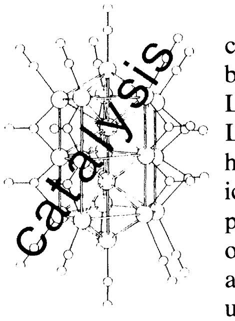
A New Picture of Surfaces Begins to Emerge

With new instrumental techniques, investigators are compiling a much clearer picture of what happens during heterogeneous catalysis



Heterogeneous catalysis, says Gabor A. Somorjai of Lawrence Berkeley Laboratory, "is the heart of most chemical and energy production technologies." Virtually all petroleum products and roughly 90 percent of chemical products are produced by reactions occurring at the surface of metals, metal oxides, silicas, and aluminas. Yet remarkably little is known about the nature of these surfaces, how gases or liquids interact with them, and how the reactions themselves occur.

True, it is possible to determine how much metal has been deposited on the surface of a support, the size of the metal particles, and their total area—and that is how most catalysts are still characterized. Only in recent years, Somarjai adds, "has the application of surface science techniques permitted the scrutiny of catalyst surfaces on the atomic scale." For the first time, "the structure, composition, and oxidation state of surface atoms may now be determined and correlated with . . . the rate, activation energy, and product distribution." The understanding gained at the molecular level "permits the design of improved catalyst formulations and holds the promise that one may 'build' new catalysts for carrying out specific chemical functions."

Many different areas of catalysis have benefited from the need for new sources of energy and chemicals. Heterogeneous catalysis, in particular, has also received impetus from the new techniques now available for studying surfaces with great precision and from the new computational techniques that have made possible better theories about the electronic interactions that occur during a catalytic reaction.* By using several of these new techniques together to look at species on the surface of a metal, says David M. Hercules of the University of Pittsburgh, "we are finally beginning to get some understanding of what is going on there." Work with the new techniques, adds John H. Sinfelt of Exxon Research and Engineering Company, "has resulted not only in significant advances of a fundamental nature, but also has aided materially in the development of new systems of major importance in industrial catalysis."

For the moment, however, most of the results are more academic in nature—or at least the results that are public knowledge, since much of the commercially critical work performed in industrial laboratories is likely to remain secret for quite some time. In general, moreover, most of the work has been done with materials that are much simpler than commercial catalysts. "Most industrial catalysts," says Bruce C. Gates of the University of Delaware's Center for Catalytic Science and Technology, "are so complex that even with a battery of techniques we won't get too far in understanding them." Those catalysts are "ill-defined structurally," adds John T. Yates, Jr., of the University of Pittsburgh, because "people had been studying them with techniques that were crude, at best. Only in the past 10 years have investigators begun to work with really good instruments and with well-defined crystals." Adds Gates: "We need to look at precisely defined systems so that we can get a better idea of what is going on in the more complex industrial systems."

To obtain a well-defined system, several investigators, including Yates, M. Albert Vannice of Pennsylvania State University, and D. Wayne Goodman of Sandia National Laboratories, have used complex pieces of apparatus, originally developed by Somorjai, in which a single metal crystal can be enclosed in a small pressure chamber in the vacuum chamber of a complex of surface science instruments. A catalytic reaction can be run at high pressures in the system and studied with some types of spectrometry that are insensitive to the presence of gases. The reaction can also be stopped at any point, and the chamber evacuated for procedures that require a vacuum.

Many industrial scientists, says John M. White of the University of Texas, have questioned this approach because they did not think that what happens on the crystal is the same as what happens "in the real world. One of the most important things that has happened in the past 3 years," he adds, "is the demonstration that there is a close correlation between results obtained on these crystals and those obtained with industrial catalysts."

