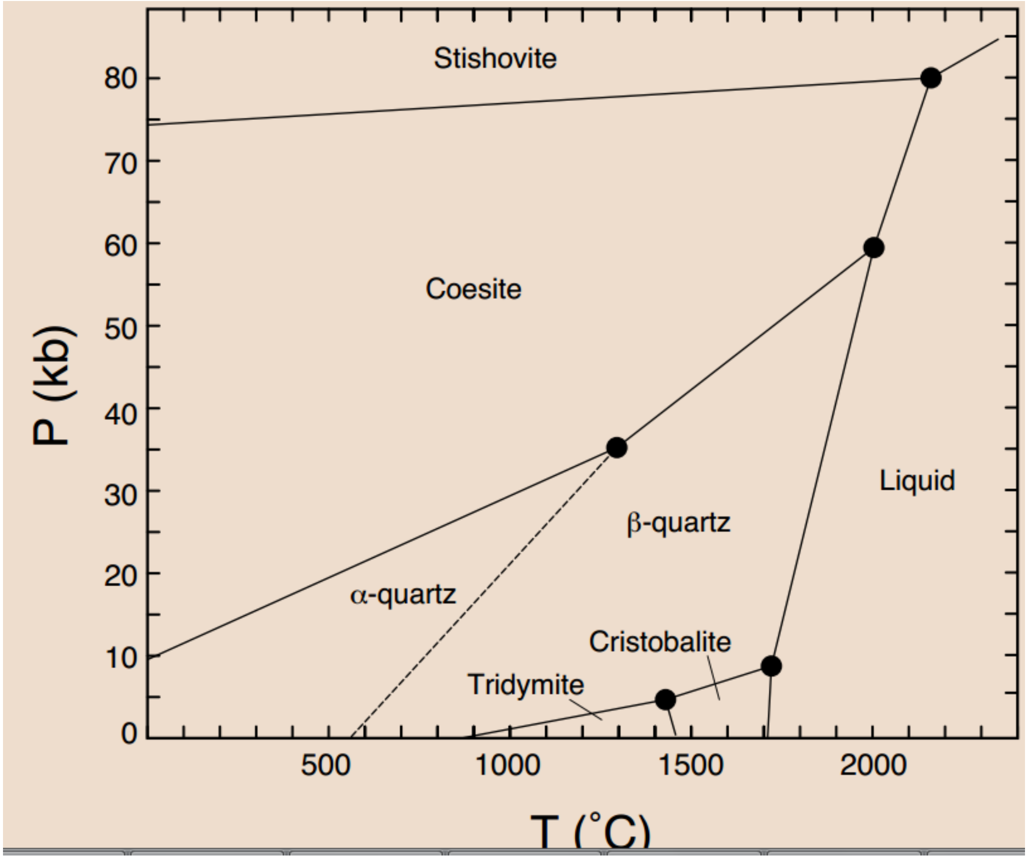
Structurally, amorphous silica is quite a covalent oxide material whose surface behavior is dominated by the chemistry of the terminal silanol groups, O_3Si-OH. Brønsted acidity of the silica’s terminal silanol is generally found weak, no protonation occurring of basic molecules.

Amorphous silica, which has dozens of industrial applications as an adsorbent and a filler, does not seem to have application as a catalyst in hydrocarbon chemistry, but is very largely used as a support for catalysts and as a binder. Recently, mesoporous silicas have been prepared. Their basic chemistry is the same as for microporous silicas.

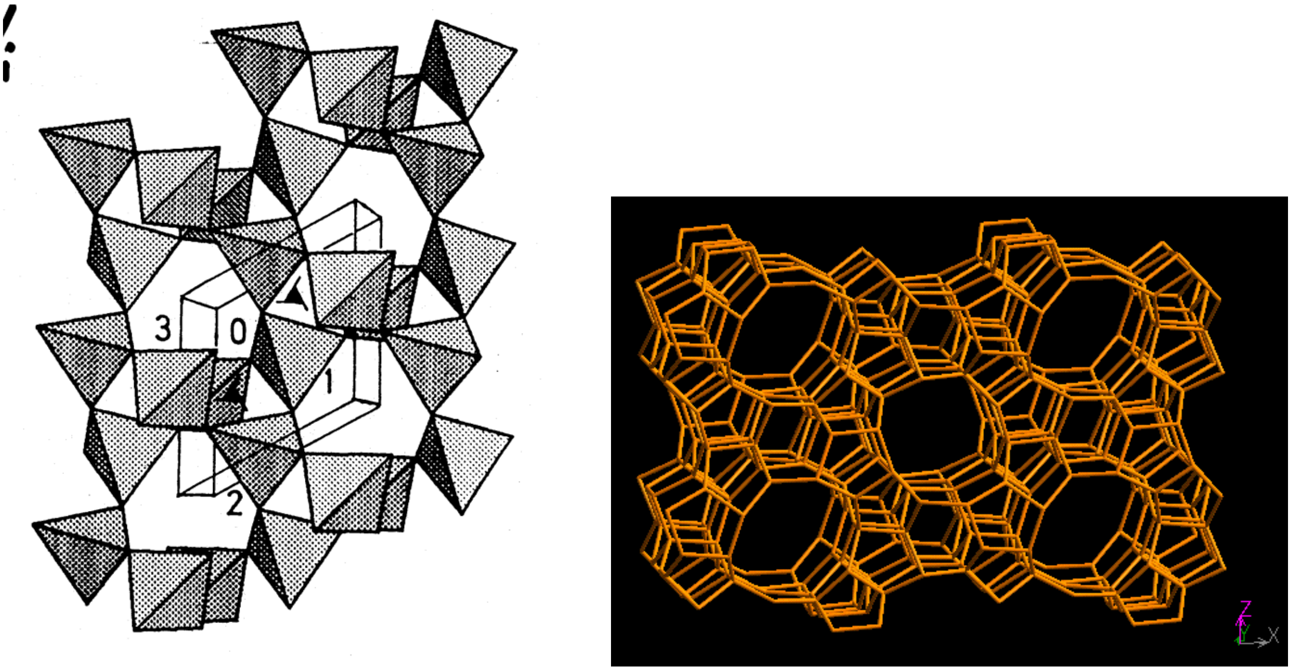
Silicalite-1 is a fully siliceous zeolite, with the MFI structure. Its crystalline framework, constituted by Si oxide tetrahedra, has an essentially covalent and hydrophobic character. When well crystalline, hydrophilic silanols, whose acidity is comparable with that of silica are present essentially at the external surface. However, when prepared in a “defective” form, nests of H-bonded silanols exist. This material has interesting application as an acid catalyst in an industrially important reaction, the vapour phase Beckmann rearrangment of cyclohexanone oxime to ε-caprolactam with the SUMITOMO process, occurring near

300°C. The active sites for this reaction, that is also catalyzed by amorphous silica but less efficiently, are thought to be external and/or internal silanol nests.

Several other fully siliceous zeolites have been synthesized in recent times



Thermodynamic stability ranges of silica polymorphs

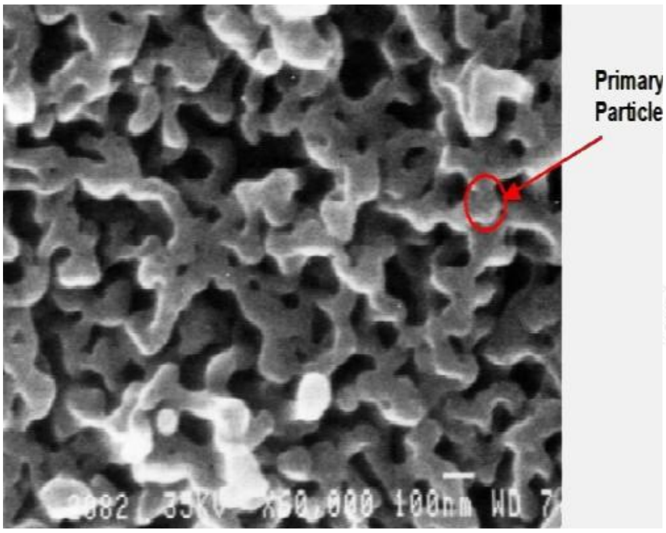


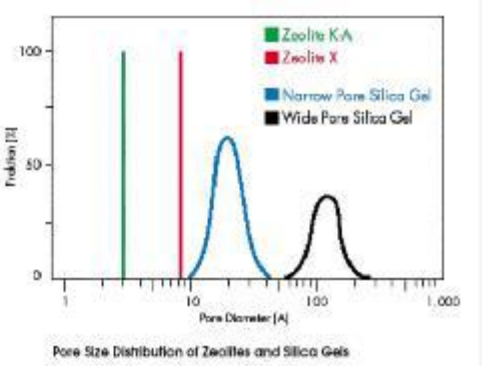
Quartz (left) and silicalite 1 (right) structures

Precipitated silicas. Although many different recipes have been proposed, precipitated silicas are commonly produced by partial neutralization of sodium or potassium silicate solutions. Sulphuric acid is mostly used, mixed with sodium silicate in water still retaining alkaline pH. Reaction is performed under stirring at 50-90 °C. The precipitate is then washed, filtered and dried. During precipitation progressive particle growth occurs up to 4-5 nm clusters, that successively agglomerate to form sponge-like aggregates. Tuning preparation procedure parameters (choice of agitation, duration of precipitation, the addition rate of reactants, their temperature and concentration, and pH of precipitation, as well as drying conditions) allows tuning of final particle size and morphology, thus surface area and porosity. Precipitates typically have a broad meso/macroporous morphology. Very high surface areas may be obtained with these procedures (up to 750 m^2/g), with pore volume in the 0.4-1,7 cm^3/g range and average pore diameter in the 4-35 nm range. Typical impurities of these materials are sodium ions (< 0,8 %) with the likely presence of iron and aluminium ions at the 500-1000 ppm level. Precipitated silica are commercially available such as the Sipernat family from Evonik and the Zeosil-Micropearl materials from Rhodia.

Silica gels. Silica gels are usually produced by dissolving sodium or potassium silicate (10-20 % silica) into an acid, such as sulphuric acid (pH ~ 0.5-2). If the particles are smaller than 100 nm they form silica sols, stabile colloidal dispersions of amorphous silicon dioxide particles that can be used e.g. as polishing agent at production of silicon surfaces in the electronic industry. A gel is formed when the molecular weight of the micelles reaches approximately 6 million , thus the hydrosol viscosity reaches the no-pour point. In a second step the liquid is removed leaving a glass-like gel which is broken down into granules and then washed, aged, and dried., with 6 % volatiles and 22 A average pore diameter.

Silica gels have pores with a wide range of diameters, typically between 5 Å and 3000 Å, and broad distributions. Silica gels synthesized with surface area as high as 800-900 m^2/g, an average pore size of about 20Å and effective pore volumes of 0,40 cm^3/g, are known as narrow pore silica gels, while wide pore silica gels are characterized by surface area ~ 400 m^2/g, average pore size of about 110Å and effective pore volumes of 1,20 cm^3/g.





Pore Size Distribution of Zeolites and Silica Gels

TEM micrograph of silica gel Grace

Fumed or pyrogenic silicas. Fumed silicas are produced by flame hydrolysis of silicon tetrachloride, a process invented in 1946 by H. Klöpfer a chemist at Degussa (now Evonik). This process consists in the reaction of $SiCl_4$ in a hydrogen-oxygen flame at high temperature, reported top be near 1100 °C (Degussa – Evonik) or 1800 °C (Cabot), producing silica and hydrogen chloride. This procedure produces very small non-porous amorphous primary particles, that tend to agglomerate in linear and branched chain-like structures. The surface area of these materials is moderately high (100-400 m^2/g) and fully external, essentially depending from the particle size that ranges 5-16 nm. The weight loss by drying is quite low, 1-2,5 % depending roughly on the surface area, the morphology being stable nearly up to 800 °C, when sintering starts. From the point of view of the metal content these materials are very pure. In particular they do not contain alkali metal impurities. Typical impuritiy of these materials are residual chlorine, and, to a low extent, aluminium, titanium and iron. A typical practical characteristic of these materials is the very low apparent density (down to 30 g/l) and the volatility of the particles.

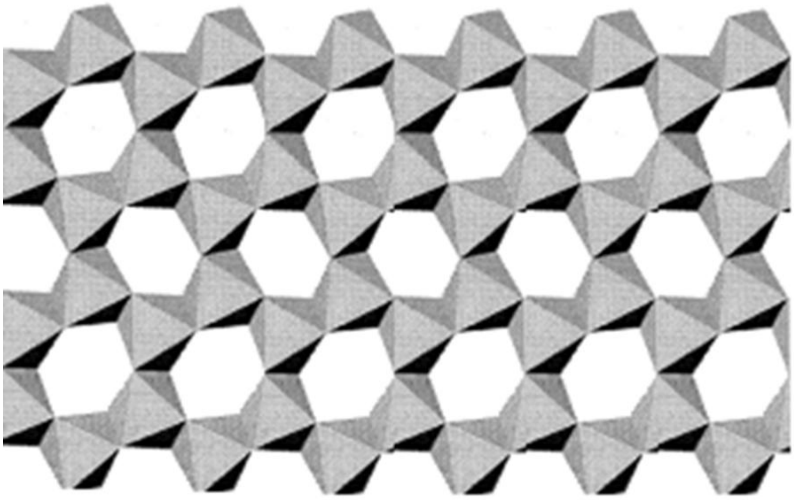
The Aluminas

Aluminum oxide is a polymorphic material. The thermodynamically stable phase is α-Al_2O_3 (corundum) where all Al ions are equivalent in octahedral coordination in a hcp oxide array. Corundum powders are applied in catalysis as supports, e.g. of silver catalysts for ethylene oxidation to ethylene oxide, just because they have low Lewis acidity, low catalytic activity (so not producing undesired side reactions), while being mechanically and thermally very strong.

All other alumina polymorphs are metastable, and may be produced from the different hydroxides or oxyhydroxide by thermal decomposition.

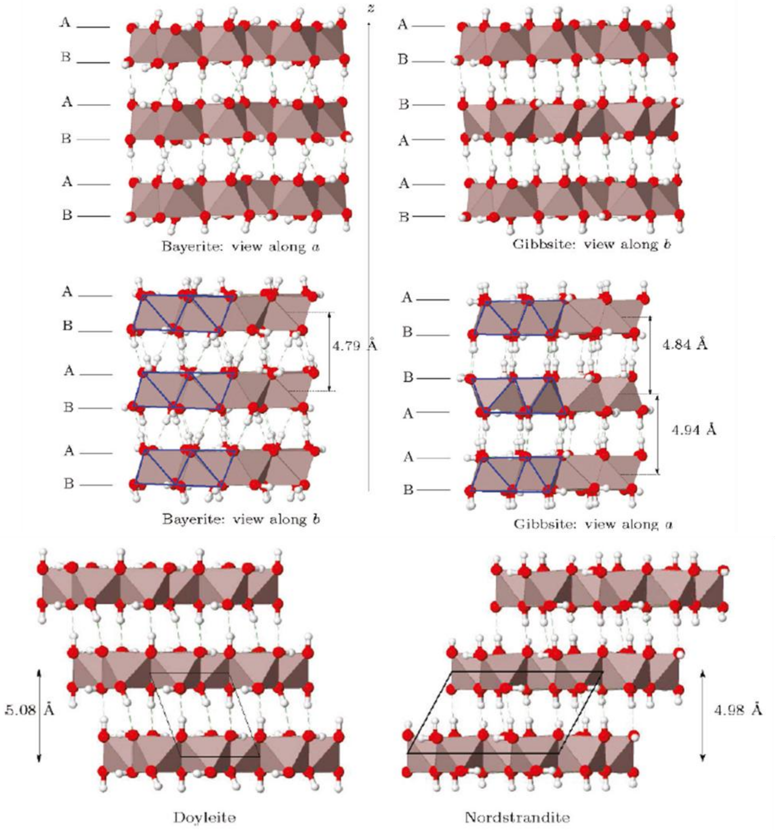
Crystal data of aluminum hydroxides and oxy-hydroxides.

mineral name	Formula	Space Group.	Z
Bayerite	α-$Al(OH)_3$	$P2_1/n$	8
Gibbsite	γ-$Al(OH)_3$	$P2_1/n$	8
Nostrandite	$Al(OH)_3$	$P\bar{1}$	4
Doyleite	$Al(OH)_3$	$P\bar{1}$or P1	2
Diaspore	α-AlOOH	Pbnm	4
Boehmite	γ-AlOOH	$P2_1/c$ or $Cmc2_1$	4
Tohdite	$5Al_2 O_3 .H_2O$	$P6_3mc$, P31c or $Cmc2_1$	2



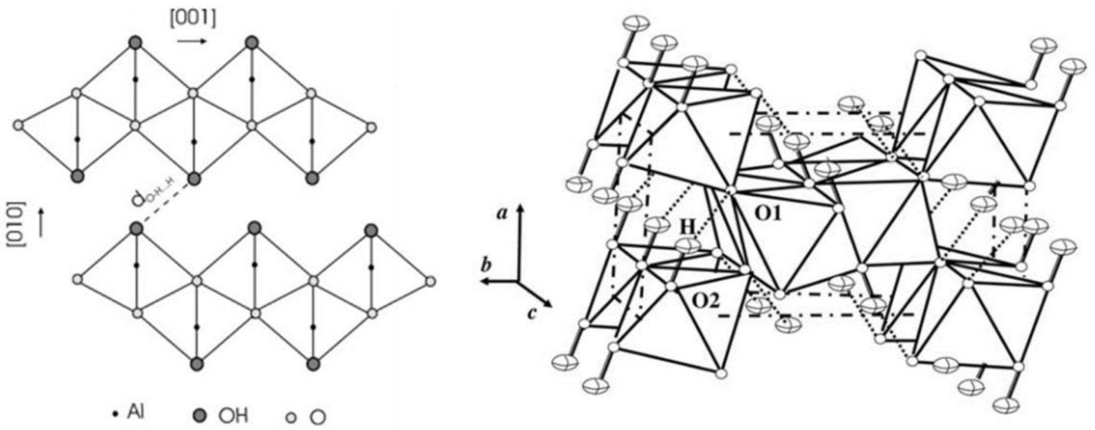
Structure of the layers common to $Al(OH)_3$ polymorphs.

Four different polymorphs are known of Al hydroxide $Al(OH)_3$: Bayerite, usually denoted as α–$Al(OH)_3$, Gibbsite, usually denoted as γ–$Al(OH)_3$, and the less common $Al(OH)_3$ polymorphs Doyleite and Nordstrandite. The four structures are closely related. They are constituted by four different stacking sequences of the same kind of layers, constituted by $Al(OH)_6$ edge sharing octahedral forming a planar pseudohexagonal pattern. Thus all Al s are octahedrally coordinated while hydroxyl-groups are bridging between two Al atoms. At both side of the layers, hydroxyl groups stand. The different $Al(OH)_3$ polymorphs are thus associated to different geometries of the H-bondings between the layers.

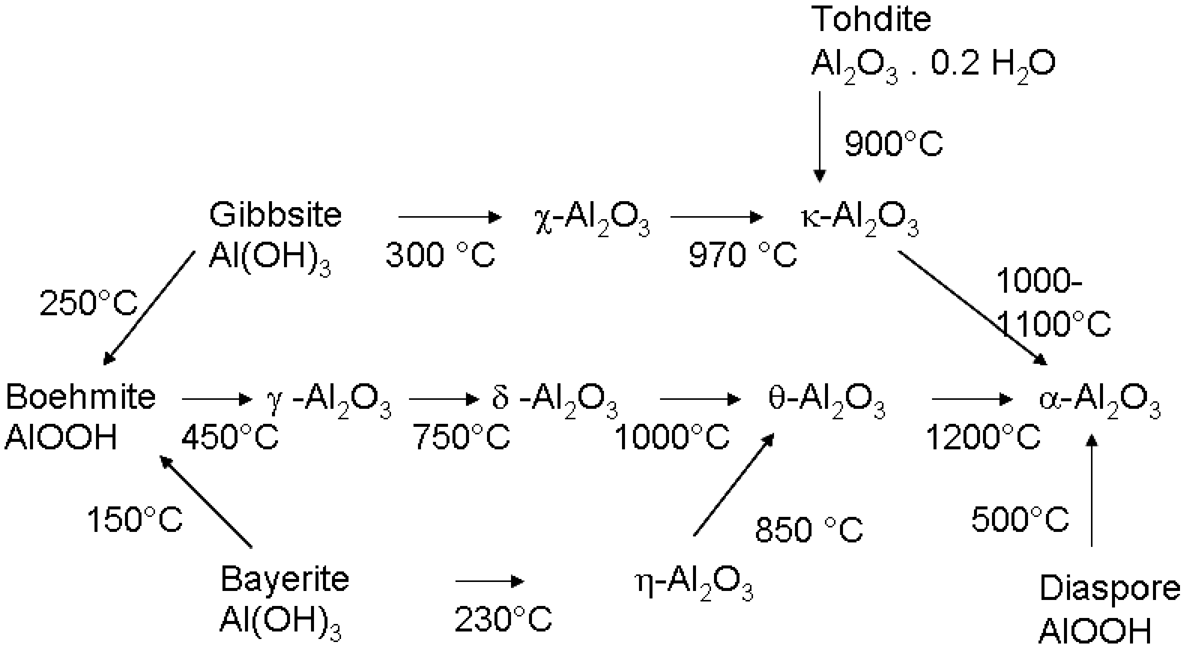


Layer staking and hydrogen bonds in Al trihydroxides $Al(OH)_3$.

Two polymorphs are known for the Al oxy-hydroxide AlOOH, diaspore, α–AlOOH , and boehmite γ–AlOOH. Boehmite has a layered structure with octahedral Al ions, tetracoordinated oxide ions and bridging hydroxyl groups. Zig-zag chains of hydrogen bonds, whose exact geometry has not been completely defined, is formed between the layers. Tohidte, with formula $Al_5O_7(OH)$ can also be considered an oxy-hydroxide.



Crystal structures of boehmite (left) and disapore (right).



Most of metastable alumina polymorphs have a structure which can be related to that of spinel, i.e. cubic $MgAl_2O_4$. γ-Al_2O_3, which is the most used form of alumina, is mostly obtained by decomposition of the boehmite oxyhydroxide γ-AlOOH (giving medium surface area lamellar powders, ~ 100 m^2/g) or of a poorly crystallized hydrous oxyhydroxide called "pseudoboehmite" at 600-800 K, giving high surface area materials (~ 500 m^2/g). The decomposition is associate to the endothermic effect in the DSC curve reported in the figure below. The materials obtained with these precipitation methods are highly microporous. γ-Al_2O_3 powders with low porosity may be obtained by flame hydrolysis of $AlCl_3$, but they show chlorine surface impurities.

Nanocrystalline boehmites are even industrially available. They may be prepared by precipitation starting from soluble Al salts, but in this case they usually contain non negligible amounts of alkali ions. Another way to obtain microporous boehmite comes from the so-called Ziegler process, industrially denoted as ALFOL process. This process is intended to produce linear fatty alcohols starting from trialkyl-aluminum formed by oligomerization reaction of ethylene with Al metal. Oxidation of aluminum trialkyls gives rise to aluminum trialkoxides that can be hydrolyzed to alcohols and bohemite. A modification of this process allows the production of aluminum trialkoxides and hydrogen from alcohols and aluminum metal. Thus, after hydrolysis, boehmite is produced while alcohols may be recycled. This way produces high purity alumina, with less than 20 ppm sodium and potassium, less than 50 ppm calcium and magnesium, less than 100 ppm iron and less than 120 ppm silicon.

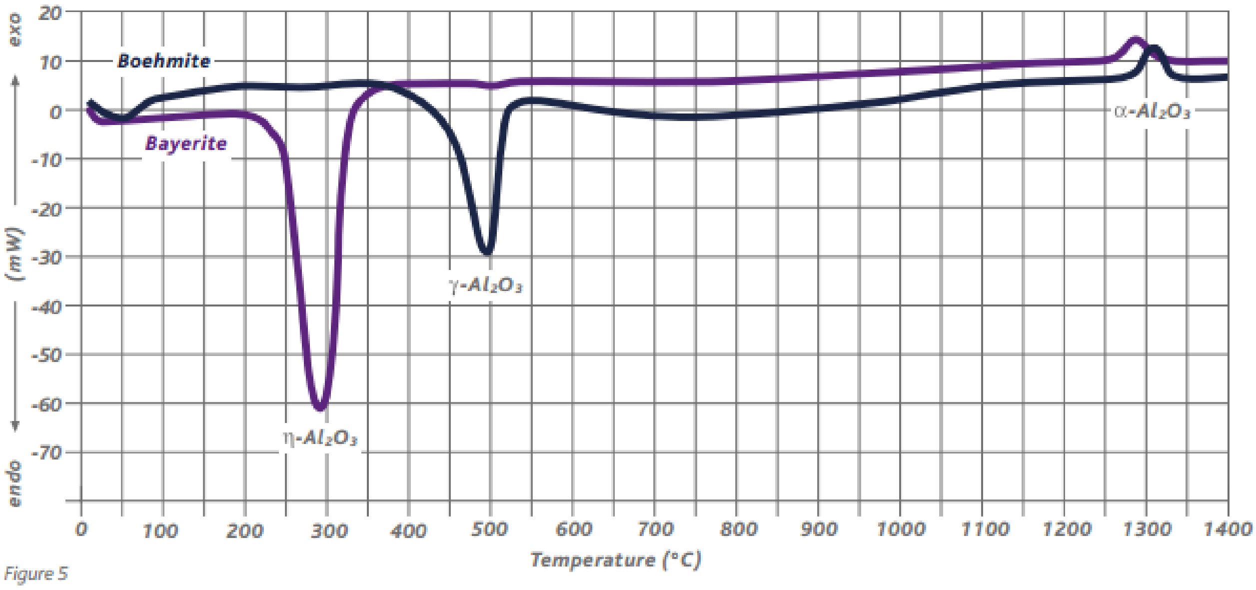
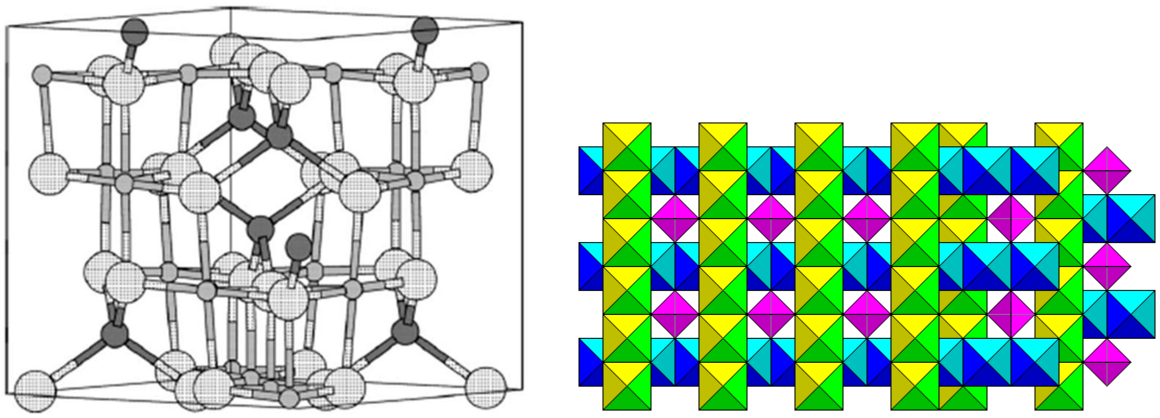
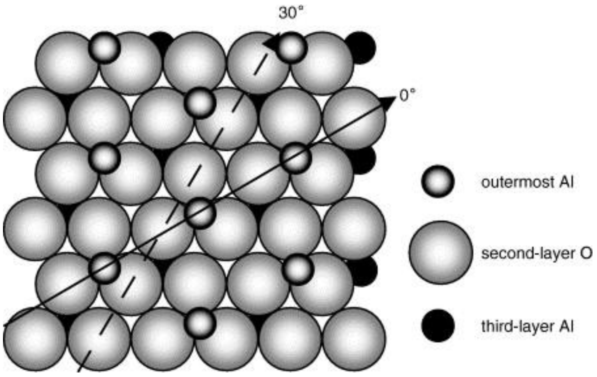


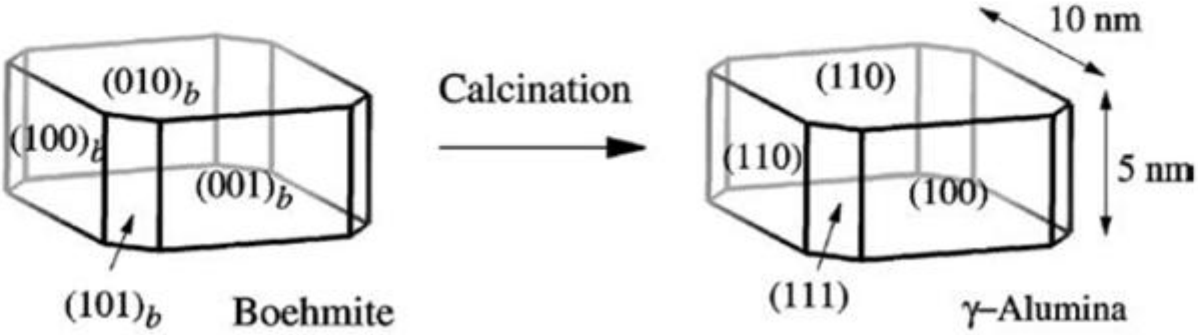
Figure 5
DSC of boehmite and bayerite aluminas



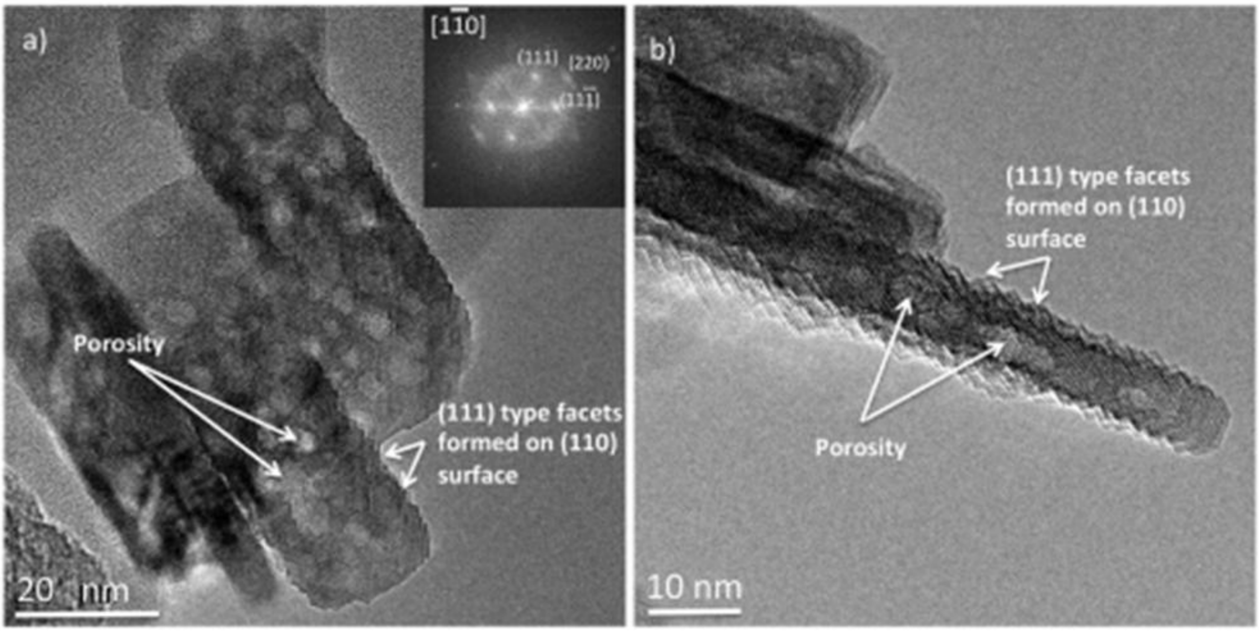
The spinel structure



The corundum structure.



Structural relationshos from boehmite and spinel



HRTEM of lamellar γ-Al_2O_3 particles.

γ-Al_2O_3 is one of the most used materials in any field of technologies. However, the details of its structure are still matter of controversy. It has a cubic structure described to be a defective spinel, although it can be tetragonally distorted. Being the stoichiometry of the "normal" spinel $MgAl_2O_4$ (with Al ions virtually in octahedral coordination and Mg ions in tetrahedral coordination) the presence of all trivalent cations in γ-Al_2O_3 implies the presence of vacancies in usually occupied tetrahedral or octahedral coordination sites.

Calcination at increasing temperatures gives rise to the sequence γ-$Al_2O_3 \rightarrow$ δ-$Al_2O_3 \rightarrow$ θ-Al_2O_3 $\rightarrow$ α-Al_2O_3. The ratio between tetrahedrally-coordinated and octahedrally coordinated aluminum ions increases upon the sequence γ- $\rightarrow$ δ- $\rightarrow$ θ-Al_2O_3. Tetrahedric Al^{3+} is near 25 % in γ-Al_2O_3, 30-37 % in δ-Al_2O_3 and 50 % (in principle) in θ-Al_2O_3. δ-Al_2O_3 is a tetragonal spinel superstructure whose unit cell is constituted by three spinel unit blocs with tetragonal deformation, likely with a partial ordering of Al ions into octahedral sites. It is formed continuously in the range 800-900 K. θ-Al_2O_3 is formed above 900 K with simultaneous decrease of the surface area to near 100 m^2/g or less. Its monoclinic structure, which is the same of β-gallia, can be derived from that of a spinel, with deformation and some ordering of the defects, with half tetrahedral and half octahedral Al ions. During the sequence γ-Al_2O_3 $\rightarrow$ δ-Al_2O_3 $\rightarrow$ θ-Al_2O_3 $\rightarrow$ α-Al_2O_3 the lamellar morphology of boehmite is mostly retained but with progressive sintering of the lamellae and disappearance of the slit shaped pores. The last step to corundum is responsible for the exothermic effect observed in the DSC curve above, typical for the polymorph transformation from a metastable phase to a thermodynamically stable phase.

η-Al_2O_3 is also considered to be a spinel-derived structure but is obtained by decomposing bayerite $Al(OH)_3$ (evident again in the DSC curve by a endothermic peak). Most authors conclude that η-Al_2O_3 corresponds to a defective spinel like γ-Al_2O_3 but with a different distribution of vacancies, namely with more tetrahedrally coordinated (35 %) and less octahedrally coordinated Al ions. This results in stronger acidity of η-Al_2O_3 with respect to γ-Al_2O_3. Calcination gives rise to the sequence η-$Al_2O_3 \rightarrow$ θ-Al_2O_3 $\rightarrow$ α-Al_2O_3.

Other metastable forms of alumina, denoted as ρ-Al_2O_3, χ-Al_2O_3 and κ-Al_2O_3 also exist and can be obtained from the hydroxides gibbsite and tohdite, but they seem to have less interest in catalysis.

The catalytic activity of transitional aluminas (γ-, η-, δ-, θ-Al_2O_3) is undoubtedly mostly related to the Lewis acidity of a small number of low coordination surface aluminum ions, as well as to the high ionicity of the surface Al-O bond. The alumina’s Lewis sites have been characterized to be the strongest among binary metal oxides. The density of the very strong adsorption sites is actually very low, near 0.1 sites/nm^2 . Taking into account the bulk density of γ-Al_2O_3, it is easy to calculate that at most one site every 50-100 acts as a strong Lewis site on γ-alumina outgassed at 400-550 °C, the large majority being still hydroxylated or not highly exposed at the surface.

Actually, the true particular sites of aluminas for most catalytic reactions are very likely anion-cation couples which have very high activity and work synergistically. The basic counterpart may be oxide anions or hydroxyl species. Actually, among the pure ionic oxides, aluminas is also one of the strongest Brønsted acids. The activity of pure γ-Al_2O_3 as a good catalyst of skeletal n-butylene isomerization to isobutylene has been attributed to its medium-strong Brønsted acidity.

Transition aluminas, mostly denoted as γ-Al_2O_3, but actually being frequently a mixture of γ-Al_2O_3, δ-Al_2O_3 and θ-Al_2O_3, or of η-Al_2O_3 and θ-Al_2O_3, have wide application as the catalyst for the Claus process, the production of sulphur from H_2S and SO_2 in the refineries.

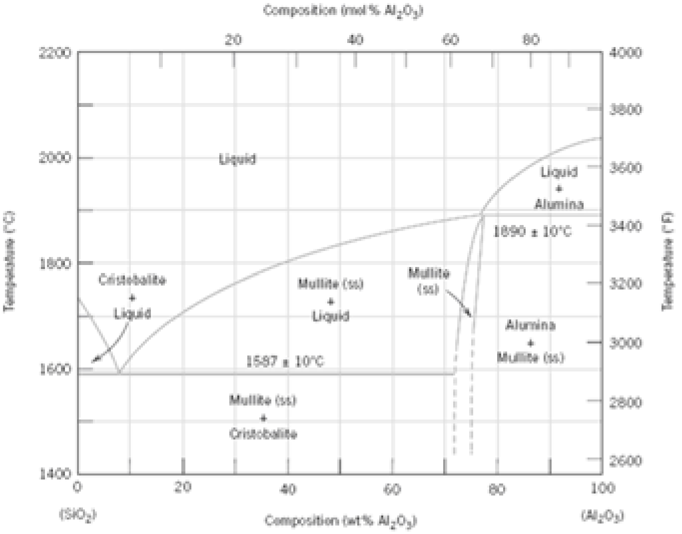
Aluminas are used as commercial catalysts of the alkylations of phenol with alcohols, such as the synthesis of o-cresol and 2,6-xylenol using methanol at 300-400 °C [42]. Aluminas are very active in the dehydration of alcohols to olefins and to ethers, such as methanol to dimethylether at 250–280 °C and 0.04–0.05 MPa, and have been used in the sixties for producing ethylene from dehydration of bioethanol.

They may be used for the dehydrofluorination of alkylfluorides which are byproducts of the HF catalyzed isobutane / butylene alkylation process. Fluoroalkanes react at 170-220°C, being converted to olefins. HF is adsorbed on the alumina to form aluminum fluoride, regeneration being needed every 6 months.

However, the main use of aluminas in hydrocarbon conversions is as an adsorbent, as a support, as a catalyst binder and as an additive (e.g. in FCC catalysis). It is also the precursor for fluorided and chlorided aluminas, which may be produced *in situ* upon halogenation, as well as for silicated aluminas (see below), borated aluminas and other "modified aluminas" produced *ex situ* by chemical treatments.

The mixed oxides of silicon and aluminum

Three polymorphic forms of Al_2SiO_5 (kyanite, andalusite and sillimanite) and mullite (whose composition ranges between 3 Al_2O_3 . 2 SiO_2 and 2 Al_2O_3 . SiO_2) are Al-rich crystalline aluminum silicates generally obtained at high temperature as sintered ceramic materials. Silicon is always tetrahedral while Al ion is octahedral in kyanite, half octahedral and half tetrahedral in sillimanite, half octahedral and half pentacoordinated in andalusite. In mullite, which is the only thermodynamically stable intermediate phase in the alumna-silica system, Al is basically octahedral but a variable amount of it occupies also tetrahedral sites. A spinel-type phase with composition 6 Al_2O_3 . SiO_2 , where Si substitutes for Al in tetrahedral coordination, has also been reported as a metastable form. These materials find significant interest in the fuield of ceramurgy.

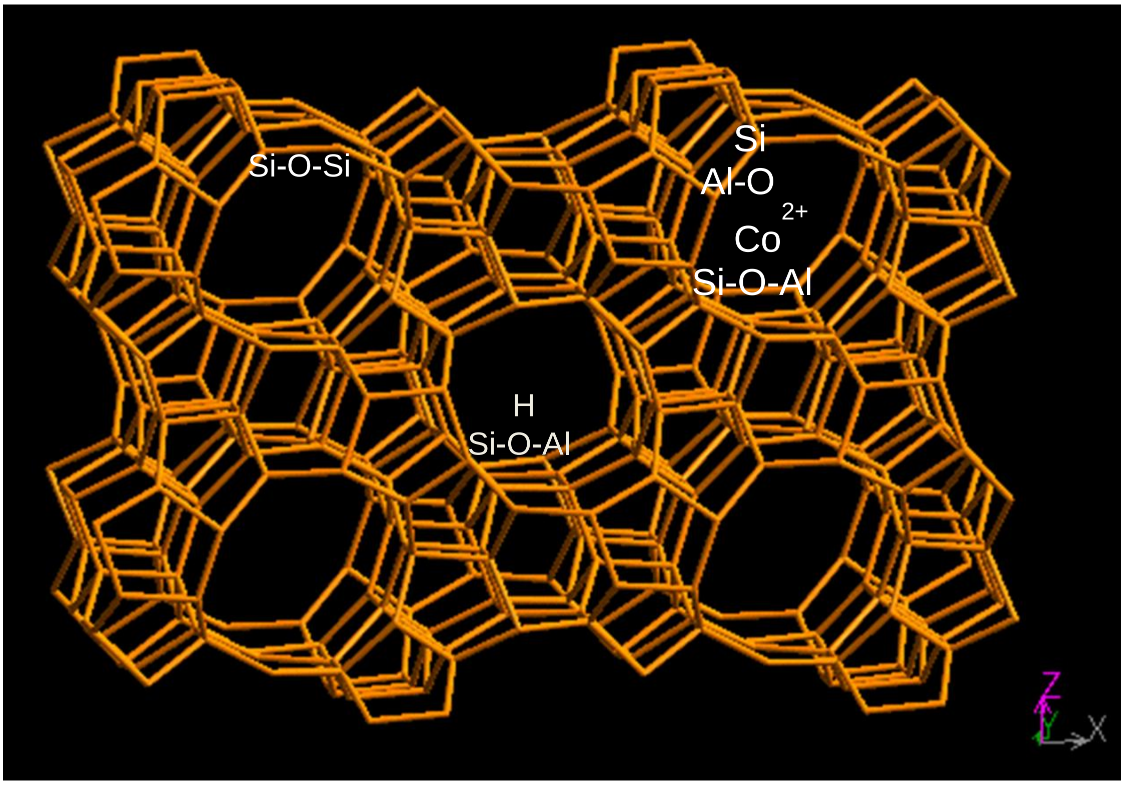


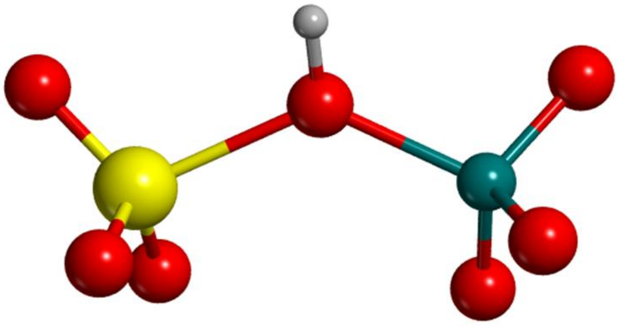
Thermodynamic stability in the alumina-silica system.

Several “mixed oxides” of silicon and aluminum have relevant role in catalysis. They are essentially amorphous or zeolitic.

The substitution of aluminum for silicon in a silica covalent network leads to a charge unbalance which must be compensated by “extra-framework” cations, mostly alkaline. This occurs in the cases of the so-called “stuffed silicas”: these alkali aluminosilicate materials have structures strictly related to the crystalline forms of silica, but with cations in the interstices to counterbalance the presence of Al ions substituting for Si. This is the case, for example, of Eucriptite ($LiAlSiO_4$, a stuffed β-quartz) or nepheline ($NaAlSiO_4$, a stuffed tridymite).

A similar mechanism also occurs in the amorphous networks of glasses, as well as in the case of zeolites. They are natural framework silicoaluminates where charge balancing cations (usually alkali or alkali earth) are located in relatively large cavities formed by the $[Si_{1-x}Al_xO_2]^{x-}$ negatively charged framework. These cavities are connected by channels that give rise to a variety of microporous structures which can be penetrated only by sufficiently small molecules, so giving rise to the “molecular sieving” effect as well as the “shape selectivity” effect in catalysis. The cations are exchangeable, so zeolites may also act as cationic exchangers. The exchange can be performed with ammonium ions which can be later decomposed into gaseous ammonia and a proton. This allows to produce protonic zeolites, which are very strong solid Brønsted acids. Today, protonic zeolites are mostly synthesized directly, by using templating agents. In this case the protons may be residual from the combustion or decompostion of the templating agents.





Protonic zeolites: acidity and shape selectivity.

Protonic zeolites are formally crystalline Si-Al mixed oxides or solid solutions of alumina in cristalline microporous silica networks, where the protons are necessary for stoichiometry. Their general formula is $H_xSi_{1-x}Al_xO_2$. The value of x is generally quite low, the protonic structures becoming unstable when Al content is relatively high, although this depends from the particular zeolite structure. The totally siliceous materials (x=0) not always can actually be sinthesised. At least 133 zeolite-type structures exist that are denoted by a 3 capital letter code by the Commission of the International Zeolite Association (IZA).

Protonic zeolites find industrial applications as acid catalysts in several hydrocarbon conversion reactions. The excellent activity of these materials is due to two main properties: a strong Brønsted acidity of bridging Si-(OH)-Al sites generated by the presence of aluminum inside the silicate framework; and shape selectivity effects due to the molecular sieving properties associated to the well defined crystal pore sizes, where at least a part of the catalytic active sites are located.

The bridging hydroxy groups Al – (OH) – Si which are located in the walls of the zeolitic cavities constitute the strong acidic sites of protonic zeolites. The proton balances the charge defect due to the Al for Si substitution in the framework. It has been recently underlined that the bridging OH’s are only detected in the interior of the zeolitic cavities, being the corresponding spectroscopic features absent in any non zeolitic material based on silica and alumina and also on the external surfaces of different zeolites (see below). Thus, the existence of the bridging hydroxy groups Al – (OH) – Si should implies the existence of the cavity. In other words, the cavities are possibly involved in the generation and/or stabilization of the bridging OH sites.

Other important properties of zeolites are their sufficient thermal stability, their quite easy reactivation when coked, mostly by burning the coke, and finally their safe disposal when non regenerable.

Most data agree suggesting that, when the Al content is relatively low, the amount of Brønsted sites in zeolites actually strictly depends on Al concentration, according to the theory. Most studies conclude that different protonic zeolites have very similar strengths, with a relevant role of local geometric factors, i.e. a relevant role of confinements effects has been suggested.

Shape selectivity. The main factor allowing molecular sieving and, consequently, shape selectivity is generally considered to be exclusively a steric effect, i.e., only molecules having a critical kinetic diameter lower than the channel diameter are allowed to enter the pores (reactant shape selectivity) and to react on an active site or, in case, to exit them and be recovered as a product of the reaction (product shape selectivity). Alternatively, transition state shape selectivity effects limit the formation of bulky transition state intermediates inside the pores that may be formed and avoid the formation of some reaction products. The molecular sieve effect is actually a dynamic phenomenon which depends on the temperature. In fact, molecules which have moderately larger diameter than the cavities may manage to access them, in particular at high temperature. However, a cut-off size exist. As for example, the access at the supercages of Y-zeolites, limited by 7.4 Å rings, can occur with molecules having up to 10.2 Å diameter.

Pretreatments. Zeolite catalysts are actually applied frequently after treatments tending to increase their stability and also, in case, to further enhance surface acidity and shape selectivity effects. These treatments, like steam dealumination, can cause the decrease of the framework Al content and the release from the framework of aluminum-containing species that contribute in stabilizing the framework, but can also contain additional catalytically active acid sites. These particles can also narrow the size of the zeolite channels or of their mouths, so improving the shape selectivity effects. Extraframework material (EF) is composed by very small particles mostly containing Al cations complexed by OH's but sometimes also involving silicate species, likely interacting with the framework walls, located in the cavities or on the external surface. It can arise from the preparation or the activation procedure or by addition of components by impregnation or ion exchange.

Various chemical treatments have also been developed to introduce mesoporosity to accelelarate diffusion of reactants and products in the catalytic mass. Additionally, different preparation methods of the same zeolite can give rise to quite different properties, due to several additional effects such as, e.g., different particle sizes and morphologies, different active site densities or different distribution of framework aluminum and, consequently, of protons from surface to bulk. In most cases the role of shape selectivity and of pretreatments such as dealumination are still imperfectly known or under debate.

Selectivation. Catalytic active sites also exist on the external surface and at the pore mouth of zeolite crystals. These sites are considered to be responsible for unwanted non-selective catalysis. In fact H-zeolites also catalyse reactions of molecules which do not enter the cavities due to their bigger size.

