CATALYSIS

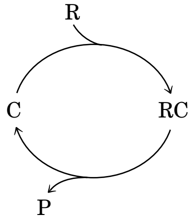
1. Introduction

Homogeneous catalysis, 324 Heterogeneous catalysis, 340 Catalysis, is the key to efficient chemical processing. Most industrial reactions and almost all biological reactions are catalytic. The value of the products made in the United States in processes that at some stage involve catalysis is approaching several trillion dollars annually, which is more than the gross national products of all but a few nations of the world. Products made with catalysis include food, clothing, drugs, plastics, detergents, and fuels. Catalysis is central to technologies for environmental protection by conversion of emissions.

This article is an introduction and survey that states the fundamental principles and definitions of catalysis, demonstrates the unity of the subject, and places it in an applied perspective. The selection of industrial catalytic processes discussed has been made for the sake of illustrating principles and representative characteristics of catalysis and catalytic processes. Details of the processes are given in numerous other articles in the *Encyclopedia*.

A catalyst is a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed itself. A catalyst changes the rate but not the equilibrium of the reaction. This definition is almost the same as that given by Ostwald in 1895. The term catalysis was coined in ~1835 by Berzelius, who recognized that many seemingly disparate phenomena could be described by a single concept. For example, ferments added in small amounts were known to make possible the conversion of plant materials into alcohol; and there were numerous examples of both decomposition and synthesis reactions that were apparently caused by addition of various liquids or by contact with various solids.

Berzelius attributed catalytic action to ill-defined forces, and the value of Ostwald's more lasting definition is that it identified catalysis as a phenomenon that was consistent with the emerging principles of physical chemistry. Now it is well recognized that catalysts function by forming chemical bonds with one or more reactants, thereby opening up pathways to their conversion into products with regeneration of the catalyst. Catalysis is thus cyclic; reactants bond to one form of the catalyst, products are decoupled from another form, and the initial form is regenerated. The simplest imaginable catalytic cycle is therefore depicted as follows:



where R is the reactant, P the product, C the catalyst, and RC an intermediate complex. The intermediate complexes in catalysis are often highly reactive and not observable.

Ideally, the catalyst would cycle forever between C and RC without being consumed. But in reality there are competing reactions, and catalysts are converted into species that are no longer catalysts. In practice, catalysts must be regenerated and replaced. Catalyst manufacture is a large industry; catalysts worth some several billion dollars are sold annually in the United States.

Catalysts may be gases, liquids, or solids. Most catalysts used in technology are either liquids or surfaces of solids. Catalysis occurring in a single gas or liquid phase is referred to as homogeneous catalysis (or molecular catalysis) because of the uniformity of the phase in which it occurs. Catalysis occurring in a multiphase mixture such as a gas–solid mixture is referred to as heterogeneous catalysis; usually this is surface catalysis. Biological catalysts are proteins, ie, poly(amino acids), called enzymes, and metalloenzymes, which are proteins incorporating inorganic components, eg, iron sulfide clusters. Some enzymes are present in cytoplasmic solution in cells and others are anchored in cell membranes or on surfaces. Traditionally, homogeneous catalysis, heterogeneous catalysis, and enzymic catalysis have been regarded as almost separate disciplines, and the language and literature have developed without much coherence and overlap.

The performance of a catalyst is measured largely by criteria of chemical kinetics, as a catalyst influences the rate and not the equilibrium of a reaction. The catalytic activity is a property of a catalyst that measures how fast a catalytic reaction takes place and may be defined as the rate of the catalytic reaction, a rate constant, or a conversion (or temperature required for a particular conversion) under specified conditions. The selectivity is a measure of the property of a catalyst to direct a reaction to particular products. There is no single definition of selectivity, but it is sometimes defined as a ratio of activities, such as the ratio of the rate of a desired reaction to the sum of the rates of all the reactions that deplete the reactants. Selectivity may also be represented simply as a product distribution. Because catalysts typically lose activity and/or selectivity during operation, they are also evaluated in terms of stability and lifetime. The stability of a catalyst is a measure of the rate of loss of activity or selectivity. In practical terms the stability might be measured as a rate of deactivation, such as the rate of change of the rate of the desired catalytic reaction or as the rate at which the temperature of the catalyst would have to be raised to compensate for the activity loss. Catalysts that have lost activity are often treated to bring back the activity, ie, reactivated; the regenerability is a measure, often not precisely defined, of how well the activity can be brought back. Technological catalysts are also evaluated in terms of cost; in a typical process, the cost of the catalyst is a small fraction of the total processing cost, often only a few cents or less per kilogram of product.

Liquid-phase catalysts are used in batch and flow reactors. Batch reactors are predominant in small-scale operations and those designed for flexibility such as pharmaceutical and fine chemicals manufacture. Flow reactors predominate in large-scale processes such as commodity chemicals manufacture and petroleum refining. Corrosion, separation, and catalyst recovery and recycle are usually important issues in these processes. Solid catalysts are used in batch and flow reactors; in most large-scale operations, solid particles of catalyst are present in fixed- or fluidized-bed reactors with gaseous or liquid reactants flowing through them (see REACTOR TECHNOLOGY).

The solids used as catalysts are typically robust porous materials with high internal surface areas, typically, hundreds of square meters per gram. Reaction occurs on the internal catalyst surface. The typical solid catalyst used in industry is a composite material with numerous components and a complex structure.

Catalytic processes are classified roughly according to the nature of the product and the industry of application, and to some degree separate literatures have developed. In chemicals manufacture, catalysis is used to make heavy chemicals, eg, ammonia and sulfuric acid; commodity chemicals, eg, acetic acid and *n*-butyraldehyde; and fine chemicals, eg, fragrances and flavorings. Catalysis is used extensively in the manufacture of pharmaceuticals. In fuels processing, catalysis is used in almost all the processes of petroleum refining and in coal conversion and related synthesis gas (CO and H_2) conversion. Most of the recent large-scale developments in industrial catalysis have been motivated by the need for environmental protection. Many processes for abatement of emissions are catalytic; automobile exhaust conversion catalysts are now the most important of all in terms of sales volume, and catalysts for conversion of nitrogen oxides in stationary power plant effluents are used on a massive scale in Japan and parts of Europe. Recent innovations in pharmaceutical manufacture involve catalysis (usually homogeneous) for asymmetric synthesis. Most of the applications of catalysis in biotechnology (qv) are fermentations, often carried out in stirred reactors with gases, liquids, and solids present; the catalysts are enzymes present in living organisms such as yeasts. There are applications of whole biological cells and of individual enzymes mounted on supports, ie, carriers, and used in fixed-bed reactors (see ENZYMES, INDUSTRIAL APPLICATIONS).

2. History

The science of catalysis is driven by technology, as it has been from the beginning. Some of the earliest known examples of controlled chemical transformations are catalytic. Fermentation (qv) was used in ancient times to make alcoholic beverages, and a number of the earliest examples of chemical technology were also exploitations of catalysis (1). For example, before the sixteenth century ether was made by distilling spirits in the presence of sulfuric acid. In 1746, nitric oxide was used as a catalyst in the lead chamber process for oxidation of sulfur dioxide to give sulfur trioxide in the manufacture of sulfuric acid. In 1781, acids were used to catalyze the conversion of starch into sugar. In 1817, H. Davy discovered that in the presence of platinum, mine gases were oxidized at low temperatures; he designed a safety lamp for miners in which the platinum glowed if the flame was extinguished (2). Many more practical discoveries were made in the 1800s (1,2).

These examples existed prior to Ostwald's 1895 definition (1), ie, before the nature of catalysis was well understood. But in 1850 Wilhelmy (3) had already made the first measurements of kinetics of catalytic reactions in an investigation of sugar inversion catalyzed by mineral acids. In the years following Ostwald's definition, just as the principles of chemical equilibrium and kinetics were becoming known, the field of catalysis became more quantitative and developed rapidly. Kinetics of surface-catalyzed reactions were measured by Bodenstein (4) just after the turn of the century. The defining work that set the stage for modern catalytic technology was the development of the ammonia (qv) synthesis process by Haber, Bosch, Mittasch, and co-workers, beginning ~1908 (1,5).

These pioneers worked out methods of catalyst testing and process development that are essentially the methods of choice today (6,7). They understood the interplay between chemical equilibrium and reaction kinetics; indeed, Haber's research, motivated by the development of a commercial process, helped to spur the development of the principles of physical chemistry that account for the effects of temperature and pressure on chemical equilibrium and kinetics. The ammonia synthesis reaction is strongly equilibrium limited. The equilibrium conversion to ammonia is favored by high pressure and low temperature. Haber therefore recognized that the key to a successful process for making ammonia from hydrogen and nitrogen was a catalyst with a high activity to allow operation at temperatures low enough for a relatively favorable equilibrium.

Bosch and co-workers (6) devised laboratory reactors to operate at high pressure and temperature in a recycle mode. These test reactors had the essential characteristics of potential industrial reactors and were used by Mittasch and co-workers (6) at BASF in Germany to screen some 20,000 samples as candidate catalysts. The results led to the identification of an iron-containing mineral that is similar to catalysts used in industry today. The researchers recognized the need for porous catalytic materials and materials with more than one component, today identified as the support, the catalytically active component, and the promoter. Today's technology for catalyst testing has become more efficient because much of the test equipment is automated and some is miniaturized. The analysis of products and catalysts is also much faster and more accurate today.

3. Homogeneous Catalysis

3.1. Characterization of Solution Processes.

There are many important examples of catalysis in the liquid phase, but catalysis in the gas phase is unusual. From an engineering viewpoint, most of the liquid-phase processes have the following characteristics in common.

Pressure and Temperature. The pressure and temperature are relatively low, typically less than ~2 MPa (20 atm) and 150°C. High pressures are used in some applications, but they require expensive thick-walled reactors. High temperatures are largely avoided because they result in high autogenous pressures and because many of the catalysts are unstable at high temperatures.

Corrosiveness. The catalyst solutions are corrosive, and the reactors, separation devices, etc, that come in contact with them must be made of expensive corrosion-resistant materials.

Separation Processes. Separation of the catalyst from the products is expensive; the process flow diagram and the processing cost are often dominated by the separations. Many soluble catalysts are expensive, eg, rhodium complexes, and must be recovered and recycled with high efficiency. The most common separation devices are distillation columns; extraction is also applied.

Gas Handling. The reactants are often gaseous under ambient conditions. To maximize the rate of the catalytic reaction, it is often necessary to minimize the resistance to gas–liquid mass transfer, and the gases are therefore introduced into the liquid containing the catalyst as swarms of bubbles into a well-stirred mixture or into devices such as packed columns that facilitate gas–liquid mixing and gas absorption.

Exothermicity. The catalytic reactions are often exothermic bond-forming reactions of small molecules that give larger molecules. Consequently, the reactors are designed for efficient heat removal. They may be jacketed or contain coils for heat-transfer media, or the heat of reaction may be used to vaporize the products and aid in the downstream separation by distillation.

There are also a number of generalizations about the chemistry of these processes. Often the reactants are small building blocks, many formed from organic raw materials, namely, petroleum, natural gas, and coal. The reactants include O_2, low molecular weight olefins, and synthesis gas (CO and H_2). In older technology, acetylene was a common building block. Many reactions are catalyzed by acids and bases, usually in aqueous solution. Many reactions are catalyzed by transition-metal complexes, usually in nonaqueous organic solvents, but sometimes in water and in ionic liquids with low melting points such as alkylammonium salts. The transition metal complex catalysts used in technology are often highly selective.

3.2. Influence of Mass Transport on Reaction Rates. When a relatively slow catalytic reaction takes place in a stirred solution, the reactants are supplied to the catalyst from the immediately neighboring solution so readily that virtually no concentration gradients exist. The intrinsic chemical kinetics determines the rate of the reaction. However, when the intrinsic rate of the reaction is relatively high and/or the transport of the reactant is relatively slow, as in a viscous polymer solution, the concentration gradients become significant, and the transport of reactants to the catalyst cannot keep the catalyst supplied sufficiently for the rate of the reaction to be that corresponding to the intrinsic chemical kinetics. Assume that the transport of the reactant in solution is described by Fick's law of diffusion with a diffusion coefficient D, and the intrinsic chemical kinetics is of the following form

$$r = k[\mathrm{C}][\mathrm{A}] \tag{1}$$

where C is catalyst and A the reactant. Then in the general case in which the diffusion influences the rate (8),

$$\eta = r/r_{\max} = \frac{1}{1 + \frac{k}{4\pi\left(\frac{R_{\mathrm{A}}+R_{\mathrm{C}}}{2}\right)D}} \tag{2}$$

where η, the ratio of the reaction rate to the maximum value that could occur, ie, the rate in the absence of a transport influence, is called the effectiveness factor, and R_{C} and R_{A} are the radii of the catalyst and reactant molecules, respectively. There are two limiting cases; if $k \ll 4\pi(\frac{R_{\mathrm{A}}+R_{\mathrm{B}}}{2})D$, then there is no diffusion influence and the rate is described by equation 1, where the concentrations are the bulk average concentrations in the solution. On the other hand, when the inequality is inverted, the rate becomes

$$r = 4\pi\left(\frac{R_{\mathrm{A}}+R_{\mathrm{B}}}{2}\right)D[\mathrm{C}][\mathrm{A}] \tag{3}$$

In the former case, the rate is independent of the diffusion coefficient and is determined by the intrinsic chemical kinetics; in the latter case, the rate is independent of the rate constant k and depends on the diffusion coefficient; the reaction is then diffusion controlled. This kind of mass transport influence is different from that characteristic of dissolution of a gas into a liquid phase.

3.3. Examples of Solution Catalysis. *Acid-Base Catalysis.* Inexpensive mineral acids, eg, H_2SO_4, and bases, eg, KOH, in aqueous solution are widely applied as catalysts in industrial organic synthesis. Catalytic reactions include esterifications, hydrations, dehydrations, and condensations. Much of the technology is old and well established, and the chemistry is well understood. Reactions that are catalyzed by acids are also typically catalyzed by bases. In some instances, the kinetics of the reaction has a form such as the following (9):

$$r = (k_0[\mathrm{H_2O}] + k_{\mathrm{H^+}}[\mathrm{H^+}] + k_{\mathrm{HA}}[\mathrm{HA}] + k_{\mathrm{OH^-}}[\mathrm{OH^-}] + k_{\mathrm{B}}[\mathrm{B}])[\mathrm{R}] \tag{4}$$

where r is the reaction rate, [R] the concentration of the reactant, and the terms on the right-hand side represent catalysis by water, hydrogen ions, undissociated acid HA, hydroxide ions, and undissociated base. Often all the terms on the right-hand side but one are negligible.

If the second term on the right-hand side in equation 4 is the only significant one, then catalysis is by hydrogen ions (hydrated protons), and the catalysis is called specific acid catalysis; the rate of the reaction is proportional to the concentration of the hydrogen ions and to the concentration of the reactant. Many examples conform to this pattern. Similarly, if the third term on the right-hand side of equation 4 is the only significant one, then the catalysis is by HA, and general acid catalysis occurs. If the fourth term is the significant one, hydroxide ions are the catalyst and specific base catalysis occurs. If the fifth term is the significant one, general base catalysis occurs.

The chemistry of acid–base catalysis involves the transfer of hydrogen ions, H^+ and sometimes H^-. In general or specific acid catalysis, the undissociated acid molecules or the hydrated protons formed by dissociation of an acid, respectively, donate protons to the reactant. The proton acceptor in an aqueous solution is a good base, often an organic compound including O, N, or S. In catalysis by bases, the reactant donates a proton to the catalyst. The proton donor in general acid catalysis may be a weak or a strong acid, and often the activity of the catalyst increases with its strength as an acid, measured by the acid dissociation constant K_a.

Donation of a proton to the reactant often forms a carbenium ion or an oxonium ion, which then reacts in the catalytic cycle. For example, a catalytic cycle suggested for the conversion of phenol and acetone into bisphenol A, which is an important monomer used to manufacture epoxy resins and polycarbonates, in an aqueous mineral acid solution is shown in Figure 1 (10).

The kinetics of the bisphenol A synthesis has been reported to be of the following form (11)

$$r = k\left[\mathrm{H}^+\right][\mathrm{A}][\mathrm{P}] \tag{5}$$

where A is acetone and P is phenol. When the reaction is carried out in the presence of low concentrations of an added compound, thioglycolic acid, $HSCH_2COOH$, the rate is increased, with the kinetics reported to be of the following form (12)

$$r = k'\left[\mathrm{H}^+\right][\mathrm{A}][\mathrm{P}](k_1 + k_2[\mathrm{T}]) \tag{6}$$

where T is thioglycolic acid, a promoter. A catalyst promoter is a substance that, although it lacks significant catalytic activity itself, increases the activity, or possibly the selectivity, of a catalyst. Promoters are common in catalysis.

In some processes, the reactant bases are too weak to be protonated significantly except in the presence of very strong acids such as fuming sulfuric acid or a mixture of concentrated sulfuric and nitric acids, ie, mixed acid.

