Heterogeneous Catalysts

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Summary. Proven catalysts exist in many different forms and with many different kinds of composition. An understanding of how catalysts function is beginning to emerge in a few areas, and some superior catalysts have been developed as a result of this knowledge. Applications of new techniques and disciplines should lead to impressive advances in the years ahead.

A catalyst is defined as a substance that accelerates a chemical reaction without itself being consumed. The degree of acceleration can be enormous, sometimes more than a factor of 10^{10}. However, the ability of certain catalysts to direct a chemical reaction is even more impressive and useful. For example, passing propylene and oxygen over bismuth oxide produces hexadiene and benzene, whereas passing the same mixture under the same conditions over a molybdate catalyst produces acrolein.

Catalysts used in commercial processes do not, in fact, remain unaltered. They have lifetimes that vary from seconds to years. Catalysts with very short lifetimes can be useful if appropriate regeneration schemes are included. For example, zeolite catalysts used for the cracking of petroleum have effective lifetimes of only a few seconds but are regenerated on a continuous basis. Catalysts that last weeks to years are also sometimes regenerated; at other times they are discarded. Many catalysts in effect are regenerable reagents. For these catalysts dynamic processes in the bulk as well as at the surface are important.

Catalysts play critical roles in energy production, transformation, storage, and utilization. They are also essential for pollution abatement, production of numerous chemical products, and in many other ways. The field of heterogeneous catalysis has become a technologically advanced field without a sound scientific foundation. Our basic understanding of how catalysts function is very limited. Materials scientists have largely ignored the field of heterogeneous catalysts, partly because the task of bringing order to the field appears overwhelming. The situation is currently changing because of the advent of many new analytical techniques and the realization of the social and economic importance of the field. Society's ability to cope with pending energy shortages during the next decades may well depend on our ability to design new and better catalysts. We can hope to provide such catalysts only if we gain an improved understanding of current catalysts.

Catalysts exist in many different forms. They can be metals, alloys or multimetallics, sulfides, oxides, nitrides, carbides, or mixtures of these. Some are single phase; others are composed of several phases. Catalysts can be used in bulk form such as gauze. Many are sufficiently crystalline to produce good diffraction patterns. Other catalysts are amorphous or are composed of particles too small to diffract. Catalysts can be electrically insulating, semiconducting, or metallic. Surface properties of catalysts are always important; frequently, bulk properties are also important.

There are hundreds of catalysts and hundreds of different reactions for which catalysts are used. Rather than attempting to survey the whole field in this article, I will present the current understanding of catalysts in several different and important areas. Recent advances in these areas have been impressive, and there is reason to be optimistic that advances in the next few years will be even more profitable.

Metal Catalysts

Many different transition metals are used as catalysts. Since most of these are easily oxidized, their use tends to be restricted to reactions of a reducing nature, for example, hydrogenation. Metals used as oxidation catalysts generally take up considerable amounts of oxygen. For example, when platinum is used as an oxidation catalyst, its surface may be largely platinum oxide (*1*).

Metal catalysts are sometimes used in bulk form as pure metal or as alloys. More commonly, metals are dispersed on supports such as silica, alumina, or carbon. If the metal is very expensive, and this is frequently the case, then such dispersion is of economic importance. The dispersion can be very great with essentially every metal atom available for catalysis.

Although a support may be used for some practical reasons such as economics or physical strength, the support may also play a critical role in the catalytic reaction.

1) Some cations tend not to be reduced to the metal on certain supports. This behavior is often encountered when iron is supported on oxides such as alumina.

2) The pore structure of the support can have considerable influence during catalysis. This occurs when a metal is supported within the pores of a zeolite structure, for example, but even the pore structure of an amorphous support can influence catalytic properties (*2*).

3) The morphology of a metal particle may be different on different supports. For example, a metal may wet some supports but not others.

4) The pattern of metal particles on the support may be governed by the surface structure of the support.

5) The supported metal may interact chemically with the support. For example, there is evidence that platinum will take aluminum into solid solution when a platinum on alumina catalyst is heated to high temperatures under hydrogen (*3*).