Although several investigators have been active in this area, work done by Goodman at Sandia and while he was at the National Bureau of Standards with Yates and others, is prototypical. Goodman has been studying the methanation of carbon monoxide and the hydrogenolysis of ethane over single crystals of nickel or ruthenium. In the first reaction, hydrogen combines with carbon monoxide to form methane and water

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

In the second, hydrogen cleaves ethane to produce two molecules of methane

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

Methanation is a particularly important reaction because it can be used to produce synthetic natural gas from coal. The mechanism by which it occurs, however, has not been very well understood. Goodman's first step was to measure the rate of methanation on the (100) and (111) surfaces (see illustration) of single nickel crystals at various temperatures. He found that the turnover numbers (the number of molecules of product produced each second divided by the number of surface atoms of catalyst) for each of the two crystal facets were virtually identical. More important, the rates were also almost exactly the same as those measured by Vannice for a nickel catalyst supported on alumina. This close correlation between single crystals and high-area catalysts, says Goodman, was "a surprise to me as well as to most everyone else in the field."

While these results may seem rather trivial, their importance cannot be underestimated. Similar measurements have rarely been made in the past because "we haven't had these techniques." The findings establish "a direct connection" between the surface chemistry of the single crystal and that of the active metal in a process catalyst in the same environment.

Goodman then examined various aspects of the reaction. He found that a carbonaceous species builds up on the surface of the nickel to a concentration of about 10 percent of a monolayer. The Auger spectrum of this carbon is virtual-

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ly identical to that of nickel carbide, indicating that the carbon dioxide dissociates as it binds to the surface, forming an activated carbon species. This carbide subsequently reacts with adsorbed hydrogen to form methane. The turnover numbers for carbide formation and reaction with hydrogen are about the same as that for methane formation. "We thus conclude," Goodman says, "that the reaction rate is determined by a delicate balance of the carbide formation and removal steps, and neither of these is rate-determining in the usual sense."

The situation is not so clear cut for ethane hydrogenolysis, which Goodman calls "the most extensively studied cracking reaction." Whereas the rate of methanation is essentially independent of the size of nickel particles on a support, investigators such as Sinfelt have found that the rate of hydrogenolysis typically decreases as the size of the particle increases (although interactions with the support complicate the picture). Such reactions have been described by Michel Boudart of Stanford University as "demanding" or "structure-sensitive."

More recently, Guy A. Martin and his colleagues at CNRS in Lyons, France, have concluded that the rate-limiting step for hydrogenolysis on a supported catalyst is adsorption of ethane by an ensemble of 15 adjacent nickel atoms free from adsorbed hydrogen. He also concluded that only a small fraction of the nickel surface is active; because large nickel particles have a high percentage of exposed (111) planes, he speculated that most of the catalysis is carried out on (100) planes and that the (111) planes are either selectively poisoned by carbon or that they are intrinsically less active.

Goodman measured the turnover number and the activation energy for hydrogenolysis on the nickel (100) surface and found that they are virtually identical to the values for methanation on the same surface. This, he says, "strongly suggests that the two reactions . . . are following the same reaction pathway and are limited by the same reaction step." The same route is also followed in the hydrogenolysis of other carbon sources, including *n*-butane and cyclopropane.