The kinetics of reactions catalyzed by very strong acids are often complicated. The exact nature of the proton donor species is often not known, and typically the rate of the catalytic reaction does not have a simple dependence on the

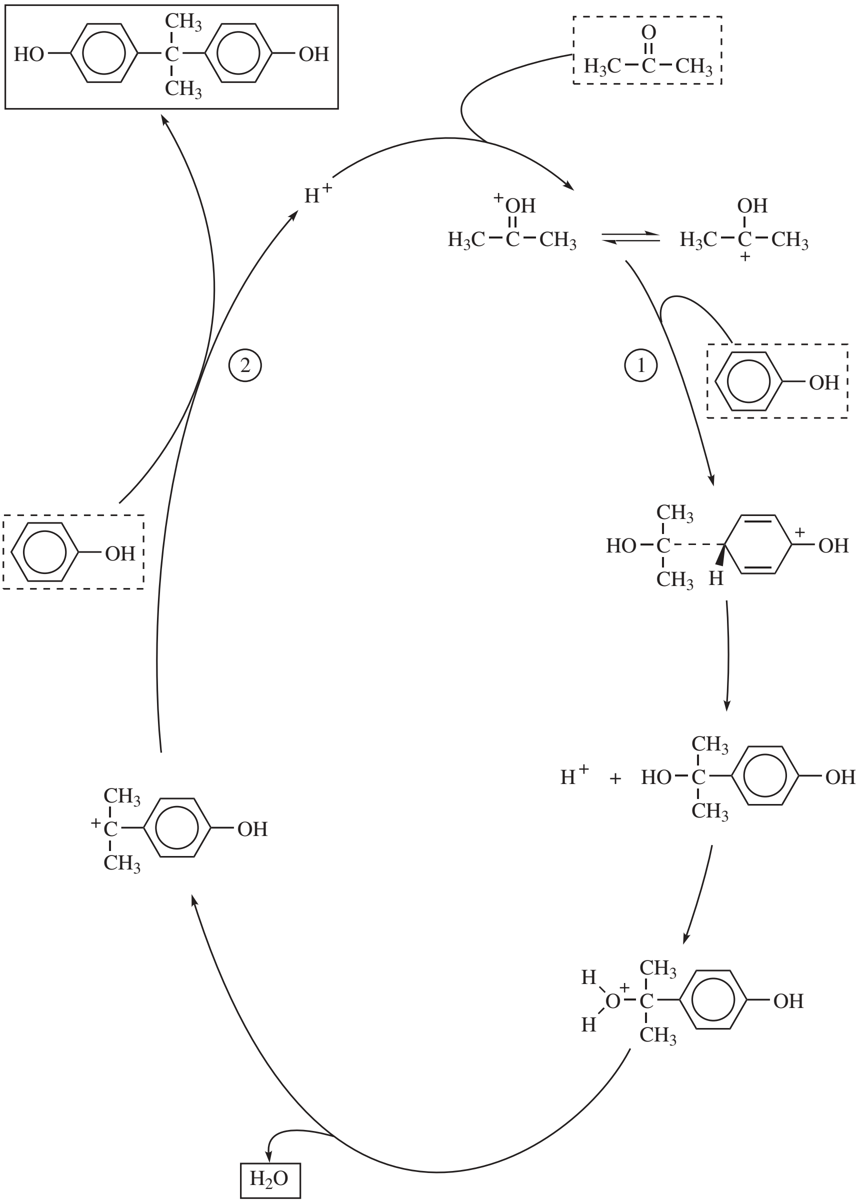


Fig. 1. Catalytic cycle for synthesis of bisphenol A from phenol and acetone in the presence of a dissociated mineral acid (10).

total concentration of the acid. However, sometimes there is a simple dependence of the catalytic reaction rate on some empirical measure of the acid strength of the solution, such as the Hammett acidity function H_0, which is a measure of the tendency of the solution to donate a proton to a neutral base. Sometimes the rate is proportional to h_0 ($H_0 = -\log h_0$). Such a dependence may be expected when the slow step in the catalytic cycle is the donation of a proton by the solution to a neutral reactant, ie, base; but it is not easy to predict when such a dependence may be found.

An important petroleum refining process, alkylation of propylene or butenes with isobutane to give high octane-number branched products, is catalyzed by concentrated sulfuric acid or hydrofluoric acid. The reactions are carried out at subambient temperatures, at which the equilibrium is favorable, in stirred, refrigerated reactors containing two-phase liquid mixtures. Most of the hydrocarbon reactants are in the organic phase, and, when the catalyst is H_2SO_4, most of the catalyst is in the aqueous phase; the reaction takes place near the liquid–liquid interface (see ALKYLATION).

In the alkylation process, the reactants are weak bases. The stronger bases in the mixture, the olefins, are protonated, forming carbenium ions. The carbenium ions are good Lewis acids, and they react with isobutane, a good hydride ion donor, to form paraffins and the relatively stable *tert*-butyl cation, ie, trimethyl carbenium ion. This is a hydride transfer reaction; such reactions are important in many acid-catalyzed hydrocarbon conversions. The *tert*-butyl cation becomes the predominant carbenium ion in the organic solution and reacts with propylene or butenes in Lewis acid–Lewis base reactions to form carbon–carbon bonds, giving C_7 or C_8 products among others. There are many C_7 and C_8 isomers formed because isomerizations are rapid. A partial cycle that illustrates the important characteristics of alkylation is shown in Figure 2 for the ethylene–isobutane alkylation. The cycle is shown for ethylene because it gives a simpler product distribution than propylene or butenes; ethylene is much less reactive than propylene or butenes because on protonation it forms a primary carbenium ion, which is much less stable than the secondary carbenium ion formed by protonation of propylene or straight-chain butenes. Ethylene is not used in the commercial alkylation processes.

Acid-catalyzed reactions of paraffins require much stronger acids than those of olefins or aromatics, because the paraffins are much weaker bases.

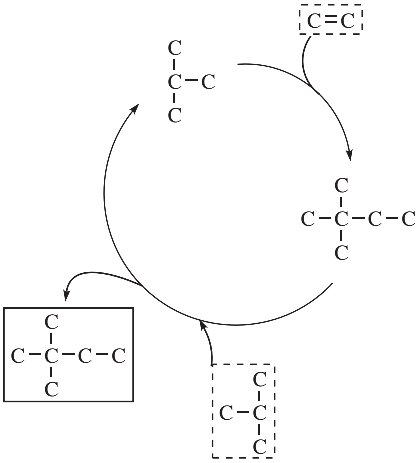


Fig. 2. Catalytic cycle for the ethylene–isobutane alkylation (10).

The only acids that catalyze reactions of paraffins alone at relatively low temperatures are combinations of Brønsted and Lewis acids; examples include $HCl + AlCl_3$, $HF + SbF_5$, and $FSO_3H + SbF_5$ (magic acid). Some of these are called superacids (13), eg, magic acid. Superacids are stronger acids than concentrated sulfuric acid and some have values of H_0 of -20 and less, whereas that of 100% sulfuric acid is only about -12. The Hammett acidity function is logarithmic; thus some superacids are more than eight orders of magnitude stronger proton donors than sulfuric acid. Hence, these superacids can protonate paraffins, even methane. They catalyze isomerization and carbon–carbon bond-forming and bond-breaking reactions at low temperatures but are not found in commercial applications, in part because of their extreme corrosiveness.

Metal Complex Catalysis. Most of the recent innovations in industrial homogeneous catalysis have resulted from discoveries of transition-metal complex catalysts. Thousands of transition-metal complexes (including organometallics, ie, those with metal–carbon bonds), are known, and the rapid development of organotransition metal chemistry in recent decades has been motivated largely by the successes and opportunities in catalysis. The chemistry of metal complex catalysis is explained by the bonding and reactivity of organic groups (ligands) bonded to the metals. The important reactions in catalytic cycles are those of ligands bonded in the coordination sphere of the same metal atom. Bonding of ligands such as CO or olefin to a transition metal activates them and facilitates the catalysis. The following reactions of transition-metal complexes account for almost all the steps in the catalytic cycles.

Ligand exchange:

$$ML_x + L' \rightleftharpoons ML_{x-1}' + L \qquad (7)$$

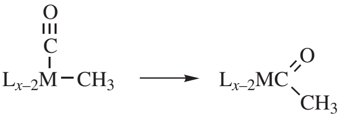
where M is metal and L and L′ are ligands. This reaction may be thermally or photochemically initiated; it may proceed by dissociation of a ligand to give a coordinatively unsaturated complex, to which another ligand is then bonded, but it may also proceed associatively, without prior dissociation of a ligand. Ligand exchange is one way in which reactants become bonded to catalysts.

Oxidative addition and reductive elimination:

$$ML_{x-2} + AB \underset{\text{reductive elimination}}{\overset{\text{oxidative addition}}{\rightleftharpoons}} ML_{x-2}AB \qquad (8)$$

The forward reaction requires an electron-rich metal in a low oxidation state that is coordinatively unsaturated. Oxidative addition provides another way for bonding of reactant ligands to a metal, and reductive elminination provides a way for products to leave a metal.

Migratory Insertion:



$$L_{x-2}M(C{\equiv}O)-CH_3 \longrightarrow L_{x-2}MC({=}O)CH_3 \qquad (9)$$

In this reaction, one ligand migrates to a neighboring ligand that then becomes formally inserted between the metal and the ligand that has migrated, creating a site of coordinative unsaturation so that another reactant ligand can be associated with the metal. The migratory insertion reaction accounts for chain-growth steps of olefin polymerization reactions.

Wilkinson Hydrogenation. One of the best understood catalytic cycles is that for olefin hydrogenation in the presence of phosphine complexes of rhodium, the hydrogenation named after the Nobel-laureate Geoffroy Wilkinson (14,15). The reactions of a number of olefins, eg, cyclohexene and styrene, are rapid, taking place even at room temperature and atmospheric pressure; but the reaction of ethylene is extremely slow. Complexes of a number of transition metals in addition to rhodium are active for the reaction.

The Wilkinson hydrogenation cycle shown in Figure 3 (16) was worked out in experiments that included isolation and identification of individual rhodium complexes, measurements of equilibria of individual steps, determination of rates of individual steps under conditions of stoichiometric reaction with certain reactants missing so that the catalytic cycle could not occur, and determination of rates of the overall catalytic reaction. The cycle demonstrates some generally important points about catalysis: the predominant species present in the reacting solution and the only ones that are easily observable by spectroscopic methods, eg, $RhCl[P(C_6H_5)_3]_3$, $RhCl[P(C_6H_5)_3]_2$ (olefin), and $RhCl_2[P(C_6H_5)_3]_4$, are outside the cycle, possibly in virtual equilibrium with species in the cycle, and not involved in the kinetically significant steps of the cycle. Often the only species that can be observed during catalysis are those that are not involved in the cycle. Consequently, elucidation of catalytic cycles is difficult, and inferences about cycles that are based on easily measured compositions of reacting solutions are usually less than well founded. The exceptions to this rule are usually the cycles of least interest, those of slow catalytic reactions.

The Wilkinson hydrogenation illustrates the roles of the oxidative addition, reductive elimination, and insertion reactions, all of which occur in the cycle (Fig. 3). Some of the properties of the rhodium phosphine complexes that explain their success as catalysts include the following: Rhodium exists in two stable oxidation states, Rh(I) and Rh(III), separated by two units. Oxidative addition and reductive elimination reactions formally require changes of two units in metal oxidation state. There are no intermediates that are so stable that they form bottlenecks in the cycle. There is an exquisite dynamic balance, and the cycle turns over rapidly with only low concentrations of the intermediates being present in a steady state. The phosphines are electron-donor ligands that are important in controlling the reactivities of the intermediates and regulating the dynamic balance. Replacement of triphenylphosphine by other phosphines leads to significant changes in the rate of the catalytic hydrogenation. The phosphines can influence the reactivities of the intermediates, and thus the rate of catalysis, by virtue of both electronic and steric effects.

Asymmetric Hydrogenation. Biological reactions are stereoselective, and numerous drugs must be pure optical isomers. Metal complex catalysts have been found that give very high yields of enantiomerically pure products, and some have industrial application (17,18). The hydrogenation of the methyl ester of acetamidocinnamic acid has been carried out to give a precusor of

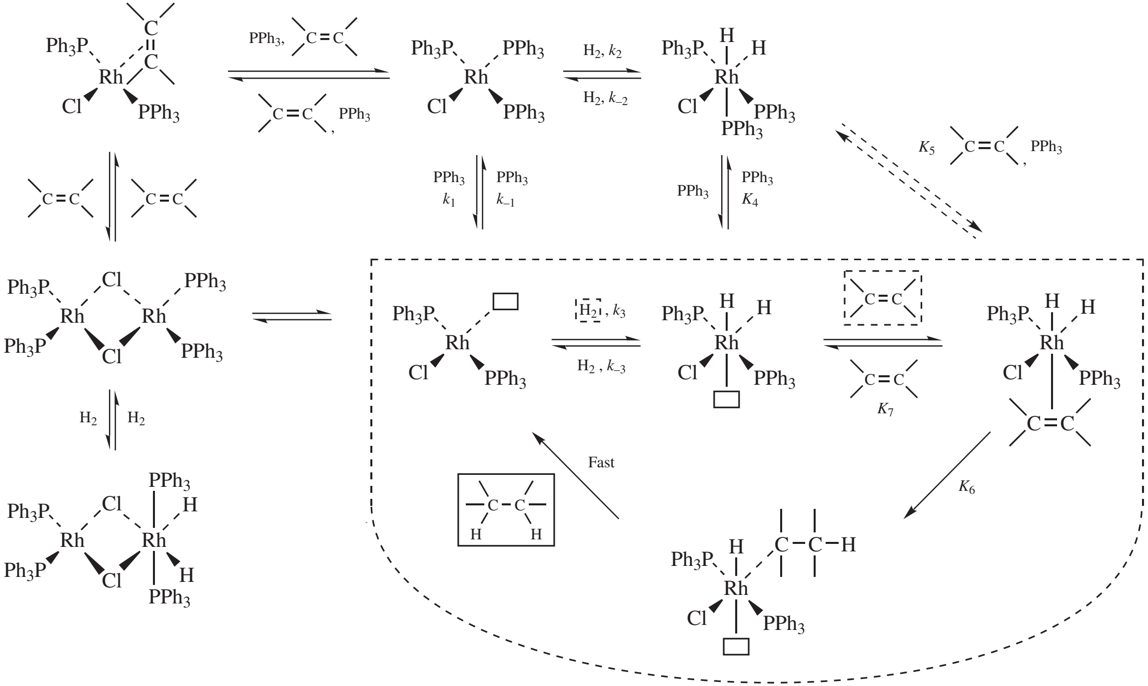
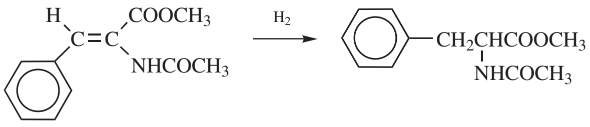


Fig. 3. Catalytic cycle (within dashed lines) for the Wilkinson hydrogenation of olefin (14,16). Ph represents phenyl (C_6H_5). Values of rate constants and equilibrium constants are as follows: $k_1 = 0.68\ s^{-1}$; $k_{-1} \geq 7\times10^4$ L/(mol·s); $K_1 \leq 10^{-5}$ mol/L; $k_{-1}/k_4 \cong 1$; $K_5 = 3\times10^{-4}$; $k_2 = 4.8$ L/(mol·s); $k_{-2} = 2.8\times10^{-4}\ s^{-1}$; $K_2 = 1.7\times10^4$ L/mol; $k_3 \geq 7\times10^4$ L/(mol·s); $k_6 = 0.22\ s^{-1}$.

L-dopa, ie, 3,4-dihydroxyphenylalanine, a drug used in the treatment of Parkinson's disease.



The strategy of the catalyst development was to use a rhodium complex similar to those of the Wilkinson hydrogenation but containing bulky chiral ligands in an attempt to direct the stereochemistry of the catalytic reaction to favor the desired L isomer of the product (17). Active and stereoselective catalysts have been found and used in commercial practice (although there is now a more economical route to L-dopa than through hydrogenation of the prochiral precursor). The 2001 Nobel Prize in Chemistry was awarded to W. S. Knowles and R. Noyori, recognizing their work on these catalysts (and to K. B. Sharpless for work on asymmetric oxidation catalysis).

Two pathways were found for the chiral hydrogenation, and they give products with different stereochemistries (19). One pathway involves the preferred mode of initial binding of the reactant to the catalyst. The other pathway involves an isomer of the reactant–catalyst complex that is formed in only small amounts, but its conversion is energetically favorable and constitutes the kinetically predominant pathway to products (9) (Fig. 4). Thus the chirality of the product is determined not by the preferred mode of the initial binding, but instead by the more favorable energetics of the pathway involving the minor isomer of the reactant–catalyst complex.

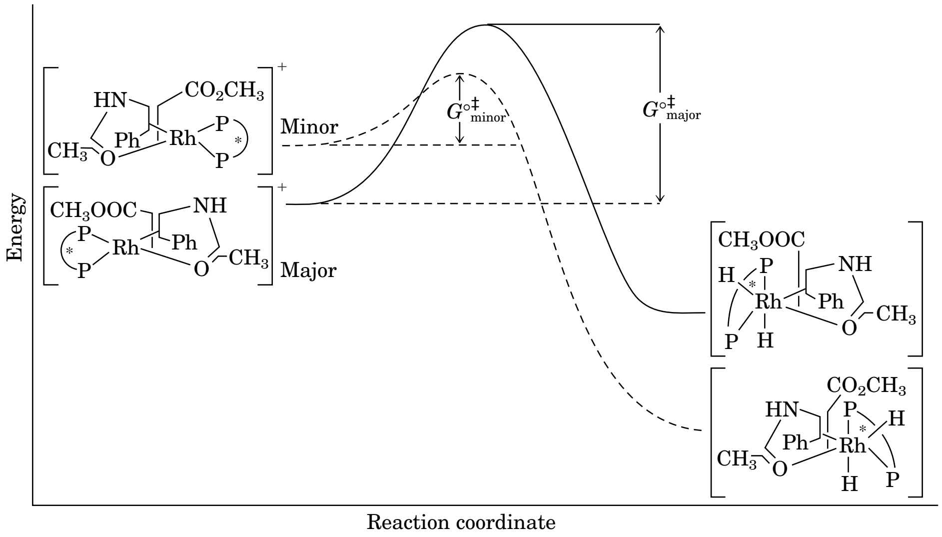


Fig. 4. Schematic representation of energy profiles for the pathways for the hydrogenation of a prochiral precursor to make L-dopa (19). The chiral disphosphine ligand is shown schematically as $\widehat{P^{*}P}$. Ph represents phenyl (C_6H_5).

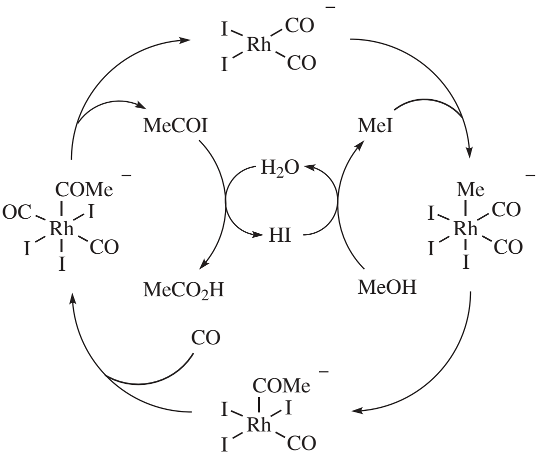


Fig. 5. Catalytic cycle for methanol carbonylation (21).