6) A spillover mechanism may be in operation. There are several different variations of this; the best known example is hydrogen spillover (*4*). Hydrogen is adsorbed and dissociated on the metal particles. This activated hydrogen then spills over on the oxide support such as silica or alumina (*5*). Organic molecules adsorbed on the oxide surface may then react with the activated hydrogen.

7) A metal-support interaction cur-

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rently receiving wide attention involves a charge-transfer mechanism. When two materials are placed in contact with each other, there is a flow of electrons from one material to the other because their Fermi levels have different energies. Thus one material assumes a positive charge, and the other a negative charge. In the case of metals in contact with insulating oxides, the electron flow will generally be from the metal to the oxide. The amount of charge transfer is difficult to measure or to predict theoretically, but it appears to depend on metal particle size as well as surface states, such as Lewis acid centers, on the support. Results from both XPS (x-ray photoelectron spectroscopy) and EXAFS (extended x-ray absorption fine structure) have indicated that metals such as platinum take on a positive charge when they are well dispersed on insulating supports such as silica, alumina, and zeolites (*6*). The effect is such that one may regard a metal as having moved to the left within a row of the periodic table. The amount of charge transfer is limited by the insulator because it does not have an abundance of empty states of appropriate energy to accept the electrons. Thus this type of charge transfer, although real, may be regarded as weak relative to some recently discovered effects.

A strong metal-support interaction is observed when a platinum group metal is supported on reduced TiO_2 (*7*). Such materials are prepared by intially supporting the metal on fully oxidized TiO_2. Subsequent hydrogen reduction at low temperature (~ 200°C) leads to a material showing normal hydrogen chemisorption. However, hydrogen reduction at higher temperatures (~ 400°C) leads to a great decrease in the ability of the catalyst to chemisorb hydrogen. Detailed studies have indicated that this is not due to a loss of metal surface area (*7*). Nevertheless, the TiO_2 becomes reduced, and the metal particles take on a negative charge (*8*). The apparent reason for this direction of the charge flow is indicated in Fig. 1. When TiO_2 is reduced, its Fermi level energy is increased until it is actually above that of the metal. Thus there is a flow of electrons from the TiO_{2-x} to the metal. This effect is stronger than the more traditional and opposite charge flow because in this case there are many available electron acceptor states on the metal. One is now in a sense moving the metal to the right within a row of the periodic table. The possibilities for this charge-transfer type of support interaction are very exciting. We can control the charge of metal particles over a considerable range, and the systematic study of resultant catalytic effects has just begun.

The catalytic behavior of a metal can differ significantly on different crystallographic faces (*9*). There is also evidence that some reactions on metals occur primarily at the edges of crystallites (*9*). Thus one might expect that catalytic properties will depend on crystallite size even if the reaction rate is normalized to metal surface area. Just such an effect is generally found for reactions that require carbon-carbon bond cleavage. The specific activity for hydrogenolysis reactions can decrease by orders of magnitude with increasing particle size. In contrast, for reactions involving carbon-hydrogen bonds, such as hydrogenation and dehydrogenation, the specific activity usually remains essentially constant with varying metal particle size (*10*). Presumably in this case the reaction occurs as rapidly on crystallite faces as on the edges.

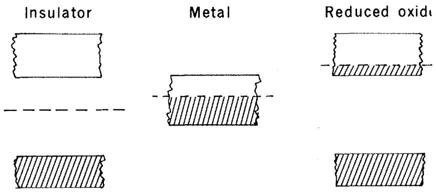

Fig. 1. Schematic energy level diagram for an insulator (for example, Al_2O_3), a metal (for example, Pt), and a reduced oxide (for example, TiO_{2-x}). Filled states are shaded, and the Fermi levels are indicated by broken lines.