A largely used strategy to avoid unwanted unselective reactivity at the external surface is to limit it by producing large well crystallized zeolite crystals. The "selectivation" of the zeolite behavior may also by obtained by inertization of the external surface through silanization with alkoxy silanes, which can destroy the external Lewis sites, precoking of the external surface and/or of the most active sites, poisoning of the external acid sites by hindered bases (such as 2,6-di-*tert*-butylpyridine), dealumination causing changes in the pore structure, etc..

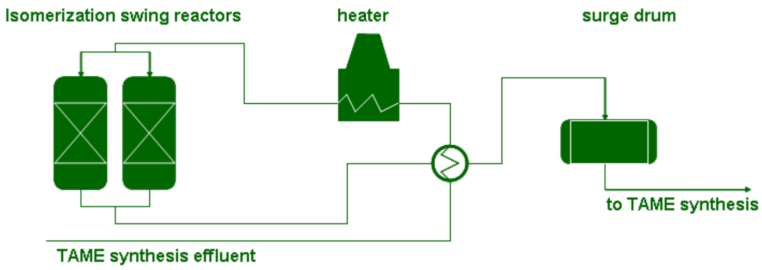
Some particular protonic zeolites applied in the industry.

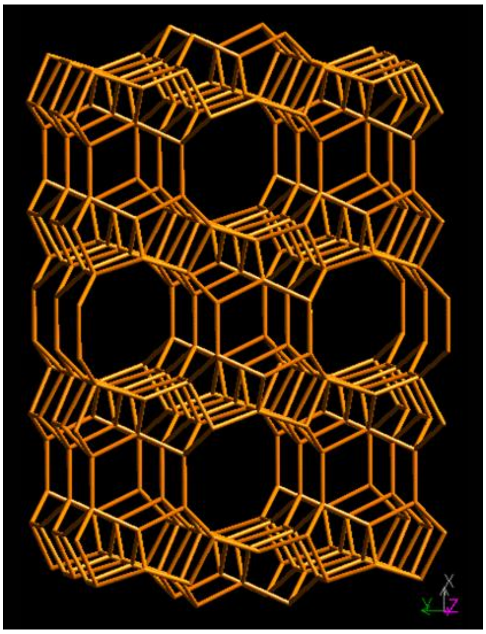
Ferrierite (H-FER).

The framework of the FER zeolite gives rise to two kinds of intersecting channels, one of which is formed by 10-membered silicate rings along [001] direction, with diameters 4.2 Å x 5.4 Å, the other being formed by 8-membered rings along [010] with diameters 3.5 Å x

4.8 Å. It is consequently denoted as a medium pore zeolite. It frequently has quite high Al content (Si/Al ratio 8) but may be also prepared in a very highly siliceous form.

H-FER zeolite focused much interest in the nineties for its high catalytic activity and selectivity for the n-butylene skeletal isomerization to isobutylene, a potentially very relevant process in view of gasoline reformulation. A commercial process, IsomPlus (Lyondell – CDTech) is available and worked industrially at least for some year. The reaction occurs near 350 °C near ambient pressure. The selectivity to isobutylene grows with time on stream when coking also proceeds and n-butylene conversion decreases progressively. Quite frequent catalyst regeneration is consequently needed, using swing reactors. One of the features of the catalyst allowing high selectivity to isobutylene is the impossible (or very highly hindered) diffusion of aromatics in the small pores of ferrierite. Aromatics are among the main products over other larger pore zeolites like H-ZSM5. It is evident that a product shape selectivity effect occurs. Theoretical data also suggested that a transition state shape selectivity effect may occur, just limiting the possibility of formation of C8 adducts that can crack unselectively giving rise to C_3 + C_5 hydrocarbons. This may be even more effective in the case of partially coked materials. so allowing improved shape selectivity.





ZSM-5 (H-MFI).

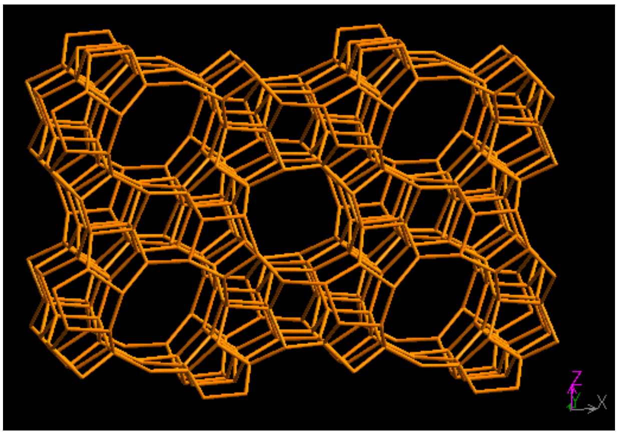
The structure of MFI zeolite contains two types of intersecting channels, both formed by 10-membered silicate rings, characterizing this material as a medium-pore zeolite. One channel type is straight and has a nearly circular opening (5.3 x 5.6 Å) along [010], while the other one is sinusoidal and has an elliptical opening (5.1 x 5.5 Å), along [100]. The Si/Al ratio may vary from infinity (Silicalite-1) to near 10.

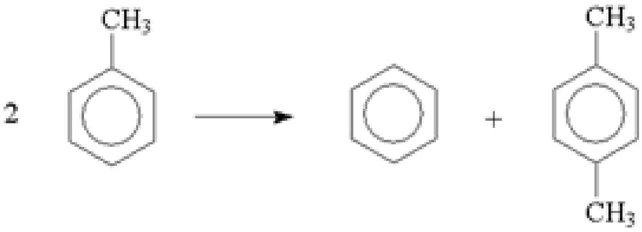
The channels of the MFI structure allow the diffusion of benzene and monosusbstituted benzenes as well as of para-xylene at ca 400°C, thus in contact with gas phase. The diffusion of ortho and meta disubstituted benzenes is far more difficult. This allows shape selectivity in favor of mono- or para-disubstituted benzenes. An example of this behavior is the application of “selectivated H-ZSM5” in the Selective Toluene Disproportionation

(STDP) process allowing the highly selective production of benzene and paraxylene from toluene. With a zeolite treated with silicon-containing compounds at the external surface (to limit reaction out of the channels), whose pore mouths may also be narrowed by silication or pre-coking, working in the vapor phase at 420-480 °C, 20-40 bar, WHSV 3-5 h^{-1} small toluene conversion per pass, the selectivity para-xylenes / total xylenes may be higher than 80 %, with cycle lengths of more than 1 year. H-MFI catalysts find a number of other applications in the field of gas-phase aromatics chemistry. They are the catalysts of the Mobil-Badger process of benzene alkylation by ethylene for the ethylbenzene synthesis, performed in the vapor phase at 390-450 °C. Interestingly, H-MFI is not a good catalyst of the benzene alkylation by propene for the cumene synthesis, producing an eccess of n-propylbenzene. This has been attributed to the high temperature needed to overcome the aromatics diffusion constraints in the 10-membered channels, that favours cumene isomerization. These constraints limit activity of H-MFI in liquid phase aromatics alkylations.

The channel size of MFI also does not allow the easy diffusion, if at all, of molecules containing the tert-butyl group. This is probably the reason for the almost total inactivity of H-MFI in isobutane / butylene alkylation whose products and intermediate species contain the tert-butyl group. For the same reason H-ZSM5-based catalysts with SiO_2/Al_2O_3 ratio of at least 20, containing ca. 40 wt% of a binder (Al_2O_3 or SiO_2), have been developed to obtain olefin oligomers with relatively high linerarity and low branching that can be applied for use as Diesel blending fuels (COD, Conversion of Olefins to Diesel, from Lurgi-Süd Chemie).

A reactant shape selectivity effect allows the use of H-MFI (usually containing also an hydrogenating metal) for the selective cracking of linear paraffins in the catalytic dewaxing of lube oils (such as the Mobil Selective DeWaxing process, MSDW). Linear paraffins enter and diffuse easily in the MFI cavities, while the entrance of branched isomers is hindered. Thus conversion of linear compounds is favored with respect to those of branched isomers.





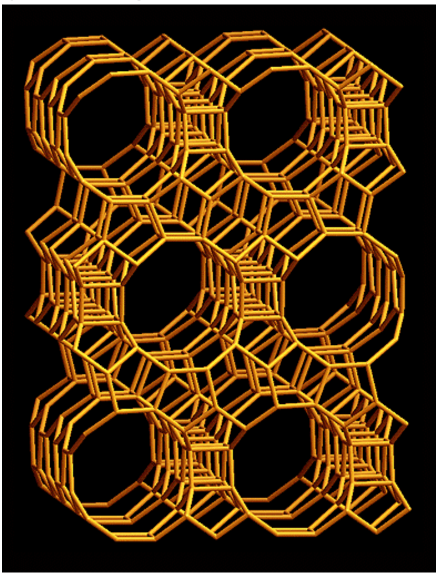
Beta zeolite (H-BEA)

The framework of BEA zeolite gives rise to two different channel types, both formed by 12-membered rings, but with a definitely different diameter, one (0.55 x 0.55 nm) in the medium pore range, the other (0.76 x 0.64 nm) in the large pore range. The Si/Al ratio is typically in the 10-30 range, although particular preparations allow this ratio range to be expanded down to 5 up to infinity.

H-BEA structure is relatively fragile and calcination or steaming above 400 °C causes progressive dealumination with deposition of extraframework aluminum (EF-Al) inside the channels**.** Chrystallographic faults are frequently observed in BEA zeolite. Actually, the structure of BEA is reported to be an intergrowth of two or three polymorph types.

The size of the larger channels of H-BEA allows quite easily the diffusion of aromatics as well as of molecules containing the tert-butyl group at low temperature (ca 200 °C), thus in contact with a liquid phase. The size of the cavity may perhaps be reduced by dealumination, producing EF material. This is considered to be beneficial e.g. for the selective acylation of 2-methoxy-naphtalene over H-BEA.

H-BEA zeolite find industrial application in the Polimeri Europa-ENI and in the UOP Q-Max^{TM} processes for the liquid-phase synthesis of cumene by alkylation of benzene with propene (see Table). In both cases H-BEA-based catalysts catalyze selectively both the alkylation reaction, in multi-fixed-bed catalytic reactors, with a large excess of benzene, and also the transalkylation reaction, where benzene reacts with polyisobutylbenzene producing additional cumene in a separate fixed bed reactor. The ENI catalyst, denoted as PBE-1, is composed of a mixture of very small and uniform beta-zeolite particles with a binder, showing both zeolite microporosity and extrazeolite mesoporosity. According to the patent literature its seems that also the Lummus/UOP EBOne liquid-phase ethylbenzene synthesis process works with a H-BEA based catalyst.



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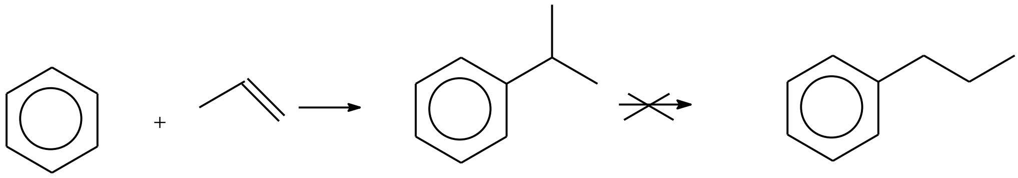
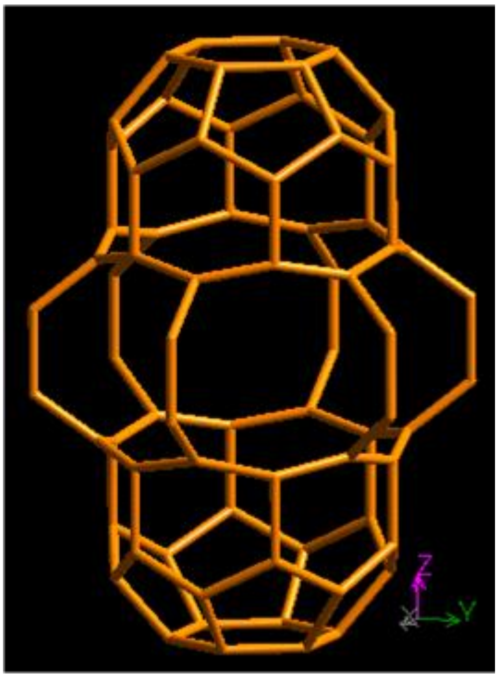


MCM-22 (H-MWW)

MCM-22 possesses a unique crystal structure denoted with the code MWW, containing two independent non intersecting pore systems. One of the channel systems contains two-dimensional sinusoidal 10-membered silicate ring channels (diameters 4.1 Å x 5.1 Å), while the other system consists of large supercages (12-membered) with dimensions 7.1 Å × 7.1 Å × 18.1 Å. The supercages stack one above another through double prismatic six-member rings and are accessed by slightly distorted elliptical 10-membered connecting channels (4.0 Å x 5.5 Å). In general, the synthesized MCM-22 zeolites crystallized as very thin plates with large external surface area, on which 12-membered hemisupercages pockets (7.0Å x 7.1 x 7.1) are exposed.

This catalyst competes with those based on H-BEA (ENI and UOP) and on H-MOR (Dow), see Table 4. The MCM-22 zeolite catalyst is more monoalkylate-selective than most large pore zeolites, and is very stable. Cycle lengths in excess of 3 years have been achieved. The excellent selectivity to monoalkylated products is attributed to the confinement effect within the 12-membered ring pore system where the reaction occurs, and the easy desorption of alkylbenzenes from the pockets. Mechanistic studies suggest that the reaction should occur in the hemisupercages exposed at the surface. If this theory is true MCM-22 should be a zeolite working mostly at its the external surface, where, however, the zeolite structure is in some way retained.



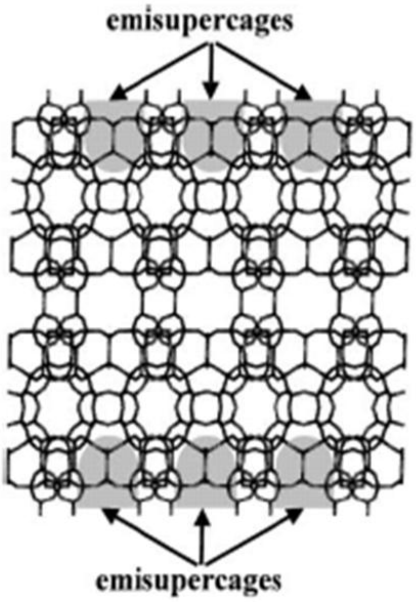


Fig. 6. MWW structure, large cavities opened to the exterior at the termination of the crystal (emisupercages).

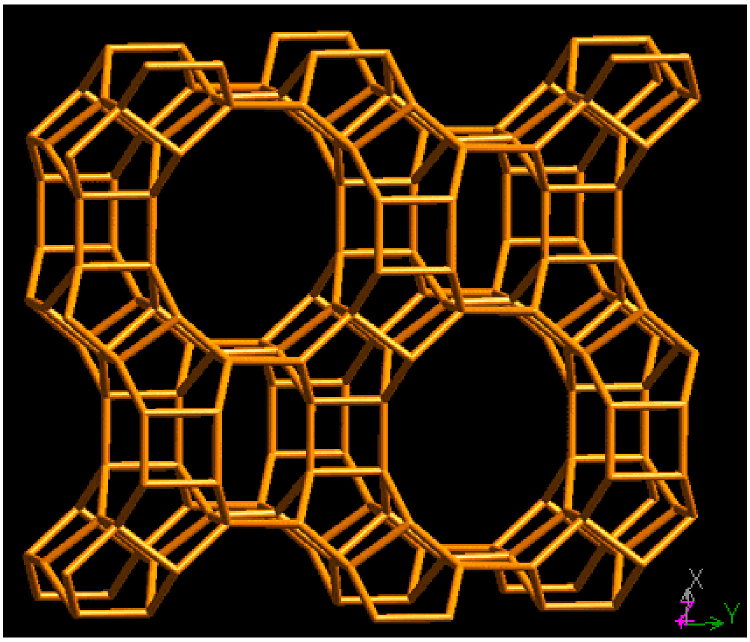
Mordenite (H-MOR)

The orthorhombic mordenite structure is characterized by nearly straight channels running along the [001] crystallographic direction, which are accessible through 12-membered silicon-oxygen rings 6.5 Å x 7.0 Å wide. Additionally, 8-ring "side pockets" exist in the [010] direction, whose opening is 3.4 Å x 4.8 Å. The side pockets connect main channels to a distorted eight-ring “compressed” channels also running parallel to the 001 direction, but having a elliptical small opening 5.7 Å x 2.6 Å wide.

Mono-substituted aromatic compounds and compounds having the tert-butyl group diffuse in the main channels, but are not allowed to enter the side pockets. Acid catalysis occurs predominantly in the main channel for aromatics, likely in the side pokets for small molecules such as light paraffins.

Dealuminated mordenite is the basic structure of commercial catalysts for C4-C6 paraffin skeletal isomerization, performed on alumina-bound Pt-H-MOR with SiO_2/Al_2O_3 ~ 15-17. Dealumination until a framework/extraframeworl Al ratio ~ 3 improves the catalytic activity. The catalyst works near 250 °C, so at a definitely higher tempertature than those based on chlorided alumina, when the thermodynamics is less favourable, but are more stable and more environmentally friendly. This agrees with the quite easy diffusion of branched molecules in the main channels.

As said, also monosubstituted benzene diffuse easily in the main channels of H-MOR, while o-disubstituted benzenes are hindered to diffuse. In agreement with this, H-MOR also catalyze selective conversions of aromatics. Dealuminated H-MOR is the catalyst of the Dow-Kellogg cumene synthesis process. Noble metal-containing H-MOR is also applied for the disproportionation of toluene to benzene + an equilibrium mixture of xylenes, generally at 20-40 bar, 380-500 °C, with excess hydrogen (H_2/hydrocarbon 1-6) and WHSV 1-6 h^{-1}.



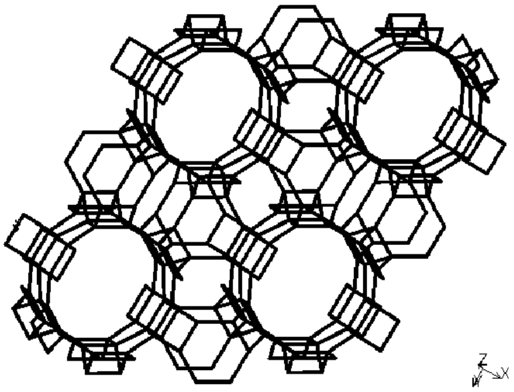
Characteristics of processes for the production of cumene by alkylation of benzene with propene

Year of development	company	catalyst	Phase	Pressure	Temperature
		$AlCl_3$/EtCl	Liquid/liquid	3-7 bar	40 °C
		H_2SO_4 < 90%	Liquid/liquid	11.5 bar	35-40 °C
1940's	UOP	Solid phosphoric acid	Vapor/solid	15-35 bar	200-250 °C
	Hüls	HF	Liquid/liquid	7 bar	50-70°C
1986-1988	Monsanto	$AlCl_3$/EtCl	Single liquid phase	10 bar	110 °C
1980s	Unocal	Y-zeolite	Gas/solid		
1992	UOP Q-Max^{TM}	H-BEA	Liquid / solid		
1992	Dow – Kellogg 3-DDM	Dealuminated H-MOR	Liquid / solid		170 °C
1994	Mobil-Raytheon	MCM-22 (H-MWW)	Liquid/solid		180-220°C
	CDTech	zeolite	Catalytic distillation		
1996	Enichem-Polimeri Europa	H-BEA	Liquid/solid	25-40 bar	150 –200 °C

Zeolite omega (H-MAZ)

Zeolite omega, a large pore zeolite with a silica–alumina ratio in the range of 4–10, is the synthetic isotype of the mineral mazzite (topological code MAZ). In its unit cell, 36 tetrahedral atoms bridged by oxygen atoms form gmelinite-type cages and 12-membered cylindrical channels along [001] direction with 7.4 Å diameters. In addition to its large pore system, secondary mesoporous structure could be created by mild dealumination, which may facilitate the transport of reactant and reduce the deposition of coke.

Zeolite omega is apparently the basic structure of modern zeolitic C4-C6 paraffin scheletal isomerization catalysts cited under development by Süd Chemie as HYSOPAR® catalysts, reported to be characterized by their outstanding tolerance of feedstock poisons such as sulphur (even more tha 100 ppm) and water with very high catalyst lifes. The catalyst is alumina-bound Pt-H-MAZ with Si/Al ~ 16, working at 250 °C with WHSV 1.5 h^{-1} and a H_2/hydrocarbon ratio of 4. Pt and hydrogen have the effect of reducing coking e hydrodesulphurizing S-containing compounds. It may be applied in the so-called CKS ISOM process licenced by Kellogg, Brown and Root. This catalyst is reported to be more effective than Pt-H-MOR commercial catalysts, and more stable than the catalysts based on chlorided aluminas and sulphated zirconia.



Industrial catalysts for light paraffins isomerization

Catalyst	S ppm	H_2O ppm	Benzene %	C7+ %	T_{reaz} °C	Note
Chlorided alumina (Pt)	0	0	< 2	< 2	130-150	Chlorided hydrocarbons needed
Sulphated zirconia (Pt)	< 20	< 20	< 2	< 2	180-210	Deactivation
Tungsta-zirconia (Pt)	< 20	< 20	< 2	< 2	180-210	
H-Mordenite-Pt	< 20	< 20	< 2	< 2	260-280	
Zeolite omega (Pt)	< 200	< 200	< 10	< 5	250-280	Benzene can be hydrogenated

Faujasite (H-FAU: H-Y, H-USY, RE-Y)

The faujasite structure is formed by wide supercages (13 Å diameter) accessed through 12-member silicate rings with 7.4 Å diameter, much smaller sodalite cages accessed through 6-member silicate rings and hexagonal prisms connecting the sodalite cages. All the catalytic chemistry of faujasites is supposed to occur in the supercages. The aluminum content in faujasite is generally very high, the theoretical Si/Al ratio being as low as 1. Faujasites with Si/Al ratio near 1 are usually denoted as X-zeolites. Faujasites with Si/Al ratio higher than 2 are usually denoted as Y-zeolites and are more stable in the protonic form, denoted as H-FAU or H-Y. The multiplicity of the hydroxy groups is ery evident. Bridging OH's located in the supercage are accessible to most molecules, while OH's located near the middle of the 6 bond rings connecting the sodalite cages, possibly weakly H-bonded through the cavity, can H-bond with molecules located in the supercages, but are unable, for steric reasons, to protonate them.

H-Y (H-FAU) zeolites for their practical application at high temperature in reaction or regeneration must be stabilized by steam dealumination, generally performed at T > 773 on the NH_4-Y precursor. The resulting materials are hydrothermally more stable (the so-called ultrastable Y zeolite, USY). Their structure and acidic properties are greatly influenced by the dealumination process which generates extraframework alumina possessing Lewis acidity and inducing enhanced Brønsted acidity within the material.

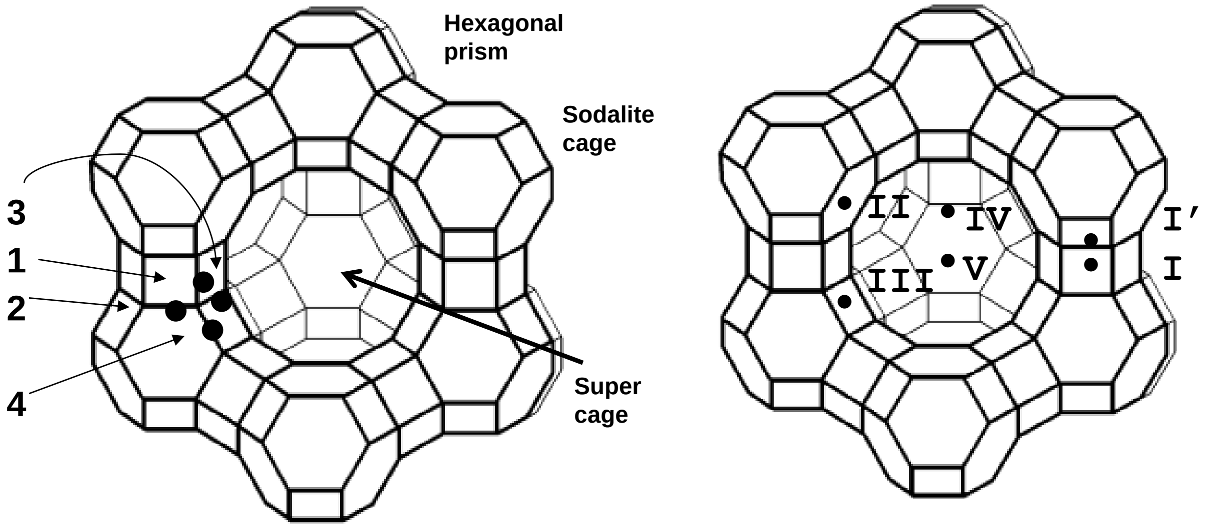
The main component of fluid catalytic cracking (FCC) catalysts today is rare-earth (RE) exchanged FAU zeolite (RE-Y or RE-USY), such as La-H-Y zeolites. They present additional OH groups in some way interactuing with the rare earths.

FCC is an authothermic process. where the strongly endothermic catalytic cracking step is coupled with the strongly hexothermic coke burning catalyst regeneration step. The catalyst continuously moves from the raiser where the cracking reaction occurs at ~ 540 °C, 2 bar, residence time ~ 3-10 sec, to the regenerator where the burning of coke gives rise to a gas rich in CO (so still useful for further heat generation by burning) and the temperature is enhanced again to 730 °C, 2 bar, residence time ~ 15 min. The catalyst must be very stable to high-temperature hydrothermal treatment to resist such a cyclic process.

Besides RE-Y and RE-.USY, the most used FCC catalyst today, several other components are present, such as an alumina or silica-alumina matrix or binder, kaolin, and H-ZSM5-containing additives to improve performances and quality of the products. To obtain a deeper cracking of sulphur compounds upon the FCC process, further additives (e.g. $ZnAl_2O_4$) may be used.

USY is also a typical component or support of hydrocracking catalysts, to provide acidity. The catalyst contains a sulphur-resistant hydrogenation phase, like Ni-W sulphide. The reaction is performed at 300-450°C under 50 to 200 atm of hydrogen. A heavy low value feed is transformed into lighter fractions. Hydrodesulphurization, hydrodenitrogenation, hydrodearomatization, hydrodealkylations occur. The wide dimension of the channels of faujasite allow quite heavy molecules to be cracked. Deactivation by coking occurs, but USY based catalyst are less easily coked than those based on silica-alumina.

USY containing Pt is probably the catalyst of the AlkyClean process proposed by Akzo Nobel / ABB Lummus for solid-catalyzed isobutane / butylene alkylation. The catalyst works at 40-90 °C and is rejuvenated in liquid phase by hydrogen-isobutane mixture, and regenerated at 250 °C by hydrogen in the gas phase. Multiple reactors are used to allow for continuous alkylate production / catalyst rejuvenation cycles. Regeneration is performed intermittently.



Positions for hydroxy groups in H-Y and of cations in exchanged Y Faujasite zeolites

Silica-aluminas (SAs).

The structural details of the oxides resulting from coprecipitation or co-gelling of Si and Al compounds are still largely unclear, if at all. Commercial materials are available with any composition starting from pure aluminas to pure silicas. The silica-rich materials are generally fully amorphous and are called “silica-aluminas” (SAs). They behave as strongly acidic materials and have been used for some decades (1930-1960) as catalysts for catalytic cracking processes, and still find relevant industrial application.

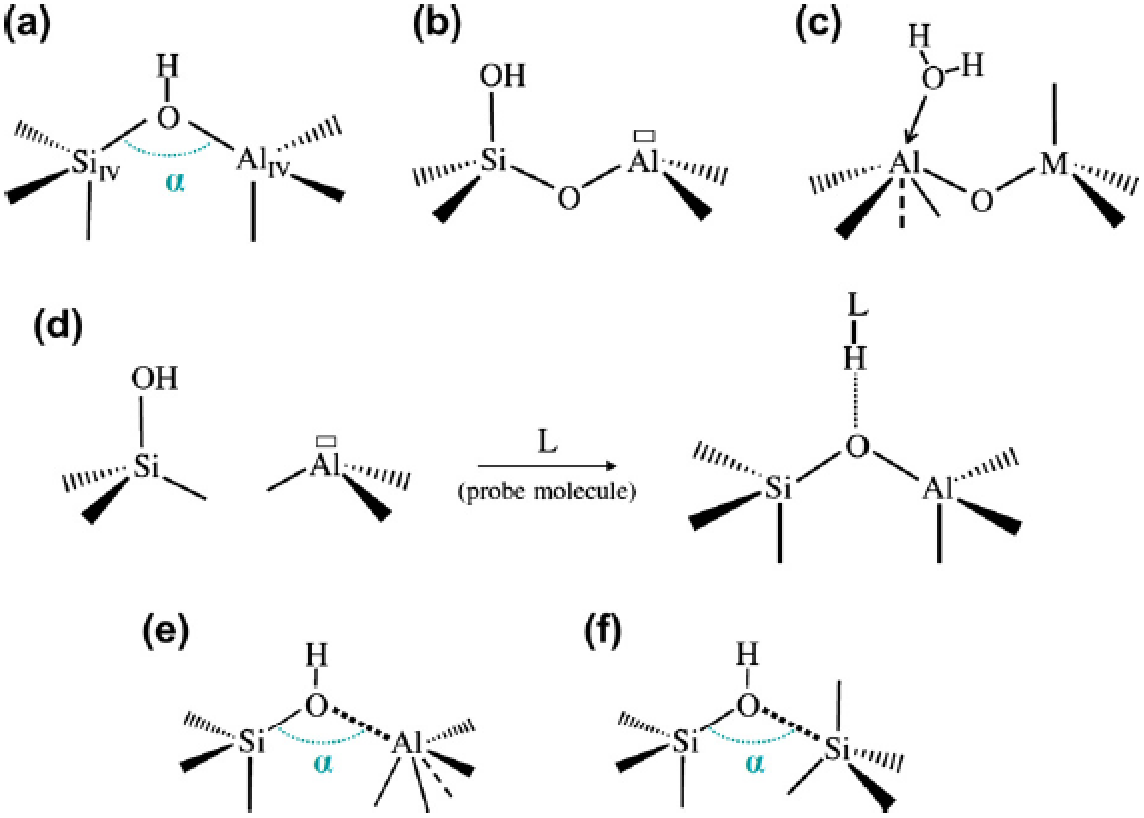
On the surface of SA, medium strength Brønsted acid sites together with very strong Lewis acid sites can be detected. Lewis sites are certainly due to highly uncoordinated Al ions and correspond to the strongest Lewis sites of transitional alumina or perhaps are even stronger, due to the induction effect of the covalent silica matrix. This makes SA also a very strong catalyst for Lewis acid catalyzed reactions. Al ions near terminal silanols can cause a revelant strengthening of the acidity of terminal silanols.

Amorphous microporous SA, used in the past for fixed and moving bed catalytic cracking starting from the fourties, still finds a number of applications as acid catalysts e.g. the dehydrochlorination of halided hydrocarbons. Also, SAs are used as supports of sulphide catalysts for hydrotreatings and of catalysts for ring opening of polycyclic compounds, useful for the improvement of the technical and environmental quality of Diesel fuels.

Mesoporous SAs containing big pores with size from few to many nm, have been developed. Different materials, denoted with the abbreviations MCM-41, FSM-16, HMS, SBA, MSU, KIT-1, MSA and ERS-8, with different mostly mesoporous pore structure, may be obtained by different preparation procedures. Although sometimes considered like very large pore zeolites, these materials are essentially amorphous SAs with non-structural although sometimes ordered mesopores. The surface chemistry of these materials appears to be closely similar to that of amorphous microporous SAs.

Several recent studies appeared concerning the possible industrial application of mesoporous SAs and the comparison with microporous SA and zeolite as catalysts for several reactions of industrial interest such as alkylation of aromatics and propene oligomerization. The catalytic activity of mesoporous SAs appear to be frequently higher than that of microporous SAs, but lower than that of zeolites. A recent contribution underlined the inverse relation of the pore sizes of mesoporous SAs and catalytic activity in n-hexane conversion showing the role of confinement effects in the acid catalysis. SAs may also act as binders in catalysts such as those for the modern FCC process.

Recently, the build-up of strong Brønsted acid centers in the walls of mesoporous SAs has been attempted, to enhance their catalytic activity and hydrothermal stability while taking advantage of their unusual porosity. This can be made with the incorporation of "zeolite seeds" in the framework. Alternatively, mesostructured SAs have been prepared by surfactant-mediated hydrolysis of zeolites, with retention of five-ring subunits, and, consequently, of Brønsted acid centers.



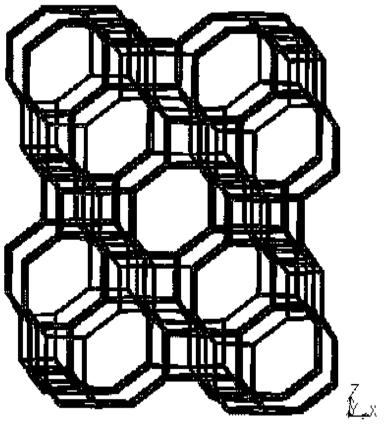
Models for Brønsted acidity in silica-alumionas.

Silicoaluminophosphates (SAPOs)

Silicoaluminophosphates (SAPO) molecular sieves are topologically similar to small or medium pore zeolites, where phosphorus, aluminium and silicon atoms occupy the tetrahedral positions. Thes materials appear to be characterized a high thermal stability. SAPO-34 is isomorphous to chabazite (CHA) whose structure is shown in Fig. 28. The chabazite topology might be described as layers of double 6-membered rings that are interconnected by units of 4-membered rings. The double 6-membered-ring layers stack in an ABC sequence. This leads to a framework with a regular array of barrel-shaped cages with 9.4 Å diameter, interconnected by 8-membered-ring windows (3.8 Å x 3.8 Å). The chabazite structure contains only one unique tetrahedral site but four different oxygen atoms in the asymmetric unit, giving four possible acid site configurations, depending on to which of the oxygen atoms the proton is attached.

The mechanism of Brosnyted acidity generation on SAPO's is the same as on zeolites, bridging hydroxyl groups being the most active sites. SAPO-34 is an excellent catalyst for the conversion of methanol to ethylene and propylene in the so called Methanol to Olefin (MTO) process. The structure of SAPO-34 along with the small sizes of certain organic molecules are keys to the MTO process, developed by UOP and Norsk Hydro. The small pore size of SAPO-34 restricts the diffusion of heavy and or branched hydrocarbons, and this leads to high selectivity to the desired small linear olefins.

Under reaction conditions, at 400-550 °C, the deactivation by coke of SAPO-34 (containing 10 % Si) is very fast although activity is completely recovered after subsequent to combustion of coke with air. The catalyst has demonstrated the degree of attrition resistance and stability required to handle multiple regenerations and fluidized bed conditions over the long term. The better performances of SAPO-34 with respect to H-chabazite as the catalyst have been related to the tunable density of acidity that allow to limit the coking rate. The catalytic performance of SAPO-34 is improved if the surfaces of the crystals are doped with silica by heating with polydimethylsiloxane or an alkyl silicate.



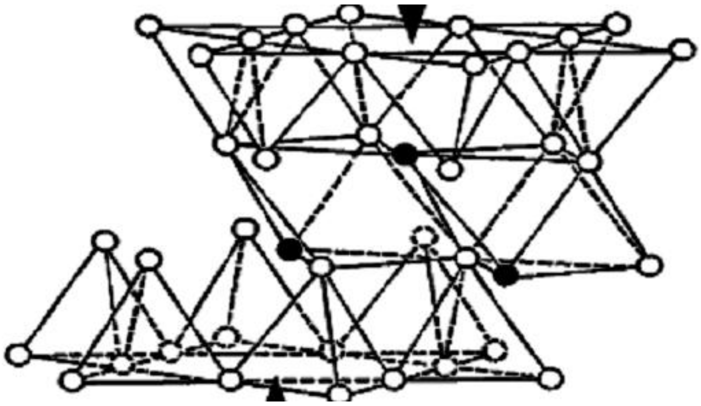
Acid catalysts from clays.

Clays may be applied in the field of adsorption and catalysis, as cheap and readily available materials. Their catalytic activity, however, is generally weak and activation procedure (e.g. acid treating and delamination) are needed to increase surface area and acidity. Kaolin is a usual component of FCC catalysts (20-50 %) and reacts with Ni and V compounds, so preserving the active component, zeolite REUSY, from contamination. Although it is generally supposed to act as a mesoporous matrix where reactant and product molecules diffuse to reach the active zeolite particles, it has been shown that kaolin, in spite of its poor acidity, participates to reaction, catalyzing the cracking of the largest molecules that do not enter the zeolite cavities

Acid treated clays.

Among the earliest cracking catalysts applied in the Houdry fixed bed catalytic cracking process were acid-activated bentonite clays, these being replaced in the 1940's by synthetic silicaluminas and in the 1960s by large pore Y-zeolites.

Smectite clays are sheet silicates in which a layer of octahedrally coordinated cations is sandwitched between two tetrahedral phillosilicate layers (2:1 layer type). To complete the coordination of the cations, hydroxy groups are also present in the layers, the theoretical formula for each layer being $Al_2Si_4O_{10}(OH)_2$. Among these clays, montmorillonites and saponites are the most widely present in nature. In the case of montmorillonites (bentonites) Mg substitutes for Al in the octahedral layers, and hydrated alkali or alkali-earth cations in the interlayer space compensate the charge defect. In saponites, additional Al for Si substitution occurs in the tetrahedral sheets .

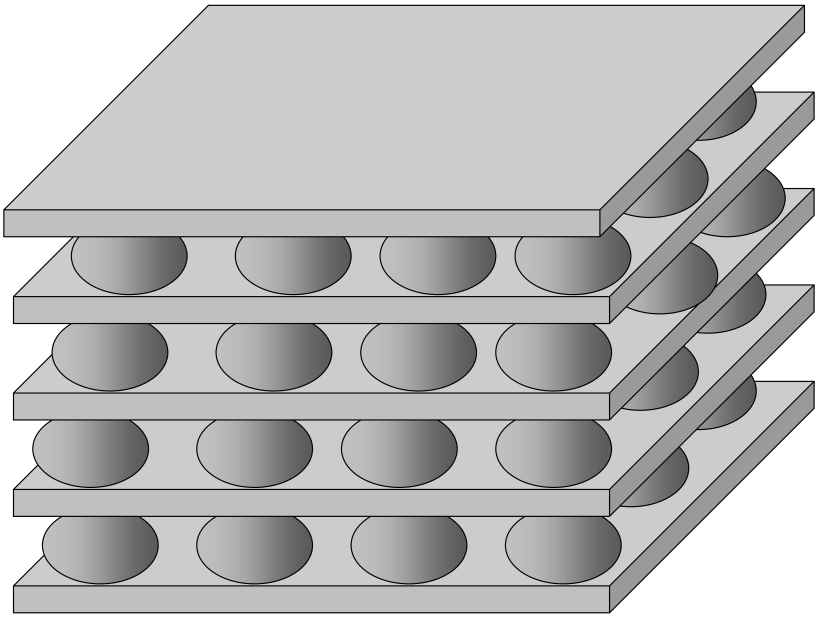


The acidity of such clays is relatively low and their surface area is also relatively low. Both acidity and surface area can be significantly enhanced by acid treatment, as done since very early times. Acid-treated monmorillonites are today commercial products and can be purchased from a variety of commercial sources. Different grades of acid-activated montmorillonites are tailored to different applications. The process by which natural calcium bentonites are acid-activated involves treatment of the uncalcined clay with mineral acids of variable concentration and for different duration at ~ 100 °C. Such a treatment leads to leaching of aluminum, magnesium and iron cations from the octahedral layer, to partial removal of aluminum ions from the tetrahedral layer that relocate in the interlayer space, and to the reduction of cation exchange capacity. During acid activation, swelling also occurs at the edges of clay platelets which open up and separate, while still remaining tightly stacked at the centre. The surface area increases notably, and pore diameters increase and assume a three-dimensional form.

Clays and acid treated clays are today largely used in the petrochemical industry mostly as adsorbants for purification and decoloration of oils. However, they are still also proposed as catalysts for several acid catalyzed reactions such as cracking of heavy fractions etherifications, esterifications, alkylation. They have also been considered for industrial applications in the field of hydroprocessing and hydroisomerization, mild hydrocracking and as support for other acid catalysts.

Pillared clays (PILC) and acidic Porous Clay Hetrostructures (PCH).

Exchanging the charge-compensating cations of a smectite clay with an oligomeric polyoxo-metal cation (like the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ Keggin-type ion) results in a two-dimensional porous material known as pillared clay (PILCs). Upon heating, the cationic pillars form oxide clusters that permanently open the clay layers, creating an inter-layer space of molecular dimensions and a well-defined pore system.



The pillaring process may generate Brønsted and Lewis acid centres in the inter-layer region of the clay, depending upon the starting clay and the pillaring agent. If the pillaring process is repeated on a pillared clay, the cation exchange capacity (CEC) of which was previously restored, both thermal stability and the number of acid sites were found to increase. The intercalation of the aluminum Keggin ion between the layers, and the following pillaring process, is quite different in the tetrahedrally substituted saponite and in the octahedrally substituted montmorillonite

. In montmorillonites the proton released during calcination can migrate into the octahedral sheets’ vacant sites but this does not occur in saponites, where they remain located in the inter-layer spacing. Moreover, pillars in pillared saponite are presumably strongly anchored to the layer by covalent Al–O–Al while in pillared montmorillonites there is no evidence of this pillar/layer anchoring.

Efforts have been made to obtain by clay pillaring large pore materials stable to regeneration treatments to perform cracking of very large molecules (> 8 Å). In any case, materials based on pillared clays are applied in some catalytic cracking processes and as molecular sieves. They may also be useful as medium-acidy supports of noble metal catalysts for Diesel and gas oil hydrotreating’. Also, the catalyitic activity of pillared clays in acid-catalysis, in particular of ethylene glycol synthesis from ethylene oxide hydration, formation of ethylene glycol ethers and of propene oxide from n-propanol appear to be of industrial interest. Further development of PILCs as industrial catalysts has been limited up to now due to inhomogeneous porosity, and difficulties in control of the preparation and of the final porosity. An interesting recent development in this field consists in the preparation of acid Porous Clay Heterostructures (PCH) by the surfactant-directed assembly of mesostructured silicas and silicaluminas in the two dimensional galleries of

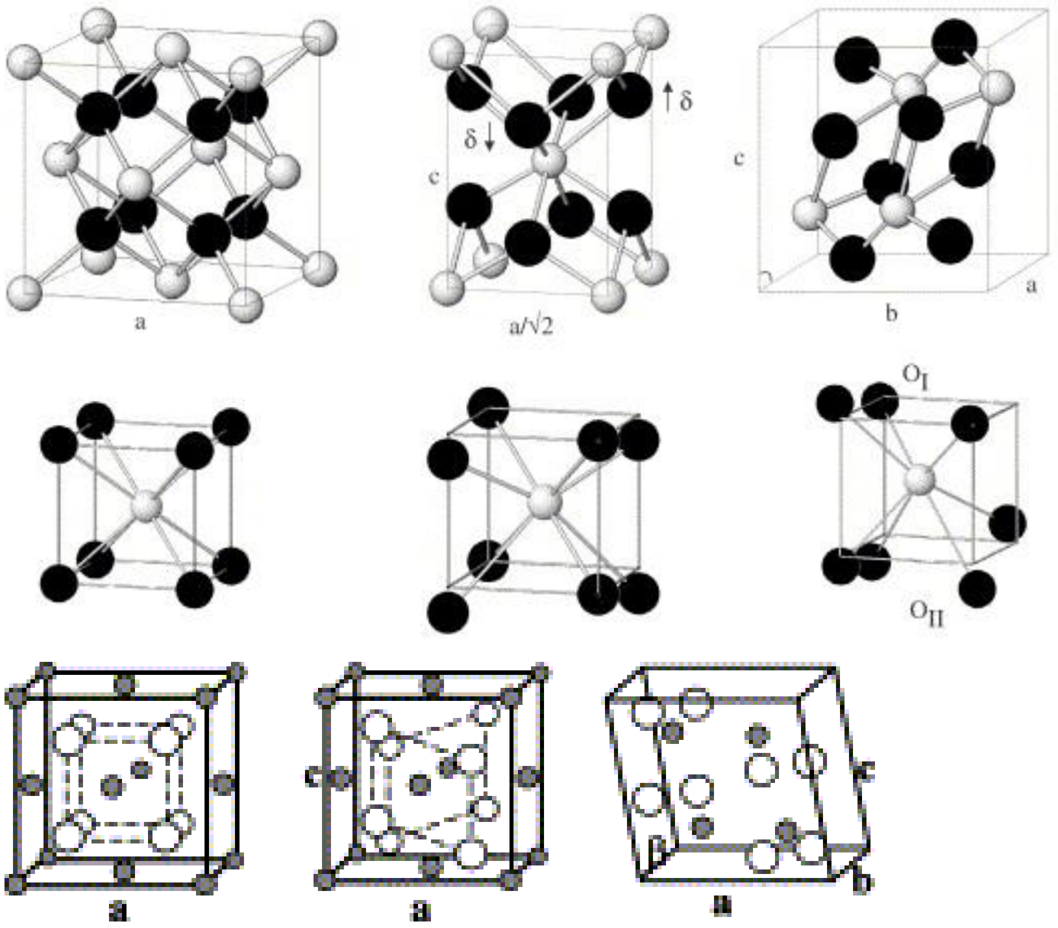
2:1 layered silicates. These materials are reported to have strong acidity, stability to 750°C and a particular porous structure.

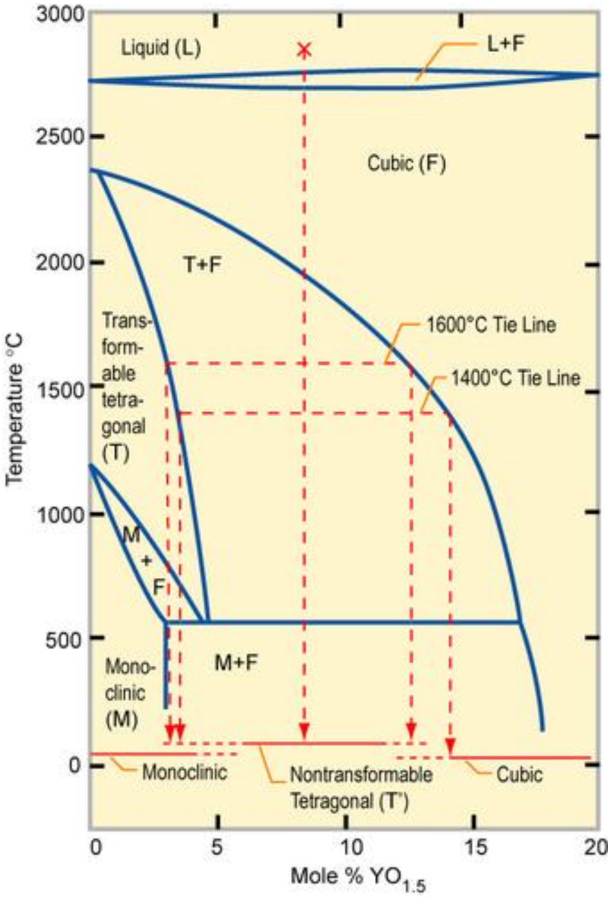
Pure and mixed or supported transition metal oxides: titania, zirconia, tungsta and their combinations.

The oxides of tetravalent transition metals, such as zirconias and titanias, are definitely ionic network solids. The ionicity of their metal-oxygen bond, associated to the medium size of the cations, corresponds to the formation of Lewis acid-base surface character, while the Bronsted acidity of their surface hydroxy groups is definitely weak. The Lewis acidity of these catalysts is medium-strong, lower than that of alumina.

Zirconia is a polymorphic material. It presents three structures which are thermodynamically stable in three different temperature ranges. Monoclinic zirconia (baddeleyite) is the room temperature form, tetragonal zirconia is stable above 1200 K while cubic zirconia is stable above 2400 K. Tetragonal and cubic zirconia, however, may exist as metastable forms at room temperature, mostly if stabilized by dopants such as Yttrium. Frequently, zirconia powders as prepared are mixed tetragonal and monoclinic. Several characterization studies have been performed on pure zirconias and showed it is a typical ionic material, characterized by medium Lewis acidity, significant surface basicity and very low Brønsted acidity, if at all.

