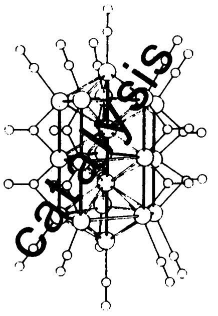
Catalysis: "No Longer a Black Art"

Increased funding, faster computers, and new surface science instruments stimulate great progress in catalysis research



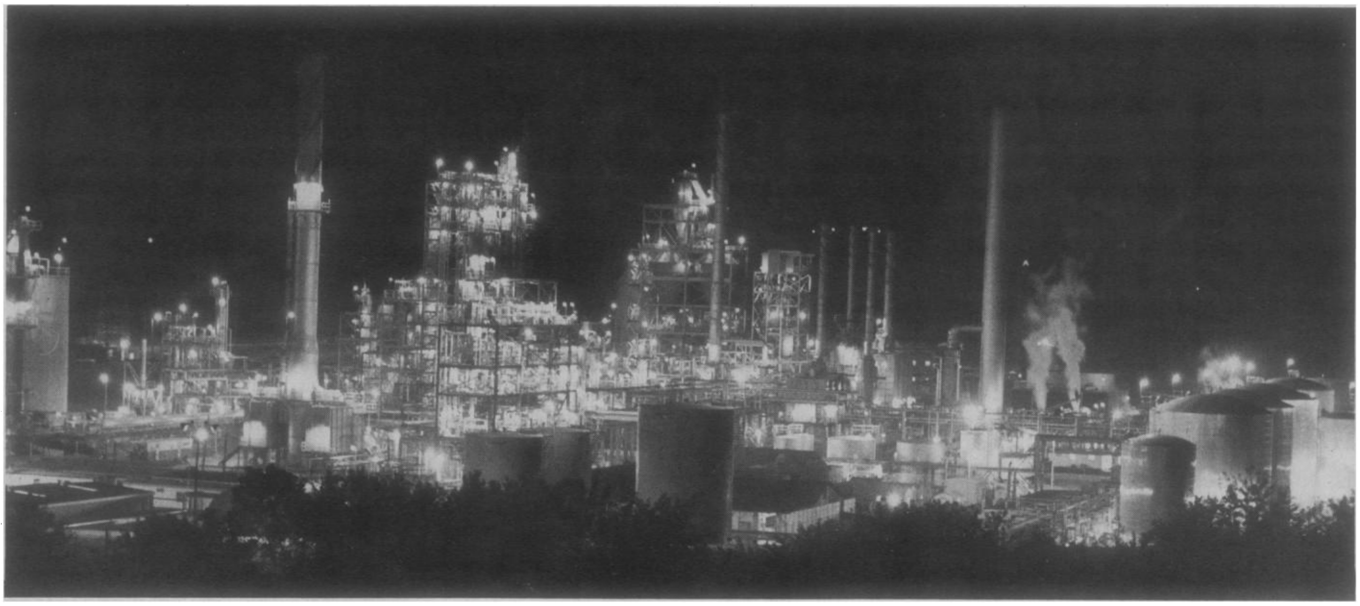
From laboratory to laboratory, from city to city, the theme is remarkably consistent. "When you got into catalysis in the past," says Alvin B. Stiles of the Center for Catalytic Science and Technology (CCST) at the University of Delaware, "you were talking to a bunch of dummies. We knew that a catalyst takes this and gives you that. The why of everything in between we didn't know. We still don't know much, but we're beginning to learn." Says Bryant W. Rossiter of the Eastman Kodak Company: "Catalysis is leaving the realm of alchemy and entering the field of science." Adds Edward Hayes of the National Science Foundation (NSF): "It is still pretty much of an art to design and optimize new catalysts and to improve upon existing catalysts, but it is no longer a black art."

"The study of catalysis is undergoing a renaissance," says F. Dee Stevenson of the Department of Energy (DOE). That renaissance, surprisingly, is being led in large part not by the artisans of the industrial chemical laboratories but by the ivory tower intellectuals of academe. These investigators are bringing a wealth of new analytical and computational techniques to the study of simple model systems in the hope that their findings can be applied to the largely undefined catalysts used by industry. "Fifteen years ago," says Mark Bateau of CCST, "many industrial scientists viewed these efforts as being largely philosophical in nature, somewhat akin to the question of how many angels can dance on the head of a pin." Today, adds John T. Yates, Jr., of the University of Pittsburgh, those same industrial scientists are finding the efforts "precisely relevant," and companies are buying and improving the instruments that have proved themselves in academic laboratories.