Methanol Carbonylation. An important industrial process catalyzed by rhodium (and more recently iridium) complexes in solution is methanol carbonylation to give acetic acid.

$$CH_3OH + CO \rightarrow CH_3COOH \tag{10}$$

The catalytic cycle (Fig. 5) (20,21) is well established. The CH_3I works as a cocatalyst or promoter because it undergoes an oxidative addition with $[Rh(CO)_2I_2]^-$, and the resulting product has the CO ligand bonded cis to the CH_3 ligand; these two ligands are then poised for a migratory insertion reaction. When the catalyst is iridium instead of rhodium, a similar cycle pertains, but the reaction of $[H_3CIr(CO)_2I_3]^-$ with CO to give $[H_3CCOIr(CO)_2I_3]^-$ is rate determining (21). The migratory insertion in the iridium complex can be accelerated by the addition of either methanol or a Lewis acid (SnI_2); each appears to facilitate substitution of an iodide ligand by CO, resulting in faster methyl migration. The greater stability of $[H_3CIr(CO)_2I_3]^-$ than of $[H_3CRh(CO)_2I_3]^-$ accounts for the different characters of the reactions catalyzed by the two metals (21).

Methanol carbonylation is one of only a few industrially important catalytic reactions for which the quantitative reaction kinetics is known (22).

$$r = k[CH_3I][\text{Rh complex}] \tag{11}$$

Here, for the rhodium-complex-catalyzed reaction, $k = 3.5 \times 10^6 \exp(-E_{act}/RT)$ and R is the gas constant, T is the absolute temperature, and E_{act} is 61.5 kJ/mol (14.7 kcal/mol). Because the reaction is zero order in the reactants, a stirred reactor has no disadvantage in comparison with a tubular flow reactor with respect to the efficiency of use of the reactor volume. A stirred reactor might therefore be preferred to facilitate rapid heat transfer and good gas–liquid contacting for rapid gas–liquid mass transfer, ie, dissolution of the CO into the reactant solution.

The reaction is carried out in a polar solvent, as the intermediates are anionic. Water is present from the following reaction, which achieves virtual equilibrium:

$$CH_3OH + HI \rightleftharpoons CH_3I + H_2O \tag{12}$$

Water is also formed in the acid-catalyzed dehydration of methanol to give dimethyl ether. The solution is acidic because of the presence of the HI.

The process flow diagram (23) (Fig. 6) is characteristic of those for homogeneous catalytic processes in being dominated by the separations devices. The products are purified by distillation, and several columns are required because the boiling point of the product acetic acid is near the middle of the boiling range of the product mixture; both the light products, including unconverted CO, CH_3I, and dimethyl ether, and the heavy rhodium complex must be recovered and recycled efficiently for the process to be economical. Corrosion is also a concern, and the reactor, separations devices, and lines are made of expensive stainless steel alloys.

For years, researchers have attempted to minimize the problems of separation and corrosion by using catalysts that are solid analogues of the metal complexes used in solution. The early attempts were not successful, in large measure because the rhodium complex was leached from the support (typically a

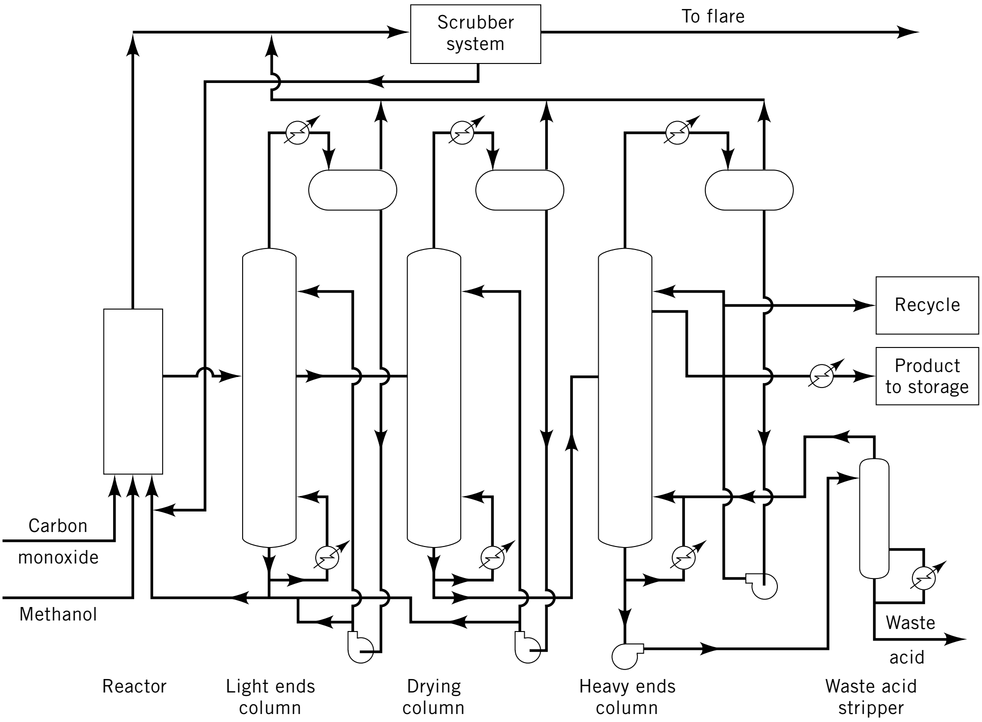
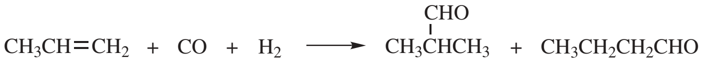


Fig. 6. Process flow diagram for methanol carbonylation catalyzed by a rhodium complex to make acetic acid (23).

cross-linked polymer with pendant phosphine groups) and the polymer was not sufficiently stable. Recent work with more stable vinyl pyridine resins as supports has led to stable catalysts and apparently to a viable industrial process (24); this is important as perhaps the first successful application of a supported catalyst that is nearly analogous to a molecular metal complex catalyst.

Olefin Hydroformylation (The Oxo Process). One of the most important industrial applications of transition-metal complex catalysis is the hydroformylation of olefins (25), illustrated for propylene:



$$CH_3CH{=}CH_2 + CO + H_2 \longrightarrow CH_3\overset{CHO}{\overset{|}{C}}HCH_3 + CH_3CH_2CH_2CHO \qquad (13)$$

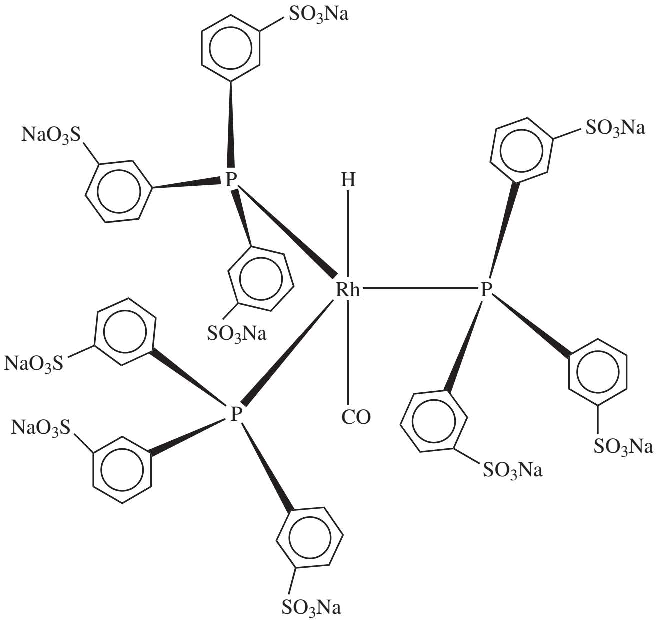
The linear isomer is more valuable than the branched isomer (see BUTYRALDEHYDE). The product aldehydes are hydrogenated to give so-called oxo alcohols; long-chain products are converted into sulfonates and used as detergents.

The oxo process was discovered in 1938 by Roelen and co-workers of Ruhrchemie. The first catalysts were cobalt carbonyl complexes formed from $[HCo(CO)_4]$. They are still used on a large scale. The process is carried out at temperatures of $\sim$150°C and pressures of $>$30MPa (several hundred atm). The high pressures are required to maintain the cobalt in the form of the soluble metal carbonyl complex; at lower pressures, cobalt metal can form and deposit on the reactor walls, possibly in a porous form that adds a significant resistance to heat transfer. Use of cobalt complexes with phosphine ligands led to processes with improved selectivities. The process flow diagram is complicated because it is expensive to separate the catalyst from the products and recycle it in the high pressure process. In the Kuhlmann process (25), the catalyst is extracted into an aqueous stream and then regenerated with acid to give $[HCo(CO)_4]$, which is absorbed into the reactant solution.

A significant advance in hydroformylation technology was made with the discovery that phosphine complexes of rhodium, similar to those used in the Wilkinson hydrogenation but incorporating H, CO, and olefin ligands as well as triphenylphosphine, have catalytic activities several orders of magnitude greater than those of cobalt; furthermore, the rhodium complexes are stable enough to be used at low pressures, typically 1.5 MPa (15 atm) at $\sim$150°C, and separated by distillation (25). Rhodium complex catalysts now are used in industrial processes for hydroformylation of propylene. When a large excess of triphenylphosphine is used as the solvent, the selectivity for the desired straight-chain product is high, with $>$95% of the aldehyde being n-butyraldehyde.

The processing costs associated with separation and corrosion are still significant in the low pressure process; for the process to be economical, the efficiency of recovery and recycle of the rhodium must be very high. Consequently, researchers have continued to seek new ways to facilitate the separation and confine the corrosion. Extensive research was done with rhodium phosphine complexes bonded to solid supports, but the resulting catalysts were not sufficiently stable, as rhodium was leached into the product solution. A successful solution to the engineering problem resulted from the application of a two-phase liquid–liquid process (26) . The catalyst is synthesized with polar $-SO_3Na$

groups on the phenyl rings of the triphenylphosphine



so that it is water soluble. In the reactor, the catalyst is largely confined to the aqueous phase and the reactants are largely confined to the organic phase; reaction likely takes place near the interface. A process flow diagram is shown in Figure 7 (26). The two liquid phases are separated downstream of the stirred reactor and the catalyst is recycled with a high efficiency. The process is applied

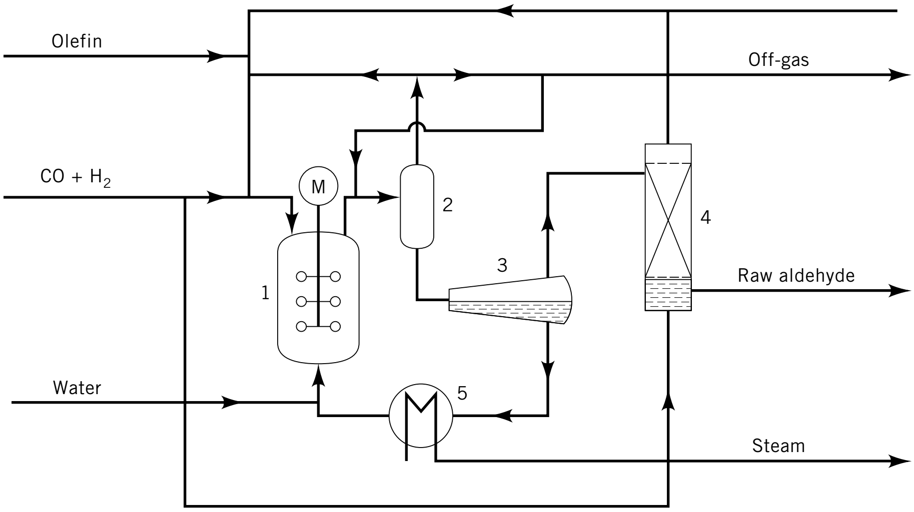


Fig. 7. Process flow diagram for the two-phase hydroformylation of propylene where 1 = reactor; 2 = separator; 3 = phase separator; 4 = stripping column; and 5 = heat exchanger (26).

commercially and is competitive with the single-phase process. It is indicative of a trend toward application of more homogeneous catalytic processes with environmentally friendly solvents such as water.

Attempts to anchor transition-metal complex catalysts to supports have been extended to reactions far beyond just methanol carbonylation and hydroformylation, but almost all the resulting catalysts have failed to find practical application. The principal difficulty is that the catalyst at each step of the catalytic cycle must be stably bonded to the support, and this is often too stringent a design criterion. Perhaps a more generally useful way to confine the catalyst in a phase separate from that containing most of the reactants is to use a second liquid phase. Water is one appealing choice, and promising work has also been done with fluorous phases (27,28).

Olefin Metathesis. The olefin metathesis (dismutation) reaction (29,30) converts olefins to lower and higher molecular weight olefins. For example, propylene is converted into ethylene and butene

$$2\,\mathrm{RCH{=\!=}CHR'} \longrightarrow \mathrm{RCH{=\!=}CHR} + \mathrm{R'CH{=\!=}CHR'} \tag{14}$$

This reaction is catalyzed in solution by complexes of tungsten, molybdenum, or rhenium in high oxidation states, eg, Re^{7+}. Examples of catalyst precursors are $[W(CH\text{-}t\text{-}C_4H_9)(OR)_2X_2]$ (31a), where X is halide. A number of catalysts require cocatalysts such as $CH_3Al_2Cl_3$.

The olefins that undergo metathesis include most simple and substituted olefins; cyclic olefins give linear high molecular weight polymers. The mechanism of the reaction is believed to involve formation of carbene complexes that react via cyclic intermediates, ie, metallacycles. An extension of the chemistry has led to efficient ring-opening metathesis polymerization (32).

Industrial olefin metathesis processes are carried out with solid catalysts (29).

The Wacker Oxidation of Ethylene to Acetaldehyde. One of the early industrial examples of organometallic catalysis in solution was described by Smidt and co-workers in 1959 (33). This is the Wacker oxidation of ethylene to give acetaldehyde (qv). It had long been known that Pd(II) complexes in solution would stoichiometrically oxidize ethylene to acetaldehyde. Smidt's insight was to make this reaction part of a catalytic cycle. The researchers created a process by closing the cycle, using an excess of an oxidizing agent, Cu^{2+}, to rapidly reoxidize the palladium that oxidized the ethylene and thereby keep palladium from plating out on the reactor walls as metal. The cycle is completed as O_2 reoxidizes the Cu^{+} formed from Cu^{2+}. The sequence of reactions is the following:

$$\mathrm{CH_2{=\!=}CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + Pd + 2\,HCl} \tag{15}$$

$$\mathrm{Pd + 2\,CuCl_2 \rightarrow PdCl_2 + 2\,CuCl} \tag{16}$$

$$\mathrm{2\,CuCl + \frac{1}{2}\,O_2 + 2\,HCl \rightarrow 2\,CuCl_2 + H_2O} \tag{17}$$

These reactions constitute the cycle; their sum gives the stoichiometry of the Wacker oxidation:

$$CH_2{=\!=}CH_2 + \frac{1}{2}\,O_2 \rightarrow CH_3CHO \tag{18}$$

This process is unusual among those involving organometallic chemistry in that it takes place in aqueous solution. In one process design, there is a single reactor in which all three reactions in the sequence take place, and the feed contains pure O_2. In another process, there are two reactors, with the ethylene oxidation (eq. 15) and the palladium reoxidation (eq. 16) taking place in one reactor and the reoxidation of Cu^+ with air taking place in the other. An advantage of the single-reactor process is the confinement of the corrosive solutions in one vessel, but this is compensated by the need for purified oxygen . The feed gas contains ethylene and oxygen, and the composition must be kept outside the explosive limits. Consequently, the feed gas is not a stoichiometric mixture, and gas recycle is necessary for economic operation. In contrast, the two-reactor process allows the use of air as a feed to the reactor where Cu^+ is reoxidized; the air flows once through the reactor and is almost all converted. Ethylene flows into the other reactor. A disadvantage of the two-reactor process is the need for corrosion-resistant materials in both reactors and the lines between them. Both designs have been successfully applied.

A process similar to the Wacker process has been applied for the oxidation of ethylene with acetic acid to give vinyl acetate, but now the principal applications are with a solid catalyst.

Free-Radical Oxidation of Hydrocarbons. The chemistry of the Wacker reaction is atypical for oxidation. A more common pattern in catalytic oxidation is a chain reaction proceeding through free-radical intermediates; hydroperoxides are common products, and they are often converted themselves into other products (34,35). Free-radical reactions are characterized by complex product distributions because O_2 has a high reactivity with organic reactants, with metal centers, and with many ancillary ligands. Metals typically play a role in an initiation process, helping to start a free-radical chain reaction; free radicals are often generated by metal-catalyzed decomposition of organic hydroperoxides. Some of the important applications of such chemistry are oxidations of petroleum-derived hydrocarbons. Catalysts include iron, manganese, cobalt, and copper in high oxidation states; a typical solvent is acetic acid. The processes include oxidation of *n*-butane to give acetic acid, formation of fatty acids from paraffin wax, and oxidation of cyclohexane to give adipic acid (qv) precursors in nylon manufacture.