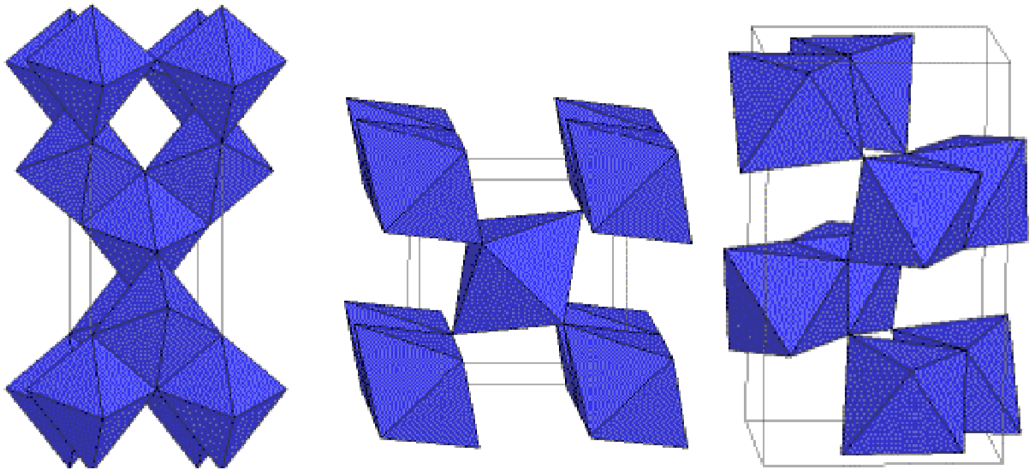
Pure zirconia or zirconia doped with alkali or alkali-earth cations is applied industrially for some alcohol dehydration and dehydrogenation reaction in the fine chemicals field. Zirconia finds many actual or potential applications as catalyst support.





Also titania is a polymorphic material: the most usual phases are anatase and rutile, the latter being always thermodynamically stable. Also titanias are highly ionic oxides with medium-high Lewis acidity, significant basicity and weak Brønsted acidity, if at all. Characterization data show that on anatase stronger Lewis acid sites are usually detectable than on rutile. Anatase is usually prepared by precipitation and is largely used in the catalysis field, e.g. as the support for vanadia-based selective oxidation catalysts as well as for vanadia-tungsta and vanadia-molybdena catalysts for the Selective Catalytic Reduction of NOx. Titania may also be used as support of sulphided hydrodesulphurization catalysts. As a catalyst, titania finds relevant application in the Claus process as an alternative to alumina in particular for the first higher temperature bed where hydrolysis of COS and CS_2 also occurs. Titania-anatase is also the basic component of most photocatalysts.

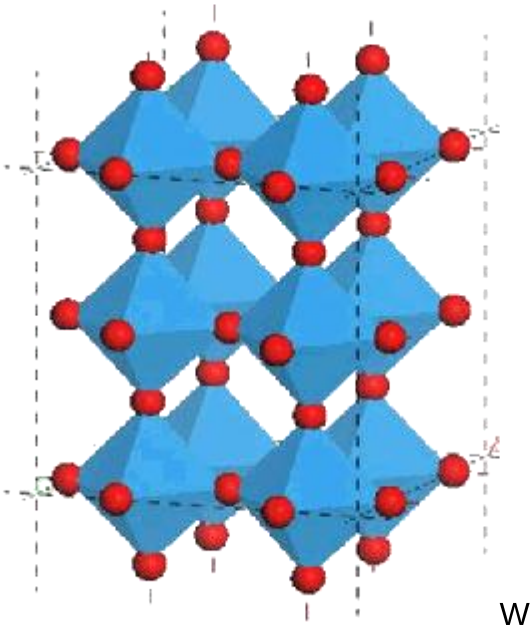
Titania and zirconia may be combined with silica and alumina, as well as each other, to give interesting and useful high-surface area and high stability materials. These materials still retain high Lewis acidity associated to the Al^{3+} , Ti^{4+} and Zr^{4+} cations, as well as medium-weak Brønsted acidity, associated to silanols and other hydroxy groups. Titania-aluminas are important materials as catalyst supports, e.g. for hydrodesulphurization catalysts.



Rutile ***Anatase*** ***Brookite***

Figure 1.1 The different polymorphs of TiO_2.

Tungsten oxide WO_3 has many crystal structures most of which however are distorted forms of the ReO_3 –type cubic structure. These structures, where hexavalent tungsten is in more or less distorted octahedral sixfold coordination, have an highly covalent character, associated to the very high charge and very low size of the W^{6+} cation. This material has very strong acidity both of the Lewis and of the Brønsted type. Pure and silica supported WO_3 have had industrial application as acid catalysts, e.g. for commercial direct hydration of ethylene to ethanol in the gas phase.



WO_3 (ReO_3) idealized structure.

Much interest has been devoted recently to tungstated oxides as catalysts. Tungstated titanias are investigated mainly in relation to their use as active components of vanadia catalysts for the selective catalytic reduction of NOx by ammonia, a reaction in which catalyst acidity plays a relevant role. Tungstated zirconia is mostly investigated in relation to its activity in the paraffin skeletal isomerization reaction. Anatase and tetragonal zirconia give rise to better catalysts than rutile and monoclinic zirconia. The presence of wolframate species on both titania and zirconia causes an increase of the Lewis acid strength, an almost full disappearance of the surface anions acting as basic sites and the appearance of a very strong Brønsted acidity. The tungstate ions on ionic oxides in dry conditions, are tetracoordinated with one short W=O bond (mono-oxo structure), responsible for a strong IR and Raman band near 1010 cm^{-1} at near or less than the monolayer coverage. This is the case of WO_3-TiO_2 supports for vanadia SCR catalysts, which usually contain ~10 % WO_3 wt/wt and have ~ 70 m^2/g. In the presence of water the situation changes very much. According to the Lewis acidity of wolframyl species, it is believed that they can react with water and be converted in an hydrated form or be polymerized. Polymeric forms of tungstate species are supposed to form at higher coverages, as an intermediate step before the formation of separate WO_3 particles.

A particular feature of tungsta-based catalysts concerns the possible reduction of tungsten oxide to lower oxidation states, that make them active catalysts also for selective oxidation. The presence of tungstate species influences very much the redox properties of vanadia-titania SCR catalysts. The hypothesis of the generation, upon reduction in hydrogen, of stronger Brønsted acid sites has been proposed. The semiconductivity of the support may influence this phenomenon.

Pt and Mn promoted WO_3-ZrO_2 catalysts are very active, e.g. in the isomerization of n-hexane at 220-250 °C. The so-called EMICT (ExxonMobil Isomerization Catalyst Technology) catalyst, based on promoted WO_3-ZrO_2, is reported to be very effective in C5-C6 paraffin skeletal isomerization at 175-200 °C even in the presence of 20 ppm of water and to be fully regenerable. In this case the redox properties of the catalyst might also be involved in the oxydehydrogenation of alkane to alkenes that later are protonated and promote a chain skeletal isomerization reaction, like for sulphated zirconia (see below). Reduced tungsten oxides are also mentioned as good catalysts for olefin methathesis.

Sulphated zirconia

Sulphation of metal oxides introduces quite strong Brønsted acidity and, in general, enhances the catalytic activity in acid-catalyzed reactions. As for exemple, sulphation of alumina enhances its catalytic activity in n-butylene skeletal isomerization.

Zirconia (tetragonal more than monoclinic), when sulphated becomes very active for some hydrocarbon conversion reactions such as n-butane scheletal isomerization. A similar behavior has also been found for sulphated zirconia-titania and, although less pronounced, for sulphated titania-anatase.

Spectroscopic studies showed that the sulphate ions on ionic oxides in dry conditions at low coverage, are tetracoordinated with one short S=O bond (mono-oxo structure). At higher coverage, disulphate species are assumed to exist, although a real proof of this probably does not exist. However, sulphate species are strongly sensitive to hydration. Lewis acidity and basicity of zirconia disappear in part by sulphation, but the residual Lewis sites are a little stronger. However, Brønsted acidity is also formed.

The very high catalytic activity of sulphated zirconia, in particular for C4-C6 paraffin isomerization, appears when a certain number of requirements is satisfied: in particular, it must be prepared by an amorphous sulphated precursor calcined at $T \geq 550$ °C in order to have tetragonal sulphated phase, and be properly activated. The catalytic activity of these materials may be enhanced by promoters such as Mn and Fe ions, which, however, do not increase the catalyst acidity.

Recent studies allowed to obtain a convincing evidence of the existence of a n-butane oxidative dehydrogenation step, probably induced by the reduction of sulphate species, during the induction period with the formation of water molecules and butylene. Protonation of butylene gives rise to the sec-butyl cation that leads to a chain mechanism. This chain may involve direct isomerization of the butyl cation and hydride transfer from n-butane (monomolecular mechanism), or dimerization of sec-butyl cation, isomerization, cracking, and hydrogen transfer (bimolecular mechanism). According to the experimental evidence that the presence of any olefins increases the butane isomerization reaction rate, it has been proposed that the skeletal isomerization reaction could occur on a “olefin modified site” (i.e. a carbenium ion) more than on the protonic site, giving rise to a bimolecular pathway having the characteristics of a monomolecular one.

Thus, the protonic acidity of these materials, arising from the presence of sulphuric acid species, is certainly strong. The presence of small amounts of water is likely required to retain surface hydroxylation. However, in parallel with what has been discussed for tungstated oxides, the semiconducting nature of zirconia (and titania to a lower extent) coupled with the reducibility of sulphate species may play an important role in the behavior of the catalyst, in non-acidic steps.

Sulphated zirconia-based catalysts have already been used in industrial application for C4 - C6 paraffin isomerization processes and are commercialized, e.g. by Süd Chemie (HYSOPAR-SA catalysts) constituted by Pt-promoted sulphated zirconia. They work at temperatures (180-210 °C) intermediate between those of the competing chlorided alumina and zeolite catalysts, similar to those of WO_3-ZrO_2 based catalysts, with final comparable performances, moderate limits in the allowed feed purity and possible regeneration.

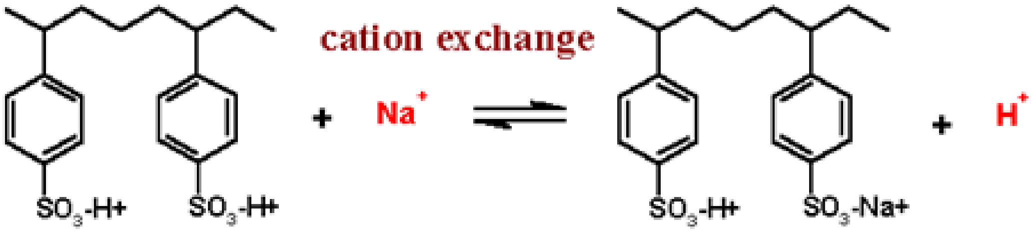
Solid acids.

Sulphonic acid resins.

Ion exchange resins have been introduced in the sixties and found today large application as catalysts in the hydrocarbon industry. The most used materials are macroreticular sulfonated polystyrene-based ion-exchange resins with 20% divinylbenzene, like the materials of the Amberlyst® family produced by Rohm and Haas. The acidity of these materials, whose surface area is near 50 m^2/g, is associated to the strong acidity of the aryl-sulphonic acid groups Ar-SO_3H. These are actually the active sites in non polar conditions, but at high water or alcohol contents in the medium, the less active solvated protons act as the acids. These materials are prepared as “gel” resins in the form of uniform beads, and as “macroporous” materials. Due to restricted diffusion, the acid sites in the gels are only accessible when the beads are swollen. “Macroporous” resins are prepared with permanent porosity, thus more acid sites are accessible also in non-swelling solvents, although diffusion of the reactant in the polymer matrix is also determinant. The number of acid sites in sulphonated polystirene is relatively high , 4.7 eq/kg for Amberlyst® -15, 5,4 eq/kg for the hypersulfonated resin Amberlyst® -36. However, the acid strength is considered to be relatively low, the Hammett acidity function being evaluated to be $H_0 = -2.2$. Another limit of these materials consists in the limited stability temperature range, < 150-180 °C. Materials with comparable activities (e.g. Dowex from Dow Chemicals, Indion from Ion Exchange ltd., India) can be found in the market.

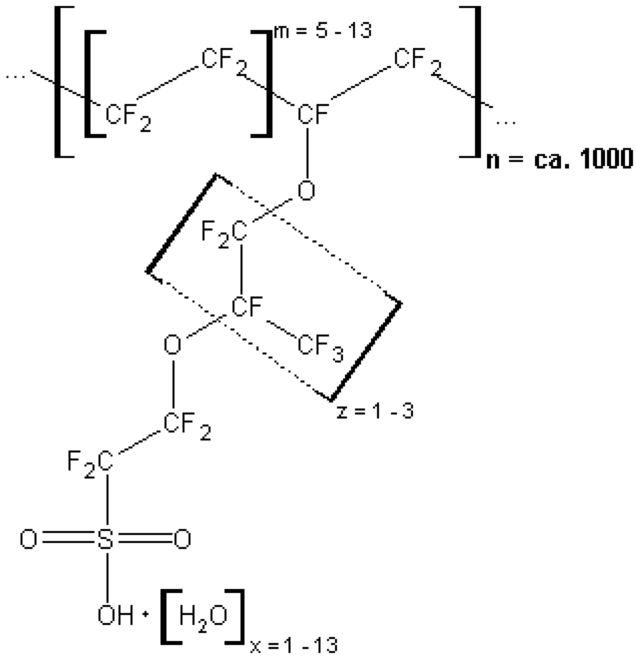
The application of these materials is limited to relatively non demanding acid catalysed reactions in the liquid phase. They are in fact the catalysts for branched olefin etherification processes such as MTBE, ETBE and TAME syntheses. In the SNAMPROGETTI process, MTBE synthesis is performed in the liquid phase at 40-80 °C e 7-15 atm C_4 cut pressure, with a water cooled multitubular reactor and an adiabatic finishing reactor in series. CD-tech proposes catalytic distillation reactors using cylindrical bales containing the ion exchange resin in the packing of the tower . The MTBE process may be modified to obtain MTBE / isobutylene dimer coproduction. The same catalysts and modified MTBE processes are applied today for isobutylene di- and trimerization. The reaction conditions are similar, but the inactive alcohol tert-butanol (TBA) is added instead of methanol. TBA does not react with isobutylene, but its presence strongly increases dimer selectivity although decreasing isobutylene conversion. Working with a real C4 cut also linear butylenes react with isobutylene to a small extent. Similar resins are also amply used in phenol alkylation processes. In this case the reaction temperature is in the range 100-130 °C. Oligomerization of propene and isoamilene can also be performed.

Suphonated polystirene polydivinylbenzene resins are deactivated by basic impurities in the feed such as nitriles (typically present in the C_4 cut after FCC), as well as by cations such as Na^+ and Fe^{3+}. Washing procedures can be applied to the catalysts to rejuvenate them. By using water cooled multitubular reactors, the hot spot due to the exothermic reaction is, when the bed is fresh, at the entrance of the tubes, but it tends to move towards the exit by increasing time on stream due to partial deactivation of the bed. This allows to follow the progressive catalyst deactivation. When the hot spot is at the exit of the bed the catalyst must be substituted. In the use of sulphonated reins for olefin oligomerization catalyst, fouling by higher oligomers may occur.



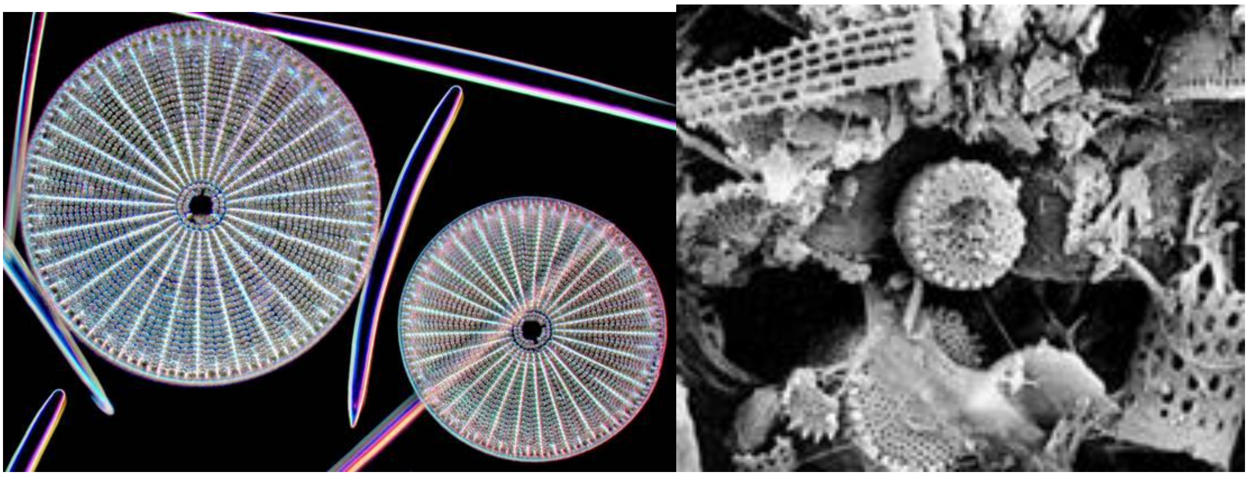
Nafion® is a strongly acidic resin produced by Dupont, a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonyl fluoride, converted to the proton (H^+) form. Nafion is definitely more acidic than polystirene-bsed sulphonic resins. This material, largely used in electrochemical processes as membrane for chlor-alkali cells and as electrolyte for proton exchange membrane fuel cells (PEMFC), may also act as a very strong Brønsted acid solid catalysts. It carries the strongly acidic terminal $-CF_2CF_2SO_3H$ group, which is however converted into solvated protons in the presence of water. This material is both chemically stable (as expected due to the fluorocarbon nature of the backbone) and thermally stable up to 280° C, at which temperature the sulfonic acid groups begin to decompose. It is commercialised in the form of membranes, of beads and of dispersions in water and aliphatic alcohols solutions.

It is generally accepted that perfluorinated resinsulfonic acids are very strong acids. However, the surface area of this material is very low, the density of the protonic sites in the pure polymer is very small (0.9 eq/kg) and their availability also is very small. Consequently, the activity of this material either in non-swelling solvents or in the gas phase is very low. This limited very much actual application in catalysis.



“Solid phosphoric acid”.

The so called “solid phosphoric acid” catalyst (SPA) has been developed by at UOP in the thirty’s. It is produced by mixing phosphoric acid 85 % with Kieselguhr (a natural form of highly pure silica) followed by extrusion and calcination. The heat treatment causes the partial polymerisation of orthophosphoric acid H_3PO_4 to pyro-phosphoric acid $H_4P_2O_7$, and higher polymers such as triphosphoric acid $H_5P_3O_{10}$, as well as the formation of silicon phosphates such as $Si_5O(PO_4)_6$, hexagonal SiP_2O_7, $Si(HPO_4)_2.H_2O$ and $SiHP_3O_{10}$. However, the real constitution of the acid phase strictly depends on water content in the catalyst which is also greatly influenced by the amount of water vapour in the feed during the reaction.



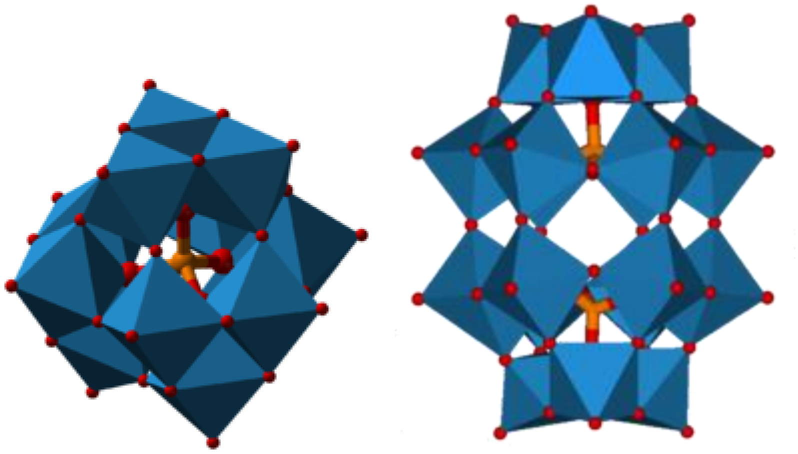
Diatoms (left) and diatomaceous earths (diatomite or kieselguhr, right) micrographs.

Free POH groups appear to be the most available to adsorbates, their Brønsted acidity is significant, but definitely lower than that of silica-alumina and zeolites.
SPA is the catalyst for gas-phase propene and isobutylene oligomerization industrial processes producing polymerate gasoline, as well as it is still used for cumene synthesis from propene and benzene. The hydration state of the catalyst affects in opposite ways the activities in olefin oligomerization and cumene synthesis and also affects strongly the catalyst lifetime. However, eccessive water in the feed leads to loss of mechanical propertries of the catalyst and its destruction, mostly due to the hydrolysis of silicon phosphates. Acid leaching and coking are additional causes of deactivation. Reaction temperature for industrial propene and isobutylene oligomerization to trimers and tetramers (UOP, IFP processes) is 150 –250 °C at 18-80 atm, with relatively high space velocities to limit coking. 250-300 ppm water in the feed are recommended and catalyst life may be more than 1 y. Multiple fixed bed or multitubular reactors are used.
SPA can also be used to produce Diesel-range olefin oligomers. The selectivity to such products has been shown to have a peak when the concentration of pyro-phosphoric acid $H_4P_2O_7$ in the catalyst become relatively high, and space velocities are low. Recently, the preparation of the catalyst has been modified to improve the crushing strength, which is controlled by the relative amounts of the silicon ortho- and pyrophosphate phases present. A new commercial catalyst was formulated which requires no binders and showed a 30% increase in catalyst lifetime.
For gas-phase UOP cumene synthesis typical reaction temperatures are 200- 260°C, at pressures 30-45 bar, with a large excess of benzene (5:1 to 10:1 benzene to propene) to limit multiple alkylation. Typical reactors are multiple fixed bed with quenching to control the hexotermic reaction temperature. 100-150 ppm of water are recommended and the catalyst life may be more than 1 y. The catalyst cannot be regenerated [232].
Solid phosphoric acid is also used for the direct hydration of ethylene to ethanol in liquid phase at 230-300 °C, 60-80 atm, and to produce other alcohols by acid-catalysed hydration of olefins. The phosphoric acid is continually lost from the carrier, and water must be supplied with the feed. However, the use of other carriers causes a diminution of the catalytic activity. .

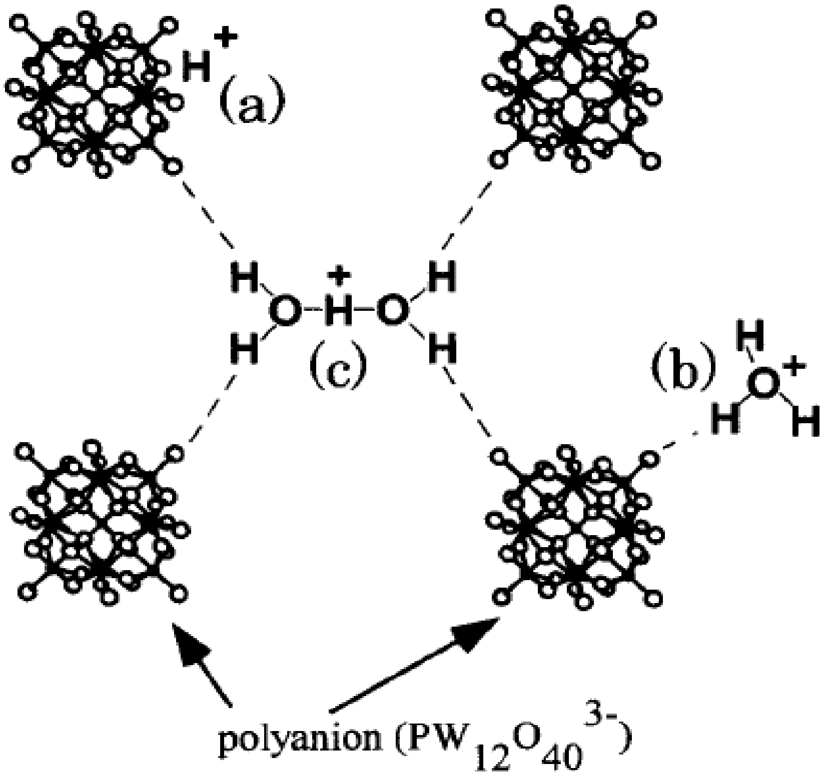
Niobic acid and niobium phosphate.
Hydrated niobium pentoxide (niobic acids, $Nb_2O_5 \cdot n\ H_2O$)) calcined at moderate temperatures of 100-300 °C are reported to show a strong acidic character with many potential applications in catalysis, displaying both Lewis and Brønsted acidity. Niobic acid is reported to crystallize as niobium oxide at 853 K, so loosing all its water and hydroxide species . The products of the combination of niobium oxide and phosphoric acid are niobium phosphates and phosphoric acid-treated niobic acid both reported to be materials potentially useful in acid catalysis. Both niobic acid and niobium phosphate find application as insoluble solid catalysts in water phase and are applied in the industry for some fine chemical acid-catalyzed processes, such as the Fructose dehydration reaction. Niobic acid and niobium phosphate are patented as alternatives to solid phosphoric acid for ethylene hydration to ethyl alcohol in the gas phase at 200 °C.

Heteropolyacids.

The most common and thermally stable primary structure of heteropolyacids is that of the Keggin unit that consists of a central atom (usually P, Si, or Ge) in a tetrahedral arrangement of oxygen atoms, surrounded by 12 oxygen octahedra containing mostly tungsten or molybdenum.. There are four types of oxygen atoms found in the Keggin unit, the central oxygen atoms, two types of bridging oxygen atoms, and terminal oxygen atoms. The secondary structure takes the form of the Bravais lattices, with the Keggin units located at the lattice positions. Heteropolyacids possess waters of crystallization that bind the Keggin units together in the secondary structure by forming water bridges. Tertiary structures can be observed when heavy alkali salts are formed.



Keggin and Wall-Dawson structures



The acidity of the heteropolyacids is purely Brønsted in nature. Since the Keggin unit possesses a net negative charge, charge compensating protons or cations must be present for electroneutrality. The acid form of heteropolyacids is generally soluble in water and acts as a liquid acid, and as a homogeneous acid catalyst in water solutions, as well as in liquid biphasic systems. Evaluation of acid strength in solution has shown that HPA's composed of tungsten are more acidic than those composed of molybdenum, and the effect of the central atom is not as great as that of the addenda atoms. Nevertheless, phosphorus-based heteropolyacids are slightly more acidic than silicon-based heteropolyacids. This gives the general order of acidity as $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ > $H_4PMo_{12}O_{40}$. A similar trend is found in gas phase catalytic experiments.

The surface area of solid HPA is generally very low (few m^2/g), and this makes accessible protons to the reactants very few. The salts of HPA's with large cations such as Cs^+, K^+, Rb^+, and NH_4^+, when obtained by precipitation from aqueous solution of the parent acid $H_3PW_{12}O_{40}$, are micro/mesoporous materials with much larger surface areas, up to 200 m^2/g . Thus, in the case of partial cation exchange, such as for $Cs_xH_{3-x}PW_{12}O_{40}$, the number of protons accessible to non polar reactant molecules is very much enhanced, and in parallel also the catalytic activity is enhanced.

According to several studies, $H_3PW_{12}O_{40}$, one of the most stable and strongest acids in the Keggin series. It has also been shown that its acid strength depends strongly on the presence of crystallization water. In agreement with this, it has been found that $H_3PW_{12}O_{40}$ and $Cs_{1.9}H_{1.1}PW_{12}O_{40}$ are very active for the isomerization of *n*-butane to isobutane at 473 K, but their catalytic activity decreased when small amounts of water were added. The Cs^+ forms of heteroplyacids are generally not soluble in water but can work as heterogeneous catalysts in liquid water or in liquid water/organic biphasic systems.

Solid heteropolyacids are active as heterogeneous catalysts for several gas-phase and liquid-phase hydrocarbon conversion reactions, and have been the object of several theoretical investigations. However, their use in the industry for gas-phase reactions seems to be still very limited, if at all, possibly due to their rapid deactivation. The commercial application of Cs-modified phosphotungstic and silicotungstic acids for the gas-phase esterification of ethylene to ethylacetate is reported.

They have been used also industrially for the hydration of olefins to alcohols, such as e.g. the syntheses of isopropyl alcohol from propene, of ter-butyl alcohol from isobutylene, and for the synthesis of poly(tetramethylene ether)glycol from tetrahydrofuran.

Other heteropolyacid structures exist besides Keggin – type phases. In particular, the so called Walls-Dawson structures, with the $H_6P_2W_{18}O_{62}$ .n H_2O stoichiometry also give rise to strong acid catalysts. The structure, known as α isomer, possesses two identical "half units" of the central atom surrounded by nine octahedral units XM_9O_{31} linked through oxygen atoms. The isomeric β structure originates when a half unit rotates $\pi/3$ around the X–X-axis. Similarly to many heteropoly-anions, the Wells–Dawson structure can be chemically manipulated to generate "holes" by removing up to six WO_6 units (from X_2M_{18} to X_2M_{12}). Wells–Dawson phospho-tungstic acid $H_6P_2W_{18}O_{62}$ shows high acidity and performs as an effective catalyst in different reactions such as MTBE synthesis, isobutane / butylene alkylation, and may catalyse reactions in liquid phase and in gas phase.

Solid Friedel-Crafts type solids.

As already cited, the classical Friedel-Crafts chemistry implies liquid-phase catalysis mostly performed with metal chloride catalysts activated by proton donor species. Due to the severe drawbacks of these catalytic systems, the substitution of these systems with solid catalysts is under development. In the field of refinery, catalysts based on solid halided aluminas are used since decades.

*Chlorided alumina.*Chloride ion at the surface of alumina, produced by adsorption of HCl or by surface decomposition of alkylchlorides, or residual from incomplete decomposition of $AlCl_3$ from the preparation method, or finally by deposition of $AlCl_3$, further enhances the acidity of alumina. Chlorided aluminas are very acidic materials, with high catalytic activity in demanding reactions, such as, e.g. isobutane / butylene alkylation .

Chlorided aluminas are used since decades as the catalytically active support for Pt-based catalysts for naphtha reforming as well as catalyst for C4 and C5 paraffin skeletal isomerization. The chlorided alumina based catalysts require the continuous addition of small amounts of acidic chlorides to maintain high catalyst activities.

For paraffin isomerization, the feed to these units must be free of water and other oxygen sources in order to avoid catalyst deactivation and potential corrosion problems. Catalysts are non-regenerable, life is usually in the range of 2–3 years. However they work at very low temperature (150-200 °C) and this allows to have more favourable equilibrium condtions, so their performances are betten than with MOR and MAZ zeolite-based catalysts or sulphated and tungstated zirconia.

In the catalytic reforming process, that works at much higher temperature (~ 500 °C) with depentanized naphtha, the chlorided alumina support acts as the catalyst of skeletal isomerization of linear paraffins as well as of alkylcyclopentanes. Also in this case chlorine compounds are fed to allow a constant chlorine content in the catalyst.

Drawbacks common to these processes concern the difficult regenerability of the catalyst, the deliquescent behaviour of aluminium chloride with the consequent leaching, corrosion and disposal problems.

Chromium and aluminum fluoride, fluorided alumina and solids containing boron trifluoride. Fluorided chromia is reported to be the most widely used catalyst precursor for large scale fluorination processes, producing fluorocarbons. The treatment of chromia with CCl_2F_2 gives rise to the formation of chromium oxide chloride fluoride species, e.g., chromium oxide halides, whose Lewis acidity is very strong. No Brønsted acidity is detected. The presence of CrF_3 and/or $CrCl_3$ phases on the activated chromia samples was not found. The partial halogenation of the surface is sufficient to provide high catalytic activity.

Fuorination of alumina with HF causes the progressive formation of AlF_3 polymorphs α-AlF_3 more than β-AlF_3. Fluorided aluminas can also be prepared by impregnation of NH_4F followed by thermal decomposition. Aluminum fluoride and fluorided aluminas are perhaps the strongest Lewis acidic solids.

Al fluoride and fluorided aluminas can be used at higher temperatures than chlorided aluminas and $AlCl_3$. They are largely used industrially in the field of the chemistry of fluorocarbons and fluorocholorocarbons..

BF_3 is also a very strong Lewis acidic compound, giving rise to Brønsted superacidic behaviour with proton-donor species. Attempts to produce stable very acidic solids based on BF_3 have been reported in the literature. Impregnation of BF_3 onto alumina gives rise to solid acids which found interesting activity in isobutane / butylene alkylation. Similar materials have been apparently used in industrial ethylbenzene synthesis catalysis (Alkar UOP process). However, leaching of BF_3 and its reactivity with water to produce volatile compounds are relevant drawbacks.

Supported liquid phase catalysts.

Attempts to produce acid solids based on liquid superacids are also in prohgress. Triflic acid (trifluoromethylsulphonic acid, $F_3C\text{-}SO_3H$) supported on silica is used in the Haldor Topsøe FBA^{TM} process of isobutane / butylenes alkylation. The reaction occurs at 273-293 K in a fixed bed reactor. The catalyst, however, may be withdrown without stop the production, and transported in a regeneration unit. Traces of acid are leached in the product, that must be purified.

4. **Basic Catalysts in the Industrial Chemistry**

Liquid bases

Metal hydroxides and their water solutions.

Most ionic hydroxides are supposed to be fully ionically dissociated in water solution. Thus the maximum obtainable concentration of hydroxide anions is determined by their solubilities. As reported in the Table the most soluble alkali hydroxides near ambient temperatures are, on molar bases, Na and Cs hydroxides. At 0 °C KOH is more soluble than NaOH, but at 100 °C NaOH is a little less than 3 times more soluble than KOH. At room or higher temperatures NaOH is the most soluble hydroxide and, consequently, concentrated soda water solutions are the most basic, allowing to produce solutions with pH in the range 13-15.

The complexation of the cation by water is likely a relevant factor in determining the solubility of metal hydroxides, and consequently the basic strengths of their saturated solutions. The cations act as Lewis acids with respect to water, forming aquo-ions H-bonded to second sphere water molecules. At least for diluted solutions, these cationic solvation complexes should be quite independent from those of the hydroxide anions.

In practice, alkali metal hydroxides (in particular sodium hydroxide, also called “caustic”, and potassium hydroxide or “caustic potash”) allow the preparation of quite dense (1-1.5 g/ml) and poorly volatile (1-13 Torr at r.t.) solutions with pH in the range 7-15.5. 2 % solutions (~ 0.5 M) have pH ~ 13, while the commercial 50 % NaOH solution, whose melting point is near 15 °C, has pH = 15.28, density 1.540 g/ml at 0°C, 1.469 at 100 °C, partial pressure of water 0.9 Torr at 20 °C. With these solutions, the partial deprotonation of very weak acids characterized by pKa ~ 20-25, such as most carbonyl compounds, can be obtained. In some cases, like for the “caustic fusion” processes, melts of dry solid NaOH (melting point 318 °C) may also be used as extremely basic media. Being also quite a cheap material, sodium hydroxide is by far the most largely used base today.

Solubilities of metal hydroxides in water.

Compound	Molecular weight (g/mol)	Solubility (g/L_{H_2O})		
		0°C	20°C	100°C
LiOH	23.95	127		175
NaOH	40.00	420	1090	3470
KOH	56.11	970	1120	1780
RbOH	102.48		(15 °C) 1800	
CsOH	149.90		(15 °C) 3955	
$Mg(OH)_2$	58.32		(18°C) 0,009	0.04
$Ca(OH)_2$	74,09	1,85	1,65	0,77
$Sr(OH)_2$	121.63	4,10		218,3
$Ba(OH)_2$	154.00	16,7	38,9	(80 °C) 1014
$Al(OH)_3$	78.00		(18°C) 0,00104	

Sodium hydroxide solutions

Water solutions of sodium hydroxide NaOH are by far the most used liquid basic catalysts. Water and sodium hydroxide monohydrate form an eutectic composition at ~ 20 % NaOH, melting near –30 °C. In the system there are two maxima in the melting point corresponding to NaOH . 3.5 H_2O (i.e. ~ 39 % NaOH , T_m ~ 15,5 °C) and to NaOH . H_2O (i.e. ~ 69 % NaOH , T_m ~ 62 °C). The melting point of the commercial 50 % soda solution is near 15 °C. NaOH has a very high solubility in water (1115 g/L, which corresponds to 52,7 % soda solution, at 25 °C). At 100 °C 3.17 kg of NaOH are soluble in 1 L of water (i.e. 76 % NaOH water solution). Soda solutions are poorly volatile quite dense liquids: the density of the commercial 50 % NaOH solution is 1.540 g/ml at 0°C, 1,469 at 100 °C. The partial pressure of water over this solution at 20 °C is 0.9 Torr.

Sodium hydroxide acts as a basic catalyst when it reacts to neutralize an acid and can be later recovered as such. This actually is frequently not true fully because an acidification step may be needed to recover the product. This step produces finally a sodium salt rather than reproducing the hydroxide. Thus, it is not always completely clear if NaOH acts as a reactant or as a catalyst. Several reaction of industrial interest using NaOH, at least formally as a catalyst can be classified as belonging to the “fine chemistry” field, thus being performed at small scales with very valuable products.

The use of sodium hydroxide has major drowbacks in corrosion problems, disposal problems and safety problems. Exposure to sodium hydroxide (dry solids or solutions) can occur when there is a spill or uncontrolled release. Transfer of solutions from tanks, handling of drums, preparations of solutions from sodium hydroxide flakes, beads, or chunks, can result in inhalation of mist or dust, splashing of liquid or dust getting into the eyes, or contact with skin. As other strong alkali substances, sodium hydroxide may cause injury to tissue by liquefaction necrosis, which is saponification of fats and solubilization of proteins, allowing deep penetration into tissue. Contact will cause severe burns with deep ulceration. Burns are less likely if the pH of the solution is less than 11.5. Repeated or prolonged contact with the skin may cause dermatitis. Sodium hydroxide aerosol can be a severe irritant of the eyes and mucous membranes.

Industrial application of sodium hydroxide.

		Final product (example)	Starting material			Intermediate product or byproduct
Caustic fusion	Metallurgy	Zirconium metallurgy	zircon minerals, $ZrSiO_4$	650 °C	Dry solid / melt	Na_2ZrO_3+ Na_2SiO_2
	Diamond mining	Recovery of diamonds	rocks (silicates)		Dry solid / melt	Sodium silicates
Caustic leaching of metal ions	Wet metallurgy	Al hydroxides / alumina	Bauxite	110-250 °C,	10-25 %	Bayer process Sodium aluminate solution
Production of sodium salts from acids	Chemical industry	Soaps (Na salts of fatty acids)	Free fatty acids		5-15 %	
		Detergents (sodium alkylbenzensulphonates)	Alkylbenzensulphonic acids			
Extraction of acidic components from / purification of organic solutions.	Paper making	Paper / cellulose	Wood chips	150-180 °C	5-10 %	Lignin
	Refinery	Alkylated gasoline (Sulphuric acid process)	Product of alkylation (Sulphuric acid process)		12 %	
	Refinery	Desulphurized gasoline or Diesel fuel	S-containing gasoline or Diesel fuel		5-25 %	Production of Na-mercaptures / disulphides
	Chemical industry	sodium phenate / phenol	Phenol-containing organic solutions			
	Food engineering	Edible vegetable oils.	Vegetable oils	40-90 °C	3-25 %	Soaps
Abatement of acid compounds from industrial and waste gases	Petrochemistry	Ethylene/propylene	Steam cracking gas		8-12%	“red oil” formation
	Refinery	Purified waste gases	H_2SO_4 contaminated gases from alkylation processes		12 %	
	Chemical industry	Purified waste gases	HCl contaminated gases from chlorination/oxychlorination processes			
	Energy production	Purified waste gases	H_2S from natural gas-biogases			
Basic reactivity in organic chemistry	Chemical industry	Vinylidene Chloride	1,1,2-thrichloroethane	60-110 °C	10-15 %	
	Polymer industry	Epoxy resins	bisphenol A (BPA) and epichlorhydrine (ECH).	100 °C, two steps	48 % caustic	
Basic catalysis.	Chemical industry	2-ethyl-2-hexenal	butanale	80°C	30 %	Mitsubishi
	Chemical Industry / Fuel production	BioDiesel (methyl esters of fatty acids)	Oils + Methanol	60-80 °C	concentrated	Lurgi
Nucleophilic reactivity.	Chemical industry	phenols	arylsulphonic acids	320-340 °C	Dry melt or 50 %	
		Benzyl alcohol	Benzyl chloride	90 °C	10 %	
		Soaps (Na salts of fatty acids)	Fats	100 °C	6-10 %	
Neutralization of waste acid solutions	Chemical industry, metallurgy	Neutral solutions to be disposed	Spent acid solutions			
Cleaning of apparata	Chemical/food industry	Clean apparata / spent soda solutions	Dirty apparata	Room – 100 °C	2-20 %	

Other hydroxides

Almost all processes performed with NaOH, as described above, can also performed with KOH with similar results, and are in fact applied with KOH in several cases. However, rarely evident advantages (or differences) come from the use of KOH instead of NaOH. One case where KOH gives different results is the soaps production process. In fact, K^+ salts of fatty acids are essentially liquid soaps at room temperature while the corresponding Na^+ salts are solid. However, a very relevant property of concentrated KOH solutions is their very high conductivity , higher than for NaOH solutions, For this reason 30-35 % KOH solutions are typical electrolytes for alkaline water electrolysis cells (AWE), for alkaline fuel cells (AFC), and for manganese dioxide-zinc alkaline batteries as well as of rechargeable Ni-Cd and Ni-Metal Hydride alkaline batteries. KOH finds also application as a component of melts for the production of industrial glasses, as well as in the production of fertilizers (such as potassium chloride, sulphate and nitrate).

$Ca(OH)_2$, also called hydrated or slaked lime, is slightly soluble in water (0.05 mol -OH/L) to give weakly basic solutions (a saturated solution at 25 °C, containing 1.8 g/L, gives a pH of 12.45). This justifies its use to neutralize acid solutions as well as to act as a basic reactant and a basic catalyst, e.g. for industrial aldol condensation reactions . However, its use instead of caustic soda is relatively rare, mainly when the use of sodium hydroxide may give rise to some safety problem. However, slaked lime finds relevant application to recover ammonia in the Solvay process for the production of soda ash (Na_2CO_3), in the "causticization" process to produce NaOH from soda ash, to regenerate soda solutions in the Bayer alumina synthesis process, in the production of magnesia as well as in water treatment processes.

The use of cesium hydroxide.in spite of its very strong solubility, is very limited likely due to its costs.

Drawbacksand in the use of hydroxides solutions.

The use and manipulation of concentrated hydroxide solutions (pH > 11.5) is associated to safety and corrosion problems. In fact the accidental contact of the human body with such solutions may cause injury to tissues with severe burns and deep ulceration. Additionally, caustic cracking susceptibility of the currently used materials (e.g. mild steel) forces to the application of more resistant and expensive materials. The application of Ni-alloys is advisable above 50-80 °C operating temperature in concentrated caustic soda.

Salts with basic hydrolysis: solutions and slurries.

Inorganic salts characterized by basic hydrolysis, i.e. the salts of weak acids, produce basic anions by dissociation, thus may also be used to increase pH in water solution. Among the most typical ones : carbonates, bicarbonates, acetates and phenates. The pK_{HB} for these anions range 4.8 – 10.25. Most of these salts have quite large solubilities. Consequently, these salts allow the formation of moderately basic solutions with pH ~ 7-13.

Sodium and potassium carbonates and bicarbonates are soluble salts characterized by basic hydrolysis. Potassium carbonate and bicarbonate are the most soluble (more than their sodium analogues) thus find larger application. These salts allow the neutralization of acids such as e.g. the production of soaps from fatty acids. Among the largest applications of potassium carbonate, the so called Hot-Potassium Carbonate (HP) process to recover carbon dioxide from hydrogen and from waste gases (Table 2). Corrosion problems are reported for these processes. Solid sodium carbonates, which are cheaper, find application as adsorbants for purification / dechlorination of incinerators waste gases.

Limestone, one of the largest constituents of the earth's crust, is a readily available and cheap mineral based on calcium carbonate, $CaCO_3$, very poorly soluble in water. Limestone, mostly in the form of slurries but also as a dry powder, finds large application in the field of Flue Gas Desulphurization (FGD) technologies, i.e. for the abatement of SO_2 from coal-fired power plant combustion waste gas and other gases. This process may produce "FGD-gypsum" which is a useful byproduct. Limestone is largely used to produce lime in the cement industry and is used to regenerate caustic in the kraft process for papermaking.

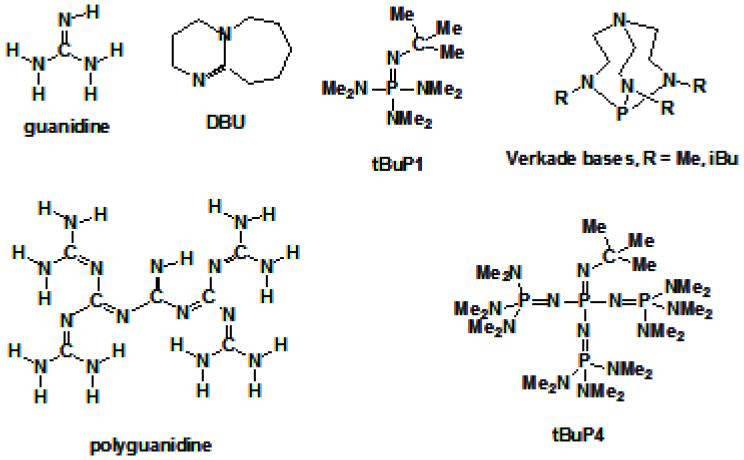
Compound	Molecular weight (g/mol)	Solubility (g/L_{H2O})		
		0°C	20°C	100°C
NH_4HCO_3	79.06	119	210	
$NaHCO_3$	84.01	69		(60°C) 164
$KHCO_3$	100.11	224		(60°C) 600
Na_2CO_3	106.00		(30°C) 505	455
K_2CO_3	138.20	1055	1105	1557
$Na(CH_3COO)$	82.04	1190		1701,5
$K(CH_3COO)$	98.14		2530	

Molecular bases.

Typical molecular bases are ammonia and N-containing organic compounds, such as amines. Ammonia is a gaseous molecule (boiling point –33.43 °C at 101.3 kPa) with very high solubility in water and weak basicity. A 1 N solution of ammonium hydroxide has a pH of 11.77 at 18 °C. A drawback of the use of ammonia solutions is associated to their relevant volatility and the toxicity and odor of ammonia vapors. The use of pure ammonia is additionally hampered by the flammability and explosivity of their mixture with air. Ammonia finds a great number of industrial applications, several of them being related to its basicity. In organic chemistry it is largely used as a nucleophilic reactant to produce, e.g. amines from alcohols. It finds also application as a base to neutralize acid solutions, such as sulphuric acid effluents from aromatic amine extraction processes from coal tar distillation fraction. Similarly, ammonia is used to neutralize sulphuric acid in the BASF process for the production of ε-caprolactam, the monomer for nylon-6. It find also large application to produce ammonium salt fertilizers.

Aliphatic amines are typically characterized by pK_{BH} roughly ranging from 8.04 for aziridine $(CH_2)_2NH$ to 11.40 for the "Hunig base", i.e. ethyl-diisopropyl amine. Thus, amines allow the production of water solutions with pH in the range 7-13. The possibility to delocalize the cation charge due to the presence of electrondonating alkyl groups is partially opposed by increased steric hindrance phenomena, as found for primary, secondary and tertiary amines. Strain tends to decrease basicity of amines. Extensive charge delocalization through delocalized π-orbitals, as it occurs in the case of protonated guanidine, makes this molecule (which is an imine, more basic than amines, with a pK_{BH} of 13.6. Aromatic and heterocyclic amines are definitely less basic than aliphatic ones.

A large number of amines have useful basic properties and may be occasionally used as basic compounds. Several amines find application as organocatalysts, in particular aymmetric compounds are useful for asymmetric synthesis. Superbasic compounds, such as those belonging to the phosphazenes family, as becoming interesting for industrial syntheses.