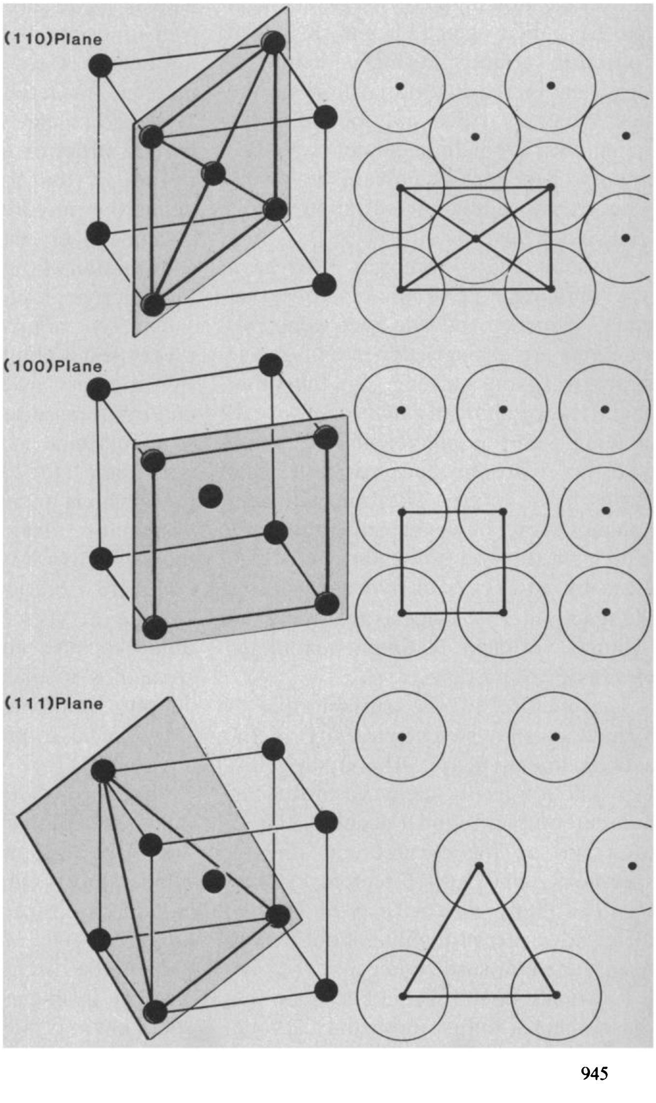
On the nickel (111) surface, however, the turnover number is substantially lower and the activation energy substantially higher than on the (100) surface. These values compare very well with those measured by Martin for large polycrystalline nickel particles supported on silica, suggesting that reaction on the (111) surface predominates on large crystallites. The most likely explanation for this difference, Goodman speculates, is the spacing between atoms on the crystal surface.

On the nickel (100) surface, the spacing between the fourfold hollow sites (that is, the sites where a carbon atom can bond equidistantly from four nickel atoms) is approximately 2.5 Å. On the nickel (111) surface, however, the distance between threefold sites is 1.4 Å. The bond length for the carbon-carbon bond in ethane is about 1.5 Å. Each carbon atom of ethane can thus settle into a threefold site on the (111) surface without appreciable stretching or dissociation; this species is relatively inert to further reaction, and the rate-limiting step is carbon-carbon scission. On the (100) surface, the adsorption of each carbon into a fourfold site breaks the carbon-carbon bond during adsorption, and the activation energy is lower. It is thus clear that the lower reaction rate on the (111) surface is intrinsic rather than due to selective poisoning.

Interestingly, W. Henry Weinberg of the California Institute of Technology has observed a similar situation for hydrogenolysis over iridium at low pressures. Weinberg observed that ethane is completely dissociated when it is adsorbed onto the (110) surface of iridium at 110 K, but exhibits virtually no dissociation on the (111) surface of iridium under the same conditions.

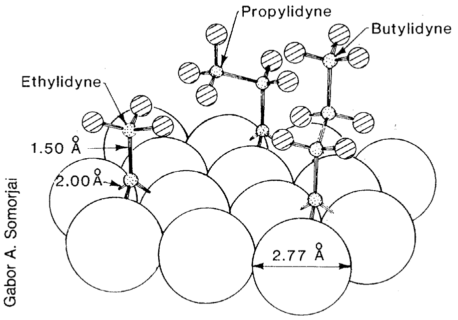
With this basic information, Goodman has also been investigating the activities of promoters and inhibitors. There has been a debate, for example, whether sulfur poisons a nickel catalyst by physically blocking the active sites or by an electronic effect. Goodman was able to demonstrate that sulfur apparently inhibits its adsorption by reducing the basicity of the *d* orbitals of nickel; there is thus a less rapid formation of surface carbon. The promoter potassium has the opposite effect, increasing the basicity and the amount of surface carbon. "The important point," he argues, "is that it is possible, at least for certain reactions, to moderate the effects of sulfur poisoning by adding potassium to the catalyst."

The importance of the carbon layer had earlier been demonstrated by So-



Crystal facets

Many metals of interest in catalysis form body-centered-cubic crystals. The crystal can be cleaved through various planes to expose different facets, which are named by their Miller indices. The (110) plane gives the most closely packed surface. The (100) plane has fourfold symmetry; that is, an atom can bind to the surface so that it is equidistant from four metal atoms. The (111) plane has threefold symmetry. Many other facets are also possible, of course. [Diagram from R. Gomer, "Surface diffusion," © Scientific American, Inc., August 1982. All rights reserved]



Gabor A. Somorjai

Alkene adsorption

Atomic surface structure of alkylidyne species adsorbed onto the (111) surface of platinum.

morjai. His studies of hydrogenolysis over single crystals of platinum provide what is probably the most detailed picture available of what happens at the catalyst surface during a reaction.