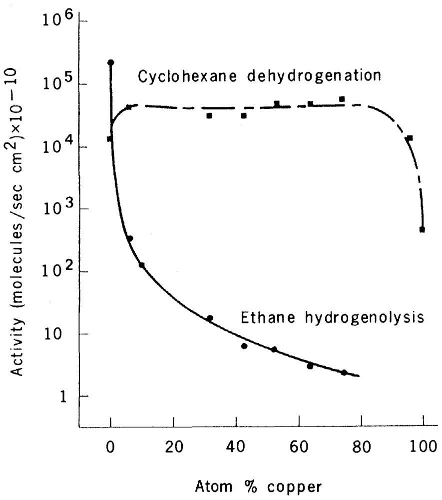

Fig. 2. Activity of Ni-Cu alloy catalysts for the hydrogenolysis of ethane to methane. [From Sinfelt (*12*)]

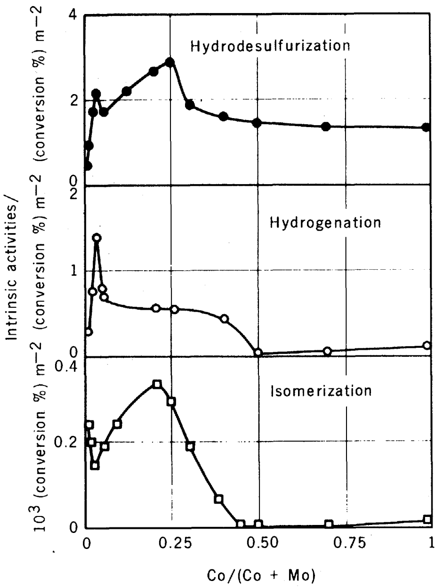

Fig. 3. Activities for hydrodesulfurization of thiophene, hydrogenation of cyclohexene, and isomerization of cyclohexane to methylcyclopentane. [After Delvaux *et al.* (*32*)]

Another variation on metal catalysts is the use of two or more metals on the same support (*11*, *12*). These are frequently referred to as bimetallic or multimetallic catalysts since the term alloy is inappropriate for isolated clusters made up of only a few metal atoms. Furthermore, the different metals may not even be in the same cluster. Originally, alloy-type catalysts were envisioned as a way of obtaining a continuous variation of properties between two metals. In fact, the catalytic properties of alloys do not generally vary linearly with changing composition (Fig. 2). The reason in the case of ethane hydrogenolysis is fairly well understood (*12*). This reaction is many orders of magnitude faster on nickel than on copper, and it is known that the surface of nickel-copper alloys is enriched with copper relative to the bulk. The surface composition of alloys is generally different from that of the bulk in a manner that is largely predictable (*13*). An interesting aspect of the surface composition is that it can be changed during catalysis because of strong chemisorption bonds of certain molecules on a specific metal of the alloy (*13*).

A reforming reaction is carried out in oil refineries to improve the octane rating of gasoline-range materials and to produce aromatics. Catalysts for this reaction were originally chromium oxide and molybdenum oxide supported on alumina. About 30 years ago platinum on alumina was found to be a much more active catalyst and to possess improved selectivity, and until about 10 years ago this was the catalyst of choice for reforming. In the late 1960's the Chevron Research Company developed a catalyst composed of platinum-rhenium on alumina, and this has properties superior to those of platinum on alumina (*11*). The initial activity of the platinum-rhenium catalyst is, in fact, no greater than that of the pure platinum catalyst. However, the high activity is maintained for a much longer time with the bimetallic catalyst. This development has had major technological consequences, and more recently a platinum-iridium bimetallic catalyst for reforming has been developed at Exxon by Sinfelt (*14, 15*). There remain many reactions for which multimetallic catalysts have not been evaluated. The number of possible metal combinations taken together with support variations leads to enormous flexibility. Undoubtedly other practical applications for such catalysts will be found. One promising area for the use of these catalysts is in the hydrogenation of carbon monoxide.

Sulfide Catalysts for Hydrodesulfurization

The hydrodesulfurization reaction is of great importance because natural gas, petroleum, and coal all contain sulfur which must be removed. This reaction can be schematically represented as

$$-CH-S- + H_2 \rightarrow -CH_3 + H_2S$$

Other reactions, such as hydrogenation or hydrodenitrogenation, usually occur simultaneously.

The most common catalyst for this reaction is frequently referred to as a cobalt molybdate catalyst. (Sometimes nickel is substituted for cobalt, and sometimes tungsten is substituted for molybdenum.) However, labeling this catalyst as cobalt molybdate is highly misleading. There are two forms of $CoMoO_4$, but neither of them is present in the working catalyst. Furthermore, despite the fact that normal preparation methods involve oxide precursors, the synthesis procedures giving best results do not involve either of the cobalt molybdates as precursors (*16*). The actual working catalyst is essentially a mixture of Co_9S_8 and MoS_2 supported on γ-Al_2O_3.