A simplified mechanism of the cyclohexane oxidation is shown in Figure 8 (36). A free-radical chain is set up, with $R\cdot$ and $ROO\cdot$ being the chain carriers (R is C_6H_{11}), as shown in the upper right of the figure. One role of Co^{3+} is suggested to be that of an electron-transfer agent undergoing a one-electron change; the role of the metal is that of a redox initiator, as cobalt cycles between the +2 and +3 oxidation states in a process that generates free radicals. As the

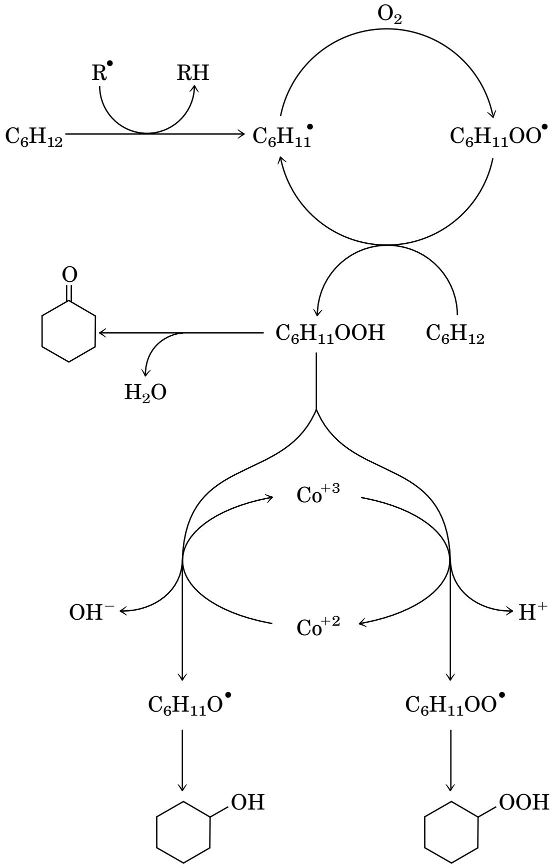
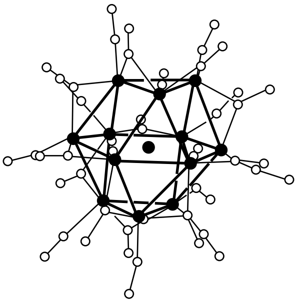


Fig. 8. Simplified mechanism for the free-radical oxidation of cyclohexane (36).

cobalt also reacts in a cycle, its role is catalytic, and only small amounts are needed.

One of the most important oxidation processes is the conversion of *p*-xylene into terephthalic acid or dimethyl terephthalate. There are numerous commercial processes, generally using air as the oxidant and cobalt and manganese salts as the catalysts (37). In one process, the oxidation takes place at ~225°C and 15 atm, and bromides are involved in the catalysis (37).

CO and H_2 Reactions. Synthesis gas (CO and H_2) can be converted into numerous organic chemicals, including acetic anhydride formed in a commercial process with a rhodium complex catalyst. Soluble rhodium catalysts are also active for synthesis of ethylene glycol along with methanol and other products (38). The process is not applied commercially because extremely high pressures are required. But the process is conceptually important because it is believed that the catalysts may be compounds with metal–metal bonds, called metal clusters. A simple metal cluster is $[Rh_{13}(CO)_{24}H_3]^{2-}$, which has the following structure:



There are many related compounds, including rhodium carbonyl cluster anions that are present in the solutions catalyzing ethylene glycol formation and which may be the catalytically active species or in equilibrium with them (38).

There are only a few well-documented examples of catalysis by metal clusters, and not many are to be expected as most metal clusters are fragile and fragment to give metal complexes or aggregate to give metal under reaction conditions (39). However, the metal carbonyl clusters are conceptually important because they form a bridge between catalysts commonly used in solution, ie, transition-metal complexes with single metal atoms, and catalysts commonly used on surfaces, ie, small metal particles or clusters.

3.4. Phase-Transfer Catalysis.

When two reactants in a catalytic process have such different solubility properties that they can hardly both be present in a single liquid phase, the reaction is confined to a liquid–liquid interface and is usually slow. However, the rate can be increased by orders of magnitude by application of a phase-transfer catalyst (39,40), and these are used on a large scale in industrial processing (see CATALYSTS, PHASE-TRANSFER). Phase-transfer catalysts function by facilitating mass transport of reactants between the liquid phases. Often most of the reaction takes place close to the interface.

Industrial examples of phase-transfer catalysis are numerous and growing rapidly; they include polymerization, substitution, condensation, and oxidation reactions. The processing advantages, besides the acceleration of the reaction, include mild reaction conditions, relatively simple process flow diagrams, and flexibility in the choice of solvents.

4. Heterogeneous Catalysis

4.1. Characterization of Surface Processes.

Most of the largest scale catalytic processes take place with gaseous reactants in the presence of solid catalysts. From an engineering viewpoint, these processes offer the following advantages, in contrast to those involving liquid catalysts: (*1*) wide ranges of temperature and pressure are economically applied. The most direct way to increase the activity of a catalyst is to increase its temperature, and high temperatures can be used economically with solid catalysts as the reactants are gases and there is no liquid phase to require a high pressure. The catalysts must be robust to withstand the high temperatures; solid catalysts are commonly used at temperatures of 500°C, and some endure temperatures several hundred degrees higher; (*2*) solid catalysts are only rarely corrosive; (*3*) the separation of gaseous or liquid products from solid catalysts is simple and costs little. It is simplest when the catalyst particles are confined in a fixed-bed reactor; when very small particles are used in a fluidized bed, they are entrained in the product stream, and a gas–solid separator is required; (*4*) the mixing and mass transport in a fixed- or fluidized-bed reactor are facilitated by the solid catalyst particles through which the reactants and products flow. If no liquid phase is present, a potentially significant mass-transfer resistance is eliminated; mass-transfer resistance in the gas phase is usually small. However, reactions take place on the internal surfaces of porous catalyst particles, and the resistance to transport through the pores is often significant; (*5*) strongly exothermic and strongly endothermic reactions are routinely carried out with solid catalysts. Fluidized-bed reactors offer the advantage of excellent mixing and high rates of heat transfer. They are commonly used when heat effects are large, eg, for oxidation reactions; alternatively, small tubes are used in bundles to minimize the distance through which the heat is transferred in a fixed bed. The catalyst particles themselves constitute a significant heat-transfer resistance, and the temperature gradients in particles are sometimes large.

4.2. Properties of Solid Catalysts. Most solid catalysts used on a large scale are porous inorganic materials. A number of these and the reactions they catalyze are summarized in Table 1 (10); a list of new processes was compiled by Armor (41).

Catalysis takes place as one or more of the reactants is chemisorbed (chemically adsorbed) on the surface and reacts there. The activity and selectivity of a catalyst depend strongly on the surface composition and structure.

The catalysts with the simplest compositions are pure metals, and the metals that have the simplest and most uniform surface structures are single crystals. Researchers have done many experiments with metal single crystals in ultrahigh vacuum chambers so that unimpeded beams of particles and radiation can be used to probe them. These surface science experiments have led to fundamental understanding of the structures of simple adsorbed species, such as CO, H, and small hydrocarbons, and the mechanisms of their reactions; they indicate that catalytic activity is often sensitive to small changes in surface structure. For example, paraffin hydrogenolysis reactions take place rapidly on steps and kinks of platinum surfaces but only very slowly on flat planes; however, hydrogenation of olefins takes place at approximately the same rate on each kind of surface site.

A few industrial catalysts have simple compositions, but the typical catalyst is a complex composite made up of several components, illustrated schematically in Figure 9 by a catalyst for ethylene oxidation. Often it consists largely of a porous support or carrier, with the catalytically active components dispersed on the support surface. For example, petroleum refining catalysts used for reforming of naphtha have ~1 wt% Pt and Re on the surface of a transition alumina such as γ-Al_2O_3 that has a surface area >100 square meters per gram. The expensive metal is dispersed as minute particles or clusters so that a large fraction of the

Table 1. **Some Large-Scale Industrial Processes Catalyzed by Surfaces of Inorganic Solids**[a]

Catalyst	Reaction
metals (eg, Ni, Pd, Pt, as powders or on supports) or metal oxides (eg, Cr_2O_3)	C=C bond hydrogenation (eg, olefin $+ H_2 \rightarrow$ paraffin)
metals (eg, Cu, Ni, Pt)	C=O bond hydrogenation (eg, acetone $+ H_2 \rightarrow$ 2-propanol)
metal (eg, Pd, Pt) Fe, Ru (supported and promoted with alkali metals)	complete oxidation of hydrocarbons, oxidation of CO_3 $H_2 + N_2 \rightarrow 2NH_3$
Ni	$CO + 3H_2 \rightarrow CH_4 + H_2O$ (methanation) $CH_4 + H_2O \rightarrow 3\ H_2 + CO$ (steam reforming)
Fe or Co (supported and promoted with alkali metals)	$CO + H_2 \rightarrow$ paraffins + olefins + $H_2O + CO_2$ + oxygen-containing organic compounds) (Fischer-Tropsch reaction)
Cu (supported on ZnO, with other components, eg, Al_2O_3)	$CO + 2H_2 \rightarrow CH_3OH$
Re + Pt (supported on γ-Al_2O_3 and promoted with chloride)	paraffin dehydrogenation, isomerization and dehydrocyclization (eg, *n*-heptane → toluene + 4 H_2) (naphtha reforming)
solid acids (eg, SiO_2-Al_2O_3, zeolites)	paraffin cracking and isomerization; aromatic alkylation; polymerization of olefins
γ-Al_2O_3	alcohol → olefin + H_2O
Pd supported on zeolite	paraffin hydrocracking
metal-oxide-supported complexes of Cr, Ti, or Zr	olefin polymerization (eg, ethylene → polyethylene)
metal-oxide-supported complexes of W or Re	olefin metathesis (eg, 2-propylene → ethylene + butene)
V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$
Ag (on inert support, promoted by alkali metals)	ethylene $+ \frac{1}{2}O_2 \rightarrow$ ethylene oxide (with $CO_2 + H_2O$)
V_2O_5 (on metal oxide support)	naphthalene $+ \frac{9}{2}O_2 \rightarrow$ phthalic anhydride + $2\ CO_2 + 2\ H_2O$ *o*-xylene $+ 3\ O_2 \rightarrow$ phthalic anhydride $+ 3H_2O$
bismuth molybdate, uranium antimonate, other mixed metal oxides	propylene $+ \frac{1}{2}O_2 \rightarrow$ acrolein propylene $+ \frac{3}{2}O_2 + NH_3 \rightarrow$ acrylonitrile $+ 3\ H_2O$
mixed oxides of Fe and Mo	$CH_3OH + O_2 \rightarrow$ formaldehyde (with $CO_2 + H_2O$)
Fe_3O_4 or metal sulfides	$H_2O + CO \rightarrow H_2 + CO_2$ (water gas shift reaction)
[$Co - Mo/\gamma-Al_2O_3$ (sulfided) {$Ni - Mo/\gamma-Al_2O_3$ (sulfided) $Ni - W/\gamma - Al_2O_3$ (sulfided)]	olefin hydrogenation aromatic hydrogenation hydrodesulfurization hydrodenitrogenation

[a] Ref. 10.

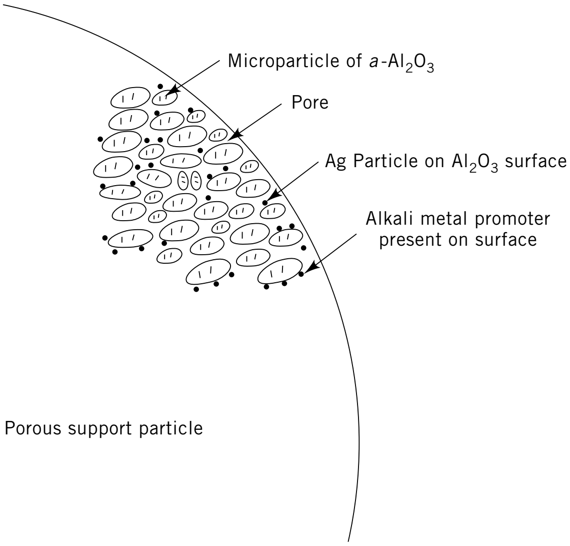


Fig. 9. Schematic representation of a catalyst for ethylene oxide synthesis (not to scale). The porous support particle consists of microparticles held together by a binder.

atoms are exposed at the surface and accessible to reactants (see CATALYSTS, SUPPORTED).

The typical industrial catalyst has both microscopic and macroscopic regions with different compositions and structures; the surfaces of industrial catalysts are much more complex than those of the single crystals of metal investigated in ultrahigh vacuum experiments. Because surfaces of industrial catalysts are very difficult to characterize precisely and catalytic properties are sensitive to small structural details, it is usually not possible to identify the specific combinations of atoms on a surface, called catalytic sites or active sites, that are responsible for catalysis. Experiments with catalyst poisons, substances that bond strongly with catalyst surfaces and deactivate them, have shown that the catalytic sites are usually a small fraction of the catalyst surface. Although most models of catalytic sites rest on rather weak foundations, some are well established. For example, NO decomposition on ruthenium takes place at steps, as shown by scanning tunneling microscopy images of individual reacting atoms on the surface (42).

Important physical properties of catalysts include the particle size and shape, surface area, pore volume, pore size distribution, and strength to resist crushing and abrasion. Measurements of catalyst physical properties (43a) are routine and often automated. Pores with diameters <2.0 nm are called micropores; those with diameters between 2.0 and 5.0 nm are called mesopores; and those with diameters >5.0 nm are called macropores. Pore volumes and pore size distributions are measured by mercury penetration and by N_2 adsorption. Mercury is forced into the pores under pressure; entry into a pore is opposed by surface tension. For example, a pressure of $\sim$71 MPa (700 atm) is required to fill a pore with a diameter of 10 nm. The amount of uptake as a function of pressure determines the pore size distribution of the larger pores (44). In complementary experiments, the sizes of the smallest pores (those 1–20 nm in diameter) are determined by measurements characterizing desorption of N_2 from the catalyst. The basis for the measurement is the capillary condensation that occurs in small pores at pressures less than the vapor pressure of the adsorbed nitrogen. The smaller the diameter of the pore, the greater the lowering of the vapor pressure of the liquid in it.

Surface areas are determined routinely and exactly from measurements of the amount of physically adsorbed (physisorbed) nitrogen. Physical adsorption is a process akin to condensation; the adsorbed molecules interact weakly with the surface and multilayers form. The standard interpretation of nitrogen adsorption data is based on the BET model (45), which accounts for multilayer adsorption. From a measured adsorption isotherm and the known area of an adsorbed N_2 molecule, taken to be 0.162 nm^2, the surface area of the solid is calculated (see ADSORPTION).

4.3. Influence of Mass Transport on Catalyst Performance. Reactants must diffuse through the network of pores of a catalyst particle to reach the internal area, and the products must diffuse back. The optimum porosity of a catalyst particle is determined by tradeoffs: making the pores smaller increases the surface area and thereby increases the activity of the catalyst, but this gain is offset by the increased resistance to transport in the smaller pores; increasing the pore volume to create larger pores for faster transport is compensated by a loss of physical strength. A simple quantitative development (46–48) follows for a first-order, isothermal, irreversible catalytic reaction in a spherical, porous catalyst particle.

If there is a significant resistance to transport of the reactant in the pores, a concentration gradient will exist at steady state, whereby the concentration of the reactant is a maximum at the particle periphery and a minimum at the particle center. The product concentration will be higher at the particle center than at the periphery. The concentration gradients provide the driving force for the transport.

As a reactant molecule from the fluid phase surrounding the particle enters the pore structure, it can either react on the surface or continue diffusing toward the center of the particle. A quantitative model of the process is developed by writing a differential equation for the conservation of mass of the reactant diffusing into the particle. At steady state, the rate of diffusion of the reactant into a shell of infinitesimal thickness minus the rate of diffusion out of the shell is equal to the rate of consumption of the reactant in the shell by chemical reaction. Solving the equation leads to a result that shows how the rate of the catalytic reaction is influenced by the interplay of the transport, which is characterized by the effective diffusion coefficient of the reactant in the pores, D_{eff}, and the reaction, which is characterized by the first-order reaction rate constant.

The result is shown in Figure 10, which is a plot of the dimensionless effectiveness factor as a function of the dimensionless Thiele modulus ϕ, which is $R(k/D_{\text{eff}})^{1/2}$, where R is the radius of the catalyst particle and k is the reaction rate constant. The effectiveness factor is defined as the ratio of the rate of the reaction divided by the rate that would be observed in the absence of a mass transport influence. The effectiveness factor would be unity if the catalyst were nonporous.

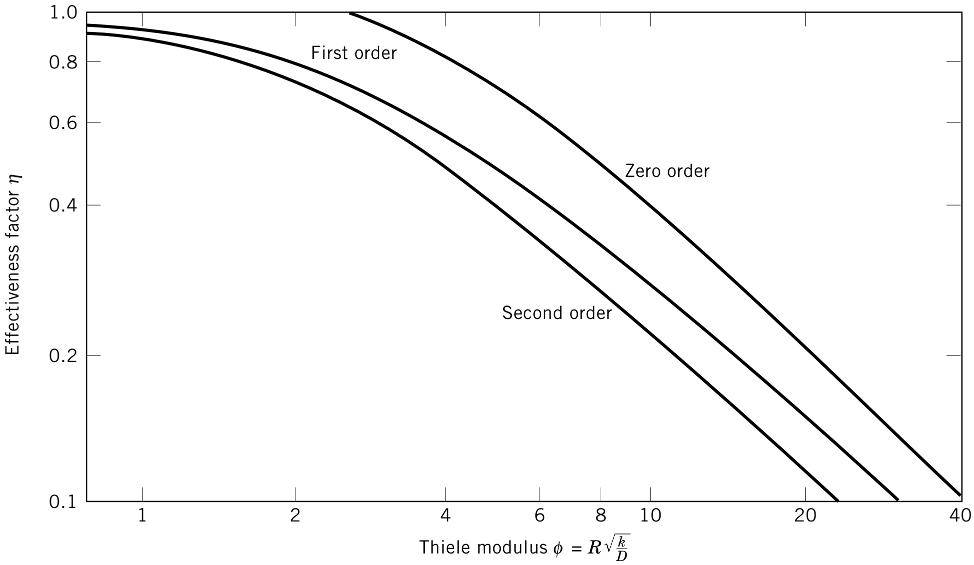


Fig. 10. The Thiele plot accounting for the influence of intraparticle mass transport on rates of catalytic reaction. The dimensionless terms η and ϕ are the effectiveness factor and the Thiele modulus, respectively, and are defined in the text.

