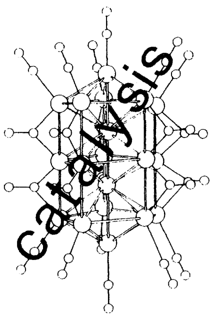
When Is a Metal Not a Metal?

Investigators searching for more selective catalysts are beginning to understand small metal clusters



"One copper atom is clearly not a metal," says Richard Smalley of Rice University. A copper dimer is also not a metal. Just as clearly, 200 copper atoms together are metallic. Most of the research on naked metal clusters addresses the problem of how many atoms must be present before a cluster takes on bulk-like properties." The answer is not yet clear. "The area between one and 100 atoms is an almost totally uncharted wilderness. Physical chemistry texts don't even tell you the length of the metal-metal bond in a dimer because that information simply hasn't been known. I'm looking forward to a substantial impact from the work we are doing now."

The work that Smalley and a few other investigators have been doing is directed to the study of the structure, physical properties, and chemistry of small "naked" metal clusters—that is, clusters with no ligands attached. Through this work they hope to compile for the first time physical and electronic data about the clusters, to model the types of reactions occurring on the surface of larger metal crystallites, and to develop more specific catalysts. The evidence suggests that they are succeeding on all counts.*

Improved specificity is a major goal for this work. In catalysis, says Bruce C. Gates of the Center for Catalytic Science and Technology at the University of Delaware, "the name of the game is selectivity." It is usually not hard to find a catalyst that will accelerate a given reaction. The problem lies in finding one that enhances the desired reaction without speeding up side reactions that yield undesired products.

A good example lies in Fischer–Tropsch chemistry, which has become virtually a "Holy Grail" for catalysis scientists because of its potential for producing chemicals and synthetic fuels from carbon monoxide and hydrogen obtained by gasifying coal. A large number of metals catalyze Fischer–Tropsch chemistry at appreciable rates, but most of them produce a distribution of products known as the Shultz–Flory distribution, which is a kinetically controlled spectrum of hydrocarbons ranging from methane to complex aromatics, waxes, and oxygenates. If the desired product is gasoline, then low-boiling hydrocarbons such as methane and ethane are of limited value, as are very high boiling compounds. "There is a broad effort in industry now," says Gates, to find catalysts that will improve Fischer-Tropsch and similar processes by minimizing the production of less desirable materials.

The problem lies in the nature of the typical industrial catalyst. Most are composed of relatively large crystallites of metal on, for example, a silica or alumina support. Each crystallite typically has a number of different crystal facets exposed, as well as edges, terraces, defects, and adatoms. For a few reactions, such as the methanation of carbon monoxide, the location and the environment of the catalytic atom or atoms is unimportant—an edge atom, for example, can carry out the reaction at the same rate as an atom in the middle of a large surface. These are structure-insensitive reactions.

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The vast majority of reactions, however, are structure-sensitive or demanding. In Fischer-Tropsch chemistry, for example, methane might (hypothetically) be formed only by edge atoms, cyclohexane would be formed at a site near a terrace, butane would be produced at a site with four adjacent atoms, and so forth. If the size of the crystallite is reduced, the number of competing reactions might also be reduced. "The dream," says Geoffrey A. Ozin of the University of Toronto, "is to produce one well-defined cluster on a well-defined support to do as selective a reaction as possible. In principle, if you have only one size and shape of cluster, you could get only one product."

The ultimate extension of this concept is to use single metal atoms. This selectivity, indeed, is one of the chief attractions of homogeneous catalysis. Again, however, most reactions of interest cannot be carried out by individual atoms; rather they require ensembles of various minimum sizes. Effort is thus being expended to prepare potential catalysts containing a small but well-defined number of atoms of one or more metals. This work has taken two different directions: the preparation of naked metal clusters and the synthesis of organometallic clusters in which ligands are attached in a precise conformation. (Both organometallic clusters and homogeneous catalysis will be the subject of future articles.)

A further advantage of working with small clusters is that the electronic properties of the metal may be substantially different from those of the bulk metal. An isolated metal atom has a higher ionization potential than an atom in bulk metal. Its electron affinity is lower. Its *d* electron orbitals are less fully filled than in the bulk metal, and its *s* orbitals are more filled. Presumably there is a gradation of these differences as the cluster grows larger, but the exact point at which the cluster becomes bulk-like has been the subject of dispute. Because these electronic properties are important in the adsorption of organic molecules and the scission of bonds, most investigators have assumed that small metal clusters may have unusual catalytic properties for electronic reasons as well as structural.