The most intriguing aspect of the cobalt-molybdenum-sulfide catalyst for hydrodesulfurization is the existence of a synergistic effect when both Co_9S_8 and MoS_2 are present. The intrinsic catalytic activity of the mixture is clearly higher than that of either end member (Fig. 3). This is true not only for the hydrodesulfurization reaction but also for the hydrogenation and isomerization reactions. The data in Fig. 3 are for unsupported sulfides, but the same type of synergistic effect exists for catalysts supported on γ-Al_2O_3.

There have been many attempts to rationalize the promoter effect of cobalt on MoS_2. Five models are discussed in a recent review by Delmon (*16*). One view is that the electrical properties of MoS_2 are altered by cobalt doping and that this in turn affects catalyst properties (*17*). Undoubtedly some doping of MoS_2 by cobalt occurs with a resulting effect on electrical properties. However, there has been no clear correlation with catalytic properties, and the maximum doping level of cobalt in MoS_2 is far below the cobalt content where the synergistic effect is most prominent.

Molybdenum disulfide has a layer-type structure, and such structures are frequently amenable to intercalation. However, it is known that cations such as cobalt and nickel do not move between the layers of MoS_2 to any significant extent. It has been proposed that there is some intercalation of these layers by cobalt or nickel at the surfaces of MoS_2 crystallites (*18*). This may well occur, and there may be implications for catalysis. However, as with the doping effect, the amount of cobalt intercalated by this mechanism is far short of that required for a completely satisfactory explanation of the synergistic effect.

Many might conclude that some ternary sulfide of cobalt and molybdenum is formed. Indeed, ternary compounds such as $CoMo_2S_4$ are known, but extensive and sophisticated studies have failed to find such compounds in catalysts used under actual reactor conditions.

One of the interesting aspects of the cobalt-molybdenum-sulfide catalysts is that the maximum synergistic enhancement occurs at different cobalt contents for different reactions (Fig. 3). This implies that different sites are involved for the different reactions, yet catalysis at these different sites is still strongly related to the synergistic effect.

Although the cobalt-molybdenum-sulfide catalyst has been extensively studied for many years in many different laboratories, the nature of the synergistic effect between Co_9S_8 and MoS_2 is not understood. One or both phases may be affected by the presence of the other. Alternatively, some sort of spillover mechanism may be involved. As with any synergistic effect of this type, catalytic properties depend not only on composition but also on the way in which these elements are put together. The microstructure of the resulting catalyst is of utmost importance.

Zeolites

Zeolites are crystalline aluminosilicates with open framework structures. These structures are so open that various organic molecules can actually diffuse in and out of the tunnels of the structures. Thus, for catalysis, a shape selectivity results since certain molecules or transition states are too large for the pores of the zeolite structures. Another important

