# Heterogeneous Catalysis: Can Surface Science Contribute?

Many believe that catalysts will be central to solving the problems of coal gasification, coal liquefaction, pollution control, and other energy related technologies. In addition, catalysts are already of considerable economic importance. Thus, the proposition that the field of heterogeneous catalysis is entering a new era imbued with a firmer scientific underpinning is both intriguing and fraught with technological implications. Although this proposition has been heard in the past, its current appearance seems to be related to the tension that exists today between practitioners of the traditional catalysis and members of the surface science community. In brief, the question is, can surface science bring its new ideas and techniques to bear on the old problem of designing better catalysts?

As the name implies, heterogeneous catalysis involves two phases: a solid catalyst (which can be a metal, semiconductor, or insulator) and gaseous or liquid reactants which react at the surface of the catalyst. Thus the interest of surface scientists in catalysis is natural. However, it is only in the last two decades that vacuum technology has advanced to the point that now ultrahigh vacuums of $10^{-10}$ torr or better can be achieved easily. At this pressure, the surface of a prospective catalytic material can be kept free from contamination for several hours, whereas previously, clean surfaces were covered by residual gases or contaminants in the vacuum system in seconds.

During this same period, various photon, electron, and ion spectroscopies that could elucidate the atomic and electronic structure of the surface layer of a specimen and of atoms or molecules adsorbed on the surface were developed. The possibility of applying these spectroscopic techniques (as well as such methods as desorption and molecular beam studies of chemisorption and reaction kinetics) to the examination of chemically and structurally well-defined single crystal surfaces has inspired a not yet crested wave of interest in surface science among both experimentally and theoretically inclined physicists, chemists, and materials scientists.

The recent fashion that scientific research "be relevant" focused the attention of surface scientists on ways of relating their research to economically and technologically important processes that occur at surfaces, such as heterogeneous catalysis. (Corrosion is an equally important example.) Thus many surface scientists have come to believe that by studying simple reactions on the surfaces of clean single crystals under controlled conditions, they can begin to isolate and understand the principles that are operative in catalytic reactions.

For their part, more traditional catalysis researchers in industrial laboratories and in academic chemical engineering departments are skeptical, pointing out that surface science has yet to produce a new catalyst. Furthermore, they explain, industrial catalysis is an enormously complex process involving high temperatures and pressures, many simultaneous reactions each undergoing many steps, and many impurities and additives, all of which are far away from the ultraclean world of the surface scientist. And, they conclude, the largely empirical approach to catalysis (which is neither unscientific nor uncharacteristic of other industrial processes) has been successful, and catalysts have been devised for a wide variety of applications that promote the desired chemical reactions with a high degree of efficiency and selectivity.

### Bridging the Gap

The process of bringing these two groups together is likely to be a gradual one, and in the last 2 years a number of workshops and meetings have been held with one goal being to start a dialogue between the physicist who will only study the surface of tungsten (not a catalytic material of great note) and the catalysis researcher who thinks of the real world. In the meantime, a few scientists are searching out a middle ground, a place where the newer experimental and theoretical tools can be applied and related to catalysis problems in the real world.

Many commercially important catalysts are in the form of small particles of metal dispersed on an insulating ceramic support. Platinum is used in the oil industry for petroleum reforming (platforming) and is being considered for automobile emission control devices. Iron is used in the synthesis of ammonia, which is central to the fertilizer industry. In the case of the reforming reactions, which convert a low-boiling fraction of petroleum into a high octane gasoline, the catalyst consists of small particles (less than 50 angstroms in diameter) supported by a porous ceramic, such as alumina ($Al_2O_3$). The platinum accounts for about 0.5 percent of the surface area of the support (which may be of the order of 200 square meters per gram). Both the platinum and the support have catalytic functions. The platinum particles in automobile emission control devices are larger than those in petroleum reformers, in part because of the relatively higher temperatures encountered in automobile exhaust systems. High temperatures cause the platinum particles to grow, and increasing the size of the particles has the adverse effect of reducing the platinum surface area and thus the catalytic activity.