Some superbasic molecules

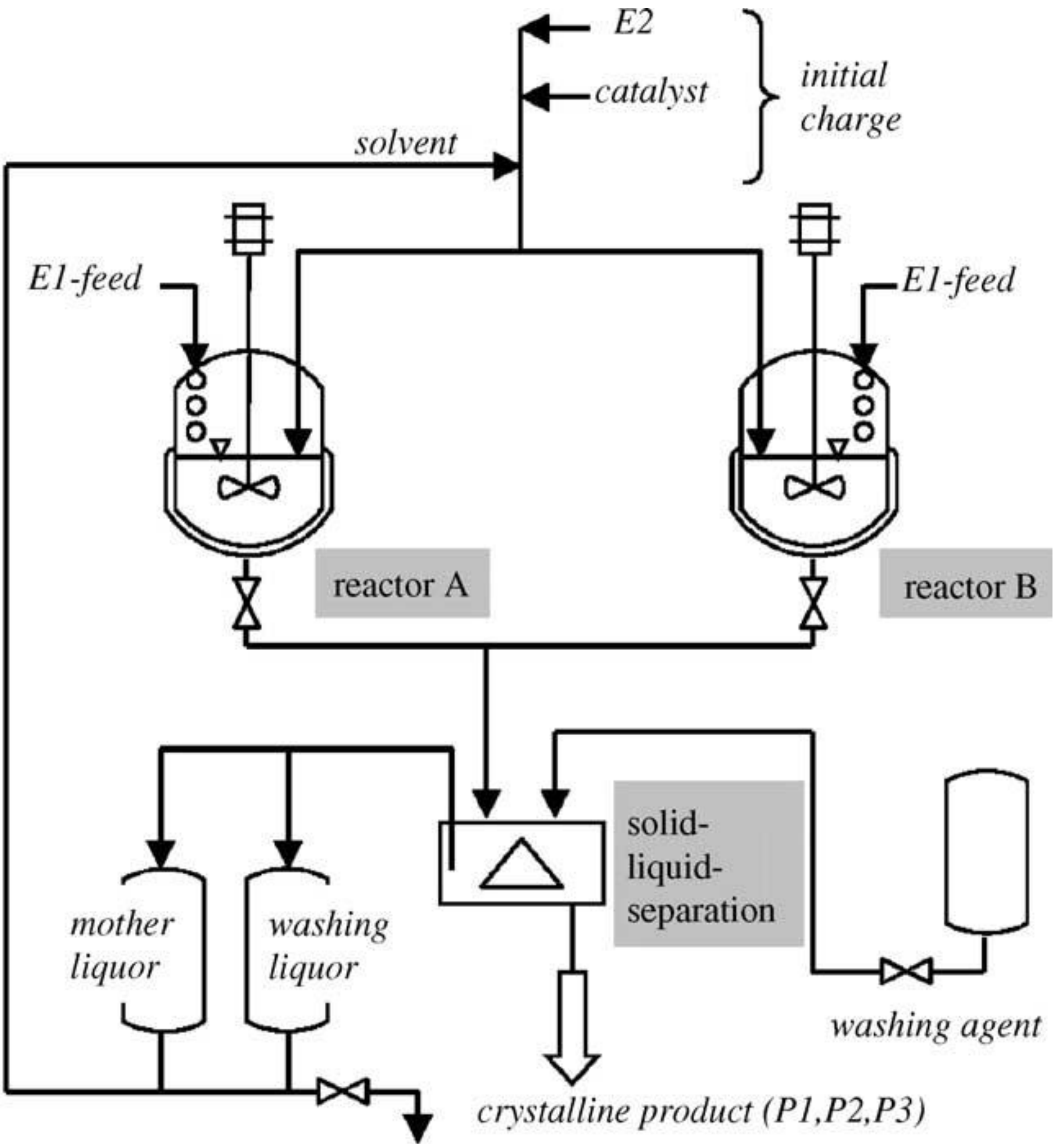
One of the most relevant applications of amines in the industrial and environmental chemistry consists in the application to wash hydrogen, methane or even waste gases to abate hydrogen suphide, mercaptans, carbonyl sulphide and / or carbon dioxide. To this purpose, the so-called “ethanolamines” are mostly applied, i.e. monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), dimethylethanolamine (DMEA), methyldiethanolamine (MDEA). These compounds have boiling points above 170 °C and do not form azeotropes with water. However they start to decompose above 200 °C. These compounds are used as 10-40 % (1-5 M) aqueous solutions giving rise to pH 8.5-12.

Other basic compounds such as phosphines, phosphine oxides and phosphine sulphides, as well as phosphate esters are used as extractants, to separate organics from water and to exctract and separate heavy metal ions. In particular, some of them find application in the separation of uranyl ion from leaching solutions in the preparation of nuclear fuels.

Obviously, limits of the use of such molecular bases consist in their toxicity, which is in some cases strong, sometimes associated to significant volatility, as well in corrosion of apparata.

Advantages I the use pf liquid bases with respect to solid bases in catalysis.

One of the few advantages in the use of liquid with respect to solid bases in catalysis is to allow the use of multipurpose plants, allowing to realize different reactions in the same plant in different times.



Multipurpose plant for aldol-like condensations with liquid catalysts.

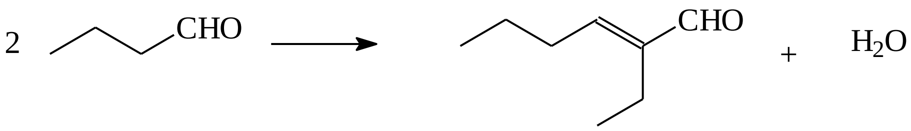
Solid Basic Materials

Alkali metal oxides.

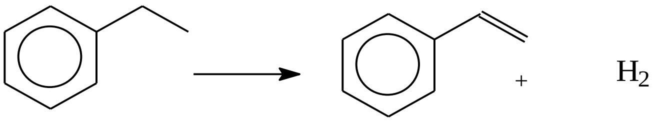
The basic reactivity of oxides of alkali metals is so high that they are essentially unstable in usual conditions, i.e. in the presence of water vapour, that is sufficient to convert them into the corresponding hydroxides, and of CO_2, that converts them into carbonates. Thus, bulk alkali metal oxides cannot normally be used as basic materials. However, alkali metal oxides can be supported or deposited over carriers, such as high surface area oxides (silica, alumina, titania, zirconia, magnesia, zeolites) or activated carbons, by impregnation / calcinations or vapor deposition procedures. They are also frequently introduced as dopants at the surface of transition metal oxides and also of metal catalysts, to introduce basicity or to reduce acidity. Potassium is frequently preferred to sodium possibly because of its definitely larger ionic size that limits reaction with supports and the formation of bulk salts. The basicity also tends to increase with cationic size, thus Cs cation giving rise to extremely high basicity.

The strong basicity of these compounds is reflected in the stability of the surface carbonates but also in the very weak acidity of the alkali ions acting as Lewis acid sites.

According to this, alkali metal – doped oxides are among the most used solid catalysts in basic catalysis, such as e.g. Na-SiO_2 for aldol-type condensations. 98 % selectivity to 2-ethyhexenal can be obtained by condensation of n-butanal over Na/SiO_2 at 400 °C, as a step in the synthesis of 2-ethylhexanol, an important intermediate in the synthsis of lubricants and plasticizers



On the other hand, many industrial catalysts are doped, sometimes heavily, by alkali to reduce acidity or to produce basic functions. Among these we can cite the iron oxide based catalysts applied to ethylbenzene dehydrogenation to styrene that may contain up to 13 % of K_2O by weight with additional small amounts of MgO and CaO.



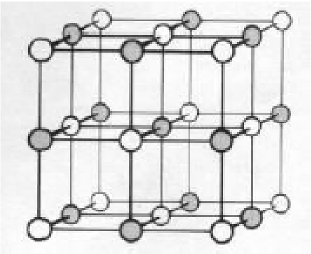
Alkaline earth oxides.

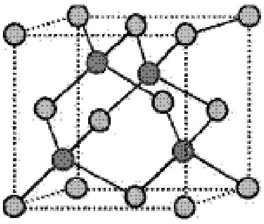
All alkaline earth oxides except BeO, whose cations are definitely larg in size, are among the strongest solid bases that may be stable as such in practical conditions. They crystallize in the rock salt type “periclase” structure, with octahedral coordination of both cation and anion. The increaing size of the cation results in an increased unit cell size as well as in an increased basicity. This is reflected, e.g. on the increased temperature for carbon dioxide desorption. On BaO full desorption of carbonates is only obtained at 900 °C.

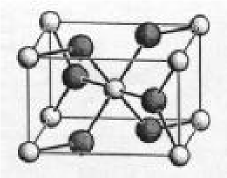
Actually, like for alkali oxides, also alkaline earth oxides are so reactive that, when prepared as fine powders, they are generally largely converted into hydroxides and carbonates, or covered by carbonates upon exposure to ambient air.

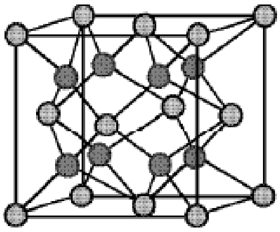
Some industrial applications of solid bases as catalysts

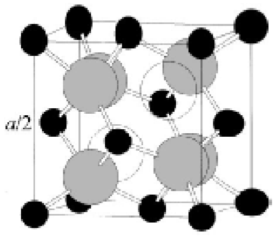
	Catalyst	Product	Reactants	Conditions	Notes
Aldol-type conversions	NaOH-SiO_2	Acrolein CH_2=CH-CHO	CH_3CHO+HCHO	300-320°C	Degussa
	CaO-BaO mixed oxide	2,2,4-trimethylpentane-1,3-diol-mono isobutyrate	isobutyraldehyde	110 °C	Chisso
	MgO-SiO_2	1,3-butadiene	ethanol	370-390 °C	
	4 % Na_2O/SiO_2, 4 % Cs_2O/SiO_2	crotonic condensation products	2-butanone (Methyl-Ethyl ketone, MEK)	325 – 400 °C	
	(Pt)-MgO-Al_2O_3 (calcined hydrotalcite)	Mesityl oxide or Methyl Isobutylketone	Acetone	120 – 250 °C condensation, dehydration,hydrogenation	Eastman
	Anionic resin Amberlite™ IRA400	pseudoionone	citral + acetone	55°C	Rohm and Haas
	Cs_2O/SiO_2	methylmethacrylate	Methylpropionate + formaldehye		Lucite alpha
Guerbet condensation	MgO-K_2CO_3-Cu	2-butyl-octanol	1-hexanol + H_2		
C-alkylation of methylaromatics with olefins	K/Al_2O_3, K/MgO Cs/carbon	isobutylbenzene	toluene + propylene	100-250°C	Phillips
	K/CaO Na/Na_2CO_3 .	5-tolyl-2-pentene	ortho-xylene + 1,3-butadiene	140 °C	AMOCO and Teijin
Olefin position isomerization	Na/NaOH/Al_2O_3	5-ethylidenebicyclo-[2.2.1]-hept-2-ene (EBH),	5-vinylbicyclo-[2.2.1]-hept-2-ene (VBH)	- 30 °C	Sumitomo
Transesterification / esterification	$ZnAl_2O_4$	Biodiesel (methyl esters of fatty acids)	Fats + methanol	200-250 °C	IFP
	Anionic resins	Biodiesel (methyl esters of fatty acids)	Free fatty acids + methanol	30-100 °C	Rohm and Haas
Dehydration/Alkylation with alcohols	Cs/SiO_2 or Na/Al_2O_3	NMP	2-pyrrolidone with methanol	300-400 °C	Mitsubishi
	MgO	2,6-xylenol	phenol with methanol	400- 450°C	General Electric
	alkali/alkaline earth-promoted alumina or zirconia catalysts	methanethiol and ethylmercaptan	alcohol with H_2S	300-400 °C	Merck
Epoxide ring opening / oxyethylation	Hydrotalcite	Alcohol polyethoxylates	Ethanol + ethylene oxide	150-180 °C	Henkel
Dehydration	Na/ZrO_2	vinylcyclohexene	1-cyclohexylethanol	350 °C	Sumitomo
	Cs-P/SiO_2	ethyleneimine	Ethanolamine	370 °C	Nippon Shokubai
Ketonization	CaO-Al_2O_3	Phenyl-1-propanone	benzoic acid with propionic acid	440 –520 °C	Union Carbide
	ThO_2 or ZrO_2	2,4-dimethyl-3-pentanone	isobutyric acid	430 °C	BASF
NOx adsorption and reaction	Pt- Ba/Al_2O_3 Pt- KAl_2O_3	N_2 + COx	NO+ hydrocarbons	200-400 °C	Toyota


rock salt

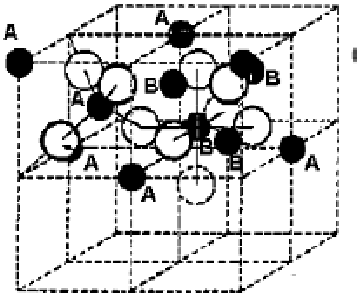

wurtzite


rutile

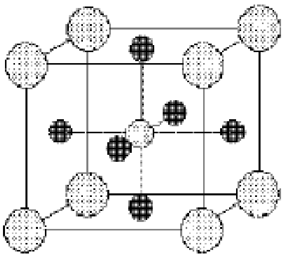

fluorite



bixbyite (1/8 unit cell)



spinel


cubic perovskite

Due to their strong basicity, alkali earth oxides cannot be covered by “monolayers” of other more covalent oxides, in contrast with what happens with ionic but less basic oxides, such as zirconia, titania, alumina. In fact, the surface of zirconia, titania, alumina can be covered by “discontinuous monolayes” of vanadate, tungstate and molybdate species, actually constituted by monomeric mono-oxo species (i.e. pyramidal low coordination complexes with one short “double” bond) predominant at low coverages in dry conditions, and polymeric species. On the contrary, with MgO such surface species are not stable and penetrate producing bulk Mg vanadate, tungstate and molybdate. The same occurs with silica-doped materials, where surface hydrogensilicate species predominate on titania, alumina and zirconia, while bulk silicates form with magnesia.

The basicity of alkaline earth oxides increases with the cation atomic number, which means by increasing cation size and decreasing its polarizing power, but also with decreasing Madelung potential, thus destabilizing the oxide anions**.** MgO and CaO free from impurities are considered to be even superbasic, following titration measurements in contact with water solution.

Different preparation methods give rise to MgO particles characterized by different morphologies and consequently different surface basicity. The catalytic activity of MgO in oxidative coupling of methane

$2\ CH_4 + O_2 \rightarrow H_2C=CH_2 + 2\ H_2O$

was found to be enhanced by Ca and Na impurities which also enhance its basicity. Calcium oxide has been found to be an excellent catalyst for biodiesel production: the performance is a little lower than with NaOH solution, but advantageously CaO is a solid.

According to their very high melting temperature (2852 °C for MgO, 2572 °C for CaO) bulk alkaline earth oxides of natural origin, such as magnesia produced by calcination of magnesite ($MgCO_3$) and Mg,Ca mixed oxides produced by calcinations of dolomite ($MgCO_3$-$CaCO_3$ solid solution) find important application as basic refractory materials.

The size of Mg^{2+} is sufficiently small to enter close packing of oxygen ions. For this reason, Mg ions can participate to the formation e.g. of mixed oxides such as spinels and ilmenites, whose oxygen packings are ccp and hcp, respectively. In relation with this, the deposition of Mg ions at the surface of normal carriers such as alumina may give rise to poor stability due to the reaction producing Mg aluminate.

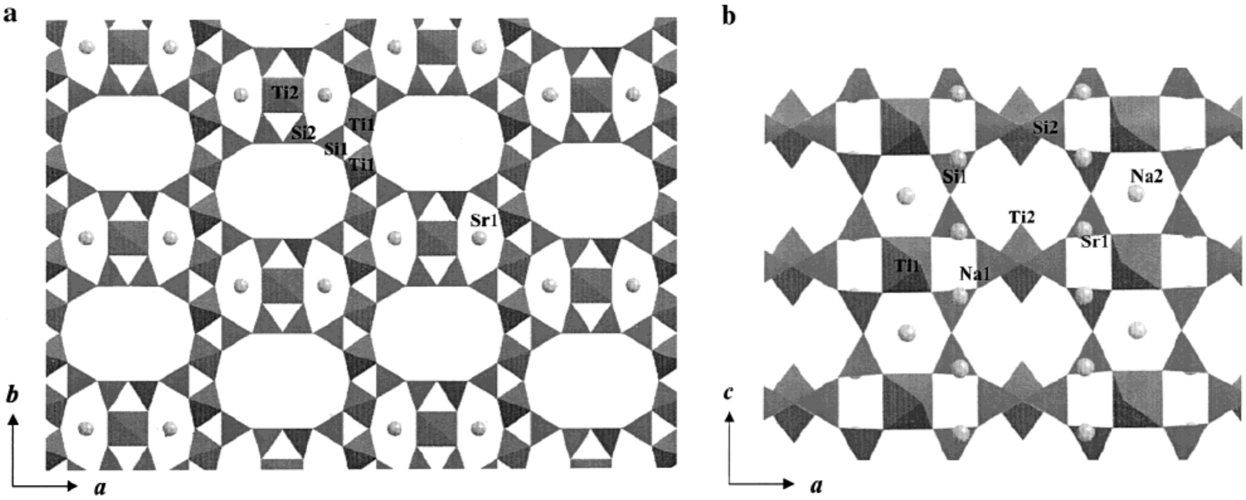
On the contrary, the size of the higher alkali earth cations is large enough to not allow the penetration into close packing of oxygen ions. According to this, Sr and Ba ions are involved in the formation of mixed oxides with less compact packing for oxide anions, such as perovskites and beta-aluminas. Additionally, Sr and Ba ions may be supported on typical oxide carriers such as alumina and titania, forming quite stable basic materials. The alkali and alkali metal cations remain exposed at the surface where their weak Lewis acidity (corresponding to strong basicity of the oxide anions) is well detectable by conventional probes. Materials belonging to the BaO-Al_2O_3 system find application as traps for nitrogen oxides in the NSR (NOx Storage and Reduction) technology for purification of waste gases of Diesel cars.

Alkali and alkali earth zeolites.

Although much work has been done on the catalytic activity of basic zeolites, it seems that, up to now, they still did not find any industrial application as catalyst. On the contrary, some of them, in particular those denoted with the IZA (International Zeolite Association) code LTA (Linde Type A) and the so-called X and Y zeolites, denoted with the code FAU, being isostructural with the natural zeolite Faujasite, have very large industrial application as adsorbents.

On the other hand, cationic zeolites may be “overexchanged”, that means that metal oxide particles may be introduced in the cavities. These particles, which in normal conditions may be carbonated and/or hydrated, may be very strongly basic if they belong e.g. to alkali oxides. This may be the case of commercial 5A zeolite (Ca,Na-LTA) where $CaCO_3$ – like particles are usually present . This is also the case of Cs oxide impregnated CsX zeolite, reported to be a very basic material.

In recent years, some interest has been devoted to a new family of solids with zeolitic structure, such as as ETS-4 (Engelhard Titanium Silicate No. 4, with formula $Na_9Ti_5Si_{12}O_{38}(OH)$. 12 H_2O) and ETS-10 (with formula $(Na,K)_2TiSi_5O_{13}.4H_2O$). ETS-4 has the interesting property of a possible tuning of the pore sizes. These materials have potentiality for adsorption and separation of even very small molecules, cation exchange and extraction of heavy metals from water.



Structure of ETS4

Transition metal, rare earth and higher valency oxides.

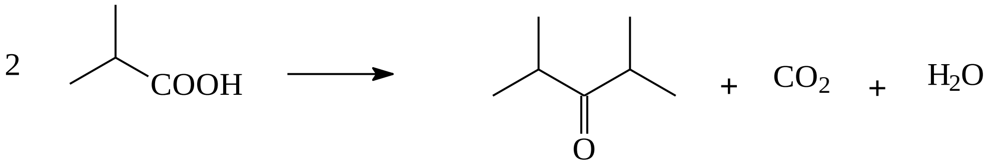
Typical metal oxides are essentially ionic network structures. This means that in the bulk and on the surface Lewis acidic cations and basic anions are present. The main factors determining the surface chemistry are the ionicity of the bond and the cation size. Low valency transition metal oxides have medium-strong acid-base properties. Relevant basicity is observed experimentally for divalent metal oxides such as wurtzite-type ZnO, tenorite CuO, as well as salt-rock type CoO and NiO. The use of some of these materials as basic catalysts is however hampered by their reducibility to the corresponding metals. Weak basicity is observed for trivalent transition metal oxides such as iron oxide and chromia. In the latter case the surface basicity strongly depends on the oxidation state, being the oxidized surface less basic than the reduced one, due to the presence of hexavalent chromate species. The basicity of ZnO and Fe_2O_3 is certainly involved in the in their reactivity towards H_2S allowing their use for gas cleanup (see below).

Stronger bases are scandia and, even more, lanthanide oxides like La_2O_3 and Nd_2O_3, in agreement with the larger cationic size. The significant basicity of rare earth sesquioxides made them the object of much imvestigation in particular in relation to the studies concerning the development of catalysts for the oxidative coupling of methane. The basicity of lanthana allows its use as catalyst of several organic reactions.

Weak basicity coupled with medium Lewis acidity is also observed for titania polymorphs anatase and rutile, while monoclinic and tetragonal zirconia have a little more pronounced basicity.

Cerium dioxide, or ceria, become quite recently a very important member of the family of catalytic oxides. It presents, when stoichiometric, the cubic fluorite structure with coordination eight for cerium ions and tetarahderal coordination for oxide anions. According to the big size of the cations, ceria presents a medium Lewis acidity and relevant surface basicity. Acually, its importance is mainly due to its slight easily reversible reducibility that produces the so called “oxygen storage capacity”. For this reason it became, as such or mixed with zirconia and alumina, a most important support for metals in oxidation reactions.

Among tetravalent metal oxides, CeO_2 has attracted much interest for its catalytic functions in the synthesis of organic compounds , which provides evidence of its relevant basicity. In fact thoria, zirconia and ceria based materials (such as CeO_2-Al_2O_3) find already practical industrial application in some dehydration and ketonization reactions, such as for the synthesis of diisopropyl ketone from isobutyric acid. CeO_2-ZrO_2 mixed oxides form a cubic solid solution in the ceria-rich side , which has relevant ability to adsorb NOx, further increased by other rare earth doping. Thoria is also reported to have strong basicity. In fact thoria, zirconia and ceria based materials find already practical industrial application in some dehydration and ketonization reactions, such as for the synthesis of diisopropyl ketone from isobutyric acid.

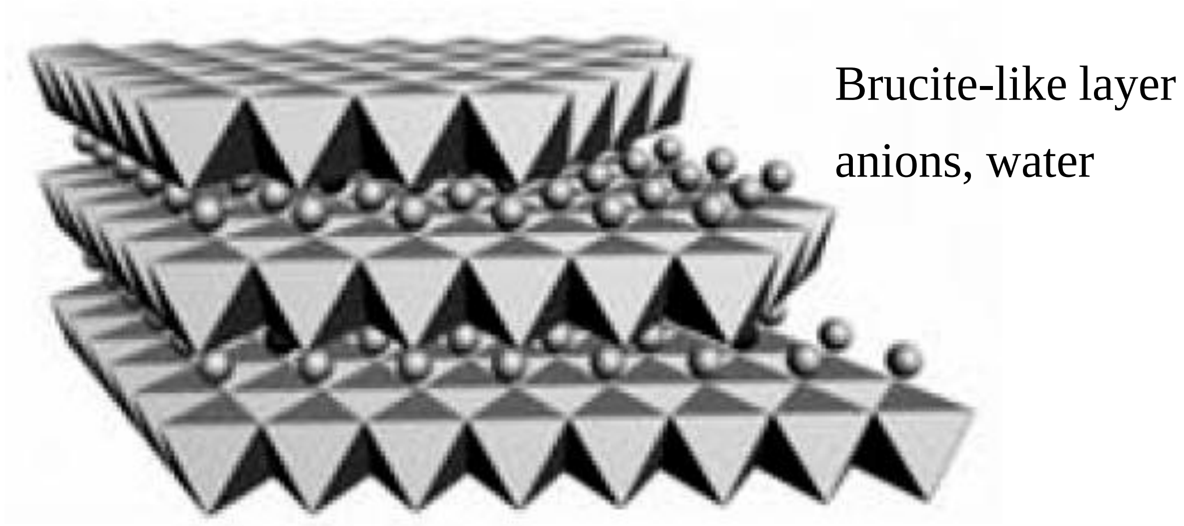


*Hydrotalcites, calcined hydrotalcites and spinels***.**

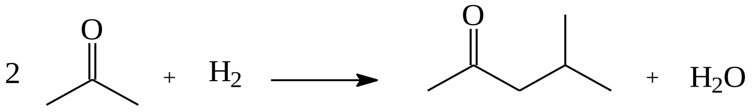
Hydrotalcite (HT, the layered double hydroxide, LDH, with formula $Mg_6Al_2(OH)_{16}CO_3$ 4 H_2O) is a natural anionic clay having interesting basic properties. Its structure is formed by brucite-like $[Mg_6Al_2(OH)_{16}]$ layers with carbonate ions and water moleculesd in the interlayer region. It is also a commercial synthesis product, used in medicine as a stomach antiacid, as well as a environmentally friendly, non-toxic and heavy metal free filler of halogenated polymers (such as PVC) to scavenge acid by-products. Hydrotalcite decompose, releasing CO_2 and water, from 260°C to 300°C, thus acting as flame-retardant and smoke suppressant. The thermal decomposition of HT gives rise to a mixed oxide whose virtual composition is 5 MgO . $MgAl_2O_4$, although these phases may give rise to mutual solid solubility, depending on decomposition temperature. In fact calcined HTs are intimate mixtures of rock-salt type and a spinel-type solid solutions.

Spinel is the mineralogical name of Mg aluminate, $MgAl_2O_4$, as well as of isostructural mixed oxides of a trivalent and a bivalent ion. Stoichiometric $MgAl_2O_4$, is essentially a normal spinel phase with tetrahedrally coordinated Mg and octahedrally coordinated Al, behaving as an important refractory material. Due to partial inversion of the spinel structure, low-coordination Al cations typical of spinel-type aluminas can be detected at the surface and produce a small density of very strong Lewis acid sites. The surface of nearly stoichiometric spinel materials show a compromise between the basic character of rock-salt-type bivalent oxides and the more or less acidic character of the corresponding sesquioxides. Excess Mg ions in the case of calcined hydrotalcites causes the predominance of the basic character of MgO. Doping with alkali may further increase the basicity of hydrotalcites.

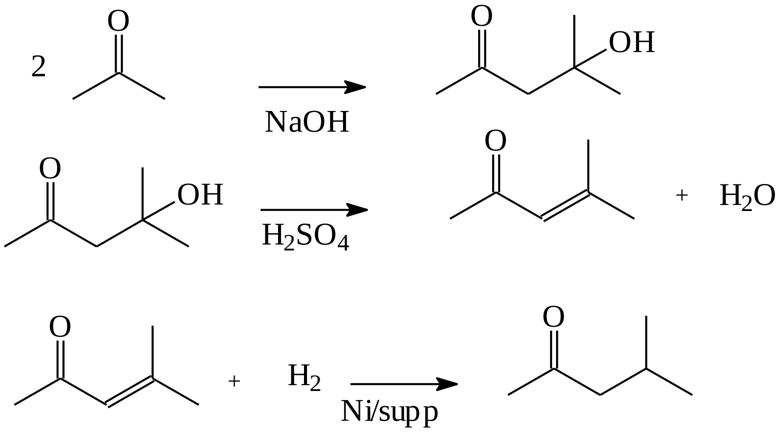
These materials, whose basic strength is somehow tunable, are very popular as basic catalysts in academic research. On the other hand, they are also used industrially, for aldol condensations such as the synthesis of, for example, methyl isobutyl ketone, MIBK, by aldol condensation of acetone followed by dehydration and hydrogenation.



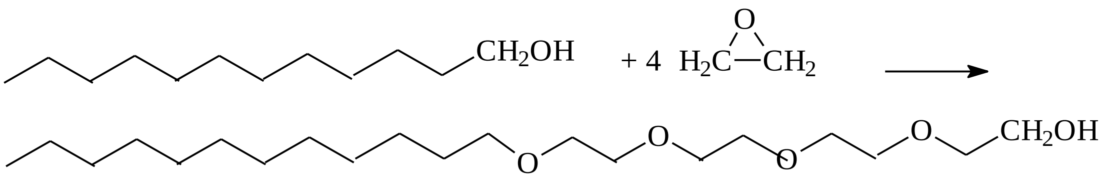
The full reaction may be performed in a single liquid phase reactor using Mg-Al hydrotalcite with 0.1 % of Pd:



This single step process substitutes the older three step one, based on catalysis by caustic, acid catalyzed dehydration and hydrogenation:



as well as for oxyethylation of alcohols with ethylene oxide with the production of non ionic polyethoxylate surfactants.



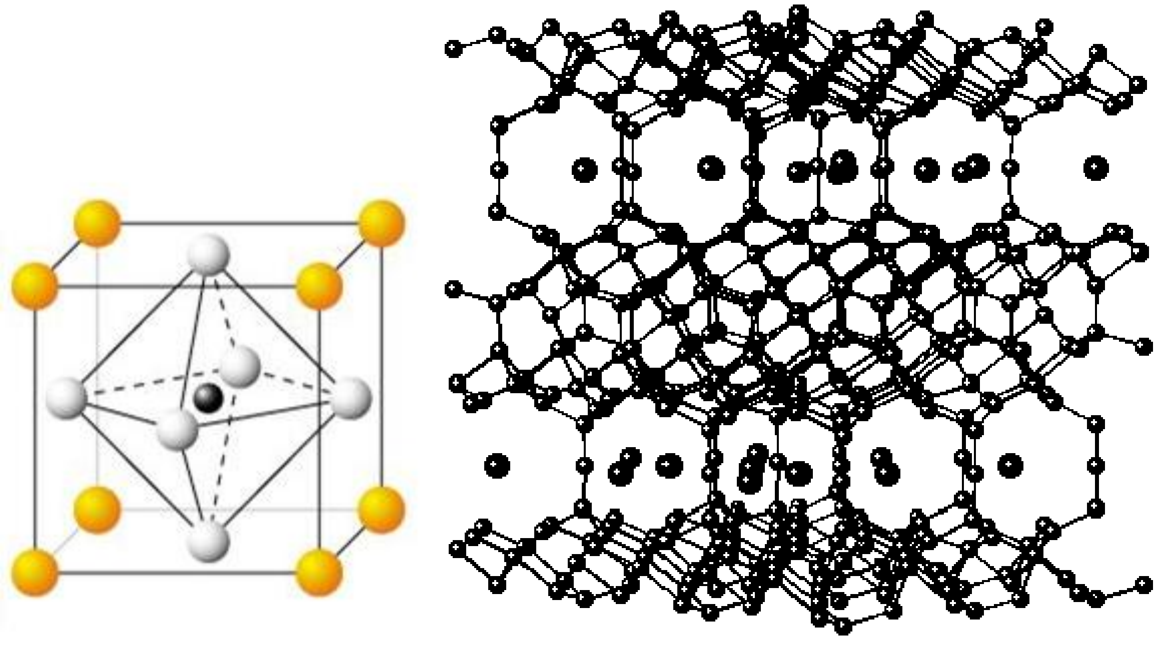
(28)

They have also been used as basic supports for noble metal catalysts, and for the abatement of SO_2 from waste gases. Mg aluminate spinels find large application as supports or components for Ni methane steam reforming catalysts just to limit surface acidity and, consequently, deactivation by coking.

According to the basic properties of both ZnO and $ZnAl_2O_4$, also Zn-Al hydrotalcite present relevant basic properties. In fact Zn-Al hydrotalcites have been patented for industrial oxyethylation. In fact Zn-Al hydrotalcite calcined at moderate temperature form poorly crystalline Zn oxides that adsorb alcohols giving rise to highly ionic alkoxide species. Zinc aluminate has also found interesting recent application as the catalyst for solid-catalyzed bioDiesel synthesis by fats transesterification with the IFP process. The use of a solid catalyst allows the distillation of methanol from the reaction medium, the separation of glycerine from biodiesel and fats, and the production of pure water and sodium free glycerine. Zinc aluminate is a component or the support of Cu-based methanol synthesis catalysts as well as methanol steam reforming catalysts.

Perovskites.

Perovskite- type phases form when small cations and large cations combine in a mixed oxide with formula ABO_3 with very different sizes. This can occur with a big bivalent and a small tetravalent cation as well as with two trivalent cations. The cubic structure of perovskite (mineralogical name of calcium titanate, $CaTiO_3$) is sometimes deformed giving rise to different tetragonal, orthorhombic and rhombohedral phases. Spectroscopic studies show that the surface is largely dominated by the large cations and this results in very basic oxide anions, at the surface of perovskites like in the cases of $BaTiO_3$, $SrTiO_3$ and several La perovskites. Evidence of this is provided by the very weak Lewis acidity of the surface cations probed by pyridine. Perovskites have been the object of much interest. These materials are thermodynamically very stable phases with several important electronic and optical properties. Among practical applications we can remind the application of LSM (i.e. lanthanum strontium manganite $La_{1-x}Sr_xMnO_3$) and similar manganite perovskites as total oxidation catalyst as well as the component of cathodes of Solid Oxide Fuel Cells.



Perovskite (left) and beta-alumina (right) structures

Beta-aluminas.

The beta aluminas and similar structures generate when a large cation (such as Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}) is mixed with a large eccess of a small trivalent one, typically Al^{3+}. The structure is constituted by slabs of the trivalent metal oxide (mostly alumina) with a spinel-type structure and ccp oxygen array, separated by layers with the very large cation and few oxygen ions to balance the charge. Along these layers ionic conductivity occurs. These materials have very high thermal stability, retaining a large surface area (i.e., >20 m^2/g), even at a temperature of 1473 K. Also in this case, as found on for Ba-β-alumina and La-β-alumina, the surface only exposes the large low valency cations, well detectable by adsorbing bases, and very basic oxygen species that adsorb CO_2 in the form of carbonates.

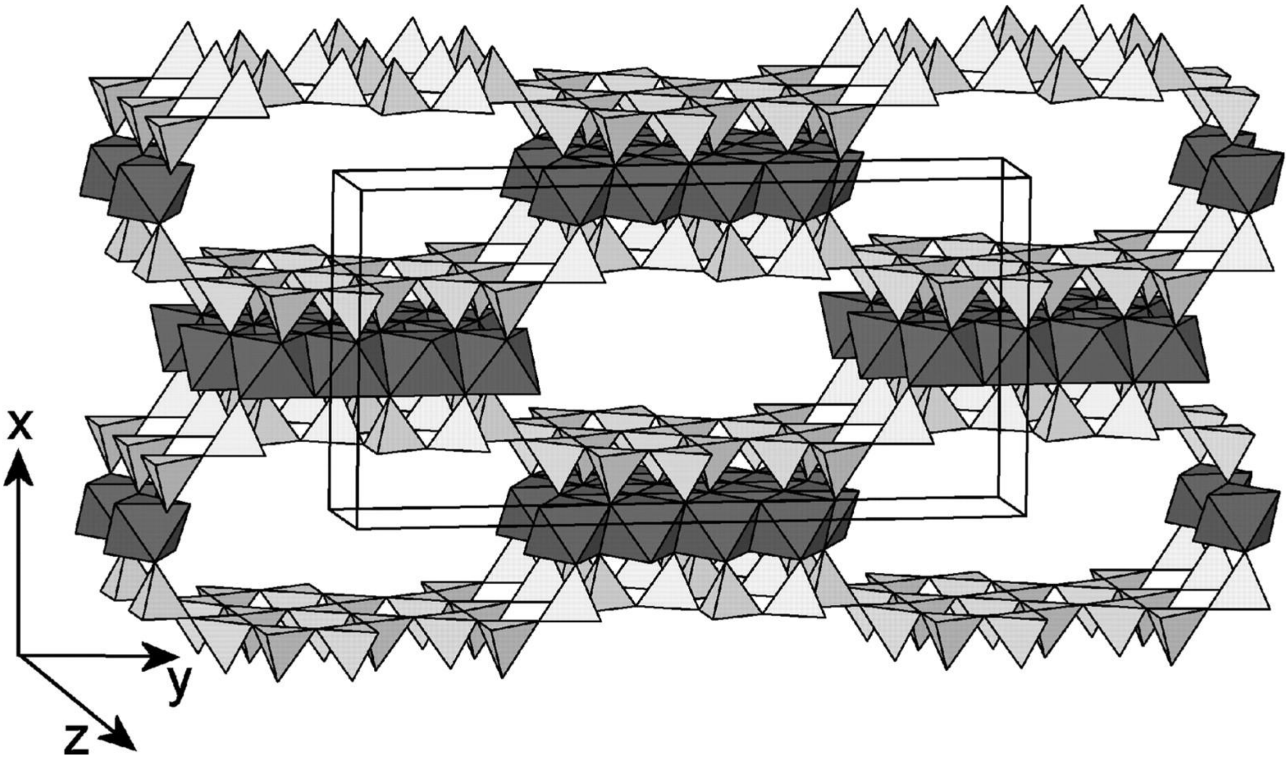
In spite of their high basicity, this property does not seem to find practical application. Beta-aluminas are industrially applied mostly in fields related to their ionic conduction, such as in secondary battery, fuel cell, thermoelectric converter, and sensor technologies. Their excellent thermal stability and high catalytic activity make hexaaluminates useful as supports or components of high temperature methane and natural gas combustion catalysts in gas-turbine applications involving temperatures up to 1773 K. Recently, they have been proposed as catalysts for abatement of N_2O through thermal decomposition. This exothermic reaction is performed at high temperature, both in end-of-pipe configuration of nitric acid and cyclohexanone oxidation processes (700 °C) and for the alternative application in the ammonia oxidation burner (1073-1173 K, wet oxidizing atmosphere).

Basic silicate clays.

Alkali and alkali earth metal orthosilicates, such as olivine (Mg_2SiO_4) and lithium silicates (Li_4SiO_4) and zirconates, besides being important refractories, find application for high temperature catalytic applications, such as biomass gasification, tar removal catalysis and high temperature CO_2 adsorption.

Smectite clays, such as montmorillonites (bentonites) and saponites, are sheet silicates in which a layer of octahedrally coordinated cations is sandwiched between two tetrahedral phyllosilicate layers. To complete the coordination of the cations, hydroxy groups are also present in the layers, the theoretical formula for each layer being $Al_2Si_4O_{10}(OH)_2$. In the case of montmorillonites (bentonites) Mg substitutes for Al in the octahedral layers, and hydrated alkali or alkali-earth cations in the interlayer space compensate for the charge defect. In saponites, additional Al for Si substitution occurs in the tetrahedral sheets. Although the presence of alkali and alkali earth ions in their structure can give rise to some basicity, surface characterization studies of untreated montmorillonite and saponite provide evidence for predominant weak acidity for the surface of these materials, The basicity can be increased significantly by chemical teeatment such as by exchanging with Cs^+ ions. Pillaring with basic materials is also possible.

Sepiolite is a hydrated magnesium silicate with the ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$, characterized by a chain-like structure producing needle-like particles, instead of plate-like particles typical of phyllosilicate clays. Most of the world production of this clay comes from deposits of sedimentary origin located near Madrid, Spain. Sepiolite is an excellent material for cat and pet litters: the popularity of sepiolite pet litters is due to its light weight, high liquid absorption and odour control characteristics.



Struttura della sepiolite

Supported metal fluorides.

According to the smaller electrophilicity of halogens (except fluorine), nitrogen, phosphorus and carbon with respect to oxygen, their bond with metals and semimetal has lower ionic character and, consequently, the corresponding binary compounds (halides, nitrides, sulphides, phosphides, carbides) are expected to show lower basicity than oxides. The strong electronegativity of fluorine is a reason for the application of KF/Al_2O_3 as a strong basic catalytic material. Other supported alkali metal fluorides, such as CsF/α- Al_2O_3 and CsF/CaO, RbF, CsF and/or KF impregnated on γ-alumina, zirconium oxide and europium oxide have been found to display good basic catalytic activity and have been patented as catalysts for the synthesis of polyglycerol..

Solid metal hydroxides and carbonates.

Very basic metal oxides are actually carbonated and hydrated in ambient conditions until high temperature. These materials, like solid NaOH, Na_2CO_3, limestone and limes, find a number of applications, as discussed above. Strong solid bases may generated *in situ* from alkaline and alkaline-earth metal carbonates by adding a small amount of acetic acid at reflux in toluene under water-free conditions, and this would result even in superbasicity, likely due to decomposition of carbonates to oxides. When used at the gas-solid interface (e.g. as catalysts) the real structure of the material (oxide, hydroxide, carbonate) depends on conditions. Alkali carbonates are frequently used as supports for alkali metallic catalysts.

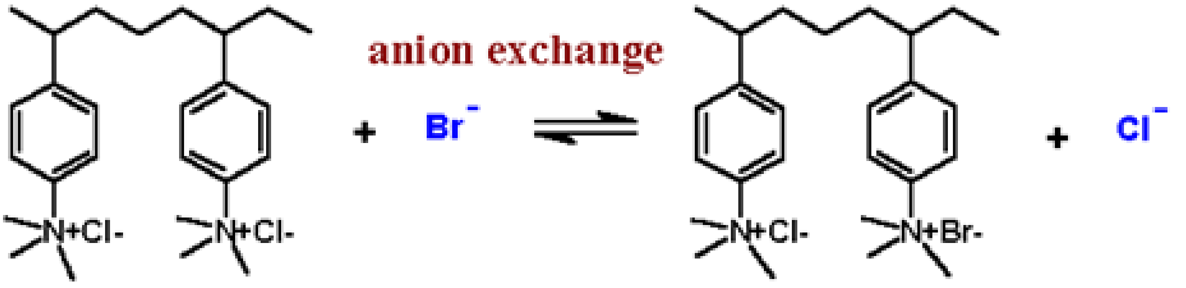
On the other hand, sodium and potassium hydroxides and also calcium compounds (oxide, carbonate) find important applications as “pure” solids for reactive melting of refractory metal oxides such as e.g. silica, zirconia, to produce melt salts in metallurgy and glass production technologies.

Activated carbons and impregnated activated carbons.

Activated carbons (ACs) are produced by pyrolysis of different carbonaceous materials such as coal, polymers,vegetables, etc. They are very high surface area materials (> 1000 m^2/g), very active in adsorption, both at the liquid-solid and at the gas solid interfaces. The real nature (waekly acidic or weakly basic) of the AC surfaces in contact with water strongly depends on pH. At low pH the basic surface sites (ketonic groups, alcoholic groups) are protonated while, at high pH carboxylic acid groups are dissociated. Additionally, the nature of inorganic matter in coal derived ACs may play also a rolein determining surface acid-base behavior. To increase adsorption ACs are frequently impregnated, e.g. by alkali oxides or carbonates, thus becoming strongly basic materials. ACs may also be used as supports for catalysts, e.g. for noble metal hydrogenation catalysts. This is used to increase reactivity towards acids.

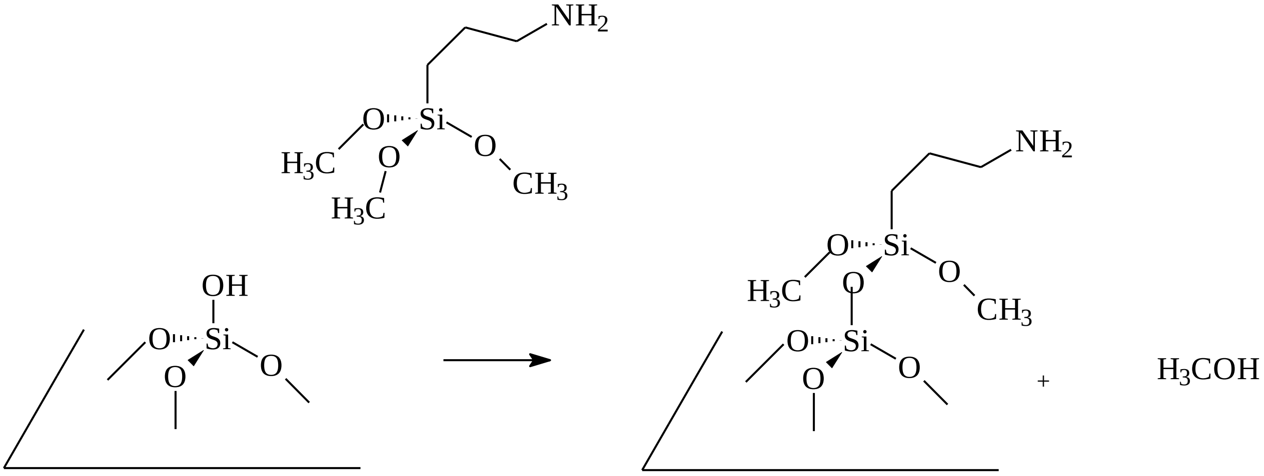
Anionic exchange resins

Ion exchange resins have been introduced in the sixties and found today large application as adsorbents and catalysts in the chemical industry. The most used materials are functionalized macroreticular polystyrene-based ion-exchange resins with 20% divinylbenzene (DVB), like the materials of the Amberlyst® family produced by Rohm and Haas. Other polymers such as acrylic -DVB copolymers as well as cellulosics are also used. Basic anion exchangers are mostly characterized by the presence of the trimethylamonium functional group bonded to the aromatic rings, counterbalanced by anions such as the hydroxide anion. These materials are active as catalysts e.g. of methanol carbonylation to methyl formate and in the Knoevenagel and aldol condensations. Resin with different compositions are also used as absorbents, e.g. in wastewater purification and heavy metal separation in metallurgy, such as in the preparation of uranium nuclear fuels and in the treatment of spent nuclear fuels. They are also used sometimes as supports for heterogeneous catalysts. One of the limits of these materials is their limited temperature applicability range (usually < 150 °C).



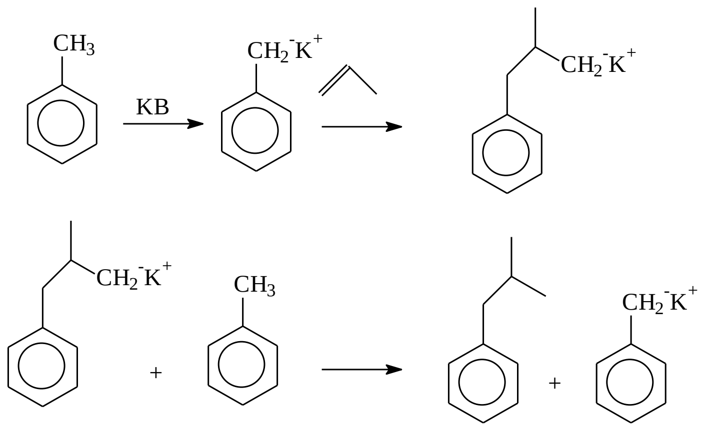
Organic bases grafted on microporous or mesoporous metal oxides and other organoinorganic solids.

The surface acido-basicity of silica-based oxides may be modified by grafting functionalized oraganosilicon compounds. Trialkoxy-silyl derivatives carrying organic functions react with surface silanol groups, producing materials carrying this function (e.g. amine or thioalcohol groups) at its surface. Similar properties may be obtained with several kinds organic-inorganic hybrid materials prepared in different ways. Mesoporous materials such as aminopropyl-modified HMS and aminopropyl-functionalized SBA-15 were prepared used to anchor organic molecules that can show basicity and activity in basic catalysis as first shown by Macquarrie. These solid materials, carrying basicity similar to that of amines, need to be used in mild conditions to avoid decomposition of the organic moieties.



Supported or solid alkali and alkali earth metals or organometallics.

As seen above, alkali and alkali earth metals, as well as their organometallics, are extremely strong bases and nucleophiles, acting as catalysts or as initiators in anionic chain reactions such as, e.g. anionic polymerizations. This reactivity is performed in dry organic solvents or in liquid ammonia, where alkali metal dissolve and ionize. Alkali metals can be deposited on solid surfaces such as on alkaline earth oxides producing solid materials with a strong reactivity and that can be considered as superbasic. Electrons released from the alkali metal atoms are assumed to be entrapped in the oxygen vacancies. Very strong reactivity has been reported for alkali metals supported on carbon materials, on alumina and on alkali carbonates, as well as for KNH_2 and $RbNH_2$ species supported on alumina. Alkali metal clusters can also be grown in the cavities of zeolites. These materials are largely used e.g. as initiator/catalysts in hydrocarbon conversion. Superbasic catalysts have been devoped by Sumitomo, based on $(NaOH)_x/Na_y/\gamma\text{-}Al_2O_3$ with x = 5-15 % wt/wt; y = 3.8 %, allowing alkylation of benzylic positions of alkylaromatics with olefins and olefin double bond isomerization at so low a temperature as –30°C. An important example of this chemistry is the production of isobutylbenzene,an intermediate for the synthesis of ibuprofen (e relevant antiinflammatory agent) by side alkylation of toluene with propene.