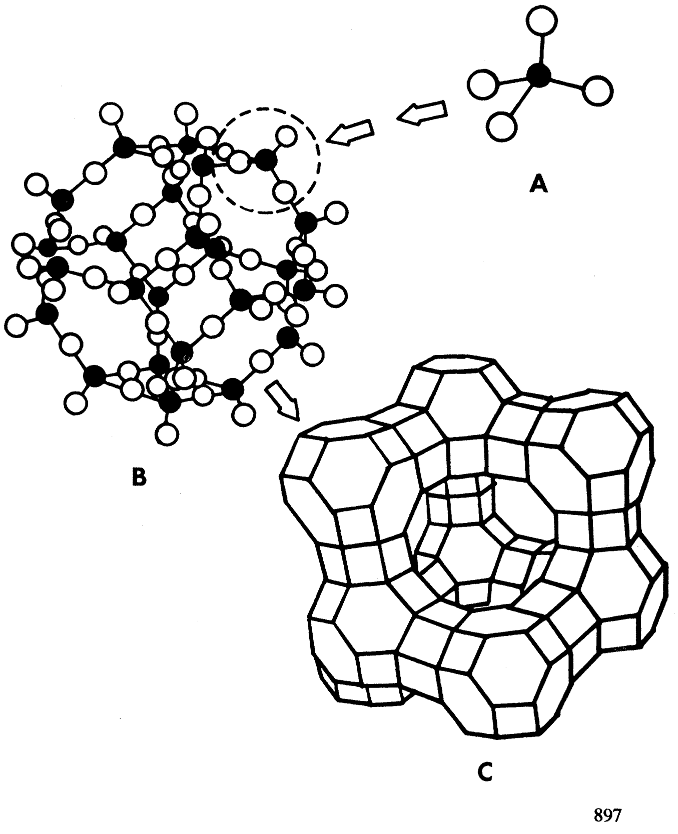

Fig. 4. The framework structure of faujasite. (A) Tetrahedral arrangement of silicon (or aluminum) atoms sharing oxygen atoms. (B) Sodalite unit consisting of 24 SiO_4^- and AlO_4^- tetrahedra. (C) Zeolite superstructure consisting of tetrahedral arrangement of sodalite units connected by oxygen bridges forming hexagonal prisms. [From Haynes (*33*)]

property of some zeolite catalysts is their exceptional acidity.

Zeolite structures are based on a framework containing silicon-oxygen tetrahedra that share corners only and are usually mixed with aluminum-oxygen tetrahedra (Fig. 4). The coordination number of all the oxygen atoms is two, and the composition of the framework is $(Si^{4+},Al^{3+})O_2$. When no Al^{3+} is present the network is electrically neutral. However, Al^{3+} is generally present, and the network has an overall negative charge which is balanced by interstitial cations or protons.

There are about 35 naturally occurring zeolites, of which about 25 have been synthesized; another 100 or so new zeolites have been synthesized during the last 30 years (*19*). The very successful gel synthesis route was developed in the late 1940's by Barrer (*20*). The gel is produced at a high *p*H from an aqueous mixture of Si^{4+}, Al^{3+}, and various alkali cations. Crystallization is normally carried out at 200° to 400°C in autoclaves. Nucleation of crystals can be rapid, irreversible, and difficult to control.

Impressive developments in zeolite synthesis have resulted recently from the use of quaternary ammonium hydroxides as a source of cations. This approach led to the first laboratory synthesis of certain naturally occurring zeolites. It has also led to the synthesis of some new and technically important zeolites such as Mobil's ZSM-5 (*21*). Another approach has been to use quaternary ammonium polymers as organic cations (*22*). Stacking faults in some zeolites cause much of the pore space to be unavailable for catalysis, but by using long-chain polymer cations these faults can be prevented so that all the pore space becomes available.

One of the most useful zeolite structures is that of the naturally occurring zeolite faujasite. The way in which this structure is built up from the tetrahedral unit is indicated in Fig. 4. The silica-to-alumina ratio is variable from about 2 to 6. Zeolites synthesized with this structure are generally referred to as either zeolite X(low silica) or zeolite Y(high silica). The free pore openings of the faujasite structure are the largest among zeolites, about 7.4 angstroms. Such pores are large enough for molecules such as the xylenes to diffuse in and out. Other zeolites have smaller pores ranging down to about 4 Å.

Acid zeolites are prepared by replacing the alkaline cations with protons. This can sometimes be accomplished by ion exchange with mineral acids. However, some zeolites, especially those with high aluminum content, are attacked by acids. Thus a better method of preparing the acid form of zeolites is by ion exchange with NH_4^+ followed by heating to drive off NH_3. Different acid sites exist in such zeolites, and some possess the acid strength comparable to that of sulfuric acid. The acid form of the faujasite zeolite was introduced into the cracking catalyst in the 1960's. Its catalytic activity is several orders of magnitude higher than that of the amorphous aluminosilicates formerly used. The use of this zeolite is currently saving the United States several hundred million barrels of crude oil per year.

Another impressive aspect of zeolite catalysts is their shape selectivity, which can be reflected in different ways.

1) If a mixture of different gases is passed over a zeolite catalyst only the smaller molecules will enter the pores and react. Thus the zeolite selectively catalyzes reactions of certain gases in the mixture.