But new instruments and new computational techniques are only part of the story. There are also powerful economic forces fueling the study of new catalysts. The need for new sources of energy and chemicals, the desire for new types of products, and potential restrictions on the availability of noble metal catalysts have proved to be potent stimuli toward the development of a better understanding of the catalytic process. "The eventual hope," says Terry Baker of Exxon Research and Engineering Company, "is to tailor-make catalysts to fit each of the developing needs."

Catalysis has been inextricably linked to industry since 1835 when Jöns Jakob Berzelius first coined the term to describe the property of chemical substances that facilitate reactions without themselves being consumed. The first and, until recently, one of the only insights into the nature of catalysis came at the turn of the century when Wilhelm Ostwald recognized that catalysts exert their effects by changing only the rate of a reaction: catalysts cannot force a reaction to occur if it is not predestined chemically. Perhaps even more important than the ability of catalysts to increase reaction rates, adds John H. Sinfelt of Exxon, is their ability to alter rates selectively so that a desired reaction is favored at the expense of competing reactions.

The era of large-scale catalysis began in 1904 with Fritz Haber's catalytic synthesis of ammonia in which he passed atmospheric nitrogen over a bed of iron particles—a process that is still used in virtually the same form. Growth began in earnest during World War II when catalytic cracking of petroleum (breaking large molecules into smaller ones) be-


Frank Hoffman

Oil from coal

New catalysts are required for production of liquid fuels from coal, as at this H-coal plant in Kentucky.

came necessary to produce high-octane fuel for high-compression engines. The trend continued after the war with the introduction of catalytic reforming (which converts linear alkanes in cyclic aromatics) to increase octane further still, and with the first large use of catalysts to produce polymers.

Today, catalysis is intimately intertwined with the economy. A recent report by the trade magazine *Chemical Business* indicates that the U.S. petroleum, chemical, and automotive industries alone used $1.36 billion worth of catalysts in 1980, the most recent year for which figures are available, with a projected growth rate of about 3.5 percent per year. Vladimir Haensel of the University of Massachusetts estimates that "Catalysis contributes directly and indirectly to products accounting for a sixth of the value of all goods manufactured in the U.S.," or more than $100 billion per year.

But the economic situation is changing, particularly as it relates to petroleum. For one thing, the amount of high quality, sweet (low-sulfur) crude oil that is being pumped from the ground is declining around the world, forcing refineries to use thicker, more sulfurous (sour) crude. According to the National Petroleum Council, the proportion of sweet crude in refineries' feedstocks will decline from 65 percent in 1969 to about 41 percent in 1990. The new oils also contain larger amounts of trace metals that poison conventional catalysts.

Simultaneously, the market for residual oil—the glutinous material left over at the end of the refining process—that has been sold as No. 6 fuel oil or sprayed on roads to hold down dust has declined precipitously. Refining the new feedstocks and upgrading residual oil to useful products, says Stiles, will require "entirely different catalyst systems."

The 1973 Arab oil embargo also brought to the United States a sudden recognition of its dependence of foreign sources of petroleum. With this recognition came a renewed interest in alternative sources of energy. The most important alternative, of course, is coal, which can be burned directly or gasified to produce a mixture of carbon monoxide and hydrogen known as synthesis gas or syngas; syngas can be converted into a variety of products, especially gasoline by a process known as Fischer-Tropsch. Fischer-Tropsch chemistry was used extensively by Germany to produce fuels during World War II and is now the basis for the Sasol liquid fuels plant in South Africa. Other alternative fuels include the very heavy oils obtained from tar sands, kerogen from oil shale, methanol obtained by fermentation of biomass, and hydrogen obtained by the photocatalyzed splitting of water. The government of New Zealand is now constructing a plant to make gasoline from methanol by a new catalytic process developed at Mobil Research and Development Company. Each of these alternatives, quite obviously, will require different catalytic systems.

The chemical industry is also beginning to shift its raw materials sources, although it is not nearly as far along as the petroleum industry. The traditional feedstocks for the chemical industry have been natural gas and the light fractions from petroleum, such as naphtha. As the prices of these supplies have risen and shortages have loomed, the industry has begun to look at other sources, particularly syngas and methanol. The best example of this change is a new plant being built in Kingsport, Tennessee, by the Eastman chemicals division to produce acetic anhydride from syngas. This plant, says Eastman's Rossiter, represents "the first major shift of feedstock from petroleum to coal and, in the long term, this trend will continue."