CH3
KB
CH2-K+
CH2-K+
CH2-K+
CH3
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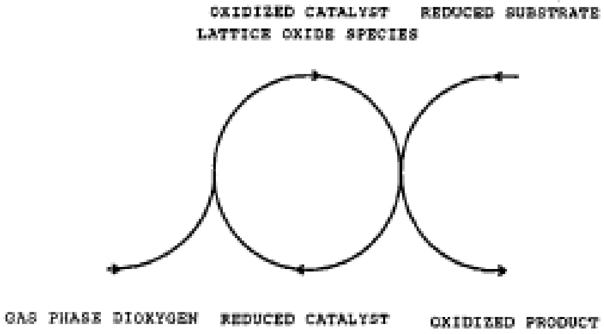
CH2-K+

5. Oxides as Oxidation Catalysts

The so-called Mars-van Krevelen or redox mechanism is widely accepted to occur in case of many oxidation reactions over metal oxide catalysts. In this case the oxidized catalyst surface oxidizes the reactant and is reoxidized by gas phase O_2 in a following step. Bulk or subsurface atomic oxide species may be active in this mechanism. In most cases oxidation catalysts are complex oxides containing reducible elements. Those reducible elements are frequently molybdenum or vanadium. To act as an oxidation catalyst the stability of the two phases must be similar allowing easy conversion of one into the other.



Scheme 1. The Mars–Van Krevelen reaction scheme for selective oxidation.

<u>Bulk mixed oxides.</u>

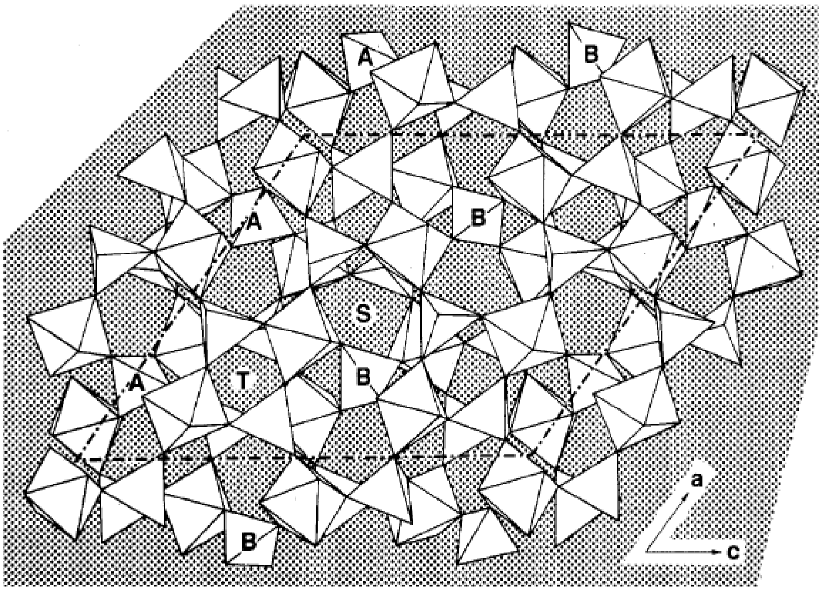
Metal molybdates.

Metal molybdates are among the most relevant families of mixed oxides applied industrially for partial oxidation reactions. The selective oxidation of methanol is an important industrial process for the production of formaldehyde

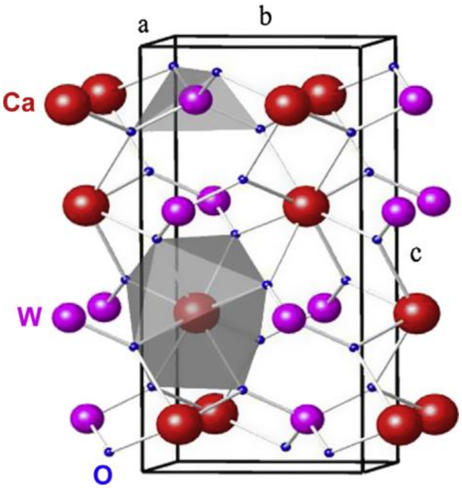
$CH_3OH + \frac{1}{2} O_2 \rightarrow CH_2O + H_2O$

One of the current industrial processes uses iron molybdate catalyst. It consists of a ferric molybdate phase ($Fe_2(MoO_4)_3$) with excess molybdena (MoO_3) so that a typical molybdenum to iron atomic ratio is 2.2:1. The typical laboratory and industrial preparation method is a coprecipitation: the catalyst can be prepared by mixing iron nitrate solution ($Fe(NO_3)_3$) with ammonium heptamolybdate ($(NH_4)_6$-Mo_7O_{24}) and adjusting the pH of the solution until both components coprecipitate. The precipitate is then filtered, washed, dried and calcined.

The complex, monoclinic room-temperature crystal structure of $Fe_2(MoO_4)_3$ consists of an open framework of octahedral FeO_6 and tetrahedral MoO_4 building blocks which are fused together by Fe-O-M0 bonds. This monoclinic structure converts into orthorombic β-$Fe_2(MoO_4)_3$ at higher temperature where the connectivity of polyhedra remains the same.



Ferric molybdate structure



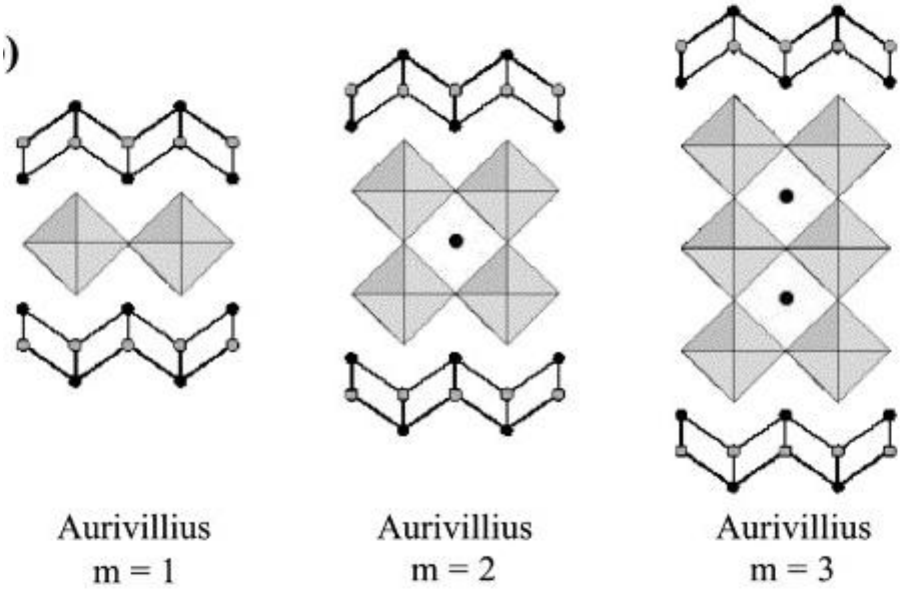
Scheelite structure of $CaMoO_4$

Although it is reported that the active phase of the catalysts is $Fe_2(MoO_4)_3$, industrial catalysts always have an excess of MoO_3. According to a recent study, the enhanced catalytic performance of bulk iron molybdate catalysts in the presence of excess MoO_3 is related to the formation of a surface MoO_x monolayer on the bulk $Fe_2(MoO_4)_3$ phase. Thus, the catalytic active phase for bulk iron molybdate catalysts is the surface MoO_x monolayer on the bulk crystalline $Fe_2(MoO_4)_3$phase and the only role of the excess crystalline MoO3 is to replenish the surface MoO_x lost by volatilization during methanol oxidation.

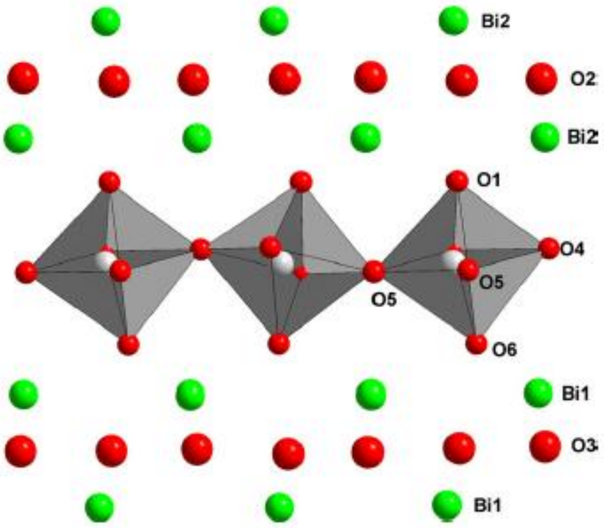
On the other hand two reduced phases, α-$FeMoO_4$. and β-FeMoO4 are found in the aged catalysts, which are not catalytically active. α-$FeMoO_4$. and β-FeMoO4 can both exist at r.t. but interconvert if pure at higher temperatures (400 °C). In the α-$FeMoO_4$phase molybdenum is octahedrally coordinated while in the β-$FeMoO_4$ phase is tetrahesdral, with a structure similar to that of scheelite.

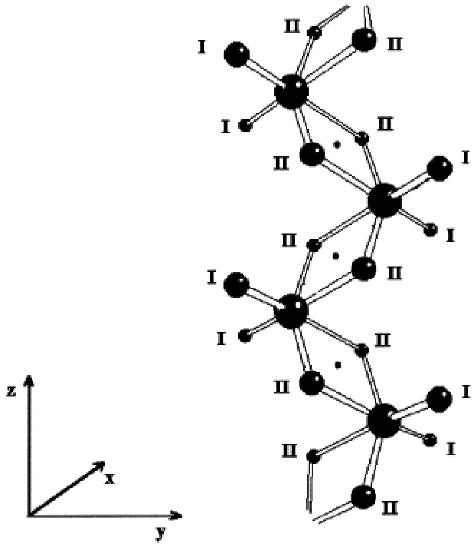
Bismuth molybdates have been developed as the catalysts for the selective oxidation of propene to acrolein and are used today also for the oxidation of isobutene to methacrolein and the oxidative dehydrogenation of butane to butadiene. Their general chemical formula is $Bi_2O_3 \cdot nMoO_3$ where n=3, 2 or 1, corresponding to the α, β and γ phase, respectively. The relative activity and selectivity of these phases are different for each reaction. Unsupported bismuth molybdates have mainly been synthesized by precipitation and solid state reaction. In the literature, different recipes for precipitation were used and the calcination was carried out at different temperatures. Pure phases were obtained under some given conditions. For example, α and γ phases were usually synthesized at 500–600 °C, β phase—$Bi_2Mo_2O_9$ was only obtained above 550 °C due to its decomposition at 540 °C to α and γ phases.

The crystal structure of γ-bismuth molybdate Bi_2MoO_6 is composed of layers of octahedral $[MoO_2]^{2+}$ and five-coordinated $[Bi_2O_2]^{2+}$ linked together by layers of $[O]^{2-}$ (Aurivillius structure). α-bismuth molybdate, $Bi_3(MoO_4)_3$ has a structure of tetrahedral coordination with cubic crystal system simila to scheelite.



Aurivillius Structures





Aurivillius structure of Bi_2MoO_6. Structure of polymeric anion in wolframite structures.

Catalysts based on bismuth molybdates are also used for ammoxidation of propylene to acrylonitrile, the very important monomer for acrylic polymers. Most recent evolution of this catalytic system implies the preparation of “multicomponent molybdates”. Industrial catalysts are based on Bi, Fe, Cr, Ni, Co, Mg molybdates where two main phases are formed: Bi/Fe/Cr trivalent scheelite-type tetrahedral molybdates constitute the active phase while Ni/Co/Fe/Mg bivalent octahedral polymolybdates with the wolframite structure act as catalysts of the reoxidation step. The catalysts are supported on silica and used in fluid bed recator.

Even more complex catalysts have been developed for propane ammoxidation, based on Mo/V/Te/Sb/Nd oxides.

Vanadyl phosphates

Another typical example of selective oxidation catalyst performed using bulk mixed oxides is the selective oxidation of *n*-butane to maleic anhydride (MA), catalysed industrially by vanadyl pyrophosphate $(VO)_2P_2O_7$ (VPP), which produces an MA molar yield of between 53 and 65 mol% at *n*-butane conversion of 80–85 mol%. While the bulk VPP is always assumed to constitute the core of the active phase, there are different hypotheses regarding the nature of the first atomic layers – i.e. those in direct contact with the gas phase. Indeed, the nature of the surface-active layer is a function of the P/V ratio used for the preparation of the catalyst. A slight excess of P with respect to the stoichiometric requirement for the VPP formation is necessary to aid the formation of the moderately active but selective δ-$VOPO_4$, that is formed during reaction on the surface of VPP. On the contrary, in stoichiometric VPP (P/V atomic ratio 1.0), the formation of highly active but quite unselective α_I-$VOPO_4$ is fostered, especially when the reaction is carried out at temperature intervals of between 340 and 400 °C. The P/V atomic ratio in the most efficient catalysts may range from 1.10 to 1.20.

Another important factor governing the catalytic behaviour of VPP is the presence of promoters. The promotional effect of Co and Fe , Bi, Nb and alkali metals has been reported. The doping of VPP with alkaline and alkaline earth metal ions leads to an increase in the effective negative charge on oxygen atoms, which is equivalent to the increase of nucleophilicity of its surface, and accelerates the rate of *n*-butane oxidation to MA.

Vanadium phosphates exist in a wide range of structural forms because of their variable oxidation states as well as the large diversity in the bonding of the VO_n polyhedra (tetrahedra, square pyramids, and distorted and regular octahedra) and the PO_4 tetrahedra. The association of different vanadium oxidation states (V, IV, and III) with their various polyhedra leads to a large diversity of the resulting structures and properties. Most attention has focused on the vanadyl hydrogen phosphate hydrate phase, $VOHPO_4{\cdot}0.5H_2O$. The topotactic transformation from the vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) to the final vanadyl pyrophosphate catalysts $[(VO)_2P_2O_7]$ is well documented. Various synthesis methods have been developed in order to obtain vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) with controlled catalytic properties. Initial catalyst preparations used water as solvent but most studies, in recent years, have concentrated on the use of alcohols as they can exhibit the duel role of solvent and reducing agent. In previous studies we have shown that very active catalysts can be prepared using an organic (VPO) and dihydrate (VPD) method. The alcohol plays a role in establishing the morphology of the vanadyl hydrogen phosphate hydrate which, since the transformation to the final catalyst is topotactic, controls the morphology of the final catalyst. We have recently reported a high-pressure solvothermal process to synthesis high crystalline catalyst precursor, $VOHPO_4{\cdot}0.5H_2O$. It was found that the alcohol used as a reducing agent can control the morphology and the best results are obtained using primary alcohols. However, precursor can be synthesized in alcohols at temperatures lower than that required by slow hydrothermal synthesis requiring the presence of surfactants as the template agent at 150 °C for 144 h.

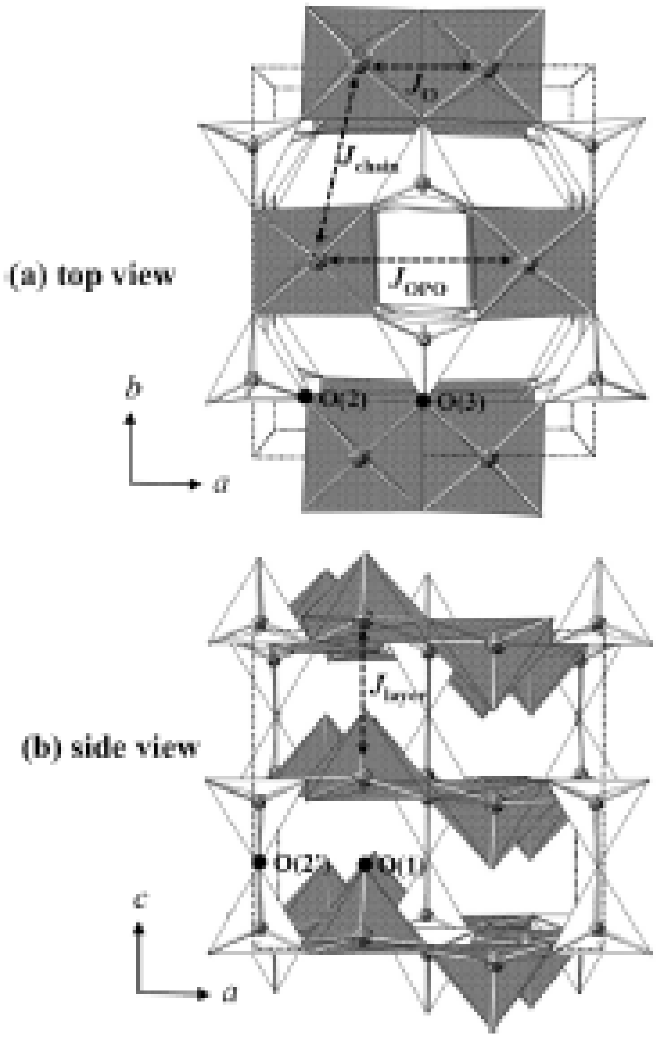
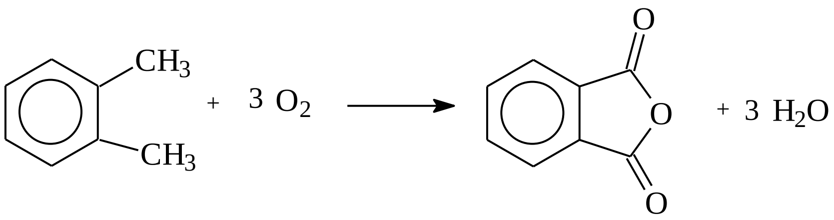


Fig. 1 Polyhedral views of the crystal structure of VOPO and the schematic description of the spin exchange couplings. The gray polyhedron represents the V_2O_8 motif (V_2O_2 ring) while the white represents P_2O_7. The bulk structure has four distinct types of oxygen: (a) O(1): forming a formal vanadyl double bond (V=O) to a single vanadium atom; (b) O(2): the doubly coordinated oxygen forming two covalent single bonds (V–O–P–O–V) that bridges the VO_5 square pyramid and the PO_4 tetrahedron along the *a* axis; (c) O(2'): the other doubly coordinated oxygen forming partial covalent bonds to the two phosphorus atoms (P–O–P) along the *c* axis; (d) O(3): the triply coordinated oxygen bridging the two VO_5 square pyramids to form the V_2O_8 motif. This type of oxygen forms P=O double bonds to the P, making only dative (donor–acceptor) bonds to the V.

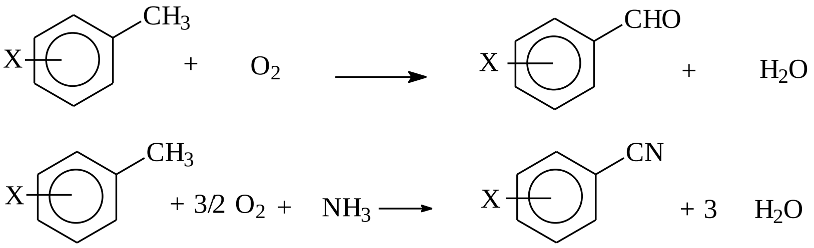
Oxides supported on oxides.

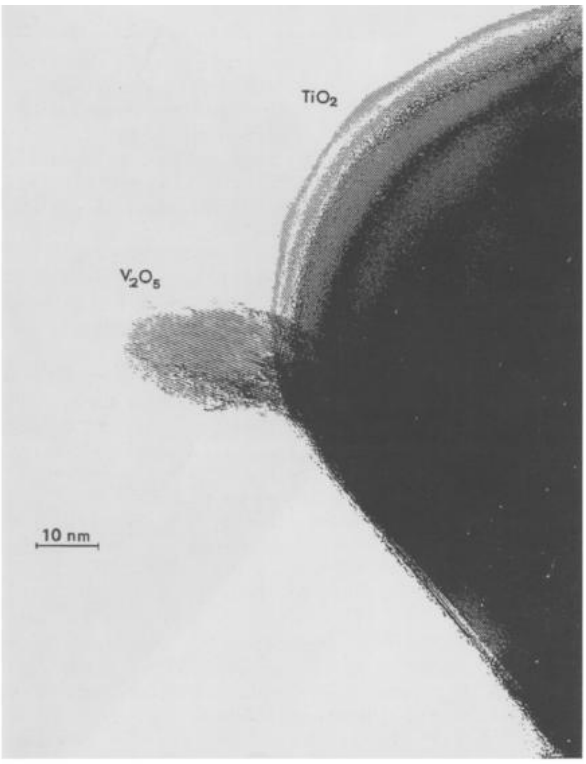
The synthesis of phthalic anhydride (precursor of phthalate esters largely used as lubricants and plasticizers) is performed industrially over vanadia catalysts (4-10 % V_2O_5 wt/wt) supported on titania (anatase polymorph) with surface area 6-25 m^2/g, alkali ions (K, Rb, Cs), Sb and P playing the role of promoters. The temperature in the bed is 360-450

°C. Although this process is well established since decades, improvements are needed from several points of view, with the need, in particular, of improving catalyst selectivity. Although the content of vanadium in induistrial catalysts is generally quite high it has been shown that sub-monolayer V_2O_5 on TiO_2 catalysts may have also good activity and selectivity if the support area is sufficiently deactivated. This catalytic system has been thoroughly characterized by IR and Raman spectroscopy.



Reactions in similar conditions allow the syntheses of aromatic anhydrides and of aromatic nitriles by oxidation and ammoxidation of toluenes and xylenes over vanadia-based catalysts such as V_2O_5 /TiO_2 or V_2O_5/Al_2O_3.





g. 6. HREM image of EL10V8 (Laboratory I-2) showing the (101) planes of V_2O_5 and TiO_2.

Another example of oxides supported on oxide catalysts is that for the SCR of Nox by ammnonia. DeNOxing of waste gases from stationary sources can be achieved efficiently by using the so-called SCR process, i.e. the Selective Catalytic Reduction using ammonia as the reductant:

$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$

Industrial catalysts are constituted by V_2O_5-WO_3/ TiO_2 or V_2O_5-MoO_3/ TiO_2 monoliths. TiO_2 in the anatase form supports a “monolayer” of V_2O_5 and WO_3 (or MoO_3) deposed by impregnation. In general, the overall surface area of the catalysts ks 50-100 m^2/g, with V_2O_5 virtual contents of 0,5-3 % w/w and MoO_3 or WO_3 contents of 8-12 % w/w . Typical reaction temperature is around 350 °C.

In all cases it has been found that the best catalysts contain nearly a full “monolayer” of vanadium plus tungsten (or molybdenum) oxides over the TiO_2-anatase support. The amount of vanadium oxide is variable but generally very small (at least in the most recent catalyst formulations). Most authors believe that vanadium oxide species are nearly “isolated” and ly between polymeric tungsten oxide species.

The choice of TiO_2-anatase as the best support for SCR catalysts seems to have at least two main reasons. i) SO_2 is usually present in the waste gases of power stations and in the presence of oxygen it can be oxidized to SO_3 and can give rise to metal sulphates by reacting with oxide catalyst supports. TiO_2 is only weakly and reversibly sulphated in conditions approaching those of the SCR reaction in the presence of SO_2 and the stability of sulphates on its surface is weaker than on other oxides such as alumina and zirconia. Consequently, TiO_2-based industrial catalysts are partially and reversibly sulphated at their surface upon SCR reaction in the presence of SO_2, and this sulphation even enhances the SCR catalytic activity. ii) It seems ascertained that supporting vanadium oxides on titania-anatase gives rise to very active oxidation catalysts, more active than those obtained with other supports. This has also been found for V_2O_5-TiO_2 (anatase) “monolayer” type catalysts for the selective oxidation of ortho-xylene to phthalic anhydride. The reason for this activity enhancement can be found on the good dispersion of vanadium oxide on titania giving rise to “isolated” vanadyl centers and “polymeric” polyvanadate species and also on the semiconductor nature of titania, whose conduction band is not very far from the d-orbital levels of Vanadyl centers, located in the energy gap. So, titania-anatase is an activating support, and gives rise to catalysts that are stable against sulphation or even improved upon sulphation.

All authors agree that ammonia is strongly adsorbed and activated on the catalysts, later reacting with gas-phase or weakly adsorbed NO.

In spite of their lower combustion activity with respect to noble metal based catalysts, base metal based catalysts, such as $MnOx/Al_2O_3$, are commercially used for catalytic combustion of oxygenated VOCs. Manganese-based catalysts, copper and nickel and combinations thereof such as unsupported Mn_3O_4, as well as Mn oxides supported on carriers such as alumina, titania and zirconia,

Zeolite catalysts for the abatement of NOx and N_2O.

Zeolites containing transition metal centers have redox activities and find interesting catalytic activity in several oxidation reactions. They are practically used for several slightly different reactions for the abatement of NOx (Denoxing) in flue gases. Several metal containing zeolites are used for the SCR of NOx by ammonia in automotive waste gas treatments.

The denitrification of waste gases can be obtained also using methane or other hydrocarbons as a selective reductant of NOx to nitrogen:

$CH_4 + 2\ NO + O_2 \rightarrow CO_2 + N_2 + 2\ H_2O$

This reaction represents formally an oxidation of methane by O_2 and NOx. Co-containing zeolites, such as Co-MFI and Co-FER, were found to be particularly active for this reaction.

Iron zeolites have been found to be very efficient for the abatement of nitrogen oxides in a number of different configurations. Fe-ZSM5 is active in the abatement of NOx by reacting with ammonia catalyzing efficiently the normal SCR reaction

$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$

as well as the so-called Fast SCR reaction, i.e. the reduction of NO+NO_2 mixture by ammonia

$4\ NH_3 + 2\ NO + 2NO_2 \rightarrow 4\ N_2 + 6\ H_2O$

This reaction can be useful in denoxing flue gas from diesel cars after a first step of oxidation of NO to NO_2. Cu-ZSM5 is also active for this reaction . However, Fe-ZSM5 can also catalyze the normal NH_3-SCR reaction, and used for this purpose in the so called EnviNOx technology to abate NOx from waste gases of nitric acid plants . On the other hand, Fe-ZSM5 is also useful to abate N_2O in two different modes: simple decomposition at 425-525 °C, formally:

$N_2O \rightarrow N_2 + ½\ O_2$

which is favored by the co-presence of NOx (NO+NO_2), or reduction by hydrocarbons

$(3n+1)\ N_2O + C_nH_{2n+2} \rightarrow (3n+1)\ N_2 + nCO_2 + (n+1)\ H_2O$

at ca 350-400 °C (Uhde deN2O process), which is instead unfavoured by the copresence of NOx .

Fe-ZSM-5, containing samples (both prepared by isomorphous substitution or post-synthesis ionic exchange) usually present a complex mixture of Fe sites with different nuclearity (from isolated to oxidic clusters, passing through dimers and small oligomers), different oxidation (Fe^{2+}, Fe^{3+} and maybe even Fe^{4+}) and coordination state.

6. Metal oxides in hydrogenation and dehydrogenation reactions.

A number of oxides adsorb significantly hydrogen and show useful activity as catalysts for hydrogenation and dehydrogenation reactions. Adsorption of hydrogen on metal oxides is mostly reported to be heterolytic, occurring on exposed cation-oxide couples, and being strongly favoured by the basicity of the oxide species. Thus hydrogen dissociation produces a metal hydride species on cationic centers and a new hydroxyl group on an oxide site. The best known case is that of ZnO which is an active catalyst in hydrogenations, such as methanol synthesis, as well as in dehydrogenation reactions. Well evident surface hydride species have been observed by different techniques, both of the terminal Zn-H type I, which is more weakly adsorbed, and of the bridging Zn-H-Zn type II, which is more strongly adsorbed, formed together with new OH groups.

Heterolytic dissociation of hydrogen has also been observed on chromia (Cr_2O_3), where only terminal hydride species where found and their combination ZnO-Cr_2O_3, as well as other mixed chromites such as Co-Cr and Mn Cr oxides, where both terminal and bridging species were found.

Two terminal hydride species have also been found to be formed by hydrogen adsorption on gallium oxide polymorphs , and assigned to hydride species bonded to tetrahedral and octahedral Ga ions, respectively.

Dissociative adsorption of hydrogen was also observed on zirconia, where terminal mono hydride Zr-H and dihydride H-Zr-H species as well as bridging species (ZrHZr) were found. Dissociative adsorption of H_2 was also observed to occur on defect sites of MgO.

The results reported above suggest that the reducing species upon hydrogenation catalysis on oxides are surface hydride species. This mechanism seems mainly involve quite hardly reducible cations on ionic oxides, i.e. with some surface basicity.

A different approach has been proposed in other cases, and may occur in particular in de-oxygenation reactions such as reduction of carboxylic acids. In this case an “inverted” version of the so-called Mars-van Krevelen mechanism, or redox mechanism, can occur. This mechanism is well evident in the case of oxidation reactions, implying the reduction of the catalyst surface by the substrate and its re-oxidation by oxygen. In the case of hydrogenation reactions, the redox mechanism implies that hydrogen may reduce the oxide surface forming water. The surface may be re-oxygenated by the substrate which is consequently de-oxygenated. Thus this mechanism is possible on the oxides of partially reducible cations, such as e.g. Ce^{4+} and Fe^{3+}.

In recent years, interest is growing on the use of ceria as hydrogenation catalyst. In particular it has been found to be active for the hydrogenation of alkynes to olefins. The adsorption of hydrogen on ceria has been studied by DFT calculations. These studies have shown that H2 may adsorb dissociatively on CeO2(111) with a relatively low activation barrier (0.2 eV) and strong exothermicity . Hydrogen dissociation is supposed to lead to two OH groups. Indeed, during hydrogenation reaction an increase of absorption in the OH stretching region of the IR spectra bands was observed. This is a mechanism of oxidative adsorption leading to the reduction of cerium ions to the trivalent state. This mechanism of adsorption may be seen as the precursor of the deoxygenation redox mechanism discussed above, being water easily formed from the hydroxyl groups of the reduced surface, and desorbed.

The two latter mechanisms, both implying the oxidation of hydrogen and the reduction of the metal centers, are parallel to those are supposed to occur in the case of hydrodesulphurization over sulphide catalysts (see below).

It can be supposed that inverse mechanisms with the same intermediate states can be applied in the case of dehydrogenation reactions. In fact, catalysts based on zinc, chromium and gallium oxide are supposed to be able to abstract hydrides from organic molecules, with the intermediate formation of metal-hydride surface species. These species will give rise to gaseous hydrogen after abstraction of a proton. On the other hand, dehydrogenation on more reducible oxides (e.g. ferric oxide) would occur with reduction of the surface and its reoxidation by eviolution of hydrogen.

$$\begin{array}{lclcll}
\text{H-H} & & H^{-} & & & \\
M^{n+}\ O^{=} & \rightarrow & M^{n+}\ \ {}^{-}OH & & &
\end{array}$$

$$\begin{array}{lclcll}
\text{H-H} & & & & & \\
O^{=}\ O^{=} & & {}^{-}OH\ \ {}^{-}OH & & O^{=} & +\ H_2O \\
M^{n+}\ M^{n+} & \rightarrow & M^{(n-1)+}\ M^{(n-1)+} & \rightarrow & M^{(n-1)+}\ M^{(n-1)+} &
\end{array}$$

$$\begin{array}{lclcll}
\text{H-H} & & & & & \\
S^{=}\ \ S^{=} & & S^{=}\ \ {}^{-}H\ \ {}^{-}SH & & & \\
M^{n+}\ M^{n+} & \rightarrow & M^{(n-1)+}\ M^{n+} & & & \\
 & & \uparrow\downarrow & & & \\
\text{H-H} & & & & & \\
S^{=}\ \ S^{=} & & {}^{-}SH\ \ {}^{-}SH & & S^{=} & +\ H_2S \\
M^{n+}\ M^{n+} & \rightarrow & M^{(n-1)+}\ M^{(n-1)+} & \rightarrow & M^{(n-1)+}\ M^{(n-1)+} &
\end{array}$$

Hydrogen adsorption site	Hydrogen insertion site site	De-oxygenation de-sulphurization site

Mechanisms of hydrogen adsorption on oxides and sulphides

Fe oxide-based catalysts for high temperature water gas shift (HTWGS).

Since decades the high temperatures water gas shift process using iron oxide based catalysts is applied to convert CO and water to CO_2 and hydrogen. These catalysts have been developed at the industrial level in spite of the relatively high temperature limit for catalytic activity (350-400 °C), mainly because of their resistance to significant amount of sulphur in the feed. In this temperature conditions, the conversion of this exothermic reaction is still significantly limited by thermodynamics, thus 1-3 % CO still remain in the treated gas, depending on the number of fixed bed used.

The original composition of HTWGS is based on Cr-stabilized iron oxides. Under reaction conditions Fe_2O_3 (haematite) is reduced to Fe_3O_4 (magnetite) which is stabilized morphologically and structurally by near 10 % of chromium, producing a spinel structure with a composition $Fe[Fe_{2-x}Cr_x]O4$, with medium-low surface area (10-50 m^2/g). In the most recent formulation, 1 % copper is added to the catalyst, improving catalytic activity. It has been concluded that copper metal is present in working conditions, mainly acting as an activator for iron oxide. Further additives may also be present.

Most authors are in favour of the redox mechanism that implies that CO reduces two surface ferric ions to the ferrous state and deoxygenates the surface, thus producing CO_2.

Water would reoxygenate the surface, reoxidizing two ferrous ions to the ferric state and producing hydrogen. This is a Mars-van Krevelen type mechanism.

K-Fe oxides for ethylbenzene dehydrogenation

Styrene, one of the prominent industrial monomers, is mostly produced by catalytic dehydrogenatiion of ethylbenzene , previously prepared by alkylation of benzene with ethylene. In the BASF process the reaction is typically performed at 710 °C after preheating the feed to about 590 °C in a multitubular reactor with a steam/ethylbenzene ration of 1.2. Alternatively, in the Dow process, two adiabatic reactors, working between 640 and 580 °C, with intermediate heat exchanger to recover reaction heat, are used. Many catalysts have been described for this reaction, but those actually applied in the industry are based of potassium-promoted ferric oxide, with surface area of 2 m^2/g. The Shell 105 catalyst dominated the market for many years. This catalyst, whose initial compostion was reported to be 93% Fe_2O_3, 5 % Cr_2O_3, 2 % KOH was later enriched in potassium until the compoistion 84.3 % Fe_2O_3, 2.4 % Cr_2O_3, 13.3 % K_2CO_3. The composition of a recent industrial catalyst is ~ 70 % Fe_2O_3, ~ 11 % CeO_2, 13-11 % K_2O, with CaO, MgO and MoO_3 all 2-1.5 %.

The basic components in the catalyst would favour the abstraction of a proton from the benzylic position of ethylbenzene, first, while the reduction of iron ions would result in the abstraction of the second hydrogen atom with two electron (formally an hydride species). The surface is regenerated by desorption of hydrogen and formal regeneration of ferric ions, as it occurs in the case of water gas shift reaction, with a Mars Van Krevelen-type mechanism.

Chromia-alumina for alkane dehydrogenation and hydrodealkylation.

Dehydrogenation of light paraffins such as propane and isobutane to produce propene and isobutene, respectively, may be performed to enhance the availability of such intermediates in refinery (to feed alkylation, polymerization and ether synthesis units) or in petrochemistry, starting from Natural Gas Liquids. Also these reactions need more than 550 °C and low pressure to allow sufficient thermodynamically limited conversion.

Chromium-oxide (typically 10-20 % by weight) deposited on alumina or on silica-stabilized transition (γ-/-δ/-θ) aluminas is the basic component of catalysts for these processes . Chromia may give rise to different structures when combined with alumina. Isolated and clustered species species together with supported chromia particles represent likely active phases. Additionally, Cr_2O_3 and Al_2O_3 may give rise to defective spinel-type solid solutions, which are also active catalysts , as well as to corundum-type solid solutions , which are inactive catalysts. The surface area of the catalysts are few tens of square meters per gram. However, the catalyst formulation includes promotion with alkali metals (e.g. 1% K2O wt), which is fundamental for increasing the chromium active sites and decreasing the surface acidity of both Cr and Al oxides. K has the best effect, if provided in the right amount.

The catalyst deactivates rapidly by coking (timescale: minutes/hours) and does not allow the use of steam in the feed. Cr_2O_3-Al_2O_3 catalysts are also applied to toluene hydrodealkylation to increase benzene production in the “aromatics loop”. The reaction is highly exothermic and the typical operating conditions (Houdry DETOL process) are 550

°C to 660 °C, and 20 to 70 bar. The typical catalysts are be based on 10-15 % chromia on alumina.

Gallium oxide based catalysts for dehydrogenations

Gallium oxides have been reported to have interesting dehydrogenation activity. Since many years Ga-zeolites, in particular Ga-ZSM5 zeolite, have been found to act as active catalysts for propane aromatization. Materials based on this catalytic system are applied in particular in the UOP Cyclar process , that converts liquefied petroleum gas (LPG) at ca 500 °C directly into a liquid, aromatic product in a single processing step. The reaction is best described as dehydrocyclodimerization, and is thermodynamically favoured at temperatures higher than 425°C. The dehydrogenation of light paraffins (propane and butanes) to olefins is the rate limiting step. Once formed, the highly reactive olefins oligomerize to form larger intermediates, which then rapidly cyclize to naphthenes. This process (developed jointly by BP and UOP) provides a route to upgrade low value propane and butane, recovered from gas fields or petroleum refining operations, into a high value, BTEX rich liquid aromatic concentrate.

Gallium oxide containing catalysts have been reported to be active also in the dehydrogenation of paraffins to olefins. The occurrence of an heterolytic cleavage of the C-H bonds producing gallium hydride and alkoxy species has been proposed. More recently, the formation of surface metal-alkyl groups by breaking paraffin C-H bonds has been reported. In particular, catalysts compositions comprising gallium, one or more alkaline or alkaline earth metals with small platinum addition, supported on an alumina are reported to allow good yields in light olefins, such as propylene from propane in a fluidized transport bed process .

A similar catalytic system based on alkalized Ga_2O_3-Al_2O_3 with manganese and silica has been later developed in a new industrial process for styrene synthesis by ethylbenzene dehydrogenation . Also in this case the process, denoted as SNOW being developed jointly by SNamprogetti and DOW, is based on a “fast raiser” reactor, where the catalyst moves entrained by the co-current hydrocarbon stream at a gas velocity of 4-20 m/s. The reaction occurs with space time 1-5 sec at 700-590 °C 34. In this case, the abstraction of an hydride species from the benzylic position of ethylbenzene is supposed to occur in the key step.

Zinc oxide for dehydrogenation reactions.

As said, zinc oxide powders are active in hydrogen adsorption as well as in catalysis of both hydrogenation and dehydrogenation reactions. The older literature reports on industrial use of zinc oxide in some relevant reactions, in particular in the dehydrogenation of alcohols. Apparently, the syntheses of acetone from isopropanol dehydrogenation , of methyl-ethyl-ketone (MEK) by 2-propanol dehydrogenation, and of butyraldehyde from 1-butanol dehydrogenation , have been performed even at the industrial level over bare ZnO catalysts or on Zn chromites, silicates and titanates. It seems that today these catalysts have been substituted by the more active Cu-ZnO or Cu-ZnO-Al_2O_3 catalysts.

ZnO/γ-Al_2O_3/H-ZSM-5 catalysts are applied in the Alpha process developed by Sanyo Petrochemical Co. Ltd, a subsidiary of Asahi Chemical, the only process tailored for the production of BTX aromatics from olefin rich feeds .

Oxide based catalysts for carboxylic acid hydrodeoxygenation

As said, a number of other oxides such as zirconia and chromia have been reported in the scientific literature to have some activities in hydrogenation and dehydrogenation reactions. Zirconia and ceria as such or in combination with titania and chromia are active in several hydrogenation/dehydrogenation processes such as the hydrogenation of carboxylic acids in vapour phase to the corresponding aldehydes. Commercial processes include the production of benzaldehyde from benzoic acid, theproduction of aliphatic aldehydes such as undecanal and 10-undecylenic aldehyde and the hydrogenation of stearic acid, pivalic acid, cyclohexancarboxylic acid and methylnicotinate, in vapour phase to the corresponding aldehydes . This reaction is supposed to occur, over oxide catalysts such as zirconia and ceria, through a Mars-VanKreveln mechanism, with reduction of the catalyst by hydrogen and its reoxygenation by the carboxylic acid.

7 Metal Catalysts

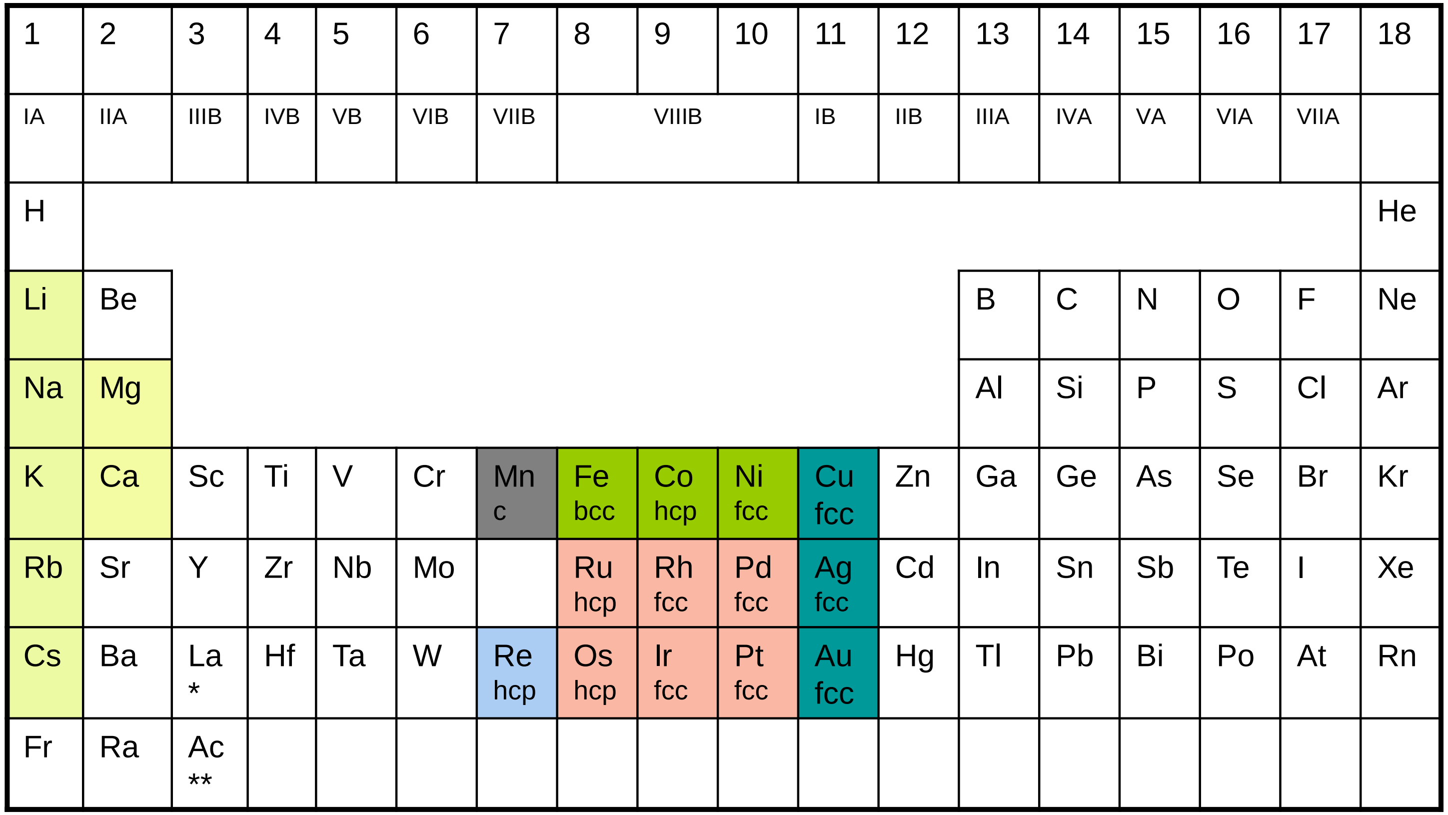
The application of two noble metals, platinum and palladium, is largely predominant over all other metals usually applied in heterogeneous metallic catalysis. These two elements have a very wide application in all fields such as hydrogenation (partial and full), dehydrogenation and total oxidation, in refinery, petrochemistry, fine chemistry and environmental catalysis. Among other platinum group metals (PGMs), whose application in homogeneous catalysis is very relevant, all other have more limited and specific applications in the field of heterogeneous metal catalysis. Rhodium finds very relevant application in the three way catalyst technology as well as in methane partial oxidation to syngas (CPO) and is an additive for silver in ammonia oxidation catalysts, iridium plays a peculiar role in selective ring opening of naphthenes, ruthenium is the base of new catalysts for ammonia synthesis but is also very active for low temperature methanation and Fischer Tropsch synthesis. Osmium, instead, does not seem to find important application in the field of solid metal catalysts. Rhenium, which belongs to group VII B (7), is almost always present as an additive in naptha catalytic reforming catalysts,

The discovery of new preparation technique revealed quite recently the possible new applications of supported gold in oxidation catalysis, such as for the low temperature and the preferential oxidation of CO and the water gas shift , in particular in the field of fuel cells technologies.

Very important is also the role of other group IB (11) metals, i.e. silver and copper. Silver catalysts play a very relevant role in ethylene and methanol partial oxidation, as well as an additive e.g. of supported Pd hydrogenation catalysts. Copper finds very large application in methanol synthesis, low temperature water gas shift, methanol steam reforming, selective hydrogenation and dehydrogenation of oxygenated compounds.

The other group VIIIB (8-10) elements (Fe, Co, Ni) have also wide application as metal catalysts. The use of bulk iron catalysts is very relevant for ammonia synthesis and HT Fischer Tropsch synhesis, Cobalt mostly for LT Fischer Tropsch synthesis and amination, nickel in almost all fields of hydrogenation catalysis and sometimes also in oxidation catalysis. As for other metal elements, their electropositive character hampers their use as metal catalysts in most conditions. A particular case is that of alkali metals which are used in non-protic highly reducing environments as basic catalysts/initiators.

Chemical elements involved in metallic catalysis



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn c	Fe bcc	Co hcp	Ni fcc	Cu fcc	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo		Ru hcp	Rh fcc	Pd fcc	Ag fcc	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La *	Hf	Ta	W	Re hcp	Os hcp	Ir fcc	Pt fcc	Au fcc	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac **															

🟥 Platinum-group metals

🟨 Alkali and alkali-earth metals
basic catalysts / initiators

Adsorption and activation of hydrogen on metals.

There is general agreement that hydrogen adsorbs dissociatively very fast on almost all relevant metal surfaces, being the dissociation of hydrogen only weakly activated or even barrierless. As for example, it has been found that when an H_2 molecule chemisorbs on a Pt surface, the antibonding σ* orbital of H_2 is completely filled by electrons from platinum. Thus, dissociative adsorption occurs non-activated, i.e. it is not kinetically hindered . Only on group 11 metals (Cu, Ag, Au) hydrogen dissociation is significantly activated and may be endothermic. On Cu/Al_2O_3 an activation energy of 42 kJ/mol was found , slightly higher than non Cu monocrystal faces. On-top, bridge or hollow sites can be occupied by atomic hydrogen species on metal surfaces.

In all cases, hydrogen dissociation gives rise to strongly bonded surface atomic hydrogen, mostly occupying hollow sites. For face centred cubic metals, (111) surfaces have been mostly investigated, while for hexagonal close packed metals, (0001) surfaces have been the object of most investigations. For body centered cubic metals most studies are on (110) faces. In all three cases, occupancy 3-fold sites is essentially favoured, although other adsorption sites such as bridge sites (such as found on Pd(100)) and top sites (such as found on Pt(111)) may be competitive with 3-fold sites. Only in the case of Ir(111) top sites appear more favoured than hollow sites for surface atomic hydrogen location.