2) On passing a gas over a zeolite

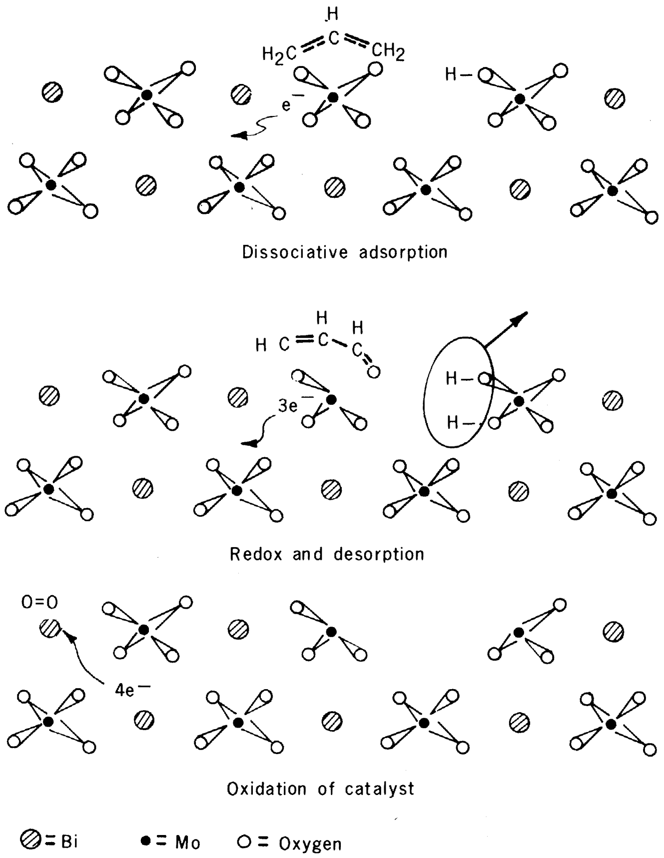

Fig. 5. Schematic of propylene oxidation showing dissociative adsorption, redox and desorption, and reoxidation of the catalyst. [After Sleight (*28*)]

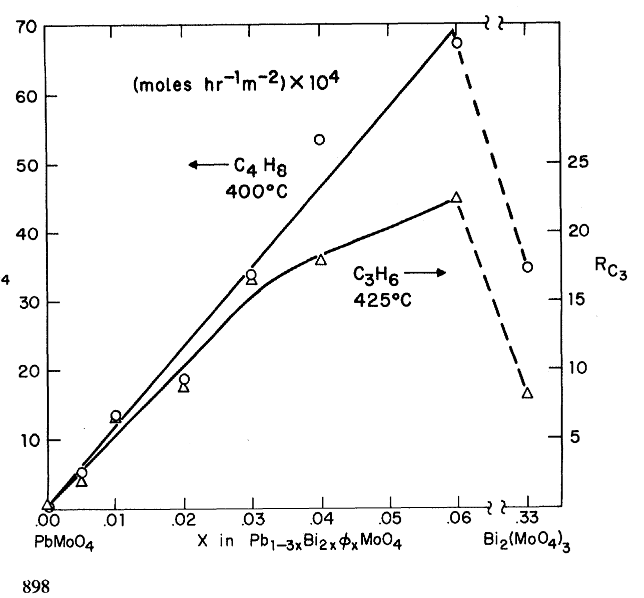

Fig. 6. Activity (*R*) for propylene oxidation to acrolein and butene oxidation to butadiene. [After Sleight and Linn (*27*)]

catalyst, some products of the reaction may be too large to leave the zeolite pores. Only the smaller molecules leave; the larger molecules stay behind and may continue to react.

3) There are also cases in which both the reactant and product gases can easily diffuse in and out of the zeolite pores but where the transition state to produce a certain product involves an intermediate which is too large for any cavity within the pore structure of the zeolite. Thus a particular reaction is effectively blocked, and shape selectivity results.

Recently, there has been a striking success based on shape-selective catalysis by a zeolite. The new synthetic zeolite ZSM-5 is an excellent catalyst for the conversion of methanol to gasoline (*21*). Pilot plants for producing gasoline by this method are now being built.