A final economic consideration is the need to import noble metals for use as catalysts. A typical catalytic converter in an automobile, for example, uses between 0.05 and 0.08 troy ounce of noble metals, either platinum or a mixture of platinum and palladium or rhodium. In 1981, according to Roger Lobenstein of the Bureau of Mines, the U.S. automobile industry used 447,000 troy ounces of platinum (at an average cost of $446 per ounce), 129,000 troy ounces of palladium (at $95 per ounce), and 30,000 troy ounces of rhodium (at $498 per ounce). Consumption of noble metals should grow rapidly because the automobile industry was severely depressed in 1981.

In that same year, the refining and chemical industries used 166,000 troy ounces of platinum and 111,000 troy ounces of palladium. Virtually all of these metals were mined in the Soviet Union and in South Africa. As much as 99 percent of the platinum used in the refining and chemical industries and a slightly smaller percentage of the palladium can be recovered and used again. The potential recovery rate for noble metals used in catalytic converters, however, is well below 50 percent, primarily because of the lack of any concerted effort to collect spent catalyst. The need for the continuing importation of these metals, says Stevenson, puts the purchasing countries at a "great strategic disadvantage. One hope is that catalysis research will lead to substitutes that will do the same thing and reduce both cost and our reliance on outside sources."

In response to these concerns, funding for catalysis research has increased substantially, although exact figures are hard to pin down. The DOE did not exist in 1973, but catalysis funding by the


Eastman Kodak Company

Chemicals from coal

Newly developed catalysts will be used at this Eastman plant in Kingsport, Tennessee, to produce acetic anhydride from gasified coal.

offices and bureaus that were subsequently incorporated into DOE was "minimal," says Stevenson. Today, that funding totals at least $20 million, with 70 percent going to basic research. Funding for surface science studies related to catalysis at NSF, says Arthur F. Findeis, has grown "steadily" over the past decade to more than $12 million. The Department of Defense and other agencies also support catalysis studies.

Funding by industry has also increased sharply, say experts, although no figures are available. The most visible sign of this increase is the healthy state of instrument companies that market large systems for the study of surfaces. Perhaps the only discouraging aspect of the funding process is reflected by the recent shortsighted retrenchments in pilot programs and demonstration facilities for alternative fuels prompted by the current glut of petroleum.

Of course, pouring money into a barren scientific field is a lot like applying fertilizer to an agricultural field in which no seeds have been planted and where no rain falls. In the case of catalysis, however, the seeds and the rain are present. The former might be considered to be the new synthetic and computational techniques for making unusual molecules and studying their properties. The latter is the plethora of new instruments that have become available.

The accessibility of computational techniques for studying catalysis systems stems, in part, from the larger, more rapid computers that have become widely available in recent years. But the ability to apply these computers to problems in catalysis has also been dependent on the development of theoretical approaches to carbon monoxide or C_1 chemistry. "Most chemical molecules of commercial interest have molecular weights of hundreds or thousands," says Rossiter, "and today are not amenable to calculations for catalysis on even the largest and fastest machines." But the carbon monoxide and hydrogen in syngas are simple molecules whose physical and electronic properties can be calculated, he says with a chuckle, "relatively easily." It is thus possible for the first time to create a theoretical model for the electronic properties of simple molecules during particular phases of a catalytic reaction, then to measure them and compare the measurements to theory. Such a process has made it possible to obtain the first real insights into what happens during a catalytic reaction.

One area where this impact has been felt is the study of clusters of metal atoms. "We have known the properties of single atoms for a long time," says Rossiter, "and also those of bulk substances, but not those of clusters containing 2 to say 200 atoms. For a long time, we couldn't make or characterize them, and there was a real question whether it was worth while to try to do so." Some preliminary computational studies and complementary model experiments, particularly by Roger C. Baetzold, John S. Hamilton, and Evgeney Shustorovich of Eastman, suggested that "Some really exciting chemistry could exist in this domain and provided a strong incentive to learn how to make the clusters." Now, says Findeis of NSF, "We can make such clusters with incredible efficiency, and we can compute their electronic character with incredible efficiency." These developments have made it possible, says Sinfelt, for the first time to conduct structure-function studies in catalytic chemistry similar to those that have provided major advances in organic chemistry.