The formation of subsurface atomic hydrogen is also possible, usually with an endothermic process. Tetrahedral and octahedral subsurface sites are occupied in this case. Only in the case of palladium, migration of hydrogen in the interior of the bulk is apparently exothermic too, due to a very large binding energy (-2.5 eV). This agrees with the data that show that only in the case of Pd a significant population of subsurface hydrogen can occur and bulk hydrides also form . At early stages the alpha phase is formed, where hydrogen atoms randomly populate small interstices in the lattice structure. At a critical point, the lattice expands, allowing hydrogen to cluster at higher density (the beta phase) , .

In the case of Ni surfaces, they also remain unreconstructed under H2 exposure. At room temperature (or above), H atoms adsorbed on Ni(100) do not show any ordering. According to DFT studies the dissociation of the hydrogen molecule is possible only over the topmost Ni atom, and the resulting H atoms may adsorb either on two free hollow sites (but the adjacent bridge sites must be free) or two bridge sites (the adjacent hollow sites must be free).

Adsorption/reaction/activation of oxygen on bulk metals.

Transition metals and/or their oxides are typical catalysts in heterogeneously catalysed oxidations. As said, oxidations can be produced in definitely oxidant conditions (excess air or oxygen) or, sometimes, in reducing conditions although an oxidant (mostly oxygen) is present. Thus, the question arises on what is the real state of the catalyst during reaction.

According to thermodynamics, metal oxides are stable at low temperature while they tend to decompose to the corresponding metals at high temperature, depending on oxygen pressure. In most cases, however, melting is forecasted in milder conditions than decomposition. Actually, base metals and most transition metal elements are stable as oxides even under high vacuum up to their melting point, frequently occurring at high temperature. Thus when these oxides are charged to the oxidation reactor, they stable as oxides and work as catalytic oxides. Some high oxidation state transition metal oxides may undergo partial decomposition to lower oxides, at moderate temperature, before melting. This is the case of Co_3O_4, that may decompose into CoO at ca 940°C and of CuO that tends to decompose around 1000 °C into Cu_2O, which last melts around 1300 °C. Thus different oxide phases may be active in oxidation catalysis.

Few transition metal oxides, usually having high oxidation states, have quite low melting point. In few cases the catalyst can work in a partially melt state. One of the most interesting case is V_2O_5/SiO_2 catalysts for SO_2 oxidation.

Selected properties of the most common noble metal oxides.4

Metal	Metal oxide		
Ru	RuO_2	1300 dec.	tetragonal
Os	OsO_2	500 dec. T	etragonal
Rh	RhO_2		tetragonal
	Rh_2O_3	1100 dec.	orthorhombic, trigonal
Ir	Ir_2O_3	1000 dec.	
	IrO_2	1100 dec.	tetragonal
Pd	PdO	750 dec.	tetragonal
Pt	PtO_2	450 (melt?)	orthorhombic
	PtO	325 dec.	tetragonal
Ag	AgO	>100 dec.	monoclinic
	Ag_2O	200 dec.	cubic
Au	Au_2O3	150 dec.	orthorhombic
Re	Re_2O_7	327 (b.p. 360)	
	ReO_3	400 dec.	cubic, hexagonal
	ReO_2	900 dec.	orthorhombic

For noble metal oxides, instead, decomposition to the metal may occur at quite a low temperature also in oxidizing atmosphere, frequently well below melting. On the other hand, noble metals are charged, sometimes, after a previous reducing pre-treatment, thus in a metallic form. Thus it is not always clear if the work catalyst is the metal or its oxide. In the Table the approximate decomposition temperatures of noble metal oxides to the corresponding metals, as reported in the literature, are summarized. On the other hand, metal oxidation to the oxide is kinetically hindered at low temperature even when the oxide is the thermodynamically stable form. Thus starting from a metal (previously produced by reduction of the oxide or other compounds using reductants such as hydrogen, CO, carbon, etc., or by decomposition of organometallics), it may remain in metallic stable or metastable state even at quite high temperature in oxidizing atmospheres or in the presence of oxidants.

However, the metals may adsorb oxygen in a reactive form. Molecular and dissociative adsorption of oxygen has been revealed by vibrational spectroscopies such as IRAS and EELS over metal monocrystal faces. In most cases, molecular adsorption is found at low temperature producing superoxo- O_2^- and peroxo O_2^{2-} molecular species. At higher temperature atomic or dissociative adsorption is found, producing surface and subsurface oxide species, as a transition state towards the formation of the bulk oxide.

Thus, for noble metal catalysts sometimes the structure during oxidation catalysis is certainly that of the metal with adsorbed oxygen species as active intermediates, while in other cases it is not clear if catalysis is done by the metal or by its oxide or by both.

Considering the elements most involved in oxidation catalysis, at least three different Rhodium oxide phases are reported: RhO_2 is apparently always a metastable phase while two polymorphs of Rh_2O_3 are reported. The hexagonal form α-Rh_2O_3, corundum structure, transforms into an orthorhombic β-Rh_2O_3 structure above 750 °C. This phase is reported to be stable in oxygen up to decompose into Rh and O_2 only at 1133 °C. In a reducing atmosphere Rh_2O_3 is reported to reduce to metallic Rhodium at about 100–150°C. Because Rh is very reactive, oxygen does not form a molecular state at low coverage on any of the clean low index surfaces, but dissociates into an atomic state. However, this atomic oxygen makes the surface less active for dissociation, so that molecular oxygen is then stable over an oxidized surface. Actually, the existence of end-on bonded molecular oxygen on Rh(111) monocrystal face has been reported to be stable but the calculated energy barrier-towards the decomposition oxygen is rather low. A minor extent of oxygen pre-occupation on a rhodium surface even enhances the ability of rhodium to decompose molecular oxygen. However, at higher initial oxygen coverages, this ability is obstructed, supporting the suggestion that oxygen coverage stagnates. The dissociation of O_2 on Rh(111) is definitely easier than on corresponding faces of less reactive metals such as Ag(111) and (even more) Au(111). Also Ruthenium oxide RuO_2 is a stable phase also at high temperature, being reported to decompose into the metal at about 1400°C. Dissociative adsorption of oxygenmany occurs on Ru monocrystal faces such as Ru(0001), which has been the object of several studies.

For Pd, in 1 mbar O_2 the $PdO \leftrightarrows Pd + ½\,O_2$ transition is expected to occur at approximately 570 °C. Accordingly, PdO is known to decompose in practice into Pd metal in the range 650 – 800 °C, depending on O_2 partial pressure and reactive gas mixture composition. molecular adsorption is observed over Pd(111) at 30 K producing two different species characterized by IR bands due to OO stretchings at 850 and 1035 cm^{-1}. These peaks are assigned to a peroxo-like state and a superoxo-like state, respectively. After saturation of these chemisorbed molecular states, a state of physisorbed oxygen is populated. Upon warming the sample above 80 K, an additional loss feature at 650 cm^{-1} develops which is assigned to a second peroxo-like molecular species. The oxygen dissociation process is completed at $T \approx 200$ K leaving a layer of atomic oxygen on the surface which is characterized by a peak at 480 cm^{-1} (Pd-O stretching) and by a 2 × 2 pattern in LEED. Oxygen atoms are adsorbed on threefold hollow adsorption sites. At 250°C data show the formation of subsurface oxygen species on Pd(111) characterized by Pd-O stretching band at 326 cm^{-1}. At and above 330°C several surface oxide phases, like Pd_5O_4, may form until Pd(111) converts into bulk PdO(101) face. It seems that easier oxidation to PdO can occur with Pd(110) face, even below 300 °C. The oxidation of Pd foils with both wet and dry oxygen is observed at relevantly lower temperature, being incipient already at 100°C and extensive at 200°C.

A similar complex situation occurs with platinum and its oxides: α-PtO_2 is the stable phase at low temperatures, metallic Pt is stable at high temperature, and in between there is a region of stability of Pt_3O_4. This region is ca. 100 K wide and at 1 atm oxygen pressure it extends from 600-700°C. Transition temperatures move to lower values at lower O_2 pressures, without qualitative changes. PtO is a metastabile phase while other PtO_2 polymorphs are stable only at high temperatures and high oxygen pressures. Accordingly, TG studies in air showed the decomposition of platinum oxide via the transitions α-$PtO_2 \rightarrow Pt_3O_4 \rightarrow Pt$ observed at 635 and 800 °C respectively. O_2 adsorbs molecularly at low surface temperature (<100 K) also on Pt monocrystal faces producing peroxy and, superoxy species. Dissociation of adsorbed O_2 begins to occur above 135 K generating an atomic oxygen species while after annealing at 230-330°C ordered surface oxide islands are observed to coexist with chemisorption structure. From density functional theory calculations a model for the surface oxide phase is revealed on Pt(110). The PtO_2 phase is found to be metastable, and its presence is explained in terms of stabilizing defects in the chemisorption layer and reduced Pt mobility. Oxidation of Pt foils also resembles that of Pd foils, being detectable already at 100-200°C.

The metal elements having the least stable oxides are gold and silver. Gold (III) oxide Au_2O_3 is reported to be more stable than Au_2O, which is only metastable with respect to the O_2 molecule and bulk Au. Au_2O_3 is reported to decompose to metallic gold at 160 °C. Experiments have shown that room-temperature, gas-phase O_2 does not readily chemisorb on macroscopic gold single crystals or supported gold clusters larger than $\sim$ 1 nm in diameter either dissociatively or molecularly, the adsorption of oxygen atoms on the surface assists in the molecular chemisorption of oxygen. In any case, steps are reported to be more reactive, adsorption on plane faces beinmg thermoneutral or even endothermic.

The binary Ag–O system contains several defined compounds: Ag_2O, Ag_3O_4, AgO, Ag_4O_3 and Ag_2O_3, among which Ag_2O is the most stable. AgO is reported to decompose into Ag_2O at low temperature (150-200 °C) while different data are reported concerning the decomposition of Ag_2O 150-400 °C). Thermodynamics forecasts stability of Ag_2O in oxygen up to ca 150 °C. On silver monocrystal faces, molecular adsorption is observed at very low temperature. The study of the interaction of oxygen with silver at higher temperature (200 °C) i.e. at temperatures significant for heterogeneous catalysis, reported on the formation of different oxygen monatomic species. Actually, oxidation of silver gives rise to Ag_2O, which has an intermediate stability. It is reported that thermodynamically silver oxidation to Ag_2O is spontaneous below ca 200 °C.

Some authors suggested the formation of surface suboxide with an approximate stoichiometry of $Ag_{1.8}O$. The situation, however, was found more recently to be more complex. Five different monoatomic oxygen species can be observed on silver at high temperature, part of wich are surface species other being subsurface species, interacting dinamycally each other.

Thus, if reaction conditions are fully oxidizing, only gold and, to a lesser extent, silver, as well as palladium and platinum only at very high temperatures, may act as metal catalysts. In fully oxidizing conditions, all other catalysts are expected to act as oxide catalysts. In contrast, for selective oxidations performed in partially reducing conditions, the real state of the catalyst may be doubtful.

Bulk metal catalysts.

Iron ammonia synthesis catalysts

Ammonia synthesis is one of the few industrial processes were unsupported metals are used. The traditional catalyst, still used in most plants, is based on bulk iron, containing several elements for activation and stabilization. It was originally obtained from a swedish magnetite mineral. The catalyst may be charged in the oxidized form (either magnetite Fe_3O_4 or wüstite FeO) or in the prereduced form, both available commercially from most producers.

Topsøe sells the KM1 unreduced catalyst, 91-95 % wt of iron oxides with 5-9 % wt K_2O, Al_2O_3, CaO and SiO_2, as well as the prereduced KM1R catalyst (89-93 % Fe,FeO). The working temperature range is 340-550 °C, with pressure range 80-600 bar.

The catalysts of the $KATALCO_{JM}$ 35 series and $KATALCO_{JM}$ S6-10 series proposed by Johnson Matthey are based on magnetite multi-promoted and/or stabilized by K_2O, Al_2O_3 and CaO. To achieve higher activity at low pressures in the region of 80 - 150 bar, $KATALCO_{JM}$ 74-1 catalysts containing also CoO as a promoter are proposed alternatively.

Süd Chemie proposes the AmoMax 10 catalyst which is a wüstite-based ammonia synthesis catalyst (98% FeO plus promoters) that, according to the firm, features significantly higher activity than magnetite-based catalysts. This high activity level is also evident at low operating temperatures, allowing improved conversion at thermodynamically more favorable conditions. AmoMax 10 is available in oxide and pre-reduced, stabilised form.

BASF Ammonia Synthesis Catalyst is a multi-promoted iron based catalyst: in its commercial form it contains $\geq$ 67% of iron in metal form with $\geq$ 2.3 % Al_2O_3, $\geq$ 2.1 % of promoter I and small amounts of oxidized iron, and three other promoters.

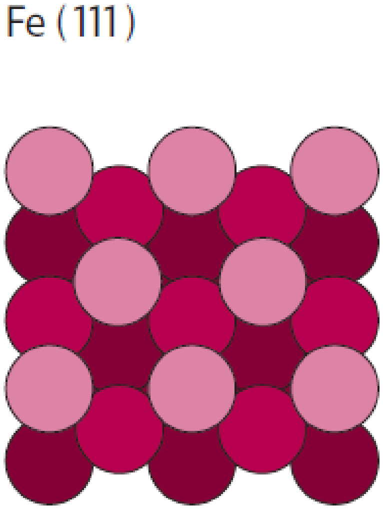
Commercial iron-based catalysts incorporate several metal oxides within the magnetite or wüstite structure that promote activity and improve stability of the operating catalyst. The most important of these are alumina and potash, which generate the so-called “doubly-promoted” catalyst. Several other oxides may also be added, for example calcium oxide, silica and magnesia. Promoters are classified as either “structural” or “electronic” depending on their mode of action.

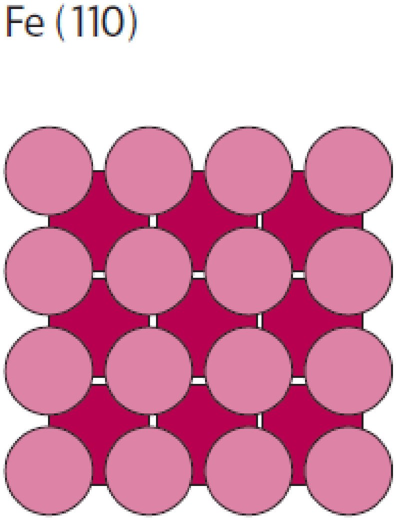
Structural promoters such as alumina and magnesia restrict the growth of iron crystallites during reduction and also during subsequent operation. They increase the thermal stability of the catalyst. Calcium oxide, and other basic promoters, react with silica impurities in the raw materials to form glassy silicates, which themselves can enhance the thermal stability of the reduced iron. The main benefit is to minimize any

neutralization of the K_2O promoter, which would reduce its effectiveness.

The presence of alkali-metal species in ammonia synthesis catalyst is essential to attain high activity. The alkali metals are “electronic” promoters and they greatly increase the intrinsic activity of the iron particles. Modern ideas on alkali-promoted ammonia synthesis catalysts show that dissociative chemisorption of nitrogen on low-index iron surfaces is extremely structure sensitive. The close packed Fe (110) plane was found to be least active, while the open Fe (111) surface was considerably more active.

Photograph of ammonia synthesis catalysts





High Temperature Fischer Tropsch synthesis catalysts

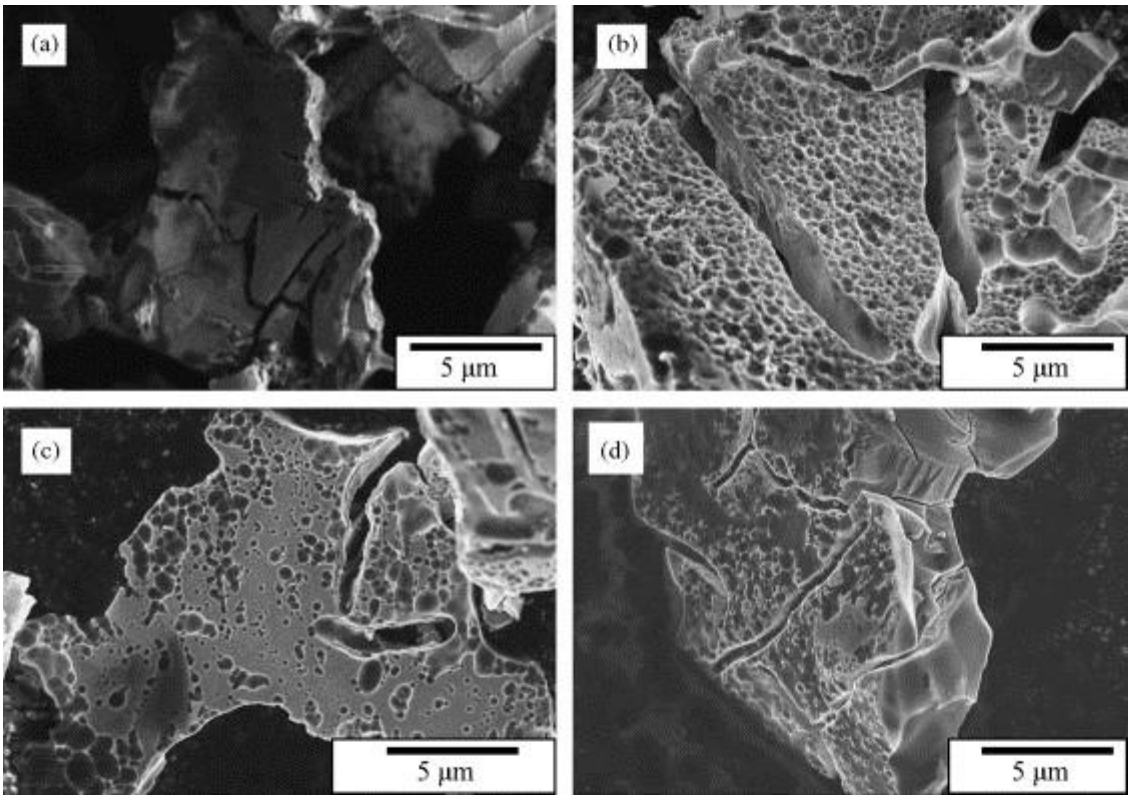
The High Temperature Fischer Tropsch process (HTFT), performed on iron-based catalysts at 300 °C, and the low temperature process performed with iron catalysts (Fe-LTFT), are also useful options. Due to their high activity for the water gas shift reaction, iron catalysts are more indicated for coal-based FT syntheses. They produce more oxygenates and a slightly different molecular weight distribution for hydrocarbons.

A typical iron FT catalyst contains also few percents of silica, copper and potassium. Copper is added to aid in the reduction of iron, while silica is a structural promoter added to stabilize the surface area but may also have a chemical effect on the catalyst properties. Potassium is considered to increase the catalytic activity for FTS and water–gas shift reactions, to promote CO dissociation and enhance chain growth, increasing olefin yield and lowering the CH_4 fraction. Under reaction conditions, the catalyst converts into mixtures of carbides, like χ-Fe_5C_2 and ε-$Fe_{2.2}C$, and magnetite Fe_3O_4, with only small amounts of α-Fe. Carbidic rather than metallic catalysis should really occur.

Nickel Raney

Another example of bulk metal used as catalyst is the so called Raney Nickel. It is prepared starting from a Ni-Al alloy produced by dissolving nickel in molten aluminium followed by cooling ("quenching"). In the activation process, the alloy, usually as a fine powder, is treated with a concentrated solution of sodium hydroxide which dissolves aluminum with the formation of sodium aluminate ($Na[Al(OH)_4]$) leaving a porous and quite impure metallic nickel powder.

Cyclohexane is produced in liquid phase like through the process developed years ago by the Institut Francais du Petrole wherein benzene and hydrogen-rich gas is fed to a liquid-phase reactor containing Raney nickel catalyst at 200-225 °C and 50 bar. The nickel suspension is circulated to improve heat removal, the benzene being completely hydrogenated in a second fixed-bed reactor. Although a good quality cyclohexane is achieved in this way, the inconvenience of a continuous consumption of catalyst is added to the generation of residues (exhausted catalyst) that forces to a later disposition of said catalyst as dangerous residue. However, the most serious disadvantage of this technology lies in the fact that low reaction temperature prevents the full exploitation of the enormous amount of caloric energy generated by hydrogenation, which in gas phase process is totally recoverable.



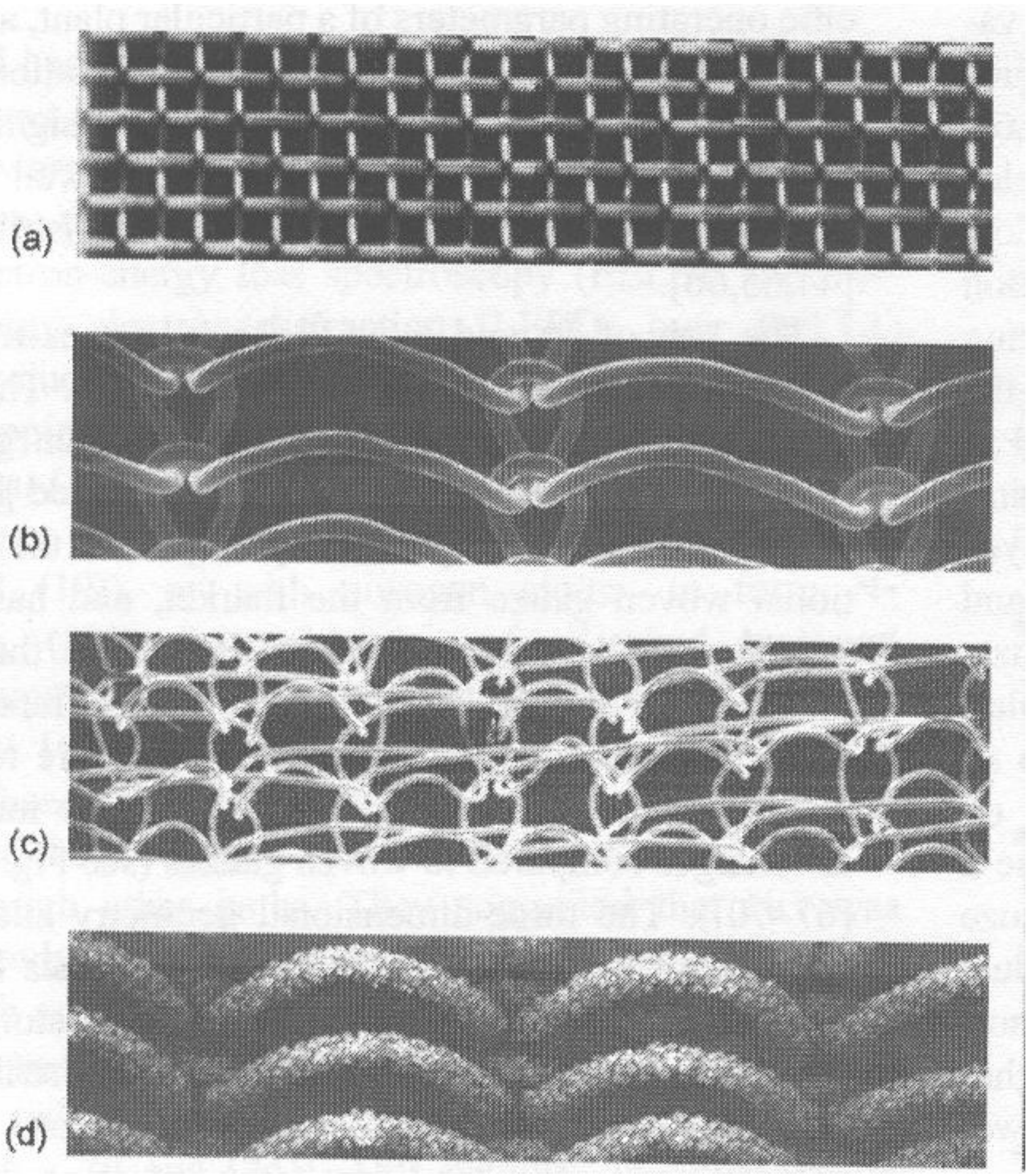
SEM images of different Raney nickel

Catalytic metal gauzes.

Ammonia oxidation by air to nitrogen monoxide is performed industrially as the first step in the production of nitric acid (Ostwald process). The reaction is carried out at 800-1000 °C, 1-12 bar with 10-14 % NH_3 in air using Pt-based gauze pads, in order to reduce the contact time to limit the further reaction of NO with ammonia and oxygen, to N_2. To reduce Pt loss as volatile PtO, other metals such as Rh and Pd are usually alloyed to Pt. The typical composition may be 5-10 % Rh, 0-15 % Pd, sometimes 0.5 % Ru. Microaddition of other elements such as B and Y are reported to limit crystal growth, with a positive effect on catalytic activity. The gauzes, of the woven or the knitted type, are produced using 0.06-0.07 mm diameter wires.

Similar catalysts and reactors are used for the Andrussow process, i.e. the synthesis of hydrogen cyanide by methane ammoxidation. Silver gauzes may be used for the production of formaldehyde by high temperature oxidation /dehydrogenation of methanol.

Figure 10.12. Installation of gauze pad—checking for wrinkles.


(a)
(b)
(c)
(d)

Supported metal catalysts.

Supports for metal catalysts.

The following materials are most commonly used industrially for supporting catalysts:

a) Aluminas. As reported in chapter 6.4.3, when applications require relatively low reaction temperature (< 500 °C), high surface area γ-, δ- or η-Al_2O_3 are common industrial catalyst supports ($S_{BET} > 150\ m^2/g$) . These are typically highly ionic and highly dispersing catalyst carrier. These supports, however, are characterized by high acidity and reactivity, thus not applicable when very reactive compounds are present in the reactant mixture. They are also unstable at temperatures > 500 °C, tending to convert into θ-Al_2O_3 or α-Al_2O_3 with loss in surface area. For these reasons, less reactive and more stable lower surface area aluminas are used in several applications, such as θ-Al_2O_3 (S_{BET} 50-100 m^2/g), α-Al_2O_3 or α-Al_2O_3/θ-Al_2O_3 mixed phases ($S_{BET} < 50\ m^2/g$).

b) Metal aluminates. Mg and Ca aluminates, with spinel and β–alumina structures, are also largely used as refractory, stable and quite unreactive carriers for high temperature applications such as steam reforming, partial oxidation, autothermal reforming and catalytic total oxidations. The surface area of these materials may be low or very low and dispersion of their surface is frequently not high.

c) Silicas. According to their ionic character, are typically non dispersing carriers in spite of their high surface areas. They have usually give rise to medium-size supported metal particles. These supports have quite high termal stability and high chemical inertness.

d) Titanias and zirconias. These are support with weak redox properties, medium acido-basicity, high dispersing ability, and high reactivities towards the metal, giving rise to Strong Metal-Support Interaction effects (SMSI). Titania (anatase) and monoclinic zirconia (baddeleyite) have limited thermal stability tending to convert into more stable phases rutile and tetragonal/cubic zirconia.

e) Ceria. Ceria is a typical support or support component characterized by redox properties and oxygen storage capacity, useful for redox reactions. This, however, gives also rise to some instability. In any case, ceria has high dispersing ability for metal sites and some surface basicity.

f) Zinc oxide. Zinc oxide has some hydrogenation/dehydrogenation activity. It is largely used as an activating support, in particular for copper and palladium hydrogenation catalysts. It gives rise to some kind of activating effect. Reduced Zn is supposed to have a synergy with copper metal for methanol synthesis and water gas shift, while the formation of Pd-Zn alloy is very likely in the case of the corresponding Pd based catalysts.

g) Magnesia. Strongly basic support, it is quite unstable in the presence of CO_2 and water. As a catalyst support it suffers of quite a low surface area and poor mechanical strength. In spite of this it is reported to be an excellent support for some metal catalysts.

h) Zeolites. Zeolites have high dispersing ability for cations. After reduction, the size of the metal particles may be limited by the size of the cavity. They may allow to associate metal catalysis with shape selectivity. They also allow to associate metal and strong protonic acid catalysis, or even metal and basic or neutral acid-basic catalysis when alkali-cationic zeolites are used (ex. Pt-K-zeolite catalysts for aromatization reactions).

i) Carbons. Different forms of carbons such as activated carbons, graphite, …, are used as supports mainly for noble metal catalysts. They are used mainly for low temperature liquid phase applications, or gas phase applications in reducing atmospheres. They dispersing ability may be tuned, depending from carbon pretreatment (oxidizing or reducing).

j) Calcium carbonate and barium sulphate. Are the supports of Pd in the so-called Lindlar catalysts, Pd-Pb/$CaCO_3$ and Pd-Pb/$BaSO_4$, applied in organic chemistry for selective hydrogenations of C≡C bonds to C=C bonds.

Industrial supported metal catalysts for hydrogenation reactions.

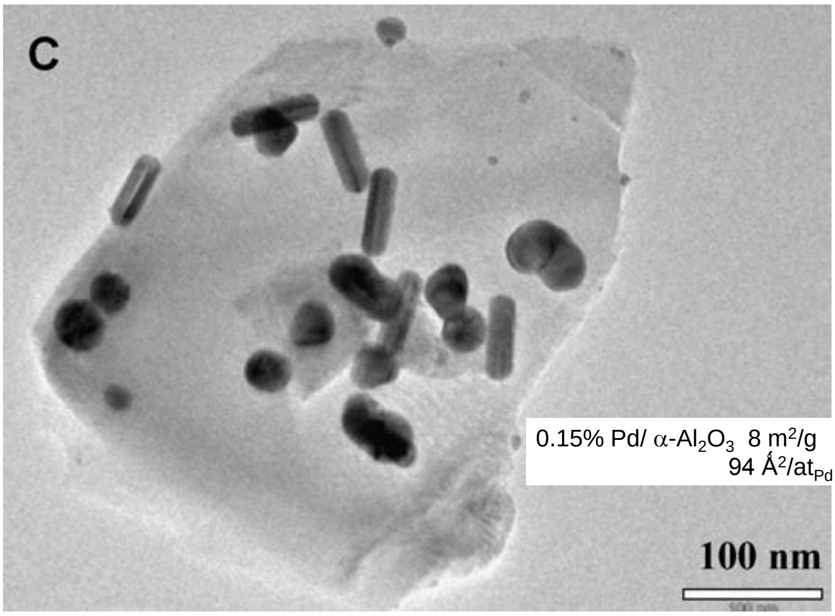
Many metals, including platinum group metals, nickel, cobalt, iron, copper, etc. are active in hydrocarbon hydrogenation. However, some noble metals are far more active, but quite easily deactivated in particular by sulphur compounds. For these reasons the catalyst composition for hydrocarbon hydrogenation is strongly dependent on the amount of sulphur impurities in the feed. Palladium, and, to a lesser extent, platinum are the choice catalysts for hydrogenation of clean feeds while nickel is mostly used for hydrogenation of medium sulphur containing feeds. Bimetallic noble metal catalysts or other modified noble metal catalysts may also have interesting resistance to medium-low concentrations of sulphur. Feeds which are heavily contaminated by sulphur may be hydrogenated over typical hydrotreating sulphide catalysts, such as alumina, silica-alumina or zeolite supported Ni-W, Ni-Mo or Co-Mo catalysts, or bulk transition metal sulphides, among which RuS_2 is reported to be the most active.

As an example, It seems that the most usual catalyst composition for acethylene hydrogenation in the C2 cut from steam cracking (tail-end configuration, sulphur free feed) is today Ag-promoted Pd/Al_2O_3, although the actual concentration of Ag may be higher than that of Pd (es. Pd 0.03 %, Ag 0.18 % for the Süd Chemie OleMax 201 catalyst). Silver concentration must be optimal to increase selectivity without a relevant decrease in activity. Gold is also reported as a promoter for Pd, while potassium, and chromium have been reported as additional or alternative promoters.

Acetylene hydrogenation reaction is performed to purify HCl flow coming from ethylene dichloride (EDC) cracking, in the process of production of vinyl chloride monomer (VCM), e.g. in the Vinnolit process. In fact HCl is recycled to ethylene oxychlorination reactor to reproduce EDC. The presence of acetylene here would result in the production of polychlorinated byproducts. The catalysts Noblyst® E 39 H and Noblyst® E 39KHL, produced by Evonik, are specific for this application: they are both reported to be constituted by Pd on silica. May be the different reactivity of the support with respect to HCl is a key feature here.

Hydrogenation of methylacetylene and propadiene in the steam cracking C3 cut or after propane dehydrogenation must be performed to limit their content in polymer-grade propylene. This reaction may either be performed in the gas phase with multiple beds or in the liquid phase in a single bed. In both cases promoted Pd/Al_2O_3 is used but the Pd content for liquid phase use must be much higher (0.3 %) than for gas phase use (0.03 %). In gas-phase hydrogenation the reaction is controlled by means of the operating temperature, which may be between 50 and 120 °C, 15-20 bar, depending on the preparation and aging state of the catalyst. With liquid-phase hydrogenation the reaction is controlled by the hydrogen partial pressure. The operating temperature of 15 –25 °C is considerably lower in this case .

Stuides provide evidence of the formation of well defined extended metallic nanoparticles over the support surface. However, the properties of these particles differ in some ways from those of normal metal particles: as for example, negative thermal expansion for supported Pt particles. Still research is active for understanding several phenomena concerning supported metal particles.



G. Berhault, L. Bisson, C. Thomazeau, C. Verdon, D. Uzio, Preparation of nanostructured Pd particles using aseeding synthesis approach. Application to the selective hydrogenation of buta-1,3-diene, Applied CatalysisA General 327 (2007) 32-43.

Micrograph of a Pd/Al_2O_3 catalyst for 1,3-butadiene hydrogenation

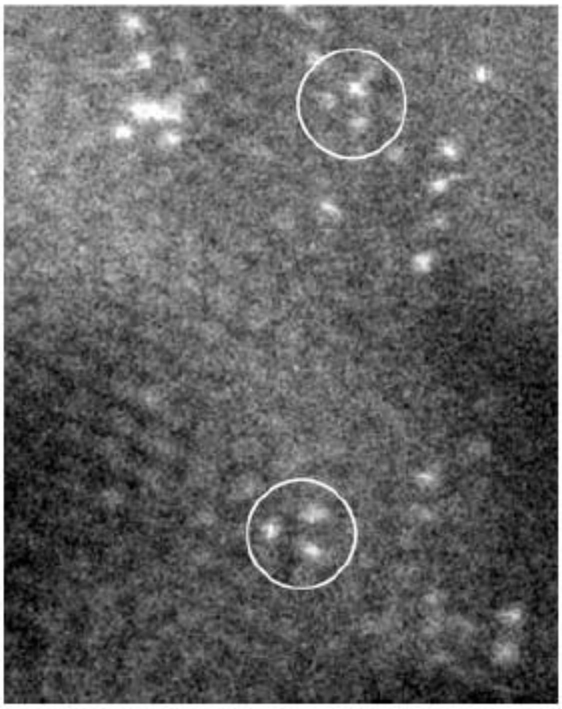


Figure 1. *Z contrast STEM image of Pt on the (110) surface of γ alumina. Two Pt_3 (trimer) structures are circled. A hint of the alumina lattice is also visible.*

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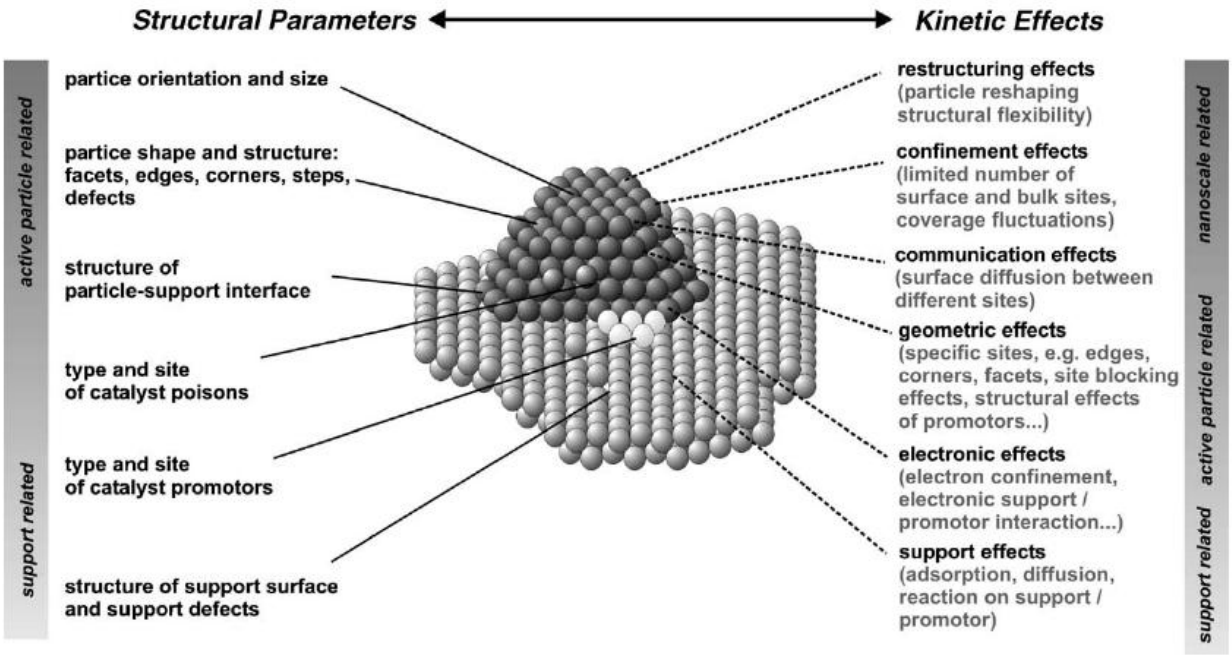
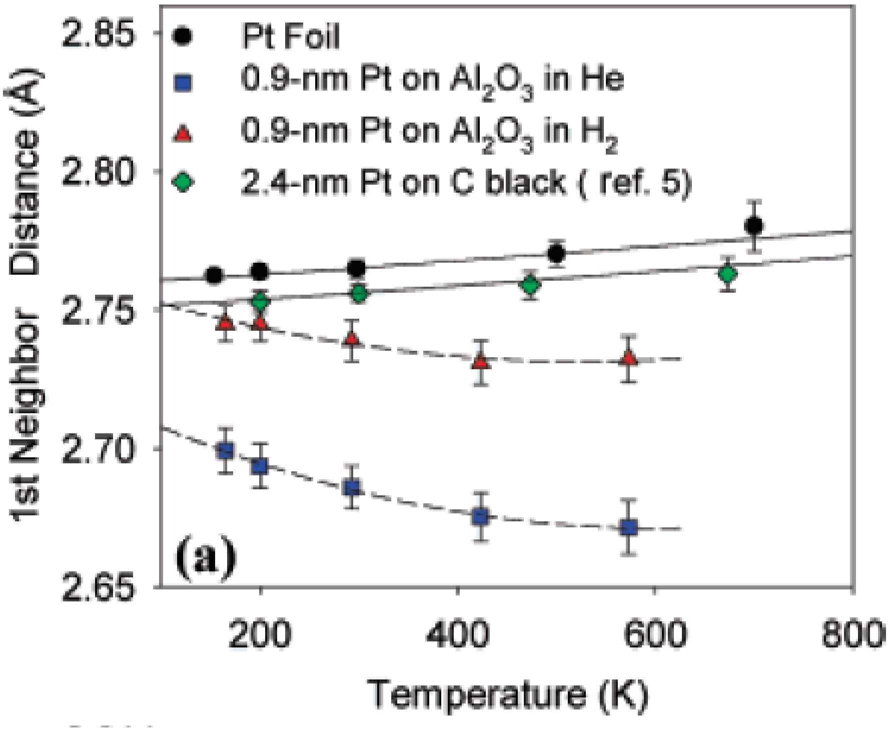


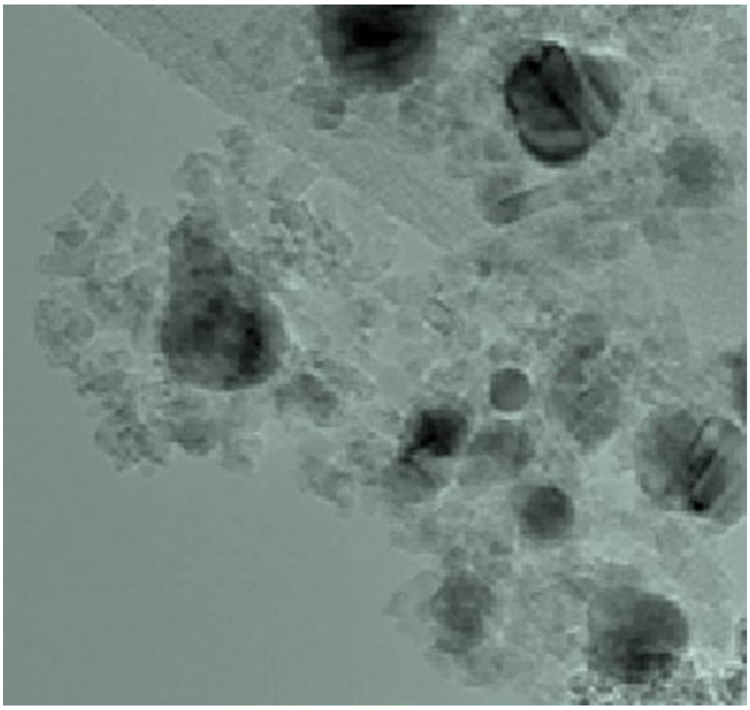
Fig. 1. Structural parameters and kinetic effects on supported metal catalysts (adapted from [73]).



Negative thermal expansion for supported Pt particles.

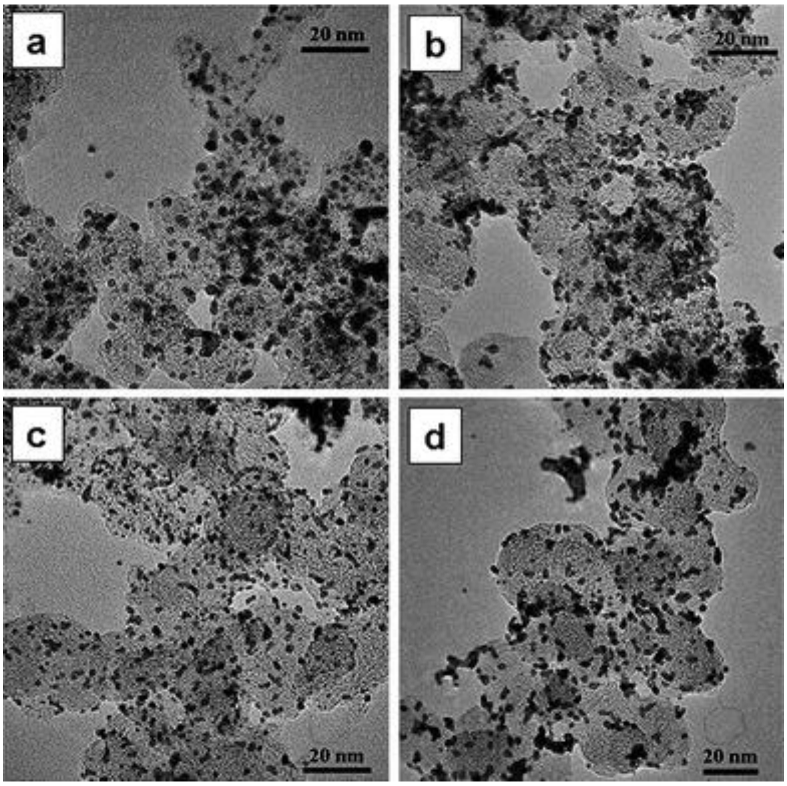
Similar problems concern the hydrogantion of aromatics. The activity of heterogeneous metal catalysts for the hydrogenation of aromatics was reported to be in order Rh > Ru >> Pt >> Pd >> Ni > Co. Pt/Al_2O_3 catalysts are used in the BenSat™ benzene saturation technology from UOP. Recently the previous UOP H-8™ catalyst has been updated in response to a demand for improved economics. The new BenSat process uses a new catalyst, the UOP H-18^{TM} catalyst, resulting in lower catalyst volume, reduced recycle, and lower precious metal requirements. According to UOP patents, its preferred form, the alumina support will comprise spheres having a surface area of from about 160 to 200 m^2/g with an apparent bulk density of from about 0.45 to 0.6. The platinum metal may be present on the catalyst in a concentration of from 0.375 to 0.75 wt. %. According to people from UOP, unlike nickel-based catalysts, platinum-based saturation catalysts are not permanently poisoned by sulfur or heavies upsets and do not cause cracking to light ends. Supported Pt catalysts compete with Ni Raney catalysts as well as supported Ni.

Partial hydrogenation of oxygen containing species is mainly performed with copper based catalysts, that allow C-O bonds to be retained.Syngases with opportune stoichiometries may be converted into methanol. Today reaction is performed at 200-250 °C, 50-150 bar, in the so-called low temperature synthesis process . Most of commercial catalysts today are based on the Cu-Zn-Al system, prepared by coprecipitation, with Cu:Zn atomic ration in the 2-3 range, and minor alumina amounts. Cu-Zn-Cr and Cu-Zn-Cr-Al systems have also been considered and used at the industrial level. The MK-121 catalyst from Topsøe contains, in the unreduced form, > 55 % wt CuO; 21-25 % ZnO, 8-10 % Al_2O_3 in the fresh catalyst, graphite, carbonates, moisture balance.



Using Transmission Electron Microscopy (TEM) it is possible to study the finer details of the structural arrangements in the methanol synthesis catalyst. The image recorded illustrates the key features of the FENCE™ technology; finely dispersed copper crystals (darker) prevented from sintering by a picket fence of metal oxide crystals (lighter).

For liquid phase hydrogenation reactions, metals supported on carbons are frequently used. One example is the hydrogenation of nitrobenzenes to anilines.



SEM of Pt catalysts supported on carbon.

In the nineties, Kellogg Brown and Root (KBR) developed a new process of ammonia synthesis based on Ru based catalysts denoted as KAAP™ (Kellogg Advanced Ammonia Process). The proprietary KAAP™ catalyst, which is manufactured and guaranteed by BASF Catalysts LLC under exclusive license to KBR, consists of ruthenium on a stable, high-surface-area graphite carbon base. According to the literature it should contain alkali and alkali earth promoters such as K, Cs, Ba. The KAAP™ catalyst is reported to have an intrinsic activity ten to twenty times higher than conventional magnetite catalyst. This allows operation at 90 bar synthesis loop pressure, which is one-half to two-thirds the operating pressure of a conventional magnetite ammonia synthesis loop. At this low pressure, only a single-casing synthesis gas compressor is needed and pipe wall thicknesses are reduced. This results in savings in plant capital equipment and operating costs.

Steam reforming catalysts.

Ni-alumina based catalysts are used industrially for several applications. In particular, Ni on alumina is used in many hydrogenation processes. As for example, Johnson Matthey offers Ni/Al_2O_3 catalysts for both stages of pyrolysis gasoline hydrogenation both operated in the liquid phase at 40-100 °C (first stage) and at 280 to 330 °C (second stage) at some tens of bar of pressure. Naphtha dearomatization and benzene hydrogenation to cyclohexane can be performed with the NiSAT® catalysts offered by Süd Chemie in the liquid phase, or with the BenSat process from Axens operating in catalytic distillation conditions on a Ni catalyst. Ni/Al_2O_3 are also used for the CO_x methanation reaction operated in the gas phase either to purify hydrogen from CO_x or to produce Substitute Natural Gas e.g. from syngas generated by biomass gasification: catalysts of this type are provided, among others, by Johnson Matthey, Süd Chemie and Topsøe. All these processes are performed, according to thermodynamics, at relatively low temperatures (usually < 673 K) and under some tens of bar of hydrogen, either in the liquid or in the gas phase.

Ni deposed on aluminate carriers are also largely used for steam reforming processes. These processes are essentially endothermic and are consequently performed at higher temperatures (673-1173 K) and moderate to low pressures. They are used industrially since decades for producing hydrogen by steam reforming of hydrocarbons both in large scale production plants and for fuel cell applications, and are under study for other hydrogen production processes such as methane dry reforming, bioethanol steam reforming and the steam reforming of tars to purify biomass-derived syngases. They may also be of interest as functional layers over the anodes of methane fuelled Solid Oxide Fuel Cells. In these cases, due to the higher reaction temperature, more thermally stable “support” phases than pure alumina are needed. For this reasons, silica, a stabilizing agent against phase transition of alumina, can be a component, while alkali and alkali earth cations (usually K, Mg or Ca) are usually present, producing aluminate spinels and beta-aluminas refractory supports. Such cations can also moderate surface acidity of the support, useful to limit growth of carbonaceous materials, but also somehow modify the character of Ni centers.