Many different cations can be exchanged into zeolites. This is frequently done to adjust the acidity in zeolites that are used for cracking. Transition metal cations exchanged into zeolites have other functions (*23*). These cations are sometimes reduced to the metal for catalyst studies or applications. Different types of activity (for example, hydrogenation activity) are introduced in this manner. Unusual and useful properties result from having such catalytic functions within the pores of a zeolite structure.

The future of catalysis by zeolites is very promising. We have only barely begun the task of evaluating zeolites for the multitude of reactions of interest. There are many different zeolites, and there are various ways in which the properties of a given zeolite can be altered. Fine tuning of the selectivity and activity is possible by many different methods, and new zeolite structures continue to be discovered.

Oxides for Selective Oxidation

Oxide catalysts are used in a variety of catalytic reactions. For the oxidation of hydrocarbons, oxides may be nonselective, complete combustion catalysts such as Co_3O_4. Alternatively, they may very selectively oxidize methanol to formaldehyde, propylene to acrolein, or butene to butadiene, for example. There are always other reactions, such as complete combustion, that might occur under the same conditions, but a good selective catalyst effectively blocks these other pathways. The most studied of the selective oxidation catalysts are the molybdates, and only these catalysts will be considered here, with olefin oxidation reactions being used as examples.

Bismuth molybdates were the first catalysts discovered for the selective oxidation of propylene to acrolein (*24*).

$$CH_3CH{=}CH_2 + O_2 \rightarrow CH_2{=}CHCHO + H_2O$$

Experiments with the use of oxygen-18 have established that the oxygen in the products originates primarily from the lattice of the catalyst (*25*). This lattice oxygen is readily available; thus, the rate of propylene oxidation is independent of the partial pressure of oxygen. This is an example of a catalyst that is, in fact, a reactant that is continually being regenerated in situ by gas-phase oxygen. Studies of the effect of deuteration of propylene on the rate of the reaction indicate that the rate-limiting step for propylene oxidation over bismuth molybdate catalysts is the dissociative chemisorption of propylene (*26*).

$$CH_3CH{=}CH_2 + O_s \rightarrow CH_2{-}CH{-}CH_2 + O_sH$$

This produces a surface allylic species, and a surface oxygen (O_s) is converted to a hydroxyl group. There is a second hydrogen abstraction, and acrolein desorbs taking a lattice oxygen (Fig. 5). Water also desorbs, and the catalyst is reduced by four electrons per propylene molecule converted to acrolein. One oxygen molecule then restores the lost electrons and the lattice oxygen. After many studies, the roles of bismuth and molybdenum in this process have become reasonably well defined.

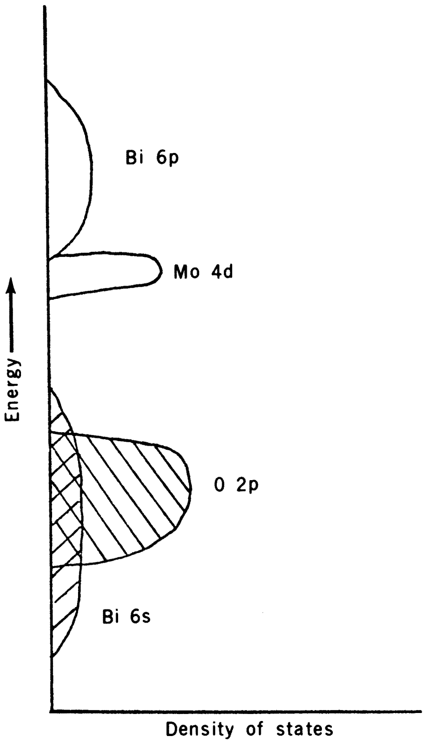

Fig. 7. Schematic energy level diagram for a bismuth molybdate.

Model studies of propylene and butene oxidation over oxides with a scheelite structure were carried out at DuPont (*27*, *28*). The scheelite structure is very simple compared to the bismuth molybdate structures, and cation vacancy defects are readily introduced. Furthermore, the bismuth-to-molybdenum ratio can be varied while retaining the same basic structure. Molybdates with a scheelite structure may be inactive, or they may be as active and selective as the bismuth molybdates (Fig. 6). In many studies the bismuth and defect concentrations were varied independently. Both the defects and bismuth enhance the reaction, but in different ways. For those catalysts with little or no bismuth, the ability of the catalyst to reoxidize itself is very poor and the rate of reaction depends on the partial pressure of oxygen. This and other data indicate that bismuth cations are the sites for catalyst reoxidation.