Below about 100°C, alkenes adsorbed to the platinum (111) surface, Somorjai finds, form alkylidyne molecules: The carbon-carbon (olefin) bond closest to the metal is perpendicular to the metal surface and its 1.5-Å length corresponds to a single bond, indicating that the dissociative process has already begun. The terminal carbon is bonded by a multiple bond of the carbyne type. This layer is ordered below 100°C, but it becomes disordered on further heating, and hydrogen is evolved. Between 200°C and 400°C, the disordered layer is composed of CH_2, C_2H, and CH fragments. Above 400°C, these fragments lose all of their hydrogen and form a graphite overlayer that destroys the catalyst activity.

In addition to that dissociation, a carbonaceous layer is also deposited on the catalyst surface, and the reaction occurs in its presence. In fact, Somorjai says, a clean platinum surface cannot readily catalyze hydrocarbon conversion reactions. Below about 120°C, this layer has an average stoichiometry of C_2H_3 and it can be rehydrogenated and removed from the surface. At higher temperatures, an increasing proportion of the layer becomes irreversibly bound to the metal, with a stoichiometry of C_2H. The activity of the metal catalyst is inversely proportional to the concentration of this tenacious layer.

Therefore, says Somorjai, "we have two seemingly contradictory observations." On one hand, the hydrogenolysis reactions are strongly dependent on the structure of the surface. On the other hand, the catalytically active surface is covered with the equivalent of a monolayer of carbonaceous deposit that masks its structure. Titration with carbon monoxide, however, indicates that a significant fraction of the surface is kept clean by an excess of hydrogen during the reaction. This suggests that there are "islands" of clean platinum surrounded by masses of carbon.

The picture of the surface that is formed is shown schematically in the accompanying figure. The hydrogenolysis reaction itself—cleavage of the carbon-carbon bond—must occur at a structural site on the clean metal surface, specifically one with threefold symmetry. The intermediates or products that form, however, probably cannot desorb from the metal surface because they are *too strongly* bound. It is likely then that these species diffuse onto the carbonaceous overlayer where they can be desorbed more readily, perhaps with the additional transfer of hydrogen. Studies by Robert Gomer of the University of Chicago as well as others show that this type of migration is exceptionally facile. The carbonaceous layer not only binds the intermediates more weakly, but it also stores about ten times as much hydrogen as the clean metal surface.

The fractional concentration of the bare metal islands, Somorjai has found, can be manipulated not only be hydrogen pressure, but also by additives such as alkalai metal promoters and by other transition metals that are used as alloying agents. Gold and tin, for example, increase the activity of the platinum catalyst and change its specificity by altering the structure and active site concentration of the bare metal islands, by aiding the rehydrogenation of the carbonaceous layer, and by slowing the dehydrogenation of the carbonaceous layer to the inactive graphitic form.

This type of picture is available only in a very small number of cases, however. Investigators are only now beginning to determine precisely how most potential reactants bind to a catalyst surface and what their fate is afterward. One investigator who is undertaking this survey in a systematic fashion is Weinberg. The most effective way to do this is to make a complete vibrational analysis of the adsorbate, he says, but this has rarely been done because the sophisticated tools were not available and because it is simply "damn hard to do." Some of his surveys have provided interesting insights.

When ethylene is adsorbed onto ruthenium, for example, it forms two methylene (CH_2) groups, even at very low temperatures. On rhodium, platinum, or palladium, however, it forms an ethylidyne molecule. Methylene is an intermediate in the Fischer-Tropsch synthesis of gasoline from gasified coal, and this dissociation may be one reason why ruthenium is a good catalyst. The relation between bonding to the metal and catalysis is very "delicate," Weinberg says; metals that are too far to the left of ruthenium in the periodic table "tear the molecule apart," while those too far to the right do not break the bond. "For the first time, these kinds of systematics are becoming understood."