Supported metals for partial and total oxidations.

Noble metal catalysts are also largely used for oxidation reactions. Most literature concerning red-ox properties of supported metal catalysts refer on the presence of metal particles of different sizes and oxide particles and their interconversion. This is in part because those species are those can be quite easily detected with common techniques such as XRD and TEM. The idea that these species only are those involved in metal catalysis allows to discuss results in parallel with surface science studies of monocrystals, and use typical theoretical approaches for modeling. However, this approach is an oversimplification. Actually the possible role of other surface species such as monoatomically dispersed metal or cationic centers or small clusters has been reported by many authors.

Among the largest productions, ethylene selective oxidation to ethylene oxide (EO) is performed over silver based catalysts. Typical catalysts may contain 8-15% by weight of silver deposed over low surface area alpha-alumina, 0.5-1.3 m^2/g with a porosity of about 0.2-0.7 cc/g. The catalyst may contain several propmoters such as 500-1200 ppm alkali metal (mostly cesium), 5-300 ppm by weight of sulphur as cesium or ammonium sulphate, 10-300 ppm of fluorine as ammonium fluoride or, alkali metal fluoride. Similar catalysts are used when oxidation is performed with air or with oxygen at 250-280 °C, ~ 20 bar. Today authors agree that in oxidizing conditions a surface oxide with stoichiometry $Ag_{1.8}O$ is formed and represents the oxidized catalyst form in the Mars Van Krevelen cycle.

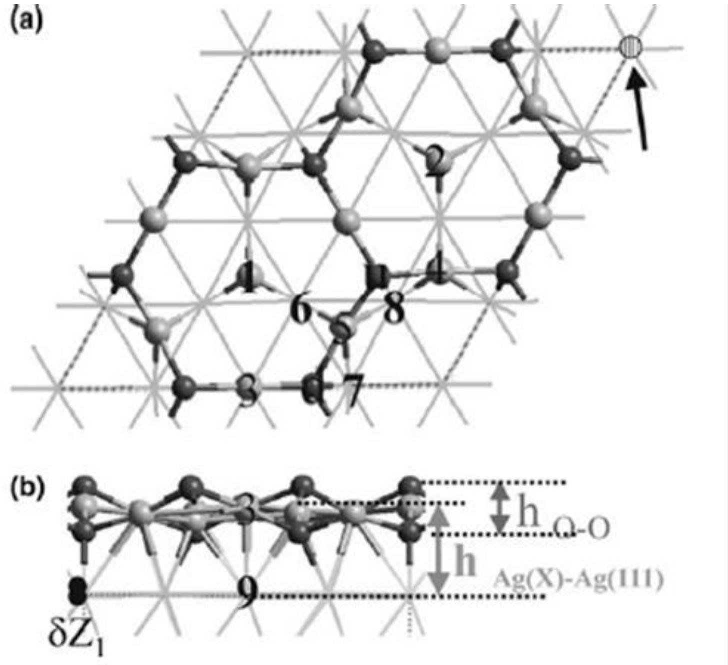
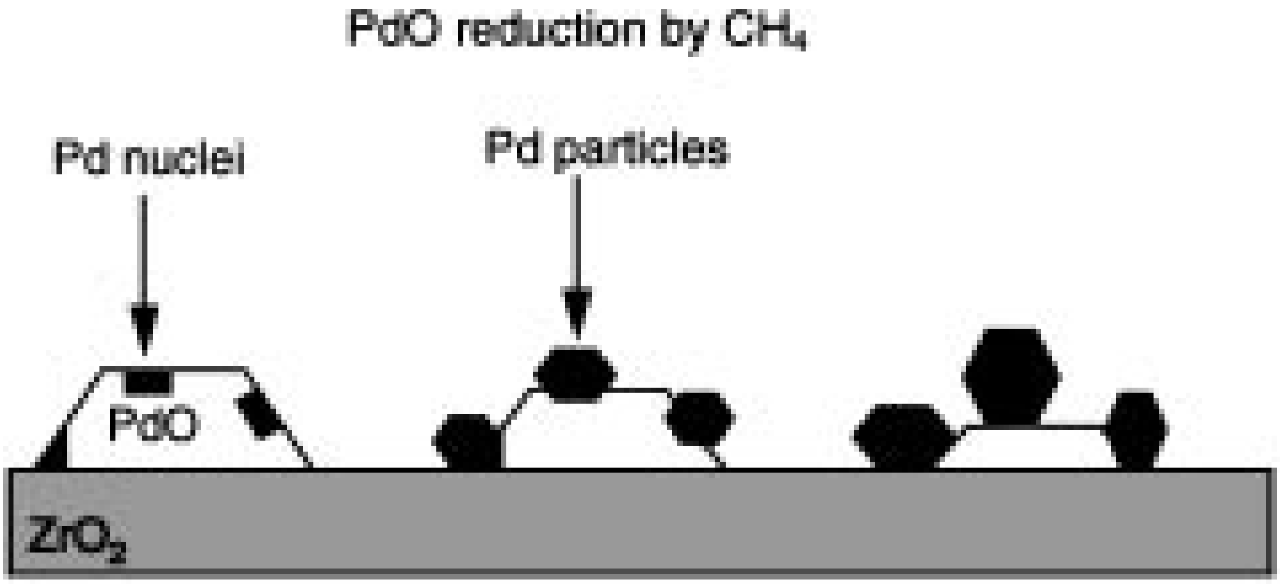
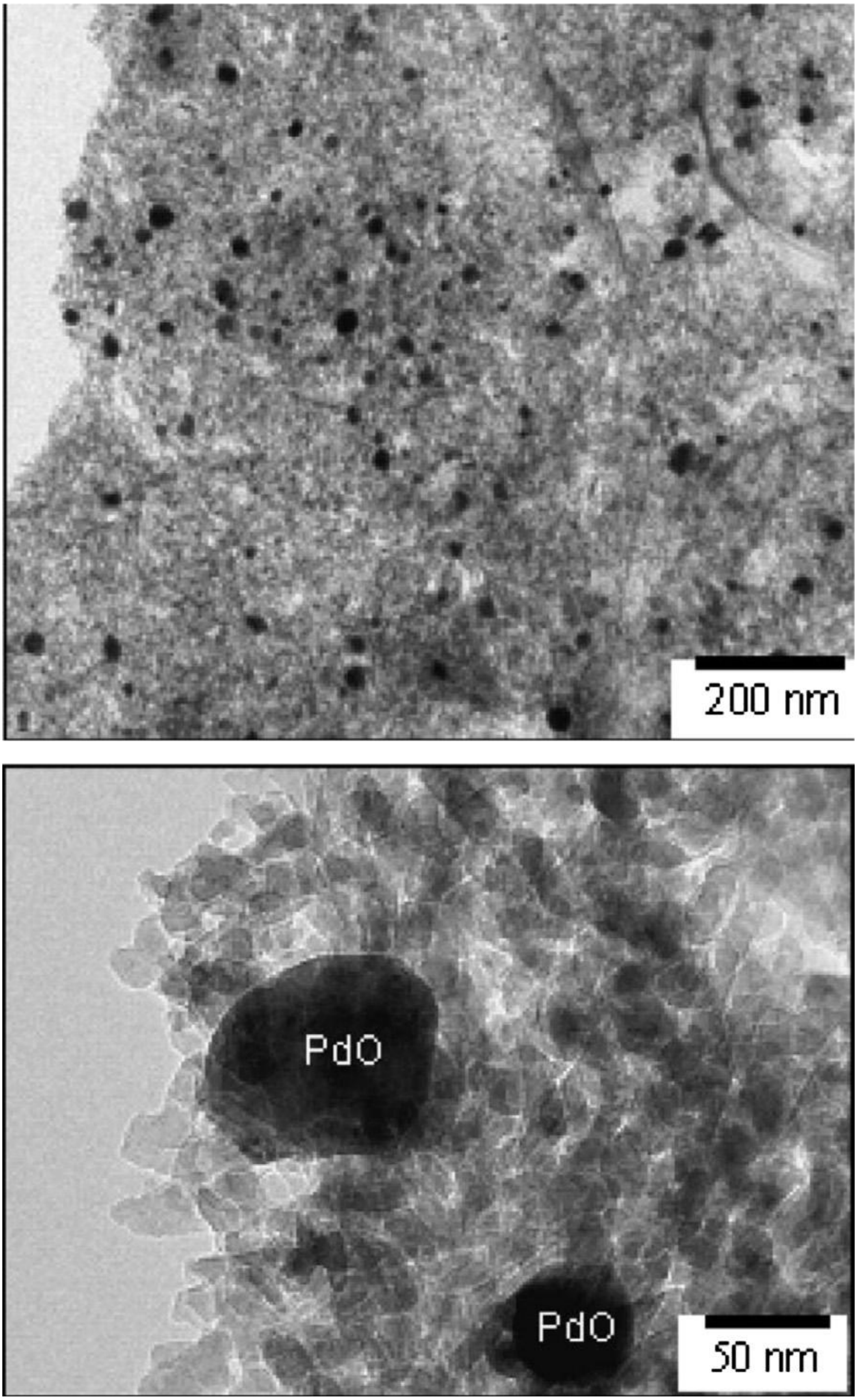


Fig. 2. Plan (a) and side (b) views of the structure of the $p(4 \times 4)$ $Ag_{1.8}O$ oxide overlayer on Ag{1 1 1}. Grey sticks represent the Ag substrate. Grey (dark grey) balls depict Ag (O) atoms in the oxide overlayer. In (a) the arrow and the hatched circle mark the location of the additional Ag atom that is present in the Ag_2O oxide overlayer.

Methane, natural gas, syngas or hydrogen combustion for energy generation may be performed in the presence of a catalyst to reduce temperature as well as NOx formation. Palladium based catalysts appear to be the most active catalysts in methane combustion. Alumina is the most largely used support, although addition of ceria is reported to be beneficial. Zirconia- and zirconia-ceria supported catalysts have also been investigated. Despite there are still some divergences in literature concerning mainly which is the most active state of the Pd-based catalysts for CH_4 oxidation, e.g. metallic Pd, PdO or a mixed phase Pd^0/PdOx, the active phase of Pd oxidation catalysts is mostly identified as PdO, which is known to decompose into Pd metal in the range 650-850 °C, depending on oxygen pressure and reactive gas mixture. The transformation of PdO into Pd is reported to negatively affect catalytic reaction by lowering conversion, CH_4 combustion activity being reversibly restored upon re-oxidation of Pd to PdO. Howevere, it is evident that Pd and PdO are not the only species present on the catalysts, and that Pd catalysts work also in conditions where Pd metal is the predominant species. Recent surface science studies showed that the chemistry of these systems is indeed very complex. The combination of Pd/Al_2O_3 with other active metallic component, such as e.g. Rh, Cu, Ni, may significantly improve low-temperature performances.


PdO reduction by CH₄
Pd nuclei
Pd particles
PdO
ZrO₂


PdO reduction by H₂
Pd
PdO
ZrO₂



TEM of a Pd/Al_2O_3 combustion catalyst

The catalytic partial oxidation (CPO) of methane, has received considerable attention for synthesis gas production because it provides close to 100% methane conversion and >90% synthesis gas yields in millisecond contact times. Compared to contact times of seconds in a steam reformer, CPO reactors can be three orders of magnitude smaller processing the same amount of synthesis gas. In addition to reduced investment costs, methane CPO supplies a H_2/CO ratio of 2/1, which is favorable for methanol or Fischer-Tropsch synthesis. Alternative applications are to produce hydrogen in refineries and filling stations.

Ni and Rh-based catalysts have been identified to be the most promising CPO catalysts, the support being a refratory ceramic material such as α-Al_2O_3, magnesia or zirconia. In contrast to supported Ni catalysts, however, Rh-based catalysts display both high activity and stability during the catalytic partial oxidation of methane to synthesis gas. Rh catalysts also show higher resistance to carbon deposition and to sulphur poisoning. However, due to the high cost of Rh, its use for commercial application is one of the key issue. Ni catalysts deactivate due to metal evaporation and formation of NiO and $NiAl_2O_4$. Pt and Ir also showed high stability, but significantly lower conversions and selectivities compared to Rh catalysts. Rapid deactivation was also observed in case of Pd coated monoliths as a result of coke deposition.

Studies reported the formation of Rh oxide rafts over the alumina surface.

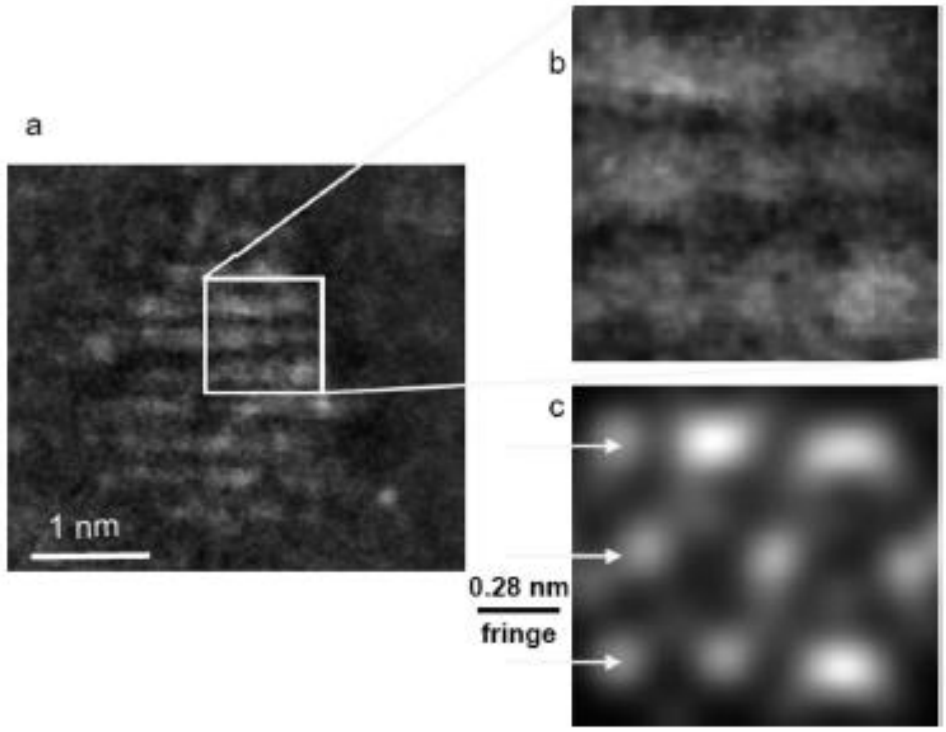


Figure 3. (a) *Z*-STEM image of Rh on γ-alumina (from ref 6). (b) Exploded view ca. 1.0 × 1.0 nm. (c) Simulated image based on optimized Rh_2O_3−II structure on γ-alumina (100) showing same area as part b.

Most of commercial VOC combustion catalysts are based on supported noble metals, which are needed to burn refractory compounds such as hydrocarbons. Alumina is the most frequent support, due to its stability at the required temperature. This is the case of the CK-304 and CK-307 catalysts (Pd/Al_2O_3 and Pt/Al_2O_3, respectively, reported to be

useful for most applications) from Topsøe. Johnson Matthey PURAVOC catalysts contain 0.3-0.5 % wt noble metal, Pt, Pd, Pt-Pd, or Rh, on alumina. The BASF RO-25 catalyst, specific for VOC combustion, is reported top contain 0.5 % Pd on alumina, with 109 m^2/g .
The aftertreatment of Otto-cycle gasoline engines is satisfactorily achieved by the so called Three Way Catalysts (TWC), a technology developed after the seventies allowing the efficient abatement of unburnt hydrocarbons (HC), CO, and NOx. The original TWC composition was Pt-Rh on alumina, deposed on ceramic monolyths. In recent years, typical TWC formulations have included Pd as the active metal, ceria–zirconia as promoters according to the Oxygen Storage Capacity (OSC) of ceria and the thermal stability of zirconia, and alumina as support as well as other minor components mainly present in order to enhance thermal stability. Perovskite materials can also be present to help limiting of noble metal sintering. The use of the different noble metal formulation (Pt-Rh, Pd-Rh, Pd only) is due in part to purely economic reasons, resulting from the high cost and scarcity of Rh and from the variable relative prices of Pd and Pt.

8.Hydrotreating Catalysts based on Sulphides

Hydrotreatments (Hydrodesulphurization and hydrocracking) is a very relevant family of processes performed in refinery to purify distillates fro sulphur and to convert heavy fractions in medium distillates. In this case sulphide catalysts are mostly used due to their stability in the presence of sulphur.

Layered bulk sulphides and their applications

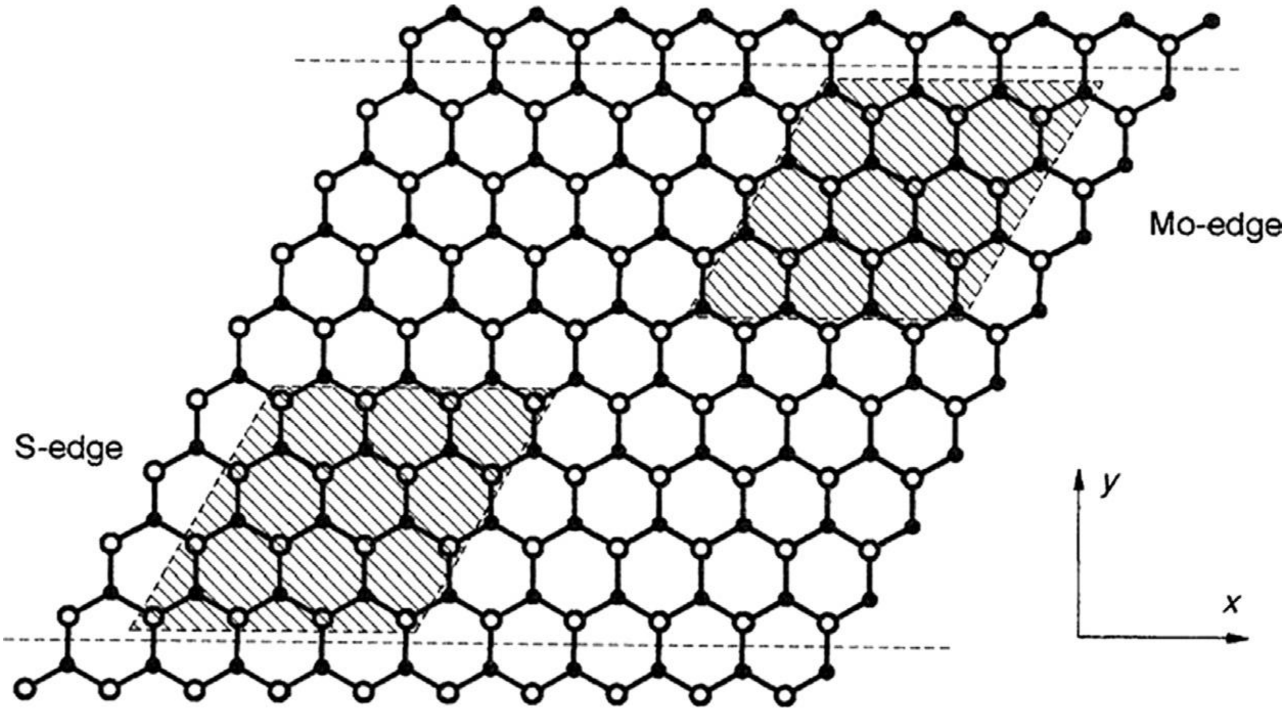
The use of unsupported metal sulphides in hydrotretament proceses may originate from the coal liquefaction process developed starting from 1920 by Bergius and coworkers. In the original Bergius process, finely grounded coal is mixed with the heavy oil and fed with the H_2 to a reactor at 673–773 K and 20–70 MPa, producing gases, light, middle and heavy oil fractions. The catalyst was constituted of bulk tungsten, molybdenum or iron sulfide.

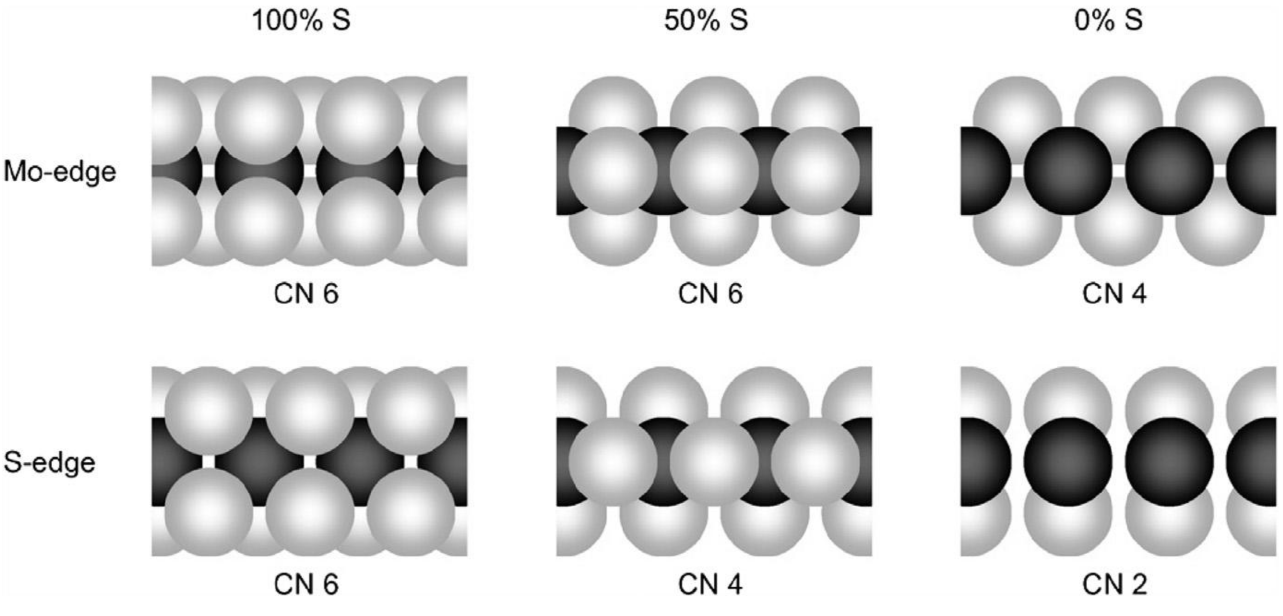
A similar system has been recently developed by the ENI group in the so called Eni Slurry Technology (EST). This technology is a slurry hydrogenation/hydrocracking process for converting oil residues (the bottom of the barrel) to lighter fractions. A catalyst precursor, consisting of an oleo-soluble molybdenum carboxylate (i.e. naphthenate or octoate), is dissolved in the feedstock and the mixture is fed to the reactor, which operates in the temperatures range 673–723 K under a total pressure of 15 MPa. H_2 is fed through a distributor located at the reactor bottom. Under these conditions, the catalyst precursor is converted to molybdenite, which is crystalline layered MoS_2, with an average particle size of a few nanometers.

Among the many bulk sulphides which are active in hydrodesulphurization and hydrogenation catalysis, those which are largely applied commercially seem to be essentially constituted by mixed molybdenum and tungsten sulphides, promoted by Ni or Cobalt, i.e. the same components of the common alumina-supported HDS catalysts but apparently in a different formulation.

Molybdenum and tungsten sulphides MoS_2 and WS_2 are isostructural layered phases. The tetravalent element forms a layer sandwiched between two two-dimensional hexagonal sulphide layers stacked over each other in an eclipsed fashion. Thus, the coordination around the metal is trigonal prismatic. Each sulfur centre is pyramidal, being connected to three Mo centres. Because of the weak van der Waals interactions between the sheets of sulfide atoms, MoS_2 has a low coefficient of friction, resulting in its useful lubricating properties.

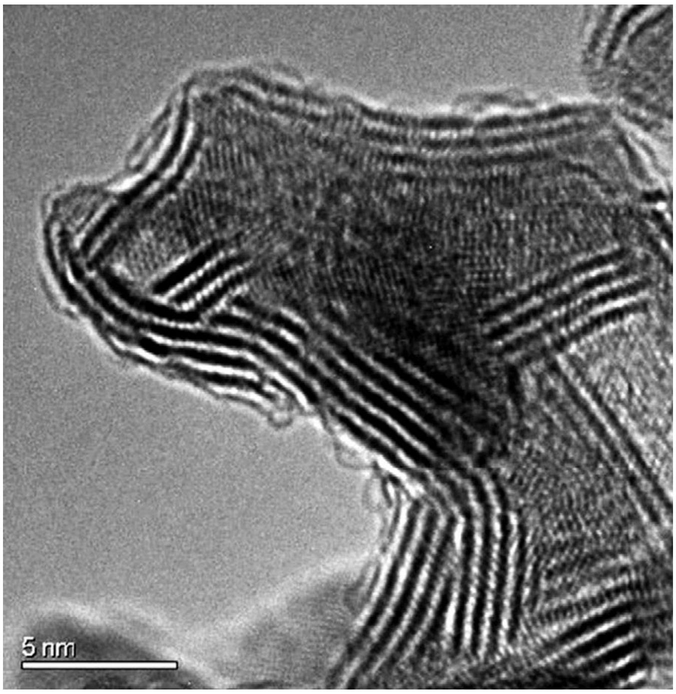
Two main polymorphs of MoS_2 are reported to exist, due to the different relative position of the slabs. α-MoS_2 (molybdenite) hexagonal (space group $P6_3/mmc$), most stable, is the most common and studied polymorph and the natural form. β-MoS_2 is the rhombohedral modification (space group R3m).





Ball model (side view) of the edges of a MoS2 slab at different sulfur loadings. Dark spheres represent Mo, light spheres S atoms. Indicated are the total sulfur coordination (%) of the edge and the coordination number (CN) for Mo in each case. For theoretical stoichiometric MoS_2 the S edge has 100% sulfur, while the Mo edge has 0% sulfur.

MoS_2 can also be prepared in poorly crystalline form, termed the "rag" structure, consisting of several stacked but highly folded and disordered S-Mo-S layers. On the other hand, line defects and stacking faults as well as nanoindentations are currently observed in MoS_2.



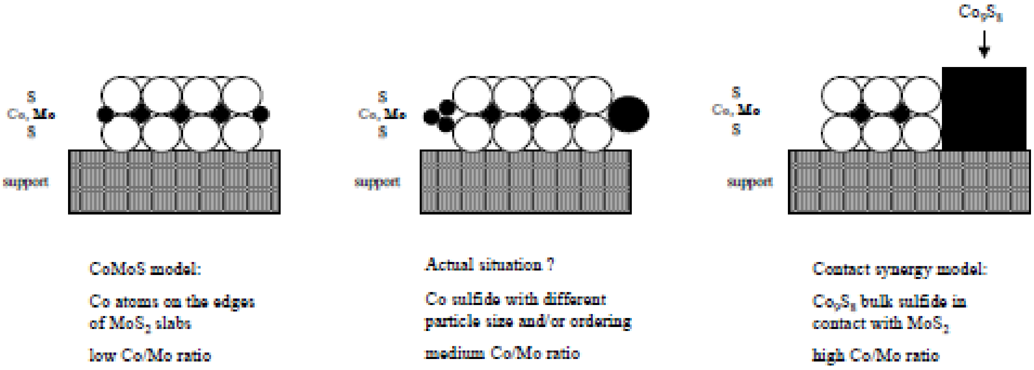
HREM micrograph on unsupported mixed NieMo sulfide showing a large curved MoS_2 stacks with numerous defects and intergrowths

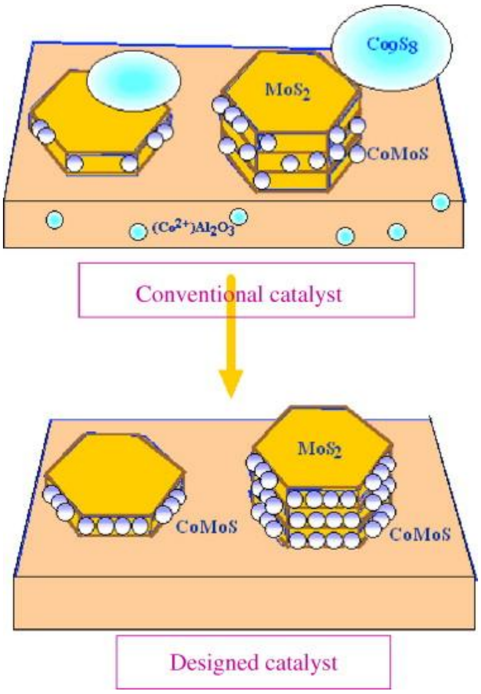
WS_2 occurs naturally as the rare mineral called tungstenite, with the same structure of molybdenite.
Commercial unsupported sulphide hydrotreating catalysts denoted as NEBULA^{TM}, (NEw BULk Activity) developed jointly by Akzo Nobel, Nippon Ketjen and Exxon Mobil in 2001, are apparently based on Ni-promoted $(Mo,W)S_2$. They are reported to be substantially more active than alumina supported catalysts.
According to the most accepted theory, mostly developed for supported MoS_2 catalysts, the catalytic chemistry of these materials should mostly occur at the lateral termination (edges) of the MS_2 slabs. Two kinds of termination should exist for stoichiometric MoS_2, the S edge ($\bar{1}010$ face), where coordinatively unsaturated sulphur is located for stoichiometric MoS_2, and the Mo- edge ($10\bar{1}0$ face) where coordinatively unsaturated Mo species are expected in stoichiometric MoS_2 . As said, hydrogen is supposed to adsorb with an oxidative mechanism at sulphur atoms while organic sulphide molecules would adsorb through the sulfur lone pair on sulphur vacancies associated to Lewis acidity of unsaturated Mo centers. The promoters Ni and Co introduce further defects and disorder in the structure perturbing the stacking of the layered sulphides, introducing curvatures and non-stoichiometry.

Supported bimetallic sulphides
The type of catalysts used for hydrotreating processes is mainly dependent on the specific reaction and process requirements. In general, catalysts for hydrotreating reactions

consist of mixed sulfides of CoMo, NiMo, or NiW supported on high surface area carriers, reactions, while NiMo sulfide catalysts are excellent in hydrodenitrogenation (HDN) and hydrogenation (HYD). NiW sulfide catalysts are very promising for hydrocracking, aromatics hydrogenation at low H_2S concentrations and conversion of alkylated dibenzothiophenes, although the high costs of these catalysts makes industrial applications less attractive. Noble metal catalysts, like e.g. Pd or Pt, have gained increasing attention due to their high hydrogenation activity. However, these catalysts are sensitive towards poisoning by sulfur compounds. Interestingly, CoW sulfide catalysts seem somehow not to be a good combination for application in industrial hydrotreating processes. In general, thespecifications of the feed and the desired products will determine which catalyst (or combination of catalysts) will be used. As already mentioned hydrotreating catalysts are among the most applied catalysts in industry and hence research effort on these catalysts is tremendous.

Despite the enormous amount of research, the structure of the active phase has been a matter of great debate. Although the presence of MoS_2- and WS_2-slabs has been generally accepted, the function and location of Co or Ni was the main subject of debate. In the past, various models were proposed for the role of the promoter; viz. the intercalation model, the pseudo-intercalation or decoration model and the remote control or contact synergy model. However, at this time (almost) everyone supports the so-called ‘CoMoS’ model, in which Co atoms decorate the edges of MoS_2-slabs .





9.Solid polymerization catalysts

Stereoregular catalytic polymerization is performed mainly to produce High Density PolyEthylene (HDPE), Linear Low Density Polyethylene (LLDPE, a copolymer of ethylene and another terminal olefin such as 1-butene, 1-hexene, 1-octene) and Isotactic PolyPropylene (PP. Other polyolefins (such as Poly-4-methyl-1-pentene (PMP)) as well as co-polymers are produced with similar processes and catalysts. Three main families of industrial catalysts exist for the processes, the so-called Ziegler-Natta catalysts, the Phillips Catalysts, and the so-called single site catalysts, the last being either homogenous catalysts or immobilized.

Ziegler-Natta type catalysts.

Ziegler Natta catalysts based on titanium chlorides, developed from the later fifties to the early sixties by K. Ziegler and G. Natta, have been improved progressively during time, coming now to the fifth or sixth generation. The modern catalysts are constituted by $TiCl_4$ supported on $MgCl_2$ and treated with $Al(Et)_3$ as the co-catalyst. The catalysts also contain a so called "internal donor" (ID) and an "external donor" (ED). ID is a Lewis base (or electron donor, e.g. an organic ester, ether, alcohol, or amine) whose presence increases the isotactic content of polypropylene by greatly diminishing the yield of the atactic one. The recent development of the catalyst is mostly associated to the choice of different ID molecules, being benzoate type, phthalate type (dibutyl- or diiosobutyl-phthalate), "diether" (2,2-dialkyl-1,3-dimethoxy-propane), or succinate. The catalyst needs very little amount of ED, usually dicyclopentyldimethoxy-silane, and in extreme cases it even works without any.

In the preparation step, the support $MgCl_2$ is impregnated with $TiCl_4$ and the ID. According to theoretical studies, defects and corners of the $MgCl_2$ support are likely anchoring sites for the catalytically active Ti-species, while the ID coordinated in the proximity of the active Ti center confer a remarkable stereoselectivity. This catalyst is activated by $AlCl_3$, favouring the partial reduction of Ti^{4+} into Ti^{3+}, thus forming the "active" $TiCl_3$ phase. The ED improves stereoregularity in the formation of isotactic PP by both activating the sites active in isotactic PP formation and by deactivating those which are active in the formation of the atactic polymer

The most broadly accepted mechanism for stereoregular polymerization on ZN catalysts is the so-called monometallic mechanism proposed by Cossee and Arlman. Polymerization would occur via two steps. First, coordination of the monomer to the active center occurs, followed by the stereospecific migratory insertion of the coordinated monomer into the titanium–carbon bond. In migratory insertion step, a vacant coordination site is regenerated, which enables further chain propagation.

The main features of the catalyst are high activity, excellent hydrogen response (i.e. ability to respond to the hydrogen pressure tailoring the chain length), narrow molecular weight distribution (MWD), and low xylene soluble content (CXS, i.e. low atactic PP production) of the polymer.

Developed for the original Montecatini slurry processes, still performed using slurry CSTR reactors operating at 5-10 bar, 75-85 °C in the presence of hexane as the solvent (HDPE Basell Hostalen process), catalysts belonging to this family can also work in loop reactors in supercritical propane at 65 bar and 85-100 °C (such as in the first step of the Borstar HDPE process) and in gas-phase fluidized bed processes at 80-90 °C, 20 bar (such as

Basell Spherilene HDPE process and the second step of the Borstar HDPE process). Similarly, for isotactic PP production loop reactors in the Borstar technology work at 80-100 °C, 50-60 °C in supercritical propene (bulk polymerization) while the second fluidized bed gas phase reactor works at 22-35 bar 80-100 °C. The Unipol PP process uses such kind of catalysts in two sequential gas phase fluid bed reactors.

Phillips type catalysts.

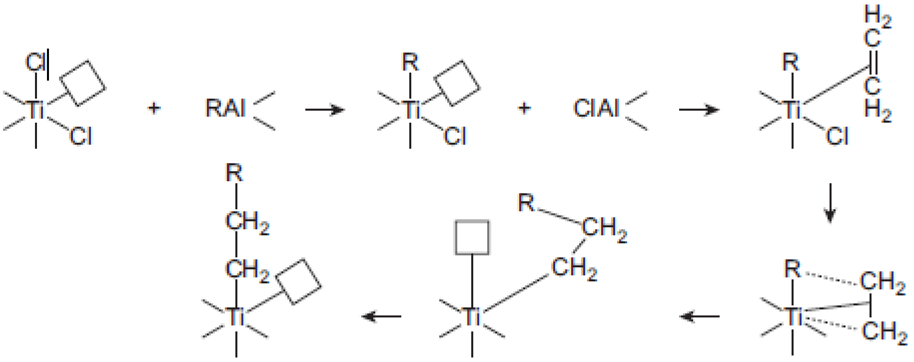
The composition of Phillips catalysts is simpler: they are constituted by chromium species on wide pore silica. The synthesis procedure implies first grafting of silica with Cr compounds or impregnation, followed by calcination producing mainly hexavalent chromate species.

The grafted Cr^{VI} species are then reduced by ethylene (industrial process) or by CO (model laboratory process), yielding anchored isolated Cr^{II} species, which are the species active in ethylene polymerization.

A number of different proposals have been done for ethylene and propylene polymerization on such catalysts. Recent studies support also for this catalyst a Cossee-Arlman-type mechanism similar to that is proposed fopr Ziegler Natta catalysts.

However, the structure of the active sites at the molecular level is far from being understood and for this reason the Phillips catalyst continues to be one of the most studied and controversial system in heterogeneous catalysis research. As a consequence of the high heterogeneity of the amorphous silica support, the Phillips catalyst allows a very broad molecular weight (MW) distribution for HDPE which gives to the polymer fine mechanical properties such as elasticity and impact resistance, and superior moldability due to its high melt viscosity.

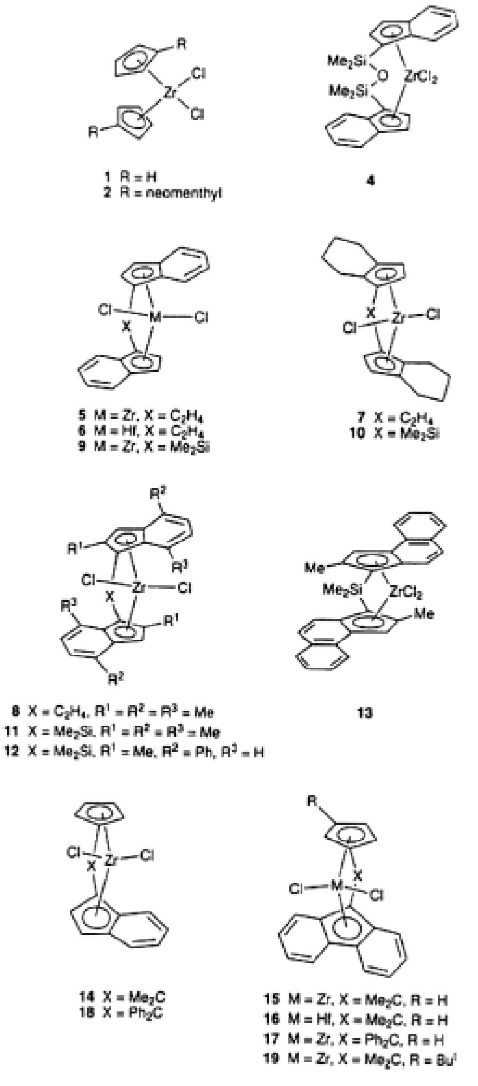
Phyllips type catalysts are most commonly used in gas-phase fluidized bed reactors for bulk polymerization (e.g. Basell Lupotech G HDPE technology) at 20-25 bar, 85-116 °C, but is now also used in loop slurry reactors (Chevron Phillips process).



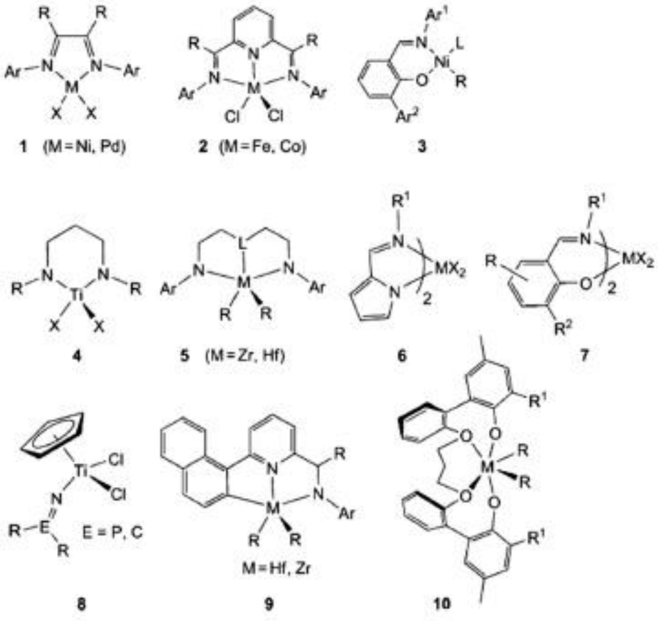
CosseeeArlman mechanism of ZieglereNatta polymerization catalysis.

Heterogenized “single-site” polymerization catalysts.

The so called single-site catalysts are mononuclear metal complexes having stereoregular olefin polymerization activity. The ability of metallocene catalysts to produce stereospecific polymerization was already known by Natta, but found practical interest when Kaminski reported their very pronounced promotion when methylaluminoxane (MAO) are used as co-catalysts. A number of substituted or non-substituted Zr,Ti and Hf cyclopentadienyl, indenyl or fluorenyl complexes were found to display excellent activiy. After the Kaminsky discovery, a number of other non-metallocene (or post-metallocene) metal complexes were found to display excellent stereospecific polymerization activity, in particular when used with activators. These metal complexes work in solution as homogeneous catalysts. Thus, liquid-phase solution polymerization processes were developed with these catalysts.



Metallocene catalysts



Post-metallocene catalysts

On the other hand, a further improvement was made when successful supporting of these “single-site” metal complexes was obtained, allowing the use of supported single site catalysts to already existing typical gas-phase or slurry polymerization processes in substitution of Ziegler-Natta and Phyllips catalysts. In fact, most of the actual HDPE, LLDPE and iPP manufacture processes can today be applied using also supported single site catalysts. According to the literature, silica and $MgCl_2$ are the most used supports for both metallocene and non-metallocene catalysts. In fact silica supported zirconocenes are used industrially for the production of LLDPE. However, a number of other supports have been cited in the open literature. Polymeric supports, such as polysiloxanes and polystyrene based materials are reported. Some industrial processes such as Mitsui

Evolue process are reported to work with supported metallocene catalysts, using fuid bed gas phase reactors. Montmorillonite-supported metallocene catalysts have been developed at the industrial level for the production of isotactic polypropylene by Mitsubishi. Among non-metallocene catalysts, those based on salicylaldimines (also denoted as phenoxy-imine, FI) ligands have been studied and described in detail. They can be heterogenized by supporting on silica and $MgCl_2$ or polymeric supports such as silicones, polystyrene and polyolefins. The Llyondel-Borstar Metocene technology is apparently associated to the use of supported non-metallocene catalysts applicable in both gas phase and slurry processes such as the Spheripol technology using a slurry loop reactor followed by a gas phase fluid bed reactor.

10.Adsorption and absorption on solids.

Adsorption is a physical chemical process due to the interaction between particles and selective medium. n solid retains some families of molecules while others are not retained. Depending on the relationship that develops between the adsorbent and adsorbed distinction is made between:

a) physical adsorption: process that quickly reaches the equilibrium is weakly exothermic and 'reversible, which generally allows for easy regeneration of the adsorbent. Are made between adsorbate and adsorbent interactions of van der Waals or weak hydrogen bonds. During the adsorption molecules adsorbed forgiveness in part their translational degrees of freedom, but not vibrational and rotational, by binding to the surface; binding to the surface can then be seen as a bond that can only be removed during a desorption process.

b) chemical adsorption: there is formation of a chemical legane, for example of coordination, between solid and molecule. This is a much more exothermic than physical adsorption, and regeneration of the adsorbent implies more energy.

c) absorption: the reaction between solid and molecule is deeper, not only superficial, and because the change of the chemical nature of both:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Especially in cases of adsorption, in addition to the chemical nature of the solid and its surface is relevant morphology and porosity, normally defined by the following parameters

a) surface area or specific surface,
b) pore size
c) the total pore volume.
d) pore size distribution

From the point of view of porosity distinguishes between different types of materials:

1. solid structural or zeolitic porosity: it is crystalline solids whose structure provides for the existence of cavities and channels of dimensions "molecular". These materials can be called "molecular sieves".
2. microporous solid: pore size <20 Å
3. mesoporous solids: pore size between 20 Å and 500 Å
4. macroporous solid: pore size> 500 Å

Gas phase adsorption processes

In the "classic" diagram these systems operate with two twin beds of adsorbent solids. While working in one of the beds adsorption, thus purifying the gas, the other regenerates. The operation can be conducted in different ways:

1. PSA (Pressure Swing Absorption) performing adsorption at high preessione and desorption at low pressure
2. VPSA (Vacuum Pressure Swing Absorption) that is operating the desorption step under vacuum,
3. TSA (Temperature Swing Adsorption), obtaining the desorption under heating.
4. Purge Swing Absorption, getting the desorption purging with a gas (water vapor, nitrogen, air). Frequently purge is realized with a heated gas or vapour, thus producing a mix of TSA and purge SA.

When the conditions of the adsorption and desorption steps are very different, in particular in terms of pressure, polybed processes are needed. The use of many beds allows to separate different depressuriazation and repressuriazation operation in steps, allowing the process to be used continuously.

The current obtained for desorption, remarkably concentrated, can be retrieved or sent to an incinerator.

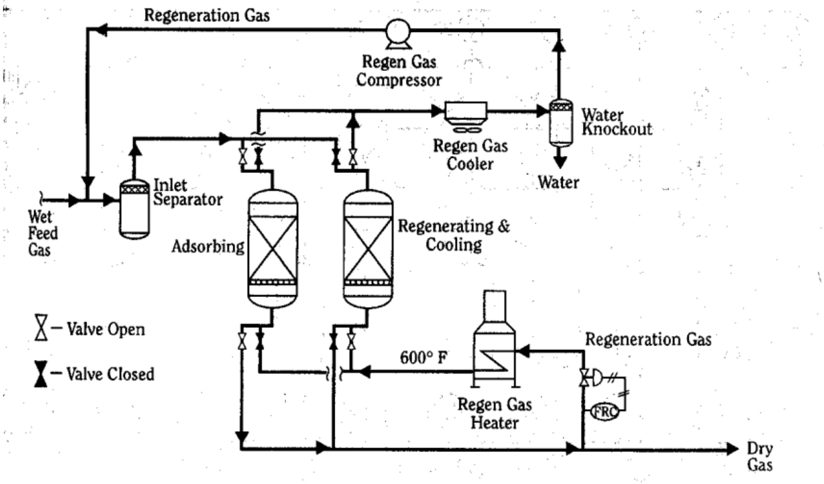


FIG. 16-49 Two-bed TSA system with regeneration equipment. (*Reprinted with permission of GPSA. Reference:* Engineering Data Book, *10th ed., Gas Processors Suppliers Association, Tulsa, 1988, Sec. 20, p. 22.*)

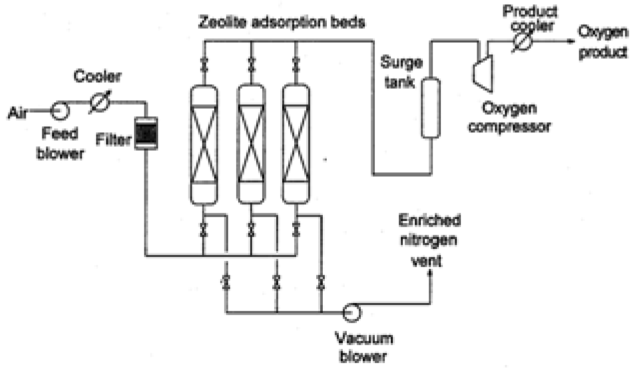
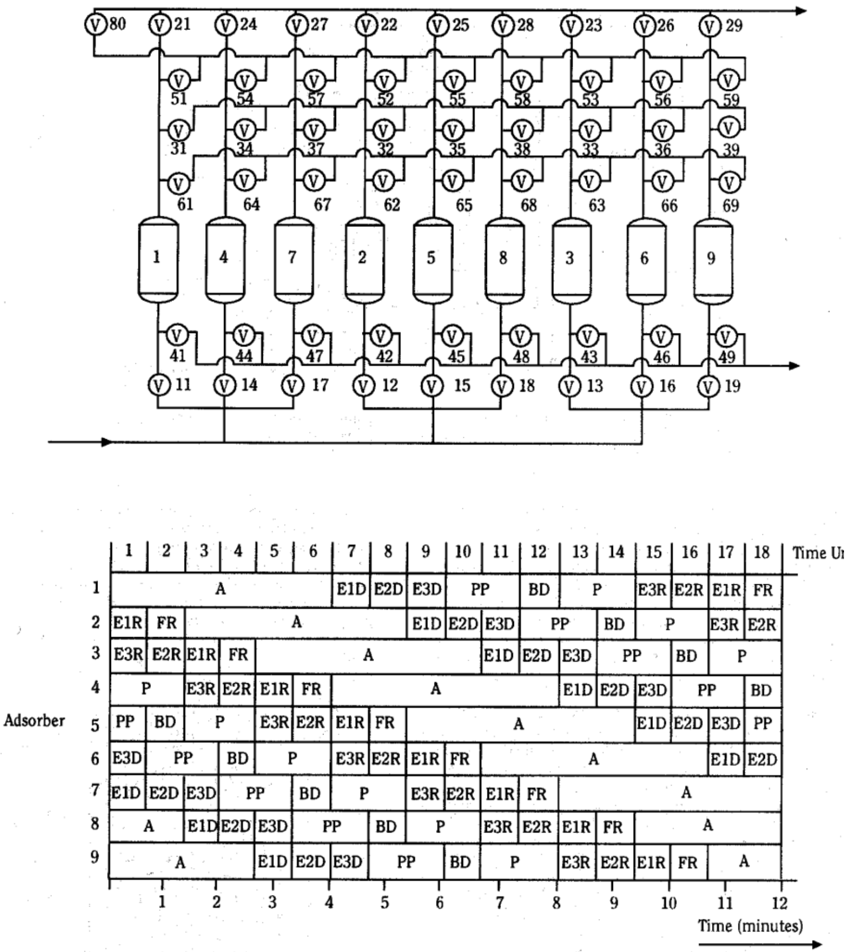


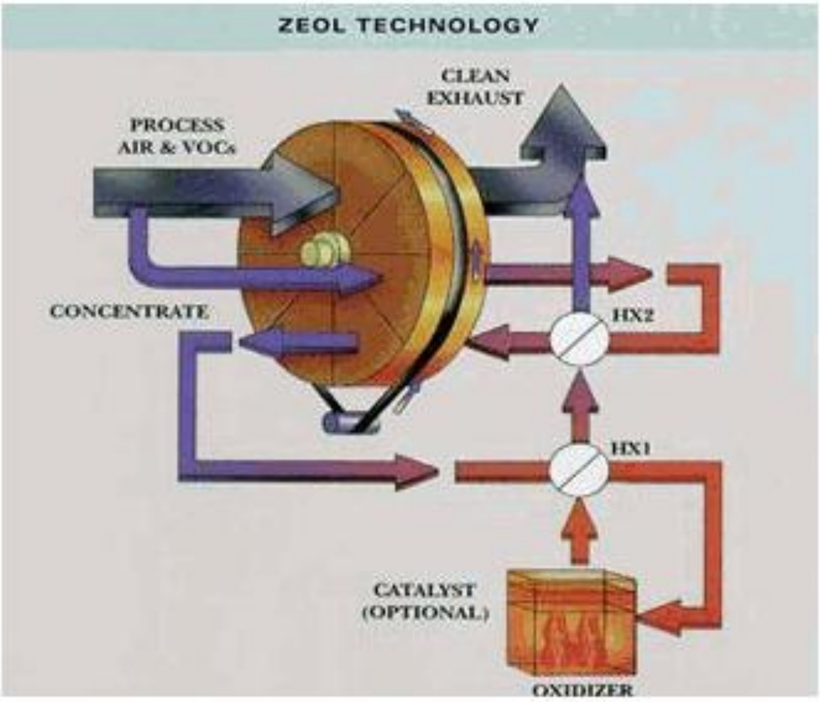
Figure 16 VPSA oxygen production unit.