The site for propylene dissociative chemisorption is probably a molybdate group. This is an electron donor-acceptor interaction with analogies in homogeneous oxidation reactions. Bismuth may play some role in propylene chemisorption, but this role is secondary to its role in reoxidation of the catalyst. It has been suggested by Grasselli (*29*) that bismuth may be the site at which the abstracted hydrogen is converted to a hydroxyl group. Very recent experiments at SOHIO indicate that the bismuth role is more important for the second hydrogen abstraction (*30*). Bismuth may also play a role in propylene chemisorption because of an inductive or electronic effect. In any case this role of bismuth can be fulfilled by other cations or by defects in the case of the scheelite structure.

Since we have a model in which reduction occurs at a molybdate group and reoxidation of the catalyst occurs at a bismuth site, a special electronic structure must exist. A schematic of the energy diagram of a bismuth molybdate is shown in Fig. 7. There are two degeneracies of energy levels. The filled bismuth 6*s* band overlaps the filled oxygen 2*p* band, and this may or may not have implications for catalysis. The overlap or hybridization of the molybdenum 4*d* and bismuth 6*p* bands has profound implications for catalysis. The working catalyst is always in a slightly reduced state. During reduction, electrons are introduced into the molybdenum 4*d* levels. However, in view of the mixing of these levels, electrons in the bismuth 6*p* band are always available at any bismuth surface site where the catalyst is reoxidized. Such valence degeneracy is a necessary requirement for catalysts where reduction and oxidation occur at different sites with different cations.

Another aspect of these catalysts is that the lattice oxygen must migrate from the site of reoxidation to the site where oxygen was removed from the lattice. We know that for the most selective oxidation catalysts this process is sufficiently fast so that it does not affect the rate of olefin oxidation. It is generally believed that oxygen mobility in bismuth molybdates is very high, but there are very few reliable data. It may be of significance, however, that the highest oxygen mobility yet observed is for bismuth oxide doped with tungsten or molybdenum (*31*).

There are many different requirements for a good catalyst for selective oxidation of olefins. There must be appropriate surface sites for allyl and hydroxyl formation and for catalyst reoxidation. There must be a special electronic structure involving valence degeneracy, and there must be high oxygen mobility. Optimization of all of these factors is a fascinating challenge for a materials scientist. Here, as with most catalysts, the developments to date have been largely empirical with subsequent rationalizaton, but recent understanding is improving this situation.

Conclusions

Heterogeneous catalysis has traditionally been a largely empirical science. Many obviously critical experiments have never been performed. This has encouraged speculation on mechanisms to run rampant. Although reliable data are now emerging at an encouraging rate, much current speculation is at odds with these observations. Many simplistic explanations of catalyst behavior have not stood the test of time. The true explanation in catalysis is generally very complex, and it may encompass several of the simplistic interpretations. A good catalyst combines many important factors, as has been illustrated for the selective oxidation catalysts. All too often we do not even have a good understanding of what these various factors are. Theoretical calculations can occasionally rationalize what we know from experiment. There is hope that such calculations may soon have some predictive value.

In view of the complexity of heterogeneous catalysts, many workers shrink from the challenge of bringing understanding to this field. However, there are now many techniques to study surface composition and structure. Advances in analytical electron microscopy make it possible to see features of catalysts that we could only ponder on a few years ago. These techniques are of immense importance, but breakthroughs will require significant contributions from scientists of different disciplines.

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A new growth technique, "edge-supported pulling," has been developed in the field of photovoltaics. A sheet of silicon is solidified between graphite filaments. Solar cell efficiencies above 13 percent air mass 1 have been attained on cells made from this material. The process offers the advantages of technological simplicity, minimal skill requirement on the part of the operator, and lower cost than other sheet methods. [*Solar Energy Research Institute, Golden, Colorado*] →