Therefore, the reaction rate is

$$r = \eta k[\mathrm{A}]_s \tag{19}$$

where η is the effectiveness factor and $[\mathrm{A}]_s$ the concentration of the reactant A at the peripheral surface of the catalyst particle. The observed reaction rate constant is not the intrinsic reaction rate constant k but the product ηk.

Figure 10 shows that η is a unique function of the Thiele modulus. When the modulus ϕ is small ($\lesssim 1$), the effectiveness factor is unity, which means that there is no effect of mass transport on the rate of the catalytic reaction. When ϕ is greater than ~ 1, the effectiveness factor is less than unity and the reaction rate is influenced by mass transport in the pores. When the modulus is large ($\gtrsim 10$), the effectiveness factor is inversely proportional to the modulus, and the reaction rate (eq. 19) is proportional to k/ϕ, which, from the definition of ϕ, implies that the rate and the observed reaction rate constant are proportional to $(1/R)(D_{\mathrm{eff}}k)^{1/2}[\mathrm{A}]_s$. This result shows that both the rate constant, ie, a measure of the intrinsic activity of the catalyst, and the effective diffusion coefficient, ie, a measure of the resistance to transport of the reactant offered by the pore structure, influence the rate. It is not appropriate to say that the reaction is diffusion controlled; it depends on both the diffusion and the chemical kinetics. In contrast, as shown by equation 3, a reaction in solution can be diffusion controlled, depending on D but not on k.

In the case of a significant intraparticle diffusion influence, the temperature dependence of the observed rate constant, the apparent activation energy, is not that of the intrinsic rate constant, ie, the true activation energy; rather, as the Thiele modulus becomes large (>10), the temperature dependence approaches that of $(D_{\mathrm{eff}}k)^{1/2}$. The temperature dependence of a diffusion coefficient is usually small, and the measured activation energy is thus about half the intrinsic activation energy. This is an important and general result: The kinetics is disguised by the transport influence. When the effectiveness factor is unity, there is no disguise, and the true activation energy is measured.

This development has been generalized. Results for zero- and second-order irreversible reactions are shown in Figure 10. Results are given elsewhere (48) for more complex kinetics, nonisothermal reactions, and particle shapes other than spheres. For nonspherical particles, the equivalent spherical radius, three times the particle volume/surface area, can be used for R to a good approximation.

Even when there is a transport disguise, the reaction order remains one for a first-order reaction. But for reactions that are not intrinsically first order, the transport disguise changes the observed reaction order; for an intrinsically zero-order reaction, the observed order becomes 1/2 and for an intrinsically second-order reaction it becomes 3/2 when $\phi \gtrsim 10$. For all reaction orders the apparent activation energy is approximately one-half of the intrinsic value in this limit.

The mass transport influence is easy to diagnose experimentally. One measures the rate at various values of the Thiele modulus; the modulus is easily changed by variation of R, the particle size. Crushing and sieving the particles provide catalyst samples for the experiments. If the rate is independent of the particle size, the effectiveness factor is unity for all of them. If the rate is inversely proportional to particle size, the effectiveness factor is less than unity and $\phi \gtrsim 10$. If the dependence is between these limits, then several experimental points allow triangulation on the curve of Figure 10 and estimation of η $\alpha\nu\delta$ ϕ. It is also possible to estimate the effective diffusion coefficient and thereby to estimate η $\alpha\nu\delta$ ϕ from a single measurement of the rate (48).

If the effectiveness factor is less than unity, the catalyst is not being used efficiently, ie, the central region is starved of reactant. The results of Figure 10 show how to increase the effectiveness factor: decrease the Thiele modulus. This can be done by some combination of the following: (*1*) decreasing the particle size R. However, if particles are too small, they may cause too great a pressure drop in a flow reactor or be entrained in the product stream; (*2*) changing particle shape to reduce the transport length. Particles with cross sections resembling clover leaves and wagon wheels have been used, for example; (*3*) increasing the effective diffusion coefficient. Larger catalyst pores accomplish this, but with a sacrifice in physical strength; and (*4*) decreasing the activity of the catalyst measured by k. This option is unappealing as researchers strive to make more active catalysts, but it may be economical to reduce the activity by reducing the loading of the catalytically active component on a support. It may also be appropriate to prepare the catalyst with the active component concentrated near the particle periphery and not in the particle interior.

Intraparticle mass transport resistance can lead to disguises in selectivity. If a series reaction A→B→C takes place in a porous catalyst particle with a small effectiveness factor, the observed conversion to the intermediate B is less than what would be observed in the absence of a significant mass transport influence. This happens because as the resistance to transport of B in the pores increases, B is more likely to be converted to C rather than to be transported from the catalyst interior to the external surface. This result has important consequences in processes such as selective oxidations, in which the desired product is an intermediate and not the total oxidation product CO_2.

Rates and selectivities of solid-catalyzed reactions can also be influenced by mass-transport resistance in the external fluid phase. Most reactions are not influenced by external-phase transport, but the rates of some very fast reactions, eg, ammonia oxidation, are determined solely by the resistance to this transport. As the resistance to mass transport within the catalyst pores is larger than that in the external fluid phase, the effectiveness factor of a porous catalyst is expected to be less than unity whenever the external-phase mass transport resistance is significant. A practical catalyst that is used under such circumstances is the ammonia oxidation catalyst. It is a nonporous metal and consists of layers of wire mesh.

4.4. Catalyst Components. Industrial catalysts are typically complex in composition and structure, consisting of catalytically active phases, supports, binders, and promoters.

Catalytically Active Species. The most common catalytically active materials are metals, metal oxides, and metal sulfides. Occasionally, these are used in pure form; examples are Raney nickel, used for fat hydrogenation, and γ-Al_2O_3, used for ethanol dehydration. More often the catalytically active component is highly dispersed on the surface of a support and may constitute no more than ~1% of the total catalyst. The main reason for dispersing the catalytic species is the expense. The expensive material must be accessible to reactants, and this requires that most of the catalytic material be present at a surface. This is possible only if the material is dispersed as minute particles, as small as 1 nm in diameter and even less. It is not practical to use minute particles by themselves, as they would be entrained in products and clog lines and pumps, and their use in a fixed-bed reactor would cause large pressure drops. Dispersion on a support may also help stabilize the catalytically active species.

Supports. The principal component of a typical catalyst is the porous support (49,50) . Most supports are robust solids that can be made with wide ranges of surface areas and pore size distributions. The most widely applied supports are metal oxides; others are carbon, kieselguhr, organic polymers, and zeolites.

The most commonly applied catalyst support is γ-Al_2O_3, one of the transition aluminas (33,51). These are defective metastable solids formed from nonporous $Al(OH)_3$ by heating it to ~500°C or more; continued heating gives the more stable δ-Al_2O_3. As the $Al(OH)_3$ is heated in air, it decomposes into an oxide with a micropore system and a surface area of hundreds of square meters per gram. The solid consists of small, crystalline primary particles; the spaces between these primary particles are micropores and mesopores. As the solid is heated to ~1100°C, there is a series of phase changes and ultimately a collapse of the pore structure and loss of almost all the internal surface area as finally the extremely hard, crystalline α-Al_2O_3 (corundum) is formed. It has a melting point of ~2100°C [see ALUMINUM OXIDE (ALUMINA)].

Transition aluminas are good catalyst supports because they are inexpensive and have good physical properties. They are mechanically stable, stable at relatively high temperatures even under hydrothermal conditions, ie, in the presence of steam, and easily formed in processes such as extrusion into shapes that have good physical strength such as cylinders. Transition aluminas can be prepared with a wide range of surface areas, pore volumes, and pore size distributions.

Macropores can be introduced into γ-Al_2O_3 by including particles of an organic material such as carbon or sawdust with the $Al(OH)_3$ (51). When the γ-Al_2O_3 is formed, the organic particles are surrounded by the alumina. The organic material is removed by burning, leaving macropores; the macropore dimensions are determined by the particle size of the organic material.

Most catalyst supports are simply nearly inert platforms that help stabilize the dispersion of the catalytically active phase. Sometimes, however, the supports play a direct catalytic role, as exemplified by the alumina used in supported Pt and RePt catalysts for naphtha reforming.

The surfaces of γ-Al_2O_3 and most other metal oxides are covered with polar functional groups including OH groups and O^{2-} ions (52). A structural model of γ-Al_2O_3 is shown in Figure 11 (53). When the solid is heated, it gives off water in a reversible process called dehydroxylation (54). As a result, surface OH groups are lost and Al^{3+}ions are exposed at the surface. The microparticles of the oxide interact strongly with each other through the surface functional groups; eg, hydrogen bonding can occur. As a result, a microporous solid consisting of such particles is a strong material. In contrast, some support materials, exemplified by α-Al_2O_3, have few surface functional groups, and a solid consisting of microparticles of such a material lacks physical strength.

Binders. To create needed physical strength in catalysts, materials called binders are added (51); they bond the catalyst. A common binder material is a clay mineral such as kaolinite. The clay is added to the mixture of microparticles as they are formed into the desired particle shape, eg, by extrusion. Then the support is heated to remove water and possibly burnout material and then subjected to a high temperature, possibly 1500°C, to cause vitrification of the clay;

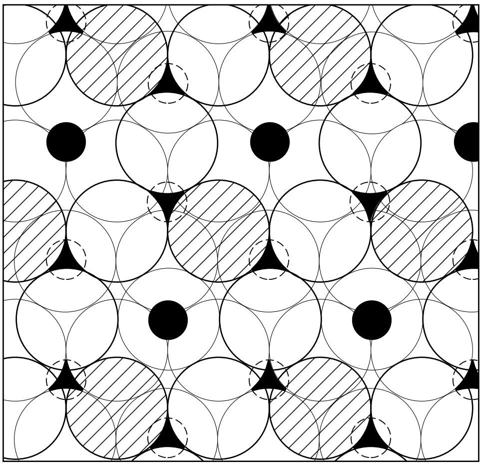


Fig. 11. Structural model of the (111) face of γ-alumina (53). The small solid circles represent Al^{3+}, the large open circles OH groups, and the hatched circles oxygen. The surface is 50% dehydroxylated.

this is a conversion of the clay into a glasslike form that spreads over the microparticles of the support and binds them together.

Promoters. Many industrial catalysts contain promoters, commonly chemical promoters. A chemical promoter is used in a small amount and influences the surface chemistry. Alkali metal ions are often used as chemical promoters, eg, in ammonia synthesis catalysts, ethylene oxide catalysts, and Fischer-Tropsch catalysts (55). They may be used in as little as parts per million quantities. The mechanisms of their action are often not well understood. In contrast, seldom-used textural promoters, also called structural promoters, are used in massive amounts in some catalysts and affect their physical properties. These are used in ammonia synthesis catalysts.

4.5. Catalyst Treatments. Catalysts often require activation or regeneration and their disposal also requires special consideration (56).

Activation. Some catalysts, eg, Ziegler olefin polymerization catalysts (57), are highly reactive in the presence of air, and some, eg, iron catalysts, are even pyrophoric; these must be handled under a blanket of inert gas. The surfaces of most catalysts are reactive and not easily maintained in an active state in the form in which they are conveniently supplied. Thus, many catalysts must be activated prior to use. The activation may be as simple as exposure to reactants under processing conditions, but some catalysts require specialized treatments. For example, catalysts used for hydroprocessing of fossil fuels are usually delivered as supported metal oxides, but in the operating state they are supported metal sulfides. Catalyst suppliers specify detailed procedures for treatment, eg, with a mixture of hydrogen and oil containing organosulfur compounds, to carry out the sulfiding properly. The details are often critical, and the catalyst manufacturer's guarantees may be void if the procedure is not carried out properly.

Deactivation. Catalysts lose activity and selectivity in many ways, and much effort in process development goes into measuring the deactivation and finding means to minimize it. Some catalysts undergo physical changes during normal operation; eg, a catalytically active phase may be transformed into an inactive phase. Catalysts also undergo sintering, which is a coalescence of particles to give larger particles, accompanied by loss of surface area. Iron sinters under conditions of ammonia synthesis, but when a textural promoter such as alumina is present, the sintering is greatly reduced. Catalyst components may be volatile and gradually vaporized during use; examples are silica used as a support and molybdenum oxides present in selective oxidation catalysts.

Catalysts commonly lose activity in operation as a result of accumulation of materials from the reactant stream. Catalyst poisoning is a chemical phenomenon. A catalyst poison is a component such as a feed impurity that as a result of chemisorption, even in small amounts, causes the catalyst to lose a substantial fraction of its activity. For example, sulfur compounds in trace amounts poison metal catalysts. Arsenic and phosphorus compounds are also poisons for a number of catalysts. Sometimes the catalyst surface has such a strong affinity for a poison that it scavenges it with a high efficiency. The poison may then adsorb strongly on the catalyst at the upstream end of a fixed-bed reactor at the beginning of operation, with a wave then moving downstream through the reactor as the upstream surface becomes saturated.

A selective poison is one that binds to the catalyst surface in such a way that it blocks the catalytic sites for one kind of reaction but not those for another. Selective poisons are used to control the selectivity of a catalyst. For example, nickel catalysts supported on alumina are used for selective removal of acetylene impurities in olefin streams (58). The catalyst is treated with a continuous feed stream containing sulfur to poison it to an exactly controlled degree that does not affect the activity for conversion of acetylene to ethylene but does poison the activity for ethylene hydrogenation to ethane. Thus the acetylene is removed and the valuable olefin is barely converted.

Because catalyst surfaces are reactive and often sensitive to their environments, they may be irreversibly changed by exposure to undesired reactants. Upsets in plant operations can lead to catastrophic losses of whole catalyst charges. A large catalyst charge that is ruined can cost hundreds of thousands of dollars as well as the cost of lost operation.

Catalysts are also deactivated or fouled by physical deposition of materials present in or formed from feeds. Sometimes massive deposits form on surfaces and block access of reactants to the catalytic sites. Coke is carbonaceous material of various compositions, often aromatic and with a high molecular weight and a typical composition of approximately CH. Coke forms on every hydrocarbon processing catalyst and on most catalysts used for organic chemical conversions. Inorganic materials are also deposited on catalysts. For example, the organovanadium and organonickel compounds in petroleum residua react to form vanadium and nickel sulfides on the surfaces of hydroprocessing catalysts. The solid deposits reduce activity by covering catalytic sites and by filling pores and restricting the entry of reactants. When the effectiveness factor for the deposition reaction is small, the pore mouths can become blocked and catalysts can suffer near catastrophic failure. Small particles of solid such as dust can also foul catalysts. This may be a problem in processes for cleanup of NO_x emissions from coal-fired power plants, and catalysts are designed in the form of monoliths (honeycombs) to minimize the effect.

Regeneration. Deactivated catalysts are treated to bring back the catalytic activity in processes called regenerations. Coke deposits are removed by controlled combustion. Often low partial pressures of oxygen are used to keep the rate of combustion and the temperature rise from becoming too large and leading to damage of the catalyst, such as by sintering. Periodic coke burn-off can be carried out many times with little damage to many catalysts. Most catalysts last for months or years between regenerations, but catalysts used for cracking of petroleum are in contact with reactants for only a few seconds; then they are separated and cycled to another reactor where they are regenerated (and then they are cycled back to the cracking reactor) (see CATALYSTS, REGENERATION).

Redispersion. Expensive catalyst components such as precious metals are used in high dispersions on supports. During operation, the small metal particles tend to sinter, ie, migrate and agglomerate, into larger particles with a loss of metal surface area and thereby a loss of catalytic activity. The metals in such catalysts may be redispersed as part of the catalyst regeneration (59). For example, after the coke is burned off a supported platinum catalyst, the catalyst may be treated with a reactive atmosphere containing chlorine and oxygen to form volatile platinum oxychloride species that are transported through the gas phase and deposited on the pore walls, where they are then treated in H_2 and reduced. The result is an increased dispersion of the platinum and a reactivated catalyst.

Reclamation, Disposal, and Toxicity. Removal of poisons and inorganic deposits from used catalysts is typically difficult and usually uneconomical. Thus, some catalysts are used without regeneration, although they may be processed to reclaim expensive metal components. Used precious metal catalysts, including automobile exhaust conversion catalysts, are treated (often by the suppliers) to extract the metals, and recovery efficiencies are high. Some spent hydroprocessing catalysts may be used as sources of molybdenum and other valuable metals.

Some catalysts are hazardous materials, or they react to form hazardous materials. For example, catalysts used for hydrogenation of carbon monoxide form volatile metal carbonyl compounds such as nickel carbonyl, which are highly toxic. Many catalysts contain heavy metals and other hazardous components, and environmentally safe disposal has become an increasing concern and expense.

4.6. Catalyst Preparation. Catalyst preparation is more an art than a science (60). Many reported catalyst preparations omit important details and are difficult to reproduce exactly, and this has hindered the development of catalysis as a quantitative science. However, the art is developing into a science and there are now many examples of catalysts synthesized in various laboratories that have nearly the same physical and catalytic properties.

Supports are often prepared first and the catalyst and promoter components added later. Metal oxide supports are usually prepared by precipitation from aqueous solutions. Nitrates are commonly used anions; alkalies and ammonium are commonly used cations. Metal oxide supports, eg, silica and alumina, are prepared in the form of hydrogels. Mixed oxides such as silica–alumina are made by cogelation. Careful control of conditions such as pH is important to give uniform products. Sol–gel processes are useful for the preparation of some high-area oxides (61).

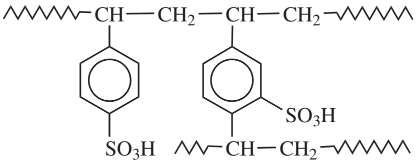
Supports are washed at controlled values of pH to remove impurities. Ions and impurities in the preparative solution are easily occluded in the solid and difficult to remove by washing. Therefore, ions that might poison the catalyst, eg, Cl^-, SO_4^{2-}, or alkali metal ions, are avoided. Many of the materials are cation exchangers, and washing does not remove cations from them. Metal ions can be removed by exchange with ammonium ions, which on heating give off ammonia and leave hydrogen ions in surface OH groups. Drying of precipitates and hydrated gels leads to evolution of gases and may generate microporosity, as described above for transition aluminas. Porosity can also be created by reduction of a nonporous oxide; porous iron can be made this way.