And then there are instruments. "In the last 15 years," says Gabor A. Somorjai of the Lawrence Berkeley Laboratory, "the explosive development of [catalysis chemistry] has resulted from the introduction of a multitude of techniques that permit the atomic scale scrutiny of the surface monolayer." Recent research breakthroughs, adds John M. White of the University of Texas, "derive in no small measure from a developing arsenal of probes; electron guns, atom guns, neutron guns, ion guns, and photon guns have been fired at surfaces to eject or scatter electrons, ions, photons, and neutral particles in almost every conceivable combination in one or another experiment. The number of techniques, about 80 in 1978, continues to increase." Some of the most important techniques are listed in the accompanying table.

Most of these techniques for surface science require high vacuums, whereas most catalytic reactions take place under high pressures. Many surfaces to be studied must thus be removed from the reaction vessel and placed in a vacuum container for analysis. This process has the potential to produce many "red herrings," says Bruce C. Gates of CCST, because the species must be very stable

Table 1. Some of the surface characterization techniques most often used to determine the structure and composition of solid surfaces. Adsorbed species present at concentrations of 1 percent of a monolayer can be readily detected. [Source: Gabor A. Somorjai, Lawrence Berkeley Laboratory]

Surface analysis method	Acronym	Physical basis	Type of information obtained
Low energy electron diffraction	LEED	Elastic backscattering of low energy electrons	Atomic surface structure of surfaces and adsorbates
Auger electron spectroscopy	AES	Electron emission from surface atoms excited by electron, x-ray or ion bombardment	Surface composition
High resolution electron energy loss spectroscopy	HREELS	Vibrational excitation of surface atoms by inelastic reflection of low energy electrons	Structure and bonding of surface atoms and adsorbates
Infrared spectroscopy	IRS	Vibrational excitation of surface atoms by absorption of infrared radiation	Structure and bonding of adsorbates
X-ray and ultraviolet photoelectron spectroscopy	XPS, UPS (ESCA)	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbates
Ion scattering spectroscopy	ISS	Elastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive and negative ions	Surface composition
Extended x-ray absorption fine structure analysis	EXAFS	Interference effects in photoemitted electron wave function in x-ray absorption	Atomic structure of surfaces and adsorbates
Thermal desorption spectroscopy	TDS	Thermally induced desorption of decomposition of adsorbates	Adsorption energetics and composition of adsorbates

to be observed and thus may be artifacts. This problem has been alleviated in part by investigators such as Somorjai, who have developed very small reaction cells that can be contained within the vacuum system of the spectrometric apparatus. While the reaction is occurring under pressure it can be studied with infrared and other techniques that are less sensitive to the presence of gases; the reaction can also be stopped at any time and the chamber evacuated to use the high-vacuum techniques. This approach, says Hayes, represents a "major improvement" in studying catalytic surfaces.

But the development of all these instruments has its own drawbacks, particularly cost. The majority of the surface science instruments cost at least $200,000 apiece. One instrument, furthermore, is seldom enough. Most of the techniques are complementary, and it may be necessary to use two, four, six, or even more techniques simultaneously or sequentially to obtain all the information necessary to deduce what is happening on the surface of the catalyst. (A saving grace is that additional techniques can often be incorporated into a major instrument for much less than the cost of a second instrument.)

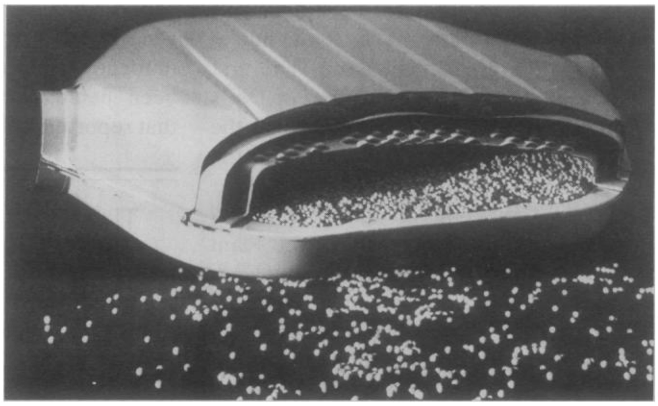
The day of the solitary scientist laboring in splendid isolation thus no longer exists for catalytic science, if, in fact, it ever did. One of the secondary themes espoused by Gates and others is the concept of "critical mass"—the idea that a certain (undefined) minimum number of both instruments and scientists must be gathered at one location before significant progress can be made. In most cases, furthermore, the scientists should represent a mix of disciplines, including both organic and inorganic chemists, chemical engineers, chemical physicists, and others. A few investigators, such as Sinfelt, caution against becoming "over-obsessed with hardware," but it seems indisputable that some of the best work is coming from laboratories where that critical mass has been achieved—including, but not limited to, CCST, Lawrence Berkeley Laboratory, the University of Pittsburgh, California Institute of Technology, Eastman Kodak Company, UOP, Inc., Mobil Research and Development Corporation, and Sinfelt's own Exxon laboratory.