Gas phase adsorption processes

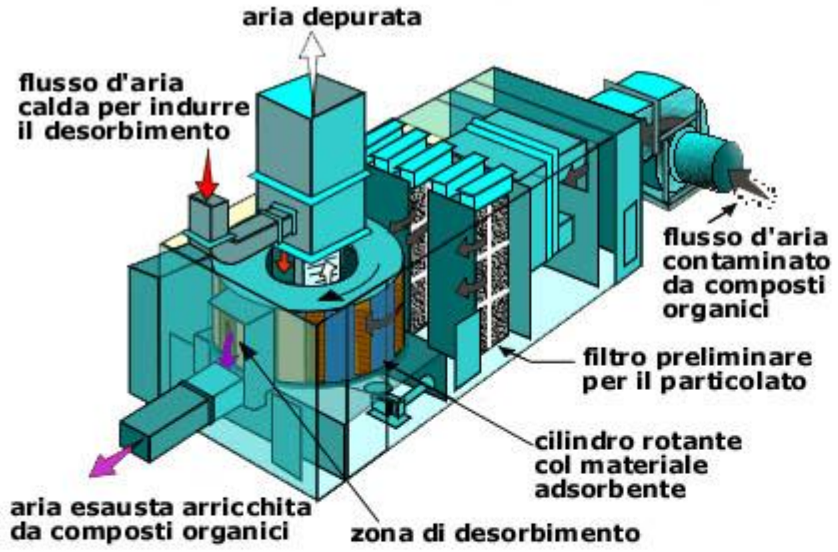


Adsorber	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Time U
1	A						E1D	E2D	E3D	PP		BD	P		E3R	E2R	E1R	FR	
2	E1R	FR	A						E1D	E2D	E3D	PP		BD	P		E3R	E2R	
3	E3R	E2R	E1R	FR	A						E1D	E2D	E3D	PP		BD	P		
4	P		E3R	E2R	E1R	FR	A						E1D	E2D	E3D	PP		BD	
5	PP	BD	P		E3R	E2R	E1R	FR	A						E1D	E2D	E3D	PP	
6	E3D	PP		BD	P		E3R	E2R	E1R	FR	A						E1D	E2D	
7	E1D	E2D	E3D	PP		BD	P		E3R	E2R	E1R	FR	A						
8	A		E1D	E2D	E3D	PP		BD	P		E3R	E2R	E1R	FR	A				
9	A				E1D	E2D	E3D	PP		BD	P		E3R	E2R	E1R	FR	A		

FIG. 16-51 UOP nine-bed polybed PSA H_2 unit: (*a*) flow scheme; (*b*) cycle diagram. (*Reference: Fuderer and Rudelstorfer, U.S. Paten number 3,986,849, 1976.*)



In particular when adsorption is used to abate vapours from air to be later incinerated, concentrators rotor can be used. It is a wheel device, packed with an adsorbent. Each section of the rotor intercepts the effluent to be purified cold and it adsorbs pollutants, then, by rotating, comes into a heated zone or traversed by a hot fluid and here releases the pollutant. This technology can be cost-effective for high flow of waste gas just concentrated in pollutants.



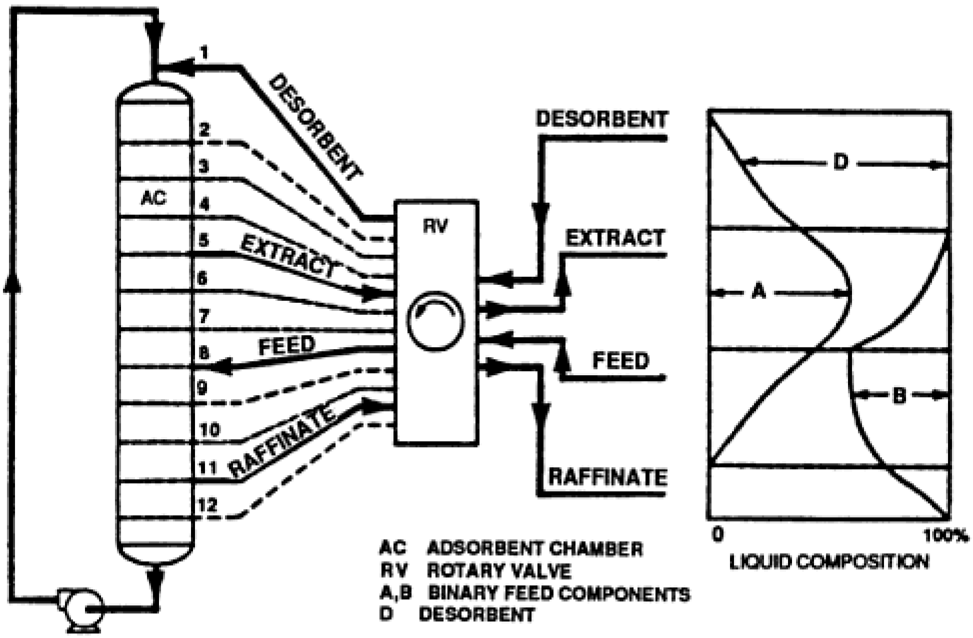
Liquid phase adsorption processes.

Adsorption is also applied to purify or separate liquids. In the most common case, twin bed purge swing adsorption is performed. In some cases the filter matter is not regenerated but disposed when saturated.

Sistema di purificazione di acque reflue con carboni attivi

A successful alternative system for commercial application is the UOP Sorbex Simulated Moving Beds Process for the separation of bulk liquid mixtures.

The bed is held stationery in one column, which is equipped with a number (perhaps 12) of liquid feed entry and discharge locations. By shifting with a rotary valve, the locations of feed entry, desorbent entry, extract (adsorbate) removal, and raffinate (non-adsorbed component) removal, a counter-current movement of solids is simulated by a downward movement of liquid.



Sorbex separation column

Industrial adsorbents

TABLE 4.1 Some Examples of Commercial Adsorption Separations*

Separation	Adsorbent
Gas bulk separations	
Normal paraffins/isoparaffins, aromatics	Zeolite
N_2/O_2	Zeolite
O_2/N_2	Carbon molecular sieve
CO, CH_4, CO_2, N_2, A, NH_3/H_2	Zeolite, activated carbon
Hydrocarbons/vent streams	Activated carbon
H_2O/ethanol	Zeolite
Chromatographic analytical separations	Wide range of inorganic and polymeric agents
Gas purification	
H_2O/olefin-containing cracked gas, natural gas, synthesis gas, air, etc.	Silica, alumina, zeolite
CO_2/C_2H_4, natural gas, etc.	Zeolite
Hydrocarbons, halogenated materials, solvents/vent streams	Activated carbon, silicalite, others
Sulfur compounds/natural gas, hydrogen, LPG, etc.	Zeolite
SO_2/vent streams	Zeolite
Hg/chlor-alkali cell gas effluent	Zeolite
Indoor air pollutants—VOCs	Activated carbon, silicalite
Tank-vent emissions/air or nitrogen	Activated carbon, silicalite
Odors/air	Silicalite, etc.
Liquid bulk separations	
Normal paraffins/isoparaffins, aromatics	Zeolite
p-Xylene/*o*-xylene, *m*-xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymeric, and affinity agents
Liquid purifications	
H_2O/organics, oxygenated organics, halogenated organics, etc.—dehydration	Silica, alumina, zeolite, corn grits
Organics, oxygenated organics, halogenated organics, etc./H_2O—water purification	Activated carbon, silicate
Odor and taste bodies/H_2O	Activated carbon
Sulfur compounds/organics	Zeolite, others
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon
Various fermentation products/ fermentor effluent	Activated carbon, affinity agents
Drug detoxification in the body	Activated carbon

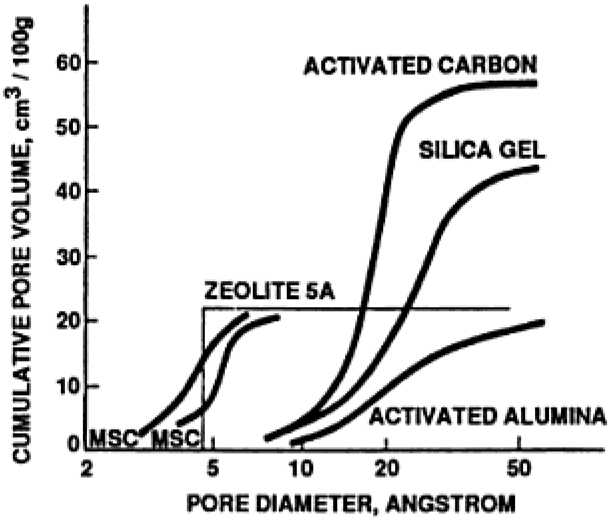
Abbreviations: LPG, liquified petroleum gas.

*Adsorbates are listed first.

Bulk separations: adsorbate concentration is greater than about 10 wt% in the feed.

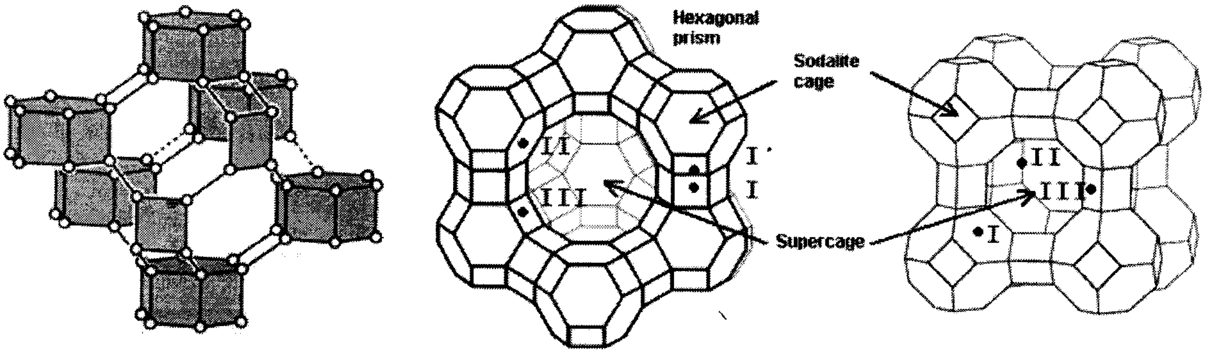
Purifications: adsorbate concentration is generally less than about 2 wt% in the feed.

Adsorbent		Pore size (Å)	S_{BET} (m^2/g)	Apparent density (g/mL)
zeolites	Chabasite	3.8 x 3.8		
	Linde 3A (KA)	4.1 x 4.1	500-700	
	Linde 4A (NaA)	4.1 x 4.1	500-700	0.7
	Linde 5A (CaA)	4.1 x 4.1	500-700	
	ZSM-5	5.5	500-700	
	Mordenite	6.5	500-700	
	Faujasite (13X, NaX))	7.4	500-700	0.7
Active carbons (ACs)		20-40	> 1000	0.6-0.8
Carbon molecular sieves		~ 5	> 1000	
Silica gels		20-50	200-500	0.7
Silicalite-1		5.5	500-700	
Mesoporosous silica MCM41		20	500-800	
llumina		30-200	200-400	
MOF		6-30	1000-2000	
TitanosilicatE ETS4				



<u>Zeolites</u>

Zeolites are porous structure silicoaluminates to adjust. The lattice is made of a structure of the formula $[Si_{1-x}Al_xO_2]^{x-}$. The basic structure of synthetic zeolites is given by a crystal consisting of tetrahedrons formed by atoms of aluminum or silicon bound to four oxygen atoms. This macromolecule is extremely stable and is characterized by possessing the spaces of uniform diameter whose size depends on the types of atoms present and the number of basic elements bonded together.



Spaces form a network of pores and internal channels occupied by alkali ions and water molecules are easily removed because they are linked by weak electrostatic forces. In general, each pore is formed by the set of 6, 8, 10 or 12 tetrahedra, which form variable diameters between 3 and 8 Angstroms (1 Angstrom is equal to 10-10 meters). So, in contrast to activated carbons that are characterized by having a set of pores and channels of different sizes and that shrink gradually developing in depth, in this case there are well-defined pore sizes.

For each aluminum takes a positive charge to balance the negative charge of the lattice. Normally these charges are given by alkali ions and / or alkaline in the cavities.. These materials act as molecular sieves, strongly adsorbing only chemical species that are small enough to enter into the cavities.. In addition, the cationic forms are used as inorganic ion exchanged.

Structure of chabasite (left), a naturally occurring zeiolite inter alia in the tuff of faujasite or zeolite 13X and zeolite Linde type A Sodium (4A). Below, adsorption isotherm of nitrogen (left) and curve of the distribution of pores in zeolites in acid form.

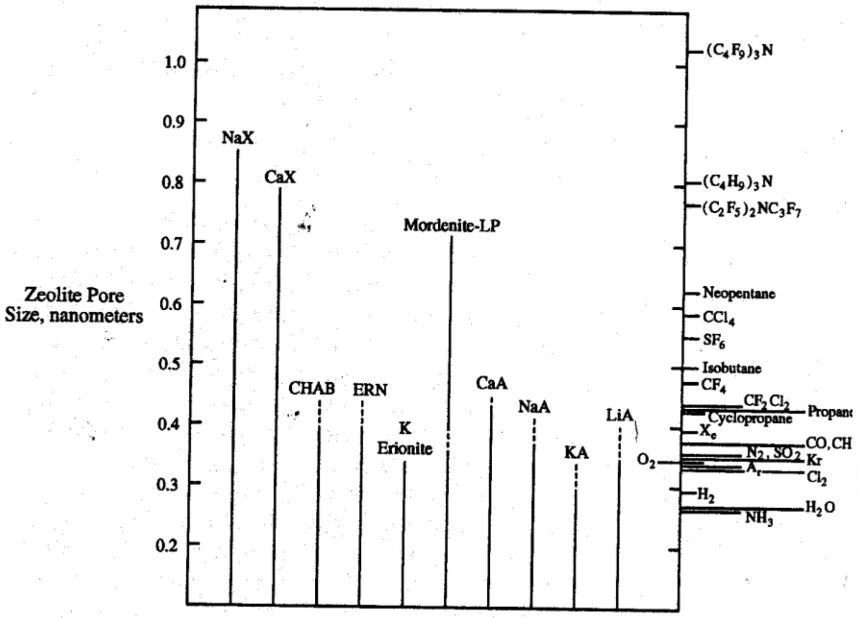


Figure 4.7 Comparison of molecular dimensions and zeolite pore sizes.

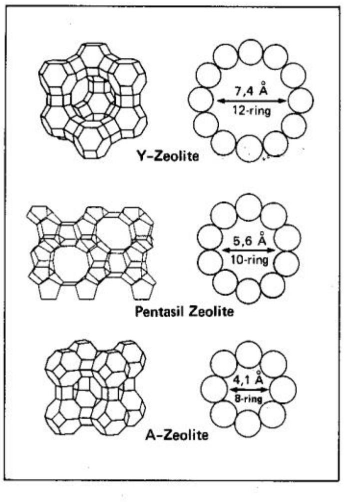
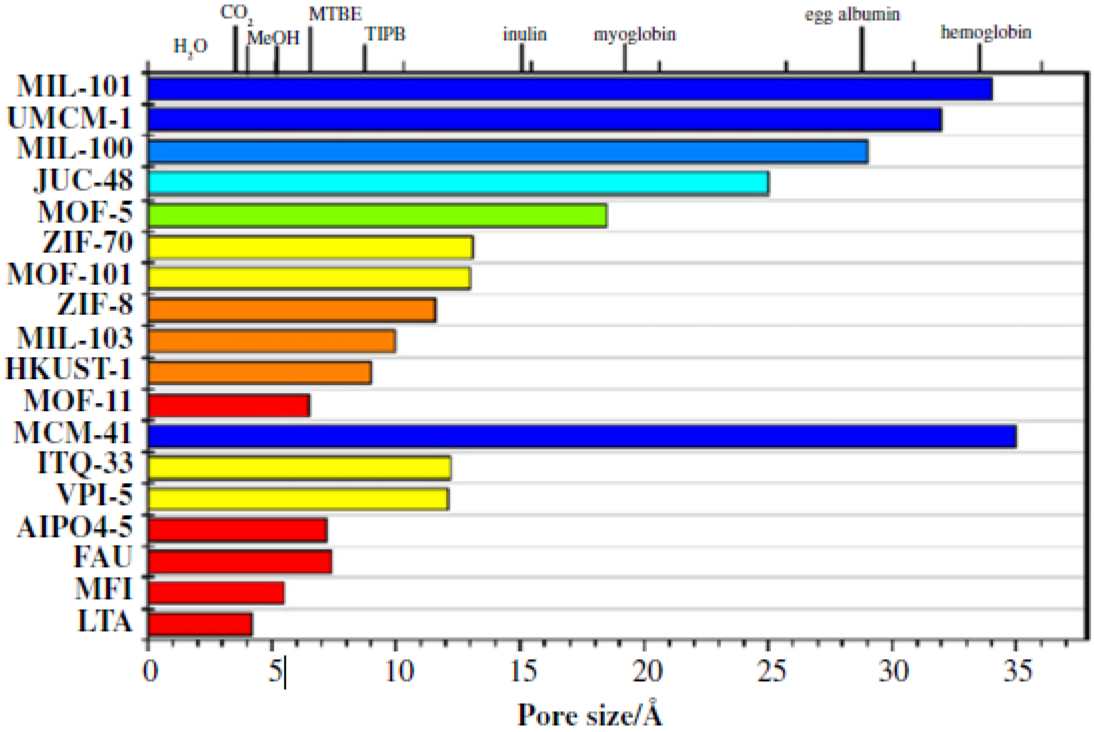


Figure 3.50: Zeolite structures with various diameters



Cavity size of zeolites, mesoporous materials and porous MOFs compared with standard aluminosilicates and aluminophosphates. Porous materials are selected arbitrarily; pore sizes are approximate due to the variety of pore shapes involved.

According to their molecular sieving properties, zeolites act as selective regenerable adsorbents for purification of gaseous streams and separation of vapours and gases. In this respect, the so called type A zeolites, denoted with the IZA (International Zeolite Association) code LTA (Linde Type A) and the so-called X zeolites, denoted with the code FAU, being isostructural with the natural zeolite Faujasite, are by far the most useful.

Sodium-faujasites, in the form of either NaX or NaY (differing for the Si to Al content and consequently for the amount of Na present), and other alkali-metal exchanged faujasites are widely applied in the industry as selective adsorbants for gas mixture separation and gas purification. The faujasite structure is formed by quite wide supercages accessed through 12-member silicate rings with 0.74 nm diameter, much smaller sodalite cages accessed through 6-member silicate rings and hexagonal prisms connecting the sodalite cages. Cations are located in different positions in the cavities depending on hydration/dehydration states or upon adsorption of different molecules. The medium Lewis acidity of the alkali and alkali earth cations, increased by the loss of ligands in dry zeolites, is the key feature for the use of these materials as regenerable adsorbants. However, the zeolite framework is also reported to display significant basicity that can cooperate in the adsorption of acid molecules. Complex interactions, where more than one cationic site and oxygen atoms cooperate in adsorption have been found.

Either in the form of powder packed beds or of membranes, alkali and alkali earth metal faujasite zeolites are used industrially for the purification of C4 cuts from nitriles and for hydrocarbon separations. The most selective adsorbant for the separation of para-xylene from meta-xylene (ortho-xylene is separated by distillation) is K,Ba exchanged Y, with Si/Al ratio ~ 2. In the UOP Parex process, the zeolite, shaped in extrudates, is put in s a single column working in the simulated countercurrent mode, where the xylene mixture and the desorbent (either toluene or paradiethylbenzene) are fed separately. Two stream are withdrawn, one rich in para-xylene,the other rich in meta-xylene. Another relevant application of Na-FAU zeoplites is the separation of air components (N_2/O_2) by pressure/vacuum swing adsorption procedures.

The structure of LTA (Linde Type A) or A zeolites consists of small “sodalite” cages, identical to those also present in the Faujasite structure, but connected differently foming larger supercages, opened each other through eight-membered oxygen rings (8MR). The sodalite cages connect to the supercages through six-membered rings (6MR), and each other through four-membered rings (4MR). Both 6MR and 4MR are too small for most molecules to pass through. The pore structure through which molecular diffusion occurs is consequently limited by the size of the 8MR that are approximately 5 Å across. The presence of charge-balancing cations (K^+, Na^+ and Ca^{2+}) reduces the effective pore size of the opening to near 3 Å (for K-LTA, also denoted as 3A) and near 4 Å (for Na-LTA, also denoted as 4A). In the case of Ca,Na-LTA (5A) only part of cationic locations is occupied, and the pore size is near 5 Å. These zeolites gained very large industrial application for drying of technical gases and liquids and for the n/i-alkane separation in discontinuous sorption processes. The potassium exchanged form, K-LTA or Linde 3A, finds relevant application in ethanol drying processes, for production of fuel grade bioethanol from starch or cellulosic biomasses fermentation, with pressure swing adsorption processes. The sodium exchanged form, Na-LTA or Linde 4A, besides being largely employed as an ion exchanger in the field of detergenc, is used for air, methane, natural gas and nitrogen purification and has also been considered for alkane/alkene separation. The calcium exchanged form, Ca-LTA (Linde 5A), finds wide application for N_2/O_2 air separation, and for separation of CO_2 from several gas mixtures such as air in spacecraft cabins, methane, natural gas and biogases. This zeolite can be applied to sequestration of CO_2 from waste gasous emissions.

Another relevant application of LTA zeolites is in the field of purification of hydrogen through pressure swing adsorption (PSA) processes. 5A molecular sieve has been found to allow the production of highly pure H_2 by adsorption and rempoval of CH_4 and CO impurities.

The separation of CO_2 from less polar gases (such as hydrogen and methane) over 4A and 5A zeolites has been the object of a recent investigation. They appear to work in a different way. In 4A zeolite the stronger adsorption occurs in the form of reversibly adsorbed carbonate ions (thus with a role of the basicity of the framework’s oxides), while in the case of 5A zeolite, reversible adsorption occurs by linear coordination of CO_2 on Ca ions acting as Lewis acid sites. In the case of 5A, the framework basic sites appear to be, in normal conditions, “poisoned” by strongly adsorbed carbonate ions.

Silica Gel

The silica gel, formally SiO_2, is the term commonly used for the colloidal silica, a polymer of silicon dioxide, when exploited for its properties dehydrating and adsorbents. The compound is produced by acidifying a solution of sodium silicate. The colloidal suspension obtained, whose degree of polymerization depends on the chemical and physical conditions maintained during the process, washed and dried, provides a white solid, granular, porous and amorphous, with variable grain size from a few millimeters up to a few microns, also called with the English name silica gel

Activated Carbon and Carbon Molecular Sieves

Activated carbons are produced by treating at a high temperature (900 ° C) in an inert atmosphere (nitrogen) in two successive stages with an intermediate cooling, and optionally in the presence of chemical compounds (eg. ZnCl2/H3PO4) of organic materials. The activated carbon can be produced from almost any organic substance with a high content of carbon, including wood, coal, peat, the shells of the coconut, etc.. Almost all organic matter with a high percentage of carbon can theoretically be activated to increase its features sorbents. In practice, however, the best candidates for active carbon contain a minimum quantity of organic material, have a long life storage conditions, must retain their properties in the circumstances of use harder, can be obtained at a low cost and are obviously capable of producing a product of high quality active once processed. Tthe wood (130,000 tons / year) is by far the most common source of activated charcoal, followed by coal (100,000 tons), the shells of coconut (35,000 tons) and peat (35,000 tonnes) are also used in large quantity, but are more expensive and less readily available

Properties of materials used in the manufacture of activated carbon (Streat et al., 1995)

Raw material	Carbon (mass %)	Volatiles (mass %)	Density ($\mathrm{cm}^3\,\mathrm{g}^{-1}$)	Ash (mass %)	Texture of activated carbon
Soft wood	40–45	55–60	0.4–0.5	0.3–1.1	Soft, large pore volume
Hard wood	40–42	55–60	0.55–0.8	0.3–1.2	Soft, large pore volume
Lignin	35–40	58–60	0.3–0.4	–	Soft, large pore volume
Nutshells	40–45	55–60	1.40	–	Hard, large micropore volume
Lignite	55–70	25–40	1.0–1.35	5–6	Hard, small pore volume
Soft coal	65–80	20–30	1.25–1.5	2–12	Medium hard, medium pore volume
Petroleum coke	70–85	15–20	1.35	0.5–0.7	Medium hard, medium pore volume
Semi-hard coal	70–75	10–15	1.45	5–15	Hard, large pore volume
Hard coal	85–95	5–15	1.5–1.8	2–15	Hard, large pore volume

"Carbon Molecular Sieves" (carbon molecular sieves) are special activated carbons by high porosity and ordered pore size centered on a dominant. Their production can be very complex and costly, often starting from polymeric materials. The material of which we see below microscopies is the product of the carbonizing sucrose inside the pores of a mesoporous silica and then dissolving the silica.

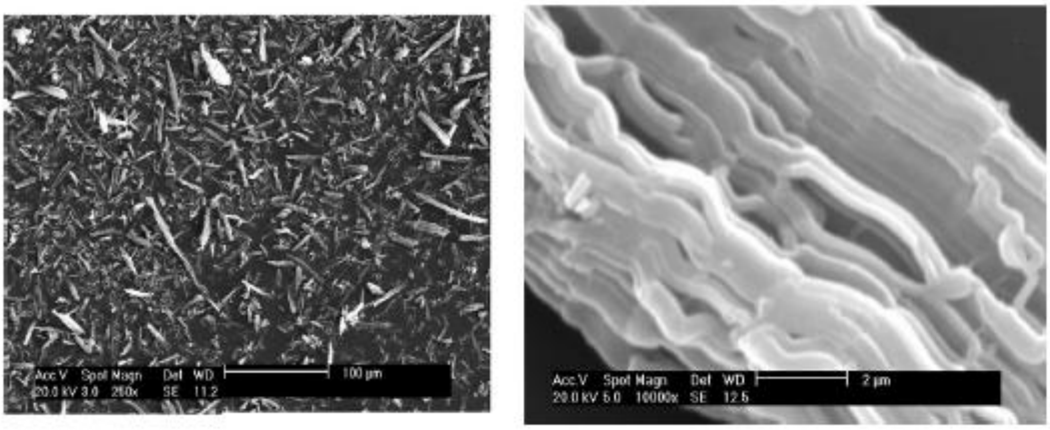


Fig. 1. SEM photo of the synthesized carbon material in two scales.

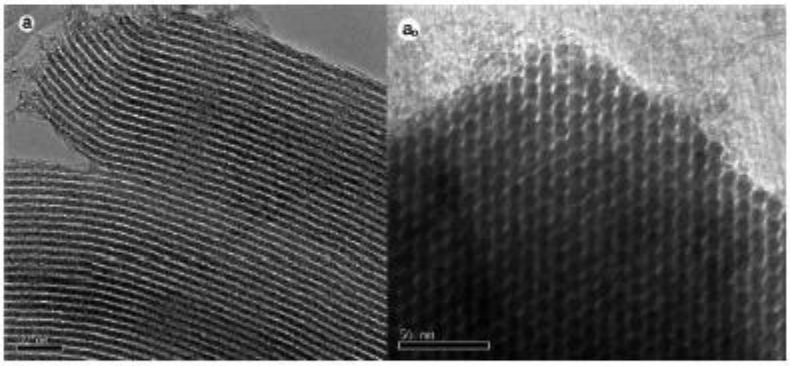


Fig. 2. TEM photos of the synthesized carbon material taken along the nanorod direction and the direction perpendicular to it (the circular black dots are nanorods).

Activated carbons for the purification of wastewater from phenolics.

Adsorptive processes are widely used in the purification of polluted streams and diluted wastewaters. Conventional fixed bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. However, regeneration may be not possible or not convenient: in this case the saturated adsorbent bed is removed and disposed or, in case, destroyed by burning in appropriate furnaces.

The most usual adsorbents for water treatment are activated carbons (AC). The adsorption capacity of AC for organic compounds depends on a number of factors, such as the physical nature of the adsorbent (pore structure, ash content, functional groups, depending on its precursor material and preparation method), the nature of the adsorbate (its solubility, pKa, functional groups present, polarity, molecular weight, size) and the solution conditions (pH, ionic strength, adsorbate concentration, oxygen availability). Therefore, two different procedures, denoted as ‘‘oxic’’ and ‘‘anoxic’’ are employed in conducting adsorption isotherm tests.

Adsorption on ACs is one of the best techniques to remove phenol and phenolics from water. The following possible interactions between the carbon surface and the phenols have been proposed: (a) electron donor–acceptor interactions between the aromatic phenolic ring and the basic surface oxygens, such as carbonyl groups; (b) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic structure; (c) electrostatic attraction and repulsion when ions are present.

Owing to the amphoteric character of a carbon surface its adsorption properties are influenced by the pH value of the solution. If adsorption takes place from unbuffered solutions, nearly neutral or weakly acidic, all three types of surface-phenol interactions may occur simultaneously. Instead, dispersion effects are predominant at low pH (< 3), when the phenolic compounds are in the non-ionized forms, and the surface groups are either neutral or positively charged. In these conditions the more polar the surface of carbon, the lower the adsorbability of phenol, the adsorption of water and phenol being competitive. For pH > pKa (e.g. at pH = 11), the phenols dissociate, forming phenolate anions, while the surface functional groups are either neutral or negatively charged. The electrostatic repulsion between the identical charges lowers the adsorption capacities. Besides, the phenolate anions are more soluble in the aqueous solution, and stronger adsorbate-water bonds must be broken before adsorption can take place.

On the other hand, the following three stages of the mechanism of phenol adsorption on ACs can be distinguished: adsorption at the infinite dilution, micropore filling, and adsorption in larger micropores and mesopores .In the range of adsorption in micropores, competition exists between micropore filling of the smallest micropores and the adsorption on active sites located in larger micropores. A temperature increase leads to vanishing of the effect of surface-chemical composition of ACs on phenol adsorption. In consequence, at higher temperatures, the porous structure of carbon determines the mechanism of phenol adsorption.

Alkali impregnated activated carbons for the purification of waste gases from H_2S.

Activated carbon, usually wide-pore carbon with a large total pore volume, and carbon molecular sieves are largely used to abate H_2S, although they are quite delicate and only allow small loadings to have acceptable lifetime. Activated carbons are in principle regenerable by mild heating during purging with inert gases such as steam or nitrogen (see Fig.4,a for a typical swing beds arrangements) . However, some authors consider them not regenerable when applied to H_2S.

Although unimpregnated carbon is also active for application as H_2S adsorbent, activated carbons impregnated with caustics (KOH or NaOH) are widely used at sewage treatment plants. Oxidation of hydrogen sulfide in the presence of caustic results in the deposition of elemental sulfur, particularly for alkaline impregnated carbons where the carbon surface pH is higher than the first dissociation constant of H_2S ($pK_a = 7.3$). If the pH is lower, sulphuric and sulphurous acids are also formed. The water film present on the carbon surface facilitates the dissolution of H_2S and its dissociation, followed by oxidation. The oxidant is likely the oxidized surface of carbon.

Although the application of impregnated carbons for hydrogen sulfide removal is very effective(typically up to 20-25 % load by weight), it is associated with a few significant disadvantages. They are as follows: (1) low temperature of self-ignition due to the exothermic reaction of caustics with CO_2 present in the air, (2) limited capacity for physical sorption due to the filling of the pore system with the impregnate, (3) special precaution has to be used due to the presence of corrosive materials, and (4) costs of caustic impregnated materials are usually higher than as received unimpregnated carbons.

Caustic impregnated carbons, when their adsorption capacity is exhausted, are generally removed from vessels and new material is loaded. Regeneration of spent AC can be employed using cold/hot waterwashing or thermal treatment to achieve recycle object, but theH_2S adsorption capacity after regeneration usually decreased remarkably. The cause is attributed that some sulfur species as elemental sulfur or sulfuric acid is strongly bound with activated sites leading to exhaust irreversibly Instead, coconut shell-based activated carbon, considered to be an alternative to activated carbons impregnated with caustics, can be regenerated in part by water washing.

Activated carbons for the removal of siloxanes from biogases..

Increasing interest is devoted recently to the use of biogases, arising from water treatment plants as well as from waste disposal plants, to produce energy. However, biogases contain several impurities, the most noxius being perhaps the presence of cyclic oligomeric methylsiloxanes. In common units, activated carbon is used to reduce the siloxane content, but since siloxanes are difficult to desorb from the material, these adsorbent beds have to be replaced regularly. This results in relevant costs. Other adsorbents used for the removal of gaseous siloxanes include molecular sieves, silica and polymer beads.

Adsorbents for mercury removal from natural gas.

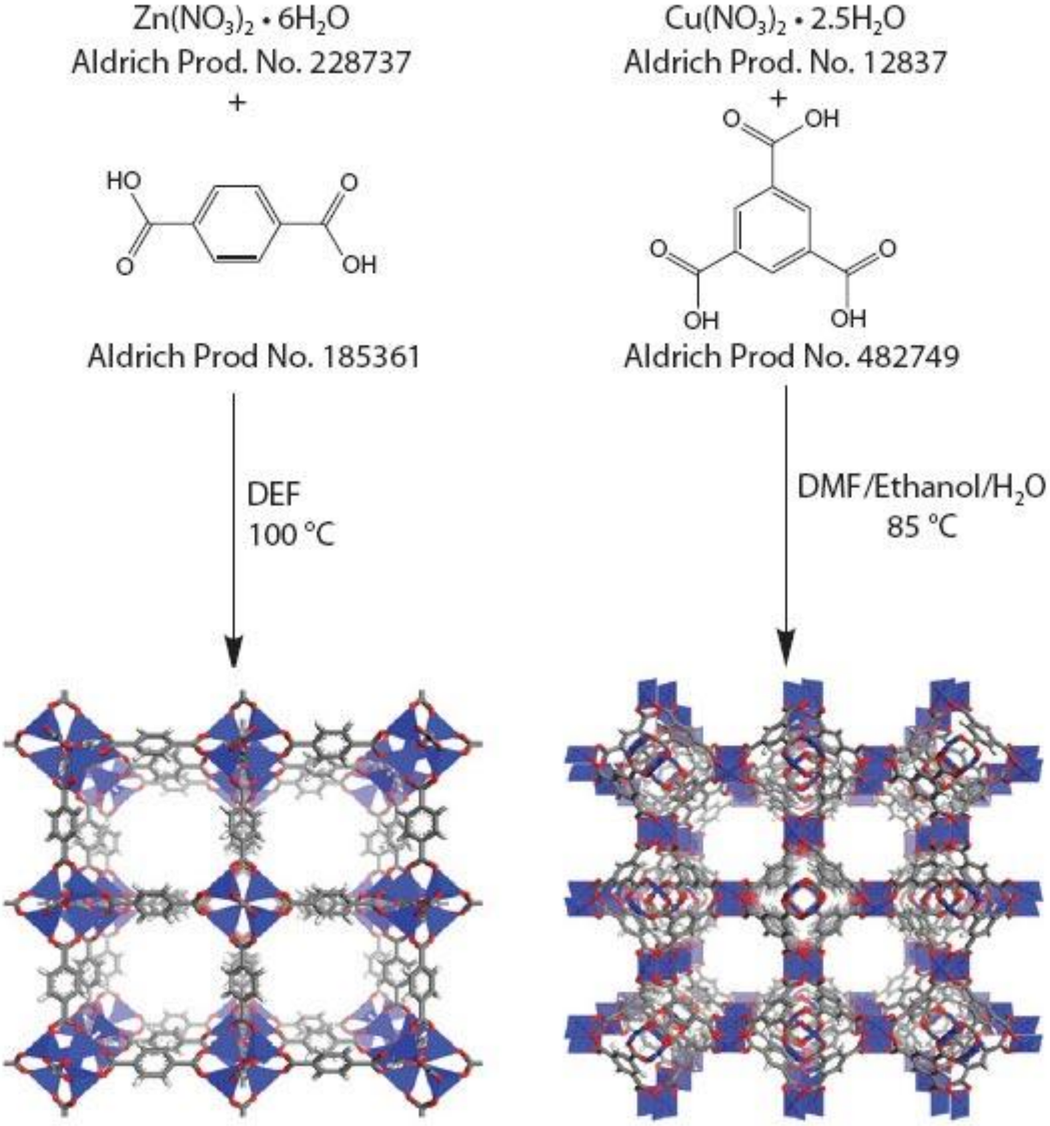
The recent development of regenerable zeolitic adsorbents for the removal of mercury from natural gas represents an interesting new application. UOP developed silver-containing zeolites, denoted as HgSIV adsorbents, with mercury removalproperties. These materials perform simultaneously both water and mercury removal. Since nearly all cryogenic plants use molecular sieve dehydrators, such as based on 4A molecular sieves (see above), the mercury removal function can be added to the dehydrator performance by replacing some of the dehydrationgrade molecular sieve. Mercury is adsorbed during the dehydration step and, when heated to the normal dehydrator regeneration temperature, releases from the silver and leaves with the spent regeneration gas. In fact, silver, like other noble metals, reacts with mercury at moderate temperatures producing amalgams, while it releases the mercury at temperatures above 227 °C. From the published data, it seems likely that the zeolite used is like 4A or 13X molecular sieve containing significant amounts of silver.

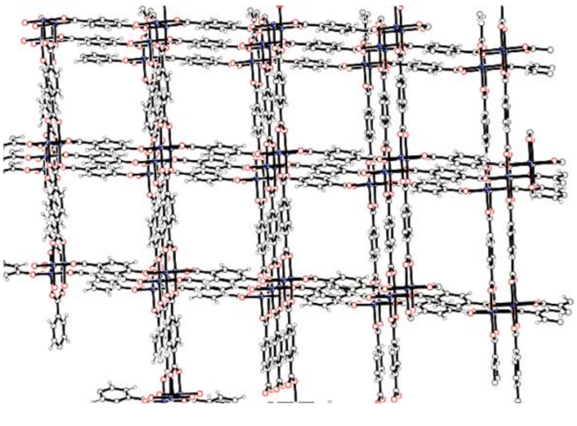
In one of the possible process configurations the regeneration gas containing moisture and mercury is first cooled to condense water and than treated with non regenerable adsorbents (such as special activated carbons) to abate and possibly recover mercury.

Silver-exchanged molecular sieves have shown great promise also in other applications ranging from antimicrobial materials to the adsorption of xenon and iodide, two key contaminants emitted from nuclear reactors.

MOFs (metal organic frameworks) and COFs (covalent organic frameworks).

MOFs are metallorganic compounds with a porous lattice. Below you look at the structure of zinc terephthalate and copper trimesato.





COFs are similar structures but built with non-metallic elements (C, Si, B).

Clays as basic adsorbants.

Clays represent natural materials that can be applied as cheap adsorbents in several technologies. Among the most used clays, we can cite kaolinite, cationic layered clays such as smectites, anionic layered clays such as hydrotalcite, sepiolite and some zeolites.

Kaolinite, whose formula is $Al_2Si_2O_5(OH)_4$, has triclinic layered structure, with quite a definit mild acidic surface character. Smectite clays, such as montmorillonites (bentonites) and saponites, are sheet silicates in which a layer of octahedrally coordinated cations is sandwiched between two tetrahedral phyllosilicate layers. To complete the coordination of the cations, hydroxy groups are also present in the layers, the theoretical formula for each layer being $Al_2Si_4O_{10}(OH)_2$. In the case of montmorillonites (bentonites) Mg substitutes for Al in the octahedral layers, and hydrated alkali or alkali-earth cations in the interlayer space compensate for the charge defect. In saponites, additional Al for Si substitution occurs in the tetrahedral sheets. Although the presence of alkali and alkali earth ions in their structure can give rise to some basicity, surface characterization studies of untreated montmorillonite and saponite provide evidence for predominant weak acidity for the surface of these materials. The basicity can be increased significantly by chemiceatment such as by exchanging with Cs^+ ions.

Sepiolite is a hydrated magnesium silicate with the ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$, characterized by a chain-like structure producing needle-like particles, instead of plate-like particles typical of phyllosilicate clays. Most of the world production of this clay comes from deposits of sedimentary origin located near Madrid, Spain. Sepiolite is an excellent material for cat and pet litters: The popularity of sepiolite pet litters is due to its light weight, high liquid absorption and odour control characteristics.

Although hydrotalcite and zeolites are natural materials, they are usually synthesized to have best purity before use. Alkali and alkali earth zeolites find application mainly as adsorbants while hydrotalcites become very popular as basic catalysts (see below).

H_2S sorbents.

The abatement of H_2S from gases may be performed with different techniques, including adsorption on solids. Commercially available solids exist for H_2S separation from natural gases and biogases, that do not allow regeneration. Mostly, they are based on iron oxides/hydroxides.

Sulfatreat 410-HP ® 361 is a “non-toxic granular material”, a combination of iron oxides (Fe_2O_3, Fe_3O_4) and an “activator oxide”, attached to a calcined montmorillonite carrier. According to the producer it can adsorb up to 25 % wt/wt and is best suited for biogases treatment. The main phenomenon is an irreversible chemical reaction between the solid and gas phase. The rates of the external diffusion, internal diffusion and surface reaction steps are relatively close, the limiting step of the process changing with experimental conditions. The apparent density of the dry adsorbent is 1000 kg/m^3. The specific surface is 5.4 m^2/g. The experimental data, performed at r.t., have proven that 1 g of adsorbent can adsorb up to 0.11 g of H_2S. It seems that the adsorbent cannot be regenerated.

Another interesting commercial product is IRON SPONGE, produced by Connelly – GPM, Inc., an hydrated iron oxide on a carrier of wood shavings and chips. IRON SPONGE is most frequently supplied with 15 pounds of iron oxide per bushel of product. Iron oxide

based materials for H_2S abatement are also Sulfur-Rite (from GTP-Merichem) and Sulfa-Bind (from ADI International Inc).
Abatement of sulphur compounds can also be achieved with Zinc-oxide based materials at temperatures intermediate from room and 400 °C. To this family belong the adsorbents of the PURASPEC family, produced by Johnson Matthey. They work in the 80-450°C temperature range allowing the abatement of H_2S, COS, aromatic and aliphatic mercaptans and sulphides. Mercury and chloride removal can also be accomplished in conjunction with sulfur removal No sulfur release by the ingress of hydrocarbons or water. A material of the same family, PURASPEC 4037, has been described by Lang et al. According to these authors, the catalyst is in the form of 0.1–0.2 in diameter spheres composed of 40–45% copper oxide and 20–30% zinc oxide by weight, with the balance being aluminum oxide. These metal oxides react with H_2S to produce metal sulfides and water vapor. A PURASPEC adsorbent has also been used successfully at $T < 200$ °C for the purification of the feed of MCFC. ZnO, and zinc ferrite as well, react with hydrogen sulphide with a true gas-solid chemical reaction. They can be regenerated by oxidation so producing streams containing sulphur oxides. Hybrid materials such as carbon-supported zinc ferrite have also been proposed.

High-temperature CO_2 sorbents.
One of the possible ways for utilization of fossil fuels such as coal without producing emissions of carbon dioxide in the atmosphere is the CO_2 capture and sequestration technology. In this process, CO_2 is captured either from the combustion gases or from hydrogen/ CO_2 mixtures produced by gasification and water gas shift. CO_2 capture can be performed with liquids (such as potassium carbonate and ethanol amines water solutions, see above) at low temperature (< 110 °C) or with solids either at low or high temperature (< 800 °C). Strongly basic oxides materials adsorb or absorb strongly CO_2 even at very high temperatures and can be regenerated by carbonate decomposition. Alkali metal oxides, in particular solids based on CaO are the most promising for this purpose. Other interesting solids for high temperature CO_2 adsorption are Li_2ZrO_3 and Li_4SiO_4.

Hot gas purification.
The high temperature removal of contaminants from hot gases such as the abatement of HCl from waste combustion, that of As_2O_3 from coal combustion gases, as well as the destructive adsorption of heavily chlorided organics such as CCl_4 may be performed over CaO based materials at 200-600 °C. In this field could also be mentioned the NOx trap technology, also called “NOx storage-reduction” (NSR), which will be treated in the next chapter.
High-temperature purification of biogases from siloxanes can be obtained using oxides such as alumina, although the resulting spent silicated adsorbant cannot be regenerated.

Adsorbants of organic sulphides in hydrocarbons purification.
Solids can be applied to abate sulphur in hydrocarbon sterams by adsorptive desulphurization. In thee so-called Phillips S Zorb technology to remove sulfur from gasoline and diesel fuels a Ni/ZnO sorbent is applied. Operating conditions are 340–410 °C, 2–20 bar, and regeneration is performed by burning the adsorbed species on the spent

adsorbant. In a similar process, called TReND, Transport Reactor Naphta Desulphurization, from RTI, Ni-Al_2O_3 adsorbent seems to be used. The IRVAD process by Black and Veatch Pritchard and Alcoa Industrial Chemicals uses an alumina-based adsorbent to counter-currently contact liquid hydrocarbon in a multistage adsorber. The adsorbent is fluidized and continuously removed and regenerated, using hydrogen, in a second column. Medium acid-base properties are likely key features of the solide to strongly adsorb both mercaptans, and sulphides, including thiophenes, while a redox function helps in the regeneration by combustion.