Catalyst components are usually added in the form of precursor metal salts in aqueous solutions. In impregnation, the support may be dried, evacuated, and brought in contact with an excess of an impregnating solution containing metal salts. The processes are complex, possibly involving some dissolution of the support and reprecipitation of structures including mixed metal species. The solid is then dried and calcined, ie, brought to a high temperature, usually in air. Alternatively, in the incipient wetness method, just enough of the impregnating solution is used to fill the pores of the support. The chemistry of the interactions of catalyst precursors with metal oxide supports is beginning to be understood. Important parameters that control the adsorption of metal complex precursors from aqueous solution are the isoelectric point of the metal oxide, the pH of the solution, and the nature of the metal complex (62). Depending on the conditions of the contact, cationic or anionic species may be adsorbed. Sometimes these are simple mononuclear (single-metal atom) species, but sometimes they are complicated polynuclear ions. The support may dissolve to some degree in the preparation solution and be redeposited in some form (perhaps with the catalyst precursor) (63). The nature of the initially adsorbed species may significantly affect the structure of the catalytic species in the resultant catalyst. After impregnation, the catalyst may be activated, for example, by drying and calcining. Promoters may be added at various stages, eg, as a final step in the preparation or just prior to operation.

Supported metal catalysts are reduced, eg, by treatment in hydrogen at temperatures in the range of 300–500°C. The reduction temperature may influence the stability of the metal dispersion.

4.7. Examples of Surface Catalysis. *Molecular Catalysis on Supports.* The term molecular catalysis is commonly applied only to reactions in uniform fluid phases, but it applies nearly as well to some reactions taking place on supports. Straightforward examples are reactions catalyzed by polymers functionalized with groups that closely resemble catalytic groups in solution. Industrial examples include reactions catalyzed by ion-exchange resins, usually sulfonated poly(styrene-divinylbenzene) (64). This polymer is an industrial catalyst for synthesis of methyl *tert*-butyl ether (MTBE) from methanol and isobutylene and synthesis of bisphenol A from phenol and acetone, among others. The former application grew rapidly as MTBE became a component of high-octane-number gasoline (see ETHERS).

The polymer has the following structure, which is shown schematically.

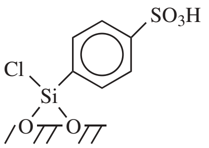


The sulfonated resin is a close analogue of *p*-toluenesulfonic acid in terms of structure and catalyst performance. In the presence of excess water, the SO_3H groups are dissociated, and specific acid catalysis takes place in the swelled resin just as it takes place in an aqueous solution. When the catalyst is used with weakly polar reactants or with concentrations of polar reactants that are too low to cause dissociation of the acid groups, general acid catalysis prevails and water is a strong reaction inhibitor (65).

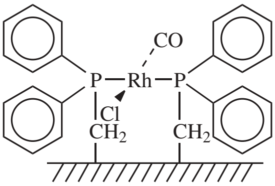
The polymer-supported catalysts are thus important conceptually in linking catalysis in solutions and catalysis on supports. The acid–base chemistry is fundamentally the same whether the catalytic groups are present in a solution or anchored to the support. The polymer-supported catalysts have replaced acid solutions in numerous processes because they minimize the corrosion, separation, and disposal problems posed by mineral acids.

Polymer-supported methanol carbonylation catalysts incorporating metal complexes, mentioned above, also behave in much the same way as their soluble analogues.

Surfaces of inorganic solids can be functionalized with catalytic groups just as organic polymers can. For example, the hydroxyl groups on the surface of silica can be used for synthesis of the following structure:



This is an ion-exchanger like the sulfonated polymer. The silica surface can also be functionalized with phosphine complexes; when combined with rhodium, these give anchored complexes that behave like their soluble and polymer-supported analogues as catalysts for olefin hydrogenation and other reactions:

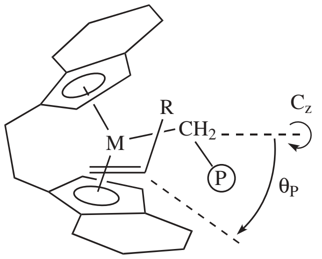


These silica-supported catalysts demonstrate the close connections between catalysis in solutions and catalysis on surfaces, but they are not industrial catalysts. However, silica is used as a support for chromium complexes, formed either from chromocene or chromium salts, that are industrial catalysts for polymerization of α-olefins (66,67). Supported chromium complex catalysts are used on an enormous scale in the manufacture of linear polyethylene in the Unipol and Phillips processes (see OLEFIN POLYMERS). The exact nature of the catalytic sites is still not known, but it is evident that there is a close analogy linking soluble and supported metal complex catalysts for olefin polymerization.

The newest industrial catalysts for olefin polymerization are supported metal complexes, metallocenes (eg, zirconocenes) promoted by aluminum-containing components such as methylalumoxane (68). These are used for polymerization of ethylene and for the stereospecific polymerization of propylene giving high yields of isotactic polypropylene; they are also used for synthesis of copolymers. The discovery and rapid development of the large new class of supported catalysts is one of the major successes of industrial catalysis in recent years.

The conceptual link between catalysis in solution and catalysis on surfaces extends to surfaces that are not obviously similar in structure to molecular species. For example, the early Ziegler catalysts for polymerization of propylene were α-$TiCl_3$. (Today, supported metal complexes are used instead). These catalysts are selective for stereospecific propylene polymerization. The catalytic sites are believed to be located at the edges of $TiCl_3$ crystals. The surface structures have been inferred to incorporate anion vacancies, that is, sites where Cl^- ions are not present and where Ti^{3+} ions are exposed (69). These cations exist in octahedral surroundings. The polymerization has been explained by a mechanism whereby the growing polymer chain and an adsorbed propylene bonded cis to it on the surface undergo a migratory insertion reaction (70). In this respect, there is no essential difference between the explanation of the surface catalyzed polymerization and that catalyzed in solution.

Stereospecific polymerization in solution and on surfaces incorporating analogous metallocenes has been explained in part by the steric restrictions of ligands bonded to the metal center. For example, the following structure, among numerous others, has been postulated as an intermediate in solution catalysis (71):



The steric constraints imposed by the bulky ligands cause the propylene to bond almost entirely with a single orientation with respect to the growing polymer chain, CH_2–Ⓟ, which leads to the stereoregular product.

The explanation for the stereospecificity of the surface catalysis, which preceded that for the solution catalysis, is based on the structure inferred for the α-$TiCl_3$ crystal edges; the locations of the Cl^- ions at the anion vacancies create an unsymmetrical environment whereby the growing polymer chain and the adsorbed propylene are oriented predominantly in a single, energetically favored way that leads to the stereoregular polymer as a result of a series of insertion reactions. The explanation is simplified, but again there is a strong conceptual link between molecular and surface catalysis. It is difficult to forge many such links because of the lack of detailed understanding of most surface-catalyzed reactions, which is a consequence of the complexity of the surface compositions and structures of solid catalysts.

4.8. Catalysis by Metals. Metals are among the most important and widely used industrial catalysts (72). They offer activities for a wide variety of reactions (Table 1). Atoms at the surfaces of bulk metals have reactivities and catalytic properties different from those of metals in metal complexes because they have different ligand surroundings. The surrounding bulk stabilizes surface metal atoms in a coordinatively unsaturated state that allows bonding of reactants. Thus metal surfaces offer an advantage over metal complexes, in which there is only restricted stabilization of coordinative unsaturation. Furthermore, metal surfaces provide catalytically active sites that are stable at high temperatures. For example, supported palladium catalysts have replaced soluble palladium for vinyl acetate synthesis; the advantages of the solid include reduced corrosion and reduced formation of by-products.

CO Oxidation Catalyzed by Palladium. One of the best understood catalytic reactions occurring on a metal surface is the oxidation of carbon monoxide on palladium:

$$2\,\mathrm{CO} + \mathrm{O_2} \rightarrow 2\,\mathrm{CO_2} \tag{20}$$

This reaction takes place similarly in automobile exhaust converters.

Carbon monoxide oxidation catalysis is understood in depth because potential surface contaminants such as carbon or sulfur are burned off under reaction conditions and because the rate of CO oxidation is almost independent of pressure over a wide range. Thus ultrahigh vacuum surface science experiments could be done in conjunction with measurements of reaction kinetics (73). The results show that at very low surface coverages, both reactants are adsorbed randomly on the surface; CO is adsorbed intact and O_2 is dissociated and adsorbed atomically. When the coverage by CO is $>1/3$ of a monolayer, chemisorption of oxygen is blocked. When CO is adsorbed at somewhat less than a monolayer, oxygen is adsorbed, and the two are present in separate domains. The reaction that forms CO_2 on the surface then takes place at the domain boundaries.

The available results are consistent with the following sequence of steps on the surface (73):

$$\mathrm{O_2} + 2\,S \rightarrow \mathrm{O_{2,ads}} \rightarrow\ 2\,\mathrm{O_{ads}} \tag{21}$$

$$\mathrm{CO} + S \rightarrow \mathrm{CO_{ads}} \tag{22}$$

$$\mathrm{CO_{ads}} + \mathrm{O_{ads}} \rightarrow \mathrm{CO_2} + 2\,S \tag{23}$$

$$\mathrm{CO} + \mathrm{O_{ads}} \rightarrow \mathrm{CO_2} + S \tag{24}$$

This depiction is vague because the exact nature of the sites S and their bonding with reactants are not known. The experimental results have led to an approximate potential energy diagram characterizing these elementary steps on the surface (Fig. 12) (73). This shows the role of the surface in providing an efficient pathway for the reaction. Most of the energy is liberated as the reactants are adsorbed; the activation energy for reaction of the adsorbed CO with the adsorbed O is relatively small, and this step is only slightly exothermic.

Ammonia Synthesis. Another well-understood reaction is the ammonia synthesis:

$$\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3} \tag{25}$$

This reaction is catalyzed by iron, and extensive research, including surface science experiments, has led to an understanding of many of the details (74,75). The adsorption of H_2 on iron is fast, and the adsorption of N_2 is slow and characterized by a substantial activation energy. N_2 and H_2 are both

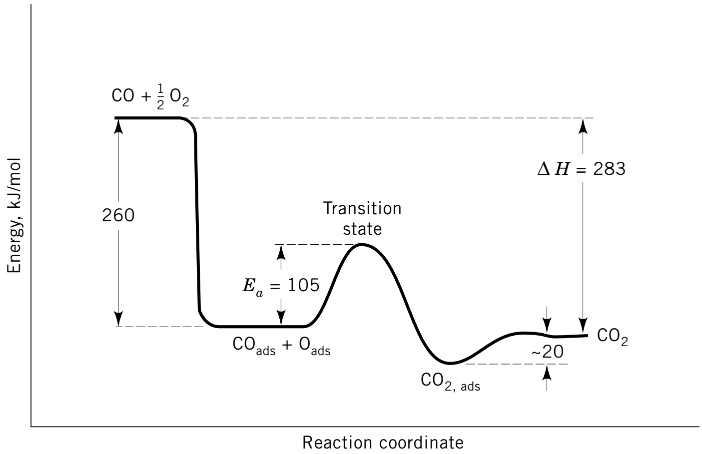


Fig. 12. Schematic potential energy diagram illustrating the changes associated with the individual reaction steps in CO oxidation on Pd (73). $E_{\mathrm{act}} = 105$ kJ/mol; $\Delta H =$ 283 kJ/mol. To convert kJ to kcal, divide by 4.184.

dissociatively adsorbed. Adsorption of N_2 leads to reconstruction of the iron surface and formation of structures called iron nitrides that have depths of several atomic layers with compositions of approximately Fe_4N. There is a bulk compound Fe_4N, but it is thermodynamically unstable when the surface structure is stable. Adsorbed species such as the intermediates NH and NH_2 have been identified spectroscopically.

The following sequence of steps explains the observations (73):

$$N_2 + 2\,S \rightarrow 2\,N_{\mathrm{ads}} \tag{26}$$

$$H_2 + 2S \rightarrow 2\,H_{\mathrm{ads}} \tag{27}$$

$$N_{\mathrm{ads}} + H_{\mathrm{ads}} \rightarrow NH_{\mathrm{ads}} + S \tag{28}$$

$$NH_{\mathrm{ads}} + H_{\mathrm{ads}} \rightarrow NH_{2,\mathrm{ads}} + S \tag{29}$$

$$NH_{2,\mathrm{ads}} + H_{\mathrm{ads}} \rightarrow NH_3 + 2\,S \tag{30}$$

where S refers to surface sites, the exact nature of which is unknown. An approximate potential energy diagram for this sequence of steps is shown in Figure 13, which shows how the catalyst facilitates the bond breaking reactions. The energy gain resulting from the formation of the strong metal–nitrogen and metal–hydrogen bonds makes the first steps endothermic. The dissociative adsorption of N_2 is rate determining, not because of a high activation energy barrier but because the frequency factor, (preexponential factor) in the rate

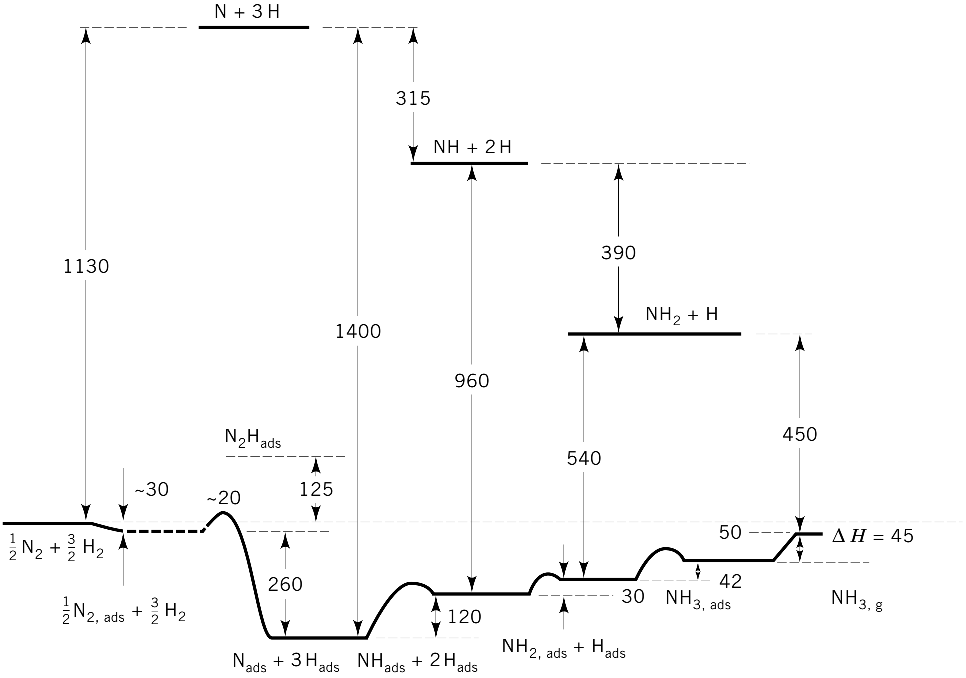


Fig. 13. Schematic potential energy diagram for the catalytic synthesis and decomposition of ammonia on iron. The energies are given in kJ/mol; to convert kJ to kcal, divide by 4.184 (73).

constant is small. The ammonia synthesis mechanism is so well understood that rates of the reaction under practical conditions have been predicted from the rate of adsorption of N_2 measured under low-pressure conditions, far from those of practical catalysis, combined with the equilibria of the other steps (75) . The prediction was within a factor of two of the observed rate of the industrial reaction. This result is a satisfying consolidation of decades of fundamental research motivated by an important catalytic process.

The industrial catalysts for ammonia synthesis consist of far more than the catalytically active iron (76). There are textural promoters, alumina and calcium oxide, that minimize sintering of the iron and a chemical promoter, potassium (~1 wt% of the catalyst), and possibly present as K_2O; the potassium is believed to be present on the iron surface and to donate electrons to the iron, increasing its activity for the dissociative adsorption of N_2. The primary iron particles are ~30 nm in size, and the surface area is ~15 m^2/g. These catalysts last for years. Some newer catalysts incorporate ruthenium instead of iron.

4.9. Catalysis by Metal Oxides and Zeolites.

Metal oxides are common catalyst supports and catalysts. Some metal oxides alone are industrial catalysts; an example is the γ-Al_2O_3 used for ethanol dehydration to give ethylene. But these simple oxides are the exception; mixed-metal oxides are more common. For example, silica–alumina was used earlier as a catalyst for cracking of petroleum and is still a component of such catalysts, and bismuth molybdates were used for ammoxidation of propylene to give acrylonitrile. Metal oxides supported on metal oxides are also commonly applied. For example, rhenium oxide, Re_2O_7, supported on alumina is used for olefin metathesis, and complicated supported oxides related to bismuth molybdates are used for ammoxidation.

Metal oxide surfaces are more complex in structure and composition than metal surfaces, and they are not so easy to characterize with some ultrahigh vacuum techniques, eg, electron spectroscopies, because they are poor electrical conductors and build up electrical charge when subjected to streams of charged particles. Consequently, understanding of catalysis on metal oxide surfaces is less advanced than understanding of catalysis on metal surfaces, although significant progress has been made (77,78).

Acid–base chemistry of metal oxide surfaces is important in catalysis and is characterized by measurements such as infrared spectroscopy with adsorbed probe molecules, eg, the base pyridine. The surfaces have both basic and acidic character (79). Both OH and O groups have base strengths ranging from weak, eg, in silica gel, to moderate, eg, in γ-Al_2O_3, to strong, eg, in highly dehydroxylated MgO. Surface OH groups are acids with proton donor strengths ranging from weak, eg, in Al_2O_3, to strong, eg, in SiO_2-Al_2O_3. Metal ions exposed at surfaces are Lewis acids. Redox properties are also important in some catalytic applications, as cations in some oxides, eg, V_2O_5, can change oxidation state. Furthermore the principles of organometallic chemistry are useful in describing the interactions of organic ligands with metal ions exposed at surfaces.