Using a transmission electron microscope, N. A. Gjostein and P. Wynblatt of the Ford Scientific Research Staff, Dearborn, Michigan, have been studying the kinetics of the growth of platinum particles at high temperatures. They found that particles 100 angstroms in diameter formed by heating a platinum film on a thin alumina substrate grew very slowly under a reducing atmosphere (such as obtains in petroleum reformers) but grew rapidly under an oxidizing atmosphere. After analyzing possible mechanisms that could explain the growth of these rather large particles, the Ford scientists have concluded that a model in which a volatile species such as platinum dioxide is transported from one particle to another either through the gas or along the substrate can account for their results. They also showed how large particles would grow at the expense of small ones.

At Stanford University, Stanford, California, J. Dumesic and M. Boudart have examined the effect of the particle size of iron catalysts, supported on magnesium oxide, on the synthesis of ammonia from hydrogen and nitrogen. They found that the catalytic activity of the iron dropped markedly as the particle size fell below 100 angstroms, thus showing, at least for the case of ammonia synthesis over iron, that too high a dispersion (small particle size) is inefficient and uneconomical. By means of Mössbauer spectroscopy, magnetic susceptibility measurements, and selective chemisorption of carbon monoxide, it was established that the source of the catalytic activity of the iron was a surface site consisting of an iron atom surrounded by seven nearest neighbors. The number of these sites decreased as the iron particle size dropped, because the sites became energetically less favorable. The iron could be restructured (at least partially) to develop the active sites by treating the particles with nitrogen—that is, nitrogen stabilized the active site.

Results of catalysis studies are often not generalizable to other catalysts. (One scientist likened understanding catalysis to finding the cause of cancer —there are just too many kinds for one mechanism to explain everything.) At the University of California, Berkeley, a team lead by G. A. Somorjai, using low energy electron diffraction (commonly known as LEED), Auger electron spectroscopy, molecular beams, mass spectroscopy, and gas chromotography, has been studying the surfaces of platinum single crystals. In large crystalline samples, sites such as that of iron with seven nearest neighbors are arrayed on crystallographic planes. Properly oriented samples can have such planes as their surface. Somorjai's group found that the catalytic activity of platinum surfaces was not associated with specific planes of this type, but was related to imperfections on such planes known as steps.

For example, the platinum plane on which the atoms are most closely packed together exhibited a much lower ability to promote the dissociation of diatomic molecules, such as hydrogen, oxygen, or carbon monoxide, than did surfaces with steps. A stepped surface is like a terraced hillside in which the terraces correspond to the close-packed planes, which in this case are a few atoms wide. Steps connect the terraces. The presence of such steps was also found to prevent graphitic layers on the platinum surface. Such layers tend to inhibit (poison) catalytic reactions.

The Berkeley researchers have also tried to relate their single crystal platinum to actual platinum catalysts by comparing the specific reaction rates for the hydrogenolysis of cyclopropane ($C_3H_6 + H_2 \rightarrow C_3H_8$) on single crystal platinum under 1 atmosphere of hydrogen with known values for small particle platinum catalysts. The good agreement obtained indicates that single crystals can be useful in catalysis investigations, at least for some reactions. The specially constructed apparatus was also designed to measure reaction rates on the same sample, both under moderate vacuum conditions ($10^{-4}$ torr or better) with a mass spectrometer and under high pressures with a gas chromatograph.

Also at Berkeley, L. M. Falicov is calculating the charge density of electrons in the vicinity of steps on the surface of transition metals, such as tungsten and platinum. Falicov's quantum mechanical calculations, which are not yet complete, suggest that the charge density near steps is most often higher than that on flat surfaces. The extra charge is typically about one-half of one electronic charge. Thus near a step, tungsten would look electronically more like rhenium or platinum to a prospective chemisorbed gas molecule. Ultimately, such calculations may provide an explanation for the results of experiments like Somorjai's.