An interesting and "unprecedented" observation by Weinberg involved the binding of acetone to ruthenium and platinum. Acetone binds to the (111) surface of platinum through the oxygen atom; this bond is relatively weak and the intact molecule can be readily desorbed. This type of binding is observed in many organometallic complexes of acetone. It binds to the geometrically identical (001) surface of ruthenium, however, in such a fashion that the carbon-oxygen bond is parallel to the surface of the metal. This type of binding has been observed primarily in organometallic complexes where there is a great deal of π bonding, and it presumably reflects the greater electron donation of ruthenium compared to platinum. This form of acetone is a precursor to dissociated CO and CH_3 moieties on the ruthenium surface. Significantly, says Weinberg, if the ruthenium is first treated with electronegative oxygen, it behaves more like platinum and both types of bonding are observed.

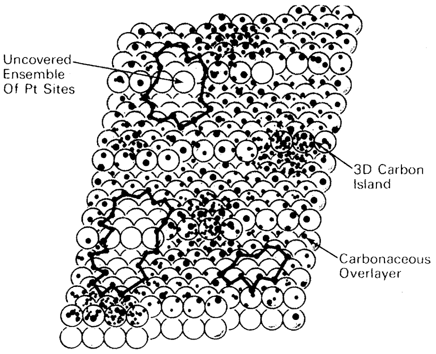
While some investigators have been cataloging how various adsorbates bind to the catalyst, some theoreticians have been trying to determine the same thing mathematically. One new theory has been proposed recently by Evgeny Shustorovich and Roger C. Baetzold of Eastman Kodak Company and Earl L. Muetterties of the University of California, Berkeley. They focus on the heat of adsorption, the total energy change when the system proceeds from an initial state of clean metal surface and free reactant to the final state in which the molecule is absorbed.

The unoccupied energy orbitals (levels) of most potential adsorbates are known to have higher energies than the highest occupied levels of electrons in transition metals. For electrons to be partially transferred from the metal to the adsorbate during binding would require that they populate a higher energy level. Because this increase in energy is rather large, Baetzold says, most investigators believe that electron transfer by this mechanism is negligible. Calculation of the wave functions of the unoccupied levels of the adsorbates, however, shows that these functions "overcompensate for the energy barrier that has to be overcome. For this reason we believe that, in general, molecules adsorbed to transition metal surfaces have a much greater acceptor function than anyone thought in the past." The new theory explains some inconsistencies between previous theories and experimental results. "The inconsistencies were not understood," he continues, "because it wasn't felt possible that significant electron transfer could follow this seemingly uphill process." Shustorovich adds that the new theory is significant in that it relates the stereochemistry of the adsorbed molecules to the unoccupied molecular orbitals. The theory has already been borne out by some preliminary experiments and has even shown where some previous experiments have been interpreted incorrectly.

One of the unusual predictions of the theory involves ammonia. "The conventional wisdom," Baetzold says, "is that ammonia is an electron donor, period. But this theory says that, under certain conditions, it may exhibit an acceptor function—and not through the nitrogen, as might be expected, but through the antibonding orbitals of the nitrogen-hydrogen bond."

Many other aspects of heterogeneous catalysis are also the subjects of extensive research, but one that surely deserves mention is the interaction between catalyst and support. Few catalytic reactions are carried out on a flat metal surface or with a slurry of catalyst particles because the dispersion—the fraction of catalyst atoms on the surface—is too low. In most cases, the metal catalyst is supported on pellets, particles, or some other form of silica, alumina, titania, or some other "inert" material, all of which can have surface areas on the order of 300 square meters per gram. On such a support, the metal can have a dispersion as high as one—that is, every metal atom will be exposed to the reaction medium. In such cases, the support may itself modify catalytic activity.