Zeolites and Catalytic Cracking. Some of the best-understood catalysts are zeolites, ie, crystalline aluminosilicates (80–82). They are well understood because they have much more nearly uniform compositions and structures than amorphous metal oxides such as silica and alumina. Here the usage of amorphous refers to results of X-ray diffraction experiments; the crystallites of a metal oxide such as γ-Al_2O_3 that constitute the microparticles are usually so small that sharp X-ray diffraction patterns are not measured; consequently the solids are said to be X-ray amorphous or simply amorphous.

Zeolites contain Si, Al, and O ions and various other cations. The structures are built up of linked SiO_4 and AlO_4 tetrahedra that share O ions. These tetrahedra are arranged in a number of ways to give the different zeolites. The structures are unique in that they incorporate pores as part of the regular crystalline structures. The pores have dimensions of the order of molecular dimensions so that some molecules fit into the pores and some do not. Hence, the zeolites are molecular sieves (qv), and they are applied in industrial separations processes to take advantage of this property. Some zeolites and their pore dimensions are listed in Table 2.

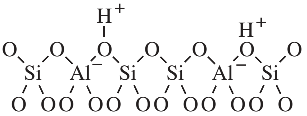
A catalytically important family of zeolites called faujasites (zeolites X and Y) is represented in Figure 14. Here the points of intersection of the lines represent Si or Al ions; oxygen is present at the center of each line. This depiction emphasizes the framework structure of the zeolite and shows the presence of the intracrystalline pore structure in which there are spaces called supercages, each with a diameter of ~1.2 nm. The pore structure is three dimensional; the supercages are connected by apertures with diameters of ~0.74 nm. Some rather large molecules can fit through these apertures (Fig. 15) and undergo catalytic reaction in the cages.

Table 2. **Zeolites and Their Pore (Aperture) Dimensions**[a]

Zeolite	CAS Registry Number	Number of oxygens in the ring	10 × Aperture dimensions, nm
chabazite	[12251-32-0]	8	3.6 × 3.7
erionite	[12510-42-8]	8	3.6 × 5.2
zeolite A		8	4.1
ZSM-5 (or silicalite)	[58339-99-4]	10	5.1 × 5.5; 5.4 × 5.6
ZSM-11		10	5.1 × 5.5
heulandite		10	4.4 × 7.2
ferrierite[b]		10	4.3 × 5.5
faujasite	[12173-28-2]	12	7.4
zeolite LTL		12	7.1
mordenite	[12173-98-7]	12	6.7 × 7.0
offretite		12	6.4

[a] The framework oxygen is assumed to have a diameter of 0.275 nm.
[b] There are also apertures with eight-membered oxygen rings in this zeolite.

The zeolite frame is made up of SiO_4 tetrahedra, which are neutral, and AlO_4 tetrahedra, which have a charge of -1. The charge of the AlO_4 tetrahedra is balanced by the charges of additional cations that exist at various crystallographically defined positions in the zeolite, many exposed at the internal surface. Zeolites are thus ion exchangers. The cations may be catalytically active. When the cations are H^+, the zeolites are acidic. Acidic zeolite Y finds enormous industrial application as a component of petroleum cracking catalysts (81). In the following simplified structure, the OH groups located near AlO_4 tetrahedra are moderately strong Brønsted acids and responsible for the catalytic activity for many reactions:



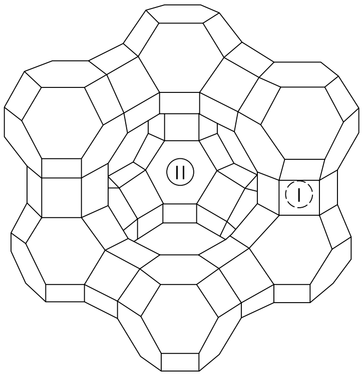


Fig. 14. Schematic representation of the structure of a faujasitic zeolite. I and II indicate cation positions.

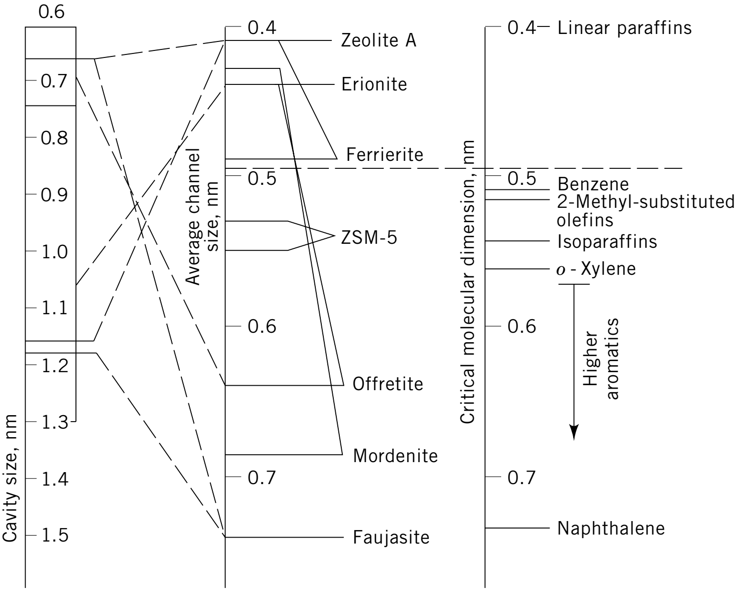


Fig. 15. Pore dimensions of zeolites and critical dimensions of hydrocarbons (82).

Zeolites are named to represent the exchangeable cations in them; eg, zeolite NaY is zeolite Y with sodium ions in the cation exchange positions.

Another catalytically important zeolite is ZSM-5. There is a three-dimensional network of pores in this zeolite, represented in Figure 16. A set of straight parallel pores is intersected by a set of perpendicular zigzag pores. These pores are smaller than those of the faujasites (Fig. 15). ZSM-5 is classified as a medium pore zeolite, the faujasites are large pore zeolites, and zeolite A (Table 2) is a small pore zeolite.

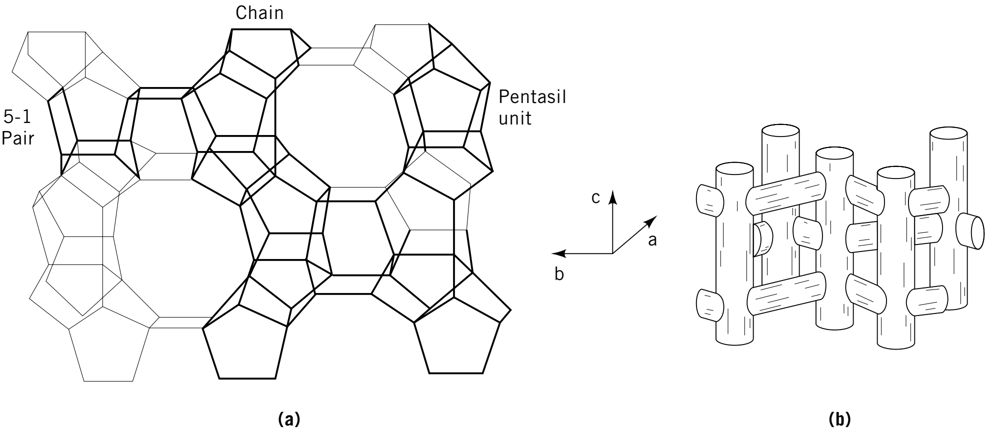


Fig. 16. Structure of the zeolite ZSM-5 (83): (**a**) framework of the zeolite; (**b**) schematic representation of the pore structure.

Both the faujasites and ZSM-5 in the acidic form catalyze many reactions that are catalyzed by other soluble and solid acids. The zeolites are not very strong acids at low temperatures, but at 500°C they are able to protonate paraffins and initiate their cracking. Almost all the catalytic applications of zeolites take advantage of their acidic properties. Activities of a family of HZSM-5 samples with different Si/Al ratios have been studied (84). When the Al contents are low, the catalytic activity is proportional to the Al content of the zeolite over a wide range of compositions. These results identify the proton-donor sites associated with the Al cations as the catalytic sites for the cracking reaction. At higher concentrations of Al in the zeolite, the dependence is no longer linear.

ZSM-5 is a component of some catalysts for cracking of petroleum (85–87), but the larger pored zeolite Y in an acidic form is the principal catalytic component. Zeolite Y is sometimes used in a form containing hydrogen ions to provide acidity and rare-earth ions such as La^{3+}, which make the structure more stable. The stability is valuable because the zeolites are deactivated in a matter of a few seconds of contact with reactant vapors in the catalytic reactor and are subjected to an atmosphere of oxygen and steam at temperatures as high as ~800°C in the regenerator where coke is burned off.

The feedstocks to crackers are petroleum fractions ranging from gas oil to residuum. They undergo a complicated set of reactions, including cracking, isomerization, disproportionation, and coke formation, that proceed through carbenium ion intermediates and give predominantly lower molecular weight products, including, eg, many in the gasoline boiling range. The patterns in the chemistry of catalytic cracking are consistent with the chemistry of hydrocarbons and carbenium ions in solution at much lower temperatures. For example, cracking of a paraffin takes place predominantly in a cycle that is initiated by formation of a carbenium ion by protonation of an olefin by the catalyst. The chain reaction is the following:

$$R^+ + R'H \rightarrow RH + R'^+ \tag{31}$$

$$R'^+ \rightarrow \text{olefin} + R^+ \tag{32}$$

The second step is a β-scission, the breaking of a carbon–carbon bond β to the charged carbon. The sum of the two reactions is the stoichiometry of the overall cracking reaction $R'H \rightarrow RH + \text{olefin}$. R^+, a relatively stable carbenium ion such as the *tert*-butyl cation, is a chain carrier. The role of the catalyst is to donate the proton to start the chain. This representation is greatly simplified.

Cracking catalysts are complex composites consisting of a support, eg, silica–alumina, and the catalytically active zeolite, present as crystallites roughly 1 μm in size dispersed in a matrix of the amorphous support (85). The catalyst particles are small, roughly 50 μm in diameter on average so that they can be fluidized by the vaporized oil entering the cracking reactor. The reactant vapors carry the catalyst particles with them; such a design is necessary because the catalyst is largely deactivated by coke after only several seconds of operation and must therefore be efficiently transported out of the reactor and into the regenerator where the coke is burned off.

The catalyst may contain ~20 wt% zeolite, and more or less is used, depending on the feedstock and operating goals. The principal component of the catalyst is the matrix, which has a relatively low catalytic activity, but it is active for cracking the molecules that are too large to fit into the zeolite pores. The matrix also plays the role of a heat-transfer medium; the cracking reactions are fast and endothermic, and the temperature of the catalyst and the rates of the reactions fall as the catalyst is carried by the oil vapors from the inlet toward the outlet of the reactor. The thermal mass of the matrix keeps the temperature drop from being too large and causing the cracking rate to fall off too quickly. After leaving the reactor, the catalyst is heated up in the regenerator where the coke is burned off and reenters the reactor at a suitably high temperature.

In addition to the matrix and the catalytically active zeolite, there are small amounts of a supported metal such as platinum on alumina, which catalyzes CO oxidation in the regenerator and minimizes the emissions of CO. There are also metal oxide components that minimize the emission of SO_x formed in the regenerator from combustion of organosulfur compounds from the oil. The metal oxides react with SO_x in the regenerator to make stable metal sulfates. Cycled with the regenerated catalyst to the reducing atmosphere of the cracking reactor, the sulfates are converted into H_2S, which is removed by scrubbing the effluent gas stream.

The discovery of new zeolites continues apace, and the newer ones tend to have larger pores than those discovered earlier (88). Zeolites can be modified by incorporation of cations in the crystalline lattice which are not exchangeable ions, but can play catalytic roles. For example, silicalite, which has the structure of ZSM-5 but without Al, incorporating Ti in the lattice, is a commercial catalyst for oxidation of phenol with H_2O_2 to give diphenols; the catalytic sites are isolated Ti cations (89).

There are numerous structures that are similar to zeolites, such as aluminophosphate molecular sieves, AlPOs, and these are finding increasing catalytic applications. A new process for removal of wax by isomerization to remove straight-chain paraffins reportedly uses a nonzeolitic molecular sieve. Unidimensional pores are selective in producing highly branched products and few cracking products; the products has a low pour point and a high viscosity index (90).

Shape-Selective Catalysis. The zeolites are unique in their molecular-sieving character, which is a consequence of their narrow, uniform pores (81,91). The transport of molecules in such small pores is different from that in the larger pores of typical catalysts. Figure 17 is a schematic representation of the diffusion coefficients of molecules in pores (92). When the pore diameters are large in comparison with the dimensions of the diffusing molecules, then molecular diffusion occurs, as it does in a fluid phase. When the pores become smaller, the interactions of the molecules with the pore walls become dominant, and Knudsen diffusion occurs. When the pores become so small that the molecules barely fit through them, then configurational diffusion occurs. This diffusion may be characterized by a substantial activation energy; the rate of diffusion is a strong function of the pore and molecule sizes in this regime. In the limit, a pore is too small for a molecule to fit in, and the diffusion coefficient becomes zero.

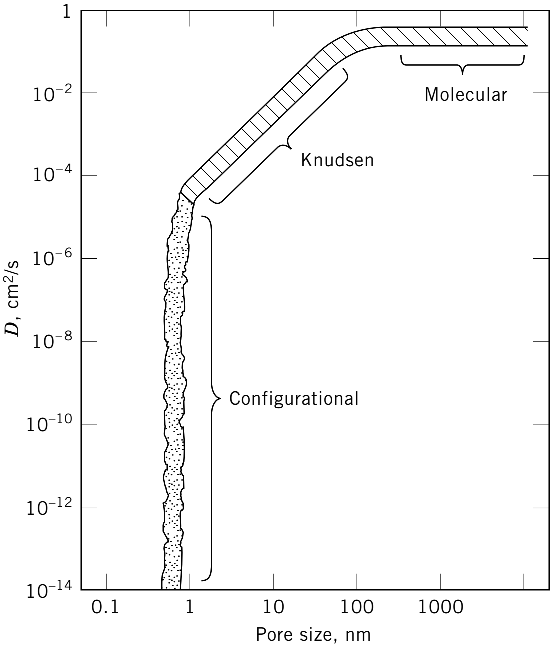


Fig. 17. Schematic representation of the regimes of diffusion in pores (92).

Catalytic processes have been developed to take advantage of the unique transport and molecular sieving properties of zeolites. The zeolite that has found the most applications is the medium-pored HZSM-5 (81,91). The term shape-selective catalysis is applied to describe the unique effects. There are different kinds of shape selectivity. Mass transport shape selectivity is a consequence of transport restrictions whereby some species diffuse more rapidly than others in the zeolite pores. In the simplest kind of shape-selective catalysis, small molecules in a mixture enter the pores and are catalytically converted whereas large molecules pass through the reactor unconverted because they do not fit into the pores where the catalytic sites are located. This statement is slightly oversimplified as there are a few catalytic sites on the outer surfaces of zeolite crystallites. Similarly, product molecules formed inside a zeolite may be so large that their transport out of the zeolite may be very slow, and they may be converted largely into other products that diffuse more rapidly into the product stream. A different kind of shape selectivity is called restricted transition state selectivity (81,91). It is not related to transport restrictions; rather, it is related to the size restriction of the catalyst pore that suppresses the formation of the transition state for a certain reaction, whereas it may not suppress the formation of a smaller transition state for another reaction. A way to diagnose the nature of the shape selectivity is to use zeolite crystallites of various sizes as the catalyst. Mass transport selectivity is influenced by the particle size; restricted transition state selectivity is not.

For example, HZSM-5 is a component of some cracking catalysts. It selectively cracks the straight-chain paraffins rather than the branched paraffins because of restricted transition state selectivity. This is a desired processing goal as the straight-chain isomers have lower octane numbers than the others and are less desirable gasoline components. In this example, the catalyst favors the reaction of the straight-chain compounds, even though they are intrinsically less reactive because they initially form secondary rather than the more stable and easily formed tertiary carbenium ions. Thus the pore size restriction reverses the pattern of selectivity that would be expected on the basis of the intrinsic chemistry alone.

Mass transport shape selectivity is illustrated by a process for disproportionation of toluene catalyzed by HZSM-5 (81,91). The desired product is *p*-xylene; the other isomers are less valuable. The ortho and meta isomers are bulkier than the para isomer and diffuse less readily in the zeolite pores. This transport restriction favors their conversion to the desired product in the catalyst pores; the desired para isomer is formed in excess of the equilibrium concentration. Xylene isomerization is another reaction catalyzed by HZSM-5, and the catalyst is preferred because of restricted transition state shape selectivity (91). An undesired side reaction, the xylene disproportionation to give toluene and trimethylbenzenes, is suppressed because it is bimolecular and the bulky transition state cannot readily form.

Mixed-Metal Oxides and Propylene Ammoxidation. The best catalysts for partial oxidation are metal oxides, usually mixed-metal oxides. For example, phosphorus–vanadium oxides are used commercially for oxidation of *n*-butane to give maleic anhydride, and oxides of bismuth and molybdenum with other components are used commercially for oxidation of propylene to give acrolein or acrylonitrile. A key to the success of a hydrocarbon oxidation catalyst is its ability to convert the hydrocarbon selectively to a partially oxidized product, rather than CO_2; this is difficult because the partially oxidized product is intrinsically more reactive than the hydrocarbon, especially when it is a paraffin.

The surface of a mixed-metal oxide exposes two kinds of metal ions in addition to O^{2-} ions and OH groups. Selective oxidation of hydrocarbons, represented schematically in Figure 18 (10), takes place on surface sites having oxygen atoms of limited reactivity, associated with the metal M_1 in the figure. These react with a hydrocarbon to give water and a partially oxidized organic compound rather than CO_2. The surface sites are reoxidized by other components of the solid catalyst rather than by O_2 directly. A second metal plays the role of an intermediary and oxygen is transported as ions through the bulk of the mixed metal oxide catalyst. A compensating transport of electrons and reaction of O_2 with the surface at sites different from those where the hydrocarbon is adsorbed make the process cyclic. Essentially this same pattern has already been illustrated by the Wacker oxidation, whereby the hydrocarbon reacts with an oxide, H_2O, in a step mediated by palladium, and a second metal, eg, copper, reacts with O_2 and then reoxidizes the palladium.