### Fivefold Symmetry of Clusters

There is a growing belief among some researchers that small particles of an element (clusters of atoms) may have a fundamentally different structure than a bulk sample of the same element, and that the difference is more than just a higher ratio of surface to volume for small particles. M. R. Hoare and P. Pal of Bedford College, University of London, found that the structure of clusters containing from 2 to as many as 55 atoms is in theory an icosahedron. The icosahedral structure has fivefold symmetry and is not allowed in bulk samples because of the requirement that a crystal structure be translationally invariant (periodic). J. J. Burton of the Exxon Research and Engineering Company, Linden, New Jersey, has also shown that a 13-atom cluster with cubic symmetry (such as that of platinum) will spontaneously transform into the icosahedral structure. Although particles of this size are difficult to examine directly, studies of rhodium clusters with a high resolution transmission miscroscope by E. B. Prestridge and D. J. C. Yates at Exxon are consistent with a structure that has fivefold symmetry. The effect of this atomic arrangement on catalysts is not yet understood.

Quantum mechanical calculations of the electronic structure of clusters of atoms which were made with a technique called the self-consistent-field $X\alpha$ scattered-wave method provide additional theoretical support for the icosahedral model. This method was originally developed as a computationally efficient method for treating polyatomic molecules and solids. Recently it has been used by K. H. Johnson of the Massachusetts Institute of Technology, Cambridge, to compute the structure of clusters of atoms. For example, R. P. Messmer of the General Electric Research and Development Center, Schenectady, New York, and Johnson, along with their associates, have been collaborating to examine clusters of nickel, copper, platinum, and palladium. Early results suggest that clusters consisting of only 13 atoms are stable in the icosahedral structure. At the same time, however, these investigators have discovered that many of the features of the electronic structure of bulk metals already appear in the clusters. They also observed that the calculated electron orbitals of atoms at the corners of the cluster were oriented so that they were especially suitable for chemisorption of gas molecules to the cluster surface. There conceivably could be some connection between the apparently high activity of such sites and the activity of steps on platinum surfaces.

In recent years, we have seen the discovery and commercial application of a type of supported catalyst for petroleum reforming and for automobile emission control known as a bimetallic or multimetallic catalyst. In the late 1960's, Chevron Research Laboratories (Standard Oil of California), Richmond, California, unveiled a reforming catalyst made with mixtures of platinum and rhenium, which led to substantial cost reductions in the reforming process by permitting operation at lower hydrogen pressures. Universal Oil Products, Des Plaines, Illinois, also developed a bimetallic catalyst. In 1972, Exxon announced multimetallic cluster catalysts and advertised a further improvement in performance. The composition of Exxon's catalyst has not been released, but some oil company observers believe that platinum and irridium are the main ingredients. Today, such bi- or multimetallic catalysts are used in most reformers. And, in the automobile industry, 1975 model cars and light trucks will have catalysts containing platinum and palladium in their emission control devices.

Credit for the development of Exxon's multimetallic cluster catalyst is attributed to J. H. Sinfelt, who began studies of highly dispersed alloy crystallites about a decade ago (previous work had been carried out on unsupported alloys). Sinfelt looked at a number of model systems composed of group VIII metals (such as nickel) and group IB metals (such as copper) and found that alloying had a major effect on the selectivity of a catalyst as well as on its activity (selectivity is the ability to catalyze preferentially one of a number of possible chemical reactions, given a set of reactants). In the course of this investigation (in which several other kinds of metal combinations were also tried), the cluster composition that Exxon now uses for reforming was discovered.

According to Sinfelt, the clusters were so small (perhaps as small as 5 or 10 angstroms in diameter) that they were difficult to characterize directly. Thus, one of the currently still controversial questions about multimetallic clusters is: Are they really alloys? Statistical arguments have been made both for and against the proposition that the separate metallic components are alloyed. Sinfelt and his co-workers showed, by means of chemisorption and catalysis studies, that the addition of small amounts of noncatalytic metals, such as copper, to active metals, such as nickel or ruthenium, caused a disproportionate decrease in the ability to catalyze the hydrogenolysis of ethane ($C_2H_6 + H_2 \rightarrow 2\,CH_4$). If the two metals were not interacting, then the activity should have been proportional to the amount of active metal. In another experiment, copper which was codeposited with ruthenium on a silica ($SiO_2$) support could not be seen by x-ray diffraction, thus indicating a very small particle size. Since copper is not normally highly dispersed—that is, does not exist in such small particle sizes on a support—the indication is that the ruthenium prevented the copper from crystallizing, which is indirect evidence that the two metals did tend to alloy.