This question is of more than academic interest because many industrial processes are dependent on the size of the catalyst crystallite. In photography, for example, the few photons striking a silver halide crystal in film produce a small cluster of silver atoms on the surface of the silver halide. On reaching the necessary size, this silver cluster acquires catalytic properties and can trigger the reduction of the entire crystal to silver by the reducing agent of the developer. Indirect evidence, say Roger C. Baetzold and John F. Hamilton of Eastman Kodak Company, suggests that the cluster "becomes catalytic, rather abruptly, at a size of a few atoms, but that thermodynamic stability does not require as large a cluster." If a smaller cluster could be made catalytic, it should be possible to make faster film.

In most applications, however, small particles typically have greater—often

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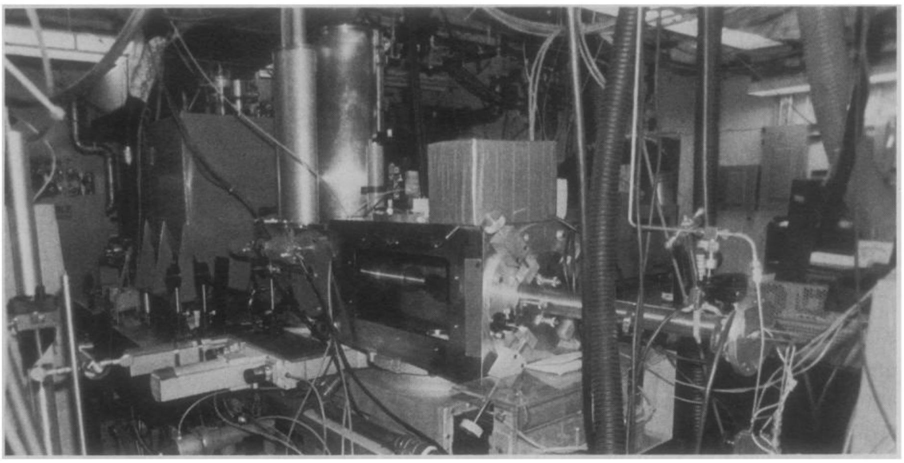


Exxon Research and Engineering Company

The supersonic metal cluster beam apparatus at Exxon Research and Engineering Company. A large flange has been removed to expose the main vacuum chamber. Behind the main chamber are the A and B chambers, each of which has a large, cylindrical liquid nitrogen trap. The time-of-flight tube is the narrower cylinder extending upward from the B chamber trap.

much greater—catalytic efficiency than larger crystallites. Manufacturers also want to minimize the use of precious metals. For both reasons, then, it becomes desirable to make catalyst crystallites on a support as small as possible and as uniform in size as possible.

This problem has presented difficulties in the past, says Baetzold, "because it was hard both to make the small particles and to characterize them spectroscopically." The former is a problem because the heat involved in conventional catalyst preparation causes the small particles to aggregate. The latter problem typically occurs because the spectroscopic signal from the support overwhelms the signal from the very small particles.

The physical properties of clusters of many nonmetals and nontransition metals are relatively well known from studies in solution and the gas phase. Among such clusters are things like P_4, Hg_4^{6-}, Sn_9^{4-}, Bi_5^{3+}, and Te_6^{6+}. At the University of Bern in Switzerland, Ernst J. Schumaker and his colleagues have pioneered in the use of hot ovens to generate beams of small clusters of sodium and potassium ions. The clusters are passed through a supersonic expansion nozzle to generate the beams and to cool them to about 300 K. James Gole of the Georgia Institute of Technology has used a similar technique to generate small clusters of copper atoms, and Sol Wexler and Steven Riley of Argonne National Laboratory have used it to generate small clusters of metals from the first row of transition elements.

But using such ovens, says Smalley, requires "a lot of art." It is difficult to get the beam established and hard to keep the orifices clean. More important, it is very difficult to get large clusters of the heavier metals and to cool the beam to low temperatures, where spectroscopy is simplified. Smalley and Andrew Kaldor, Donald Cox, and Eric Rohlfing of Exxon Research and Engineering Company have solved this problem by using a pulsed laser to vaporize a metal target in the throat of a supersonic expansion nozzle. The laser produces a localized temperature of about 10,000 K, so the technique can be used on any metal, producing clusters ranging in size from one to 200 atoms. "Our method is crude and simple," says Smalley, "and therefore it's general."

In passing through the nozzle, the clusters are cooled to about 2 K, which means that vibrations are minimized and the spectra are as simple as possible. Various types of spectroscopy are carried out during the few hundred microseconds in which the cluster is in the chamber. "It is very difficult to get a signal and information from the clusters," says Smalley, "but when it's obtained, it's definitive." The pair, using separate machines, have observed many unusual clusters, what Smalley terms "strange beasts that haven't been seen before." Kaldor says it is "like dealing with a new state of matter. We're in a transition regime from molecular species to surfaces, so I like to call what we are doing 'molecular surface science.' "