An important industrial partial oxidation process is the conversion of propylene to acrylonitrile:

$$CH_2{=\!=}CHCH_3 + \frac{3}{2}\,O_2 + NH_3 \rightarrow CH_2{=\!=}CHCN + 3\,H_2O \qquad (33)$$

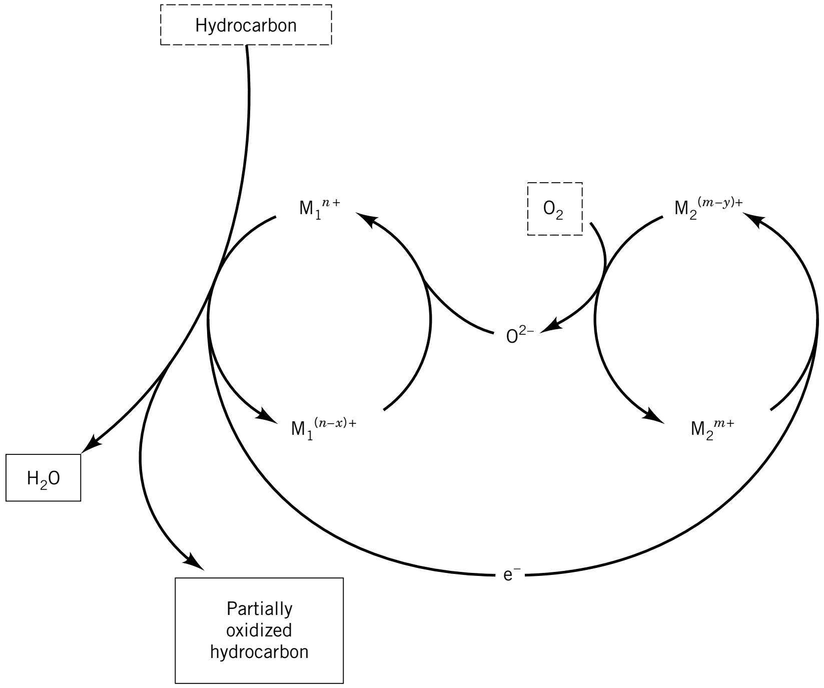
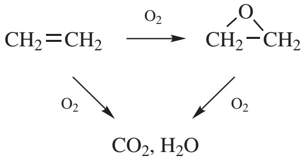


Fig. 18. Schematic representation of the catalytic cycle for ammoxidation of propylene and related reactions. M_1 and M_2 represent the two metals in a mixed-metal oxide catalyst (10).

The first catalysts used commercially to convert the propylene with high selectivity were mixed oxides of bismuth and molybdenum, referred to as bismuth molybdates. Improved catalysts consisting of a number of solid phases have been developed, with each generation becoming more complicated than its predecessor. Among the catalysts cited in a patent is the following: $Co_6^{2+}Ni_2^{2+}Fe_3^{3+}Bi^{3+}(MoO_4)_{12}$ on 50 wt % SiO_2 with some P and K (93). Silica is the support. The other components provide new functions, perhaps making the catalyst more stable. The catalysts are mechanically stable and used in fluidized-bed reactors at low pressures ~100 kPa (~1 atm), and temperatures of ~400–500°C. Years of development and improvement of catalysts for this process have led to the recognition that lattice oxygen of certain multivalent transition-metal oxides serves as a versatile, selective oxidizing agent, and these sites must be site isolated on the catalyst surface (94).

4.10. Catalysis by Supported Metals. Metals used in industrial catalysis are often expensive, and they are predominantly used in a highly dispersed form. Metal species dispersed on supports may be as small as the mononuclear chromium and zirconium complexes used for olefin polymerization, or they may be clusters containing as few as ~10 metal atoms (95), or they may be larger particles that have three-dimensional structures and resemble small chunks of metal. The surfaces of the latter expose a number of different crystal faces, and if the particles are larger than ∼5 nm the distribution of crystal faces may be almost independent of particle size and shape. The smaller clusters, however, are less like bulk metals and are more likely to have unique structures and catalytic properties. The interactions between the metals and the support may be thought of as effects comparable to the ligand effects in molecular catalysis; the catalytic properties are sensitive to the structure and size of the metal cluster (95).

Ethylene Oxidation to Ethylene Oxide. A thoroughly investigated reaction catalyzed by a supported metal is the commercially applied partial oxidation of ethylene to give ethylene oxide (96). The desired reaction is the formation of ethylene oxide, ie, epoxidation; the following reaction scheme is a good approximation:



The selective oxidation is catalyzed by silver, which is the only good catalyst. Other olefins are not converted selectively to the epoxides in the presence of silver . However, propylene epoxidation is applied commercially; the catalysts are either molybdenum complexes in solution or solids containing titanium (see ETHYLENE OXIDE; PROPYLENE OXIDE).

The ethylene epoxidation catalysts (Fig. 9) are multicomponent mixtures consisting of a support (α-Al_2O_3), the catalytically active component (silver particles), and chemical promoters (alkali metal ions such as $Cs^+$and perhaps anions such as sulfate), and a binder; the older literature also describes textural promoters. Furthermore, trace amounts of chlorine-containing compounds such as ethylene dichloride are continuously added with the feed; these compounds, like the alkali metal promoter, increase the selectivity of the catalyst for ethylene oxide. The data of Figure 19 illustrate the role of an alkali metal promoter (97). Extremely small amounts of the promoter markedly improve the selectivity of the catalyst; selectivities as high as 80% are reported. Under conditions of the catalytic oxidation, the silver surface is covered with a layer of oxygen and may be more properly described as an oxide than as a metal. There is only an incomplete understanding of the nature of the catalytic sites, the role of promoters, and the bonding of the reactants to the catalyst surface.

The support needs to be inert, which explains the choice of α-Al_2O_3; most metal oxides, including transition aluminas, catalyze unselective oxidation. The catalyst has a low surface area, ∼1 m^2/g, and large pores to minimize the influence of intraparticle diffusion, which would reduce the selectivity.

A new process for epoxidation of butadiene with a supported silver catalyst has recently been announced (98).

Naphtha Reforming and Bifunctional Catalysis. In some supported metal catalysts the support is not just an inert platform but plays an active catalytic role. This point is illustrated by catalysts for reforming of naphtha to make high octane number gasoline, a process that is a classic example of bifunctional

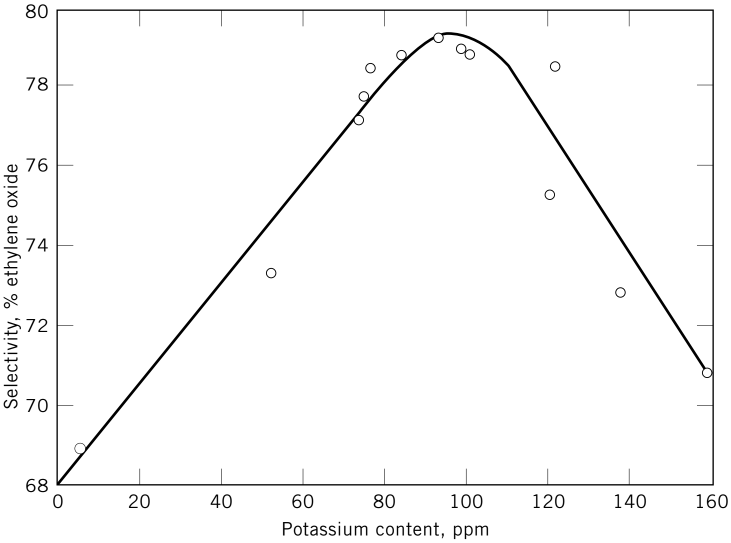


Fig. 19. Promotion of ethylene oxidation by potassium. The selectivity is the percentage of ethylene converted to ethylene oxide (97).

surface catalysis (99). The catalysts consist of metal, originally platinum (100), but now largely rhenium–platinum or tin–platinum, on a transition alumina, γ-Al_2O_3 or $\eta'''''\lambda_{-}O_3$. Platinum is chosen because it is more active than any metal except iridium in a number of reactions that increase the octane number of paraffins without substantially changing their molecular weights. These reactions include dehydrogenation, eg, conversion of methylcyclohexane to toluene, and dehydrocyclization, eg, conversion of *n*-heptane to toluene. Skeletal isomerization is also desired, but platinum has only a low activity for this reaction. Rather, the reaction is acid catalyzed. Consequently, platinum supported on an amorphous solid acid is a good catalyst.

The support must not be too strongly or too weakly acidic; chlorided Al_2O_3 is optimal. The catalyst works well for reforming although the individual functions, ie, the metal and the acid, alone do not. The metal alone does not catalyze the branching reactions; they require an acidic function to generate carbenium ions, which undergo the desired isomerization. The acidic function alone is not sufficient to generate the carbenium ions; if it were so strongly acidic, the catalyst would be deactivated rapidly by carbonaceous deposits. The metal in the catalyst catalyzes dehydrogenation of paraffins to give olefins, which are easily protonated and thereby converted by carbenium ion routes.

Some reforming processes operate with platinum on alumina catalysts at ~500°C and high pressures, eg, 5 MPa (50 atm), with the reactant stream containing predominantly hydrogen (33,99). It is unusual for a process in which hydrogen is produced to be carried out in the presence of excess hydrogen, but this is done to minimize catalyst deactivation. Coke causes deactivation, but the high partial pressure of hydrogen retards coke formation as aromatic coke precursors and coke are hydrogenated. Catalyst regeneration by controlled coke burnoff may be needed only about twice a year.

However, there is a disadvantage to the high hydrogen partial pressures that became especially apparent with the removal of tetraethyllead from gasoline and an increased need for reforming processes as a source of high octane number hydrocarbons. Aromatic compounds have high octane numbers, and the dehydrogenation of naphthenes, ie, cyclic paraffins, to give aromatics is favored thermodynamically at high temperatures and low hydrogen partial pressures. Therefore, there was an incentive to find a way to operate reforming processes economically at much lower pressures.

Low pressure operation became routine with the application of new catalysts that are resistant to deactivation and withstand the low pressures. The catalysts are bimetallic, eg, incorporating tin or rhenium as well as platinum (101,102). The structures of these catalysts are still not well understood, but they likely involve cationic forms of tin or rhenium, and the latter resists deactivation better than the monometallic catalyst, especially in the presence of sulfur-containing compounds.

There are now a number of applications of supported bimetallic catalysts. In some instances, the role of the added metal is to isolate the atoms of the other metal at the surface, thereby reducing the rates of reactions that require ensembles of the atoms as the catalytic sites. These reactions are called structure-sensitive reactions (103). Some reactions, such as olefin hydrogenation, are structure-insensitive reactions; they seem to be catalyzed by isolated metal centers on surfaces, much as the Wilkinson hydrogenation is catalyzed by mononuclear metal complexes. Iridium–platinum catalysts have been used for naphtha reforming, and one of the roles of the platinum may be to combine with the iridium in alloylike bimetallic clusters to suppress an undesired structure-sensitive reaction, viz, paraffin hydrogenolysis (103). This reaction takes place in reforming and is largely undesired because it reduces the molecular weight range.

4.11. Catalysis by Metal Sulfides.

Metal sulfides such as MoS_2, WS_2, and many others catalyze numerous reactions that are catalyzed by metals (104). The metal sulfides are typically several orders of magnitude less active than the metals, but they have the unique advantage of not being poisoned by sulfur compounds. They are thus good catalysts for applications with sulfur-containing feeds, including many fossil fuels.

Metal sulfide catalysts are widely applied in hydroprocessing of petroleum. The reactions include hydrogenation, hydrodesulfurization, and hydrodenitrogenation (105). Hydrodesulfurization is the reaction of organosulfur compounds with hydrogen to give hydrocarbons and H_2S; hydrodenitrogenation gives hydrocarbons and ammonia. Hydrodesulfurization is carried out to remove sulfur from feeds to naphtha reformers because the metals in the reforming catalysts are poisoned by sulfur. Hydrodesulfurization of heavy petroleum fractions is carried out to minimize formation of SO_x resulting from combustion of the fuels. Hydrodenitrogenation is carried out to remove basic nitrogen-containing compounds from fuels that are later hydrocracked, as hydrocracking catalysts have acidic components that are poisoned by the basic nitrogen-containing compounds.

MoS_2 is one of the most active hydroprocessing catalysts, but it is expensive, and the economical way to apply it is as highly dispersed material on a support, γ-Al_2O_3. The activity of the supported catalyst is increased by the presence of promoter ions, Co^{2+} or Ni^{2+}. The structures of the catalysts are fairly well understood; the MoS_2 is present in extremely small layer structures only a few atoms thick on the support surface, and the promoter ions are present at the edges of the MoS_2 layers, where the catalytic sites are located (106,107).

The catalysts are prepared by impregnating the support with aqueous salts of molybdenum and the promoter. In acidic solutions, molybdate ions are present largely in the form of heptamers, $[Mo_7O_{24}]^{6-}$, and the resulting surface species are believed to be present in islands, perhaps containing only seven Mo ions. Before use, the catalyst is treated with H_2 and some sulfur-containing compounds, and the surface oxides are converted into the sulfides that are the catalytically active species.

The applications of supported metal sulfides are unique with respect to catalyst deactivation phenomena. The catalysts used for processing of petroleum residua accumulate massive amounts of deposits consisting of sulfides formed from the organometallic constituents of the oil, principally nickel and vanadium (108). These, with coke, cover the catalyst surface and plug the pores. The catalysts are unusual in that they can function with masses of these deposits that are sometimes even more than the mass of the original fresh catalyst. Mass transport is important, as the deposits are typically formed with effectiveness factors less than unity, and in the extreme case the deposits block the pore mouths. Modeling of the transport–reaction phenomena has guided the preparation of catalysts with tailored pore structures to minimize the detriment of the deposits. These have been some of the most fruitful applications of the principles of chemical engineering in catalyst design and preparation.

5. Catalyst Development, Testing, and Production

Catalysts are discovered to meet processing needs and opportunities, but the discovery of a catalytic application to take advantage of some newly discovered material almost never occurs. Catalyst development is largely a matter of trial and error testing. The methodology was defined by Mittasch in the development of the ammonia synthesis process. Catalyst developers benefit from an extensive and diverse literature and often can formulate good starting points in a search for candidate catalysts by learning what has been used successfully for similar reactions. Deeper insights, such as would arise from understanding of the mechanistic details of a catalytic cycle, are usually not attained; the exceptions to this rule largely pertain to molecular catalysis, usually reactions occurring in solution. Fundamental insights were valuable in guiding the development of the process for chiral hydrogenation and that for methanol carbonylation, among others, but it would be inappropriate to infer that understanding of the fundamental chemistry led to straightforward design of the catalysts. Indeed, the initial working hypothesis about the chiral hydrogenation turned out to be incorrect. The more complicated processes of surface catalysis are for the most part only partially understood even when the processes are established and extensive after-the-fact research has been done. Creative research in catalyst discovery and development is usually the result of intuition and partial understanding combined with efficient testing and serendipity. Researchers who are repeatedly successful in finding new and improved catalysts seem to recognize needs and opportunities and notice significant exceptions to expected patterns and reason inductively by imperfect analogies.

Catalyst testing and evaluation have been revolutionized by computers, automated and miniaturized test reactors, and analytical methods. Combinatorial methods are playing an increasing role in the preparation and testing with modern equipment. Researchers can systematically prepare and screen many catalysts in a short time and efficiently determine, not only the initial catalytic activity and selectivity, but also the stability and the appearance of trace products that may indicate some new catalytic properties worthy of further development.

Catalyst design is in a primitive stage. There are hardly any examples of true design of catalysts. However, development of improved catalysts has been guided successfully in instances when the central issues were the interplay of mass transport and reaction. An example is catalysts used for hydroprocessing of heavy fossil fuels.

Almost all industrial catalysts are developed by researchers who are motivated to improve processes or create new ones. Thus the organization that first uses a new catalyst is usually the one that has discovered it. This organization, however, only rarely becomes the manufacturer of the catalyst used on a large scale. Catalysts are for the most part highly complex specialty chemicals, and catalyst manufacturers tend to be more efficient than others in producing them. Catalyst manufacturing is a competitive industry. Catalyst users often develop close relations with catalyst manufacturers, and the two may work together to develop and improve proprietary catalysts.

6. The Catalysis Literature

Catalysis is a broad, complex subject that is documented in many and varied sources. The field is rich in opportunity, in part because there is so much information that it is possible to find nuggets that competitors miss. Industrial catalysis is a competitive field, and much practical knowledge is proprietary.

The literature consists of patents, books, journals, and trade literature. The examples in patents may be especially valuable. The primary literature provides much catalyst performance data, but there is a lack of quantitative results characterizing the performance of industrial catalysts under industrially realistic conditions. Characterizations of industrial catalysts are often restricted to physical characterizations and perhaps activity measurements with pure component feeds, but it is rare to find data characterizing long-term catalyst performance with impure, multicomponent industrial feedstocks. Catalyst regeneration procedures are scarcely reported. Those who have proprietary technology are normally reluctant to make it known. Readers should be critical in assessing published work that claims a relevance to technology.

Often the catalysts described in the literature are not quite the same as those used in industrial processes, and often the reported performance is for pure single-component feeds. Sometimes the best quantitative approximations that can be made from the available literature are those based on reported kinetics of reactions with pure feeds and catalysts that are similar to but not the same as those used in practice. As a first approximation, one may use the published results and scale the activity on the basis of a few laboratory results obtained with realistic feeds and commercially available catalysts.

Catalyst suppliers are valuable sources of information. They often have extensive experience testing catalysts in long-term operation with real industrial feedstocks and may be willing to share information to improve their chances of selling a catalyst. Also they may work with a potential customer to develop catalysts that they could then supply. There is an extensive literature produced by catalyst manufacturers and organizations that license and market catalytic technology. This trade literature should be read critically as its purpose is to generate sales, but it often contains valuable information. Catalyst manufacturers and those who license and sell technology are motivated to demonstrate their technical knowledge. Their success in marketing depends on their technical reputations and their reliability in supplying catalysts and technology that consistently meet specifications.

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