More recently, R. L. Garten at Exxon has used Mössbauer spectroscopic techniques to study alloying. Mössbauer spectroscopy is of limited usefulness because it is necessary to have a suitable isotope that emits gamma rays. Iron is the most commonly used source. In collaboration with D. F. Ollis of Princeton University, Princeton, New Jersey, Garten investigated small clusters containing iron and palladium, and found unambiguous evidence for alloying in these cases. Similar studies are also under way at Exxon involving alloys of iron with platinum and other metals. Chemisorption experiments were used to show that the clusters were indeed small. In other experiments, small amounts of iron were used as a probe to study multimetallic cluster catalysts, including Exxon's commercial catalyst, and evidence was obtained for multimetallic cluster formation.

If alloying effects do occur in multimetallic clusters, then there is the possibility that the composition at the surface of the clusters may differ from the overall composition of the cluster. This kind of surface segregation effect would make correlation of observed variations in catalytic activity with cluster composition difficult. For example, Sinfelt observed apparently strong alloying effect in his experiments even when the component metals did not normally alloy with each other—that is, when they were immiscible. Although the composition of clusters is difficult to determine, again because of their small size, a number of experimenters have studied the surface composition of unsupported (bulk) samples in the hope of relating the results to small clusters.

### Alloys of Gold and Nickel

At Stanford University, F. L. Williams (now at General Motors Research Laboratories, Warren, Michigan) and Boudart, using Auger electron spectroscopy, attempted to quantitatively relate the composition at the surface of gold-nickel alloys to the overall composition of the entire sample. They found that the surfaces in a series of such alloys with increasing concentrations of nickel were largely gold-covered until the bulk composition was nearly 100 percent nickel. Exposing the surface to oxygen reversed this trend, so that the surface was enriched with nickel oxide until the bulk composition was nearly 100 percent gold.

Williams and D. Nason (now at the University of New England, Armidale, New South Wales) were able to account for these observations by means of a theory in which only nearest and second nearest neighbor bonds between like and unlike atoms were taken account of. The results of such calculations for binary alloys indicated that the alloy surface would be enriched with the component having the smaller heat of sublimation. A tendency to form strong surface bonds, as in some oxides, could override the heat of sublimation, however, so that the oxide-forming component would segregate to the surface. The difference between the surface and the bulk might be expected to become minimal for sufficiently small particles, and application of the theory to small particles indicated how the composition of the surface and the bulk would merge in small clusters.

Also at Stanford, Boudart, R. J. Madix, and W. E. Spicer are collaborating on an interdisciplinary attack on problems relating to surfaces and catalysis. One of their associates, C. R. Helms (who is now at Exxon), has used Auger electron spectroscopy to study the surface composition of copper-nickel alloys. The results on two alloys, those with bulk compositions of 50 percent nickel and 50 percent copper and of 90 percent nickel and 10 percent copper, were consistent with the theory of Williams and Nason.

At Exxon, Burton and E. A. Hyman have succeeded in quantitatively relating a theory of alloy surface segregation to experimental catalysis data. They applied the theory (similiar to that of Williams and Nason) developed at Exxon by Burton, Hyman, and D. G. Fedak to data previously obtained by Sinfelt, J. L. Carter, and Yates on the hydrogenolysis of ethane on unsupported copper-nickel alloys (about 1000 angstroms in diameter). The Exxon scientists found that a model in which two nearest neighbor nickel atoms on the surface were the sites for the adsorption of the ethane molecule could quantitatively account for the observation that the activity of the nickel for hydrogenolysis dropped precipitously as small amounts of copper were added to the nickel.

Burton also pointed out the special role of sites such as the corners and edges of a small cluster. When there are strong surface segregation tendencies, it is possible to run out of minority atoms to place at the surface of clusters of dilute alloys in which it is the minority component that goes to the surface. Thus, what atoms are available will tend to go to corners and edges before they go to other surface sites. And once again, edges and corners seem to be especially interesting.

The claim of many catalysis researchers that the modern version of surface science with its emphasis on atomic and electronic structure has yet to produce a new catalyst remains true. However, those scientists who are now working to bridge the gap between pure surface science and real world catalysis seem to be the ones who will determine whether surface science can contribute to catalysis.—Arthur L. Robinson