Given money, computer power, instruments, and a critical mass of scientists, what is being accomplished in catalysis research? A great deal, it turns out. During the next few months, *Science* will examine some of the major developments in several areas of research. Among the potential topics in which activity has been most feverish:

- Heterogeneous catalysis, the classical form of catalysis in which a reaction occurs on the surface of a solid. Heterogeneous catalysis, says White, is "an old discipline which has recently reawakened." Using the new spectroscopic techniques, scientists have been putting together the first picture of what is happening on the metal surface and why. "Ultimately," says David Hercules of the University of Pittsburgh, "We would like to be able to use spectroscopy to look at a surface and tell if it will be a good catalyst." It may also soon be possible to alter surfaces rationally. "We can begin," says D. Wayne Goodman of Sandia National Laboratories, "to think about using impurities to tailor catalysts for specific purposes."

To clean the air

This catalytic converter used on General Motors automobiles incorporates noble metals deposited on pellets of an inert support.



Engelhard Corporation

- Metal clusters, actually a subdiscipline of heterogeneous catalysis, in which clusters of a few metal atoms attached to various ligands are deposited on the surface of a support. The principal advantage of these materials is that they have a highly specific, well-defined structure; the chief disadvantage is that they are not sufficiently stable for industrial use. "We can't claim that these are technologically important yet," says Gates, "but they offer great potential for the development of designed catalysts."
- Homogeneous catalysis, in which the catalytic agent is dissolved in solution along with the reagents. Homogeneous catalysts are often "the choice of last resort" in industrial processes, says one investigator, because the reactions must often be run at high pressures to keep the catalysis in solution and because of the difficulty of recovering the catalyst from the medium. Offsetting this disadvantage in many cases, however, is the higher selectivity that can often be obtained with homogeneous catalysts. Much of the work now in progress involves ways to anchor the catalyst to a solid support for easier recovery.
- Photocatalytic reactions, particularly the use of sunlight to split water into oxygen and hydrogen. There has been much interesting research in the field recently (*Science*, 5 November 1982, p. 557), says one DOE scientist, but "the field has many land mines." The most difficult problem now, he adds, may be "to separate the science from the hype."
- Chiral synthesis, the use of asymmetric catalysts to produce only one of two possible stereoisomers. Chiral synthesis is of increasing interest in industry because of the growing use of organic molecules with optically active centers.
- Biotechnology, the adoption or adaptation of biologial processes for industrial application. Among the most relevant aspects of biotechnology are the use of enzymes bound to an inert carrier for repeated use and the modification of an enzyme's active site to change its specificity. This is a very complicated area that Rossiter, for one, terms "a basket of snakes."

Perhaps the best summary of the state of the art is offered by Sinfelt: "I think we are in a stage in catalysis that resembles the situation in physical organic chemistry 20 years ago. We're beginning to systematize observations on reactivity, correlating reactivity with structure and with electronic factors in the same manner that has brought many advances in physical organic chemistry. A lot of the spirit that went into physical organic chemistry has been important in evolving ideas about catalysis." Those discoveries are not destined to end up solely in textbooks. "There is a growing confidence," says one DOE official, "that there can be a transition from the research laboratory to the industrial plant." Meanwhile, the intellectual ferment is obviously generating great enthusiasm among the investigators. Concludes Rossiter: "I get excited just sitting here listening to someone talking about it."—**THOMAS H. MAUGH II**

The figure in the logo is the cluster anion $[Pt_{19}(CO)_{22}]^{4-}$*, one of the larger clusters known.*