"People are rapidly recognizing that the support is not inert," says Lawrence L. Murrell of Exxon. If ruthenium is supported on silica, for example, carbon monoxide is adsorbed in a ratio of three or four molecules per atom of metal. For the same metal on magnesium oxide, the ratio is only one to one, like that of platinum; this change can have a profound effect on a catalytic reaction. Murrell also cites the interaction of carbon monoxide with rhodium. When rhodium is supported on alumina, each metal atom forms a *gem*-dicarbonyl with two gas molecules. On silica, however, the ratio of carbon monoxide to metal atoms is only 1.2. From examination of the surface, Murrell concludes that the metal forms raftlike structures about 40 Å. long; *gem*-dicarbonyls form on the edges of the raft, but the center is unreactive. If a small amount of titanium oxide is added to the silica, however, the rhodium appears as small clusters in which all the surface atoms form *gem*-dicarbonyls.



Hydrogenolysis of alkenes

A model for the working surface of a platinum catalyst used in alkene hydrogenolysis as proposed by Gabor A. Somorjai of the Lawrence Berkeley Laboratory.

It is also possible, Murrell says, to "manipulate the morphology of the support to change that of the metal," inducing what has been termed a "strong metal support interaction" or SMSI. On TiO_2, for example, platinum forms small mounds that look like haystacks. If the support is reduced to Ti_4O_7, however, the platinum spreads to form a monolayer. Discoveries such as these, notes Murrell, "are setting the groundwork for tailoring catalysts to do whatever we want."

Catalyst-support interactions are also very important in hydrodesulfurization catalysts, which have become valuable because of their ability to remove sulfur from fuels. Typical catalysts contain molybdenum as the active catalyst and cobalt as a promoter; they are usually supported on alumina. Many techniques have been used to investigate these systems, says Hercules, but "despite this fact, the nature of the surface species on the catalysts is still only poorly understood."

Investigators such as Gates have shown that molybdenum is highly dispersed on the support, probably existing as a monolayer, but the exact configuration and its chemical identity were still in question. Hercules and his colleagues have found that four distinct molybdenum species can exist on the surface, depending upon the concentration of the metal and the temperature at which it is prepared. At low concentrations, the predominant species result from the interaction of molybdic acid with surface hydroxyl groups; these can contain either tetrahedrally or octahedrally coordinated molybdenum, with the latter being favored at high concentrations. Once monolayer coverage is achieved, $Al_2(Mo_4)_3$ is formed. At higher concentrations, bulk MoO_3 is observed. Each of these forms presumably has different catalytic properties, although Hercules is just now beginning to correlate structure and function.

Hercules then held the concentration of molybdenum on the catalyst constant and added increasing concentrations of cobalt. It has been known for some time that the first cobalt added reacts with the support to become chemically inert, but "the fate of the remaining cobalt was uncertain." Hercules observed that this cobalt forms a layered structure with molybdenum up to the point where equal numbers of atoms are present. Beyond that point, Co_3O_4 is formed.

Examination showed that the molybdenum-cobalt bonds are formed with the cobalt between the catalyst and the support, presumably also as a monolayer. They also found that the uptake of sulfur by molybdenum to form the activated catalyst is not affected by the presence of cobalt, so that the latter's promoting effect "does not arise from chemical changes induced in molybdenum by cobalt." Rather, the chief role of the cobalt seems to be to stabilize the molybdenum layer.

One summary of the field is offered by Weinberg. "It must always be recalled that a heterogeneously catalyzed chemical reaction, occurring under realistic industrial conditions, is very complicated indeed. Moreover, both the types of catalytic reactions as well as the types of catalysts are so diverse that no 'general theory' of catalysis is to be expected either from the experimental laboratory of the surface chemist or from the numerical calculations of the theorist." Nonetheless, he concludes, "With the advent and the further development and intelligent application of a plethora of experimental techniques capable of examining the detailed nature of a solid surface, important advances toward a better understanding of heterogeneous catalysis will almost certainly be forthcoming."—**THOMAS H. MAUGH II**

Additional Reading

1. G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, Ithaca, N.Y., 1981).
2. W. H. Weinberg, *Survey of Progress in Chemistry* (Academic Press, New York, 1983), vol. 10, p. 1.
3. J. M. White, *Science* **218**, 429 (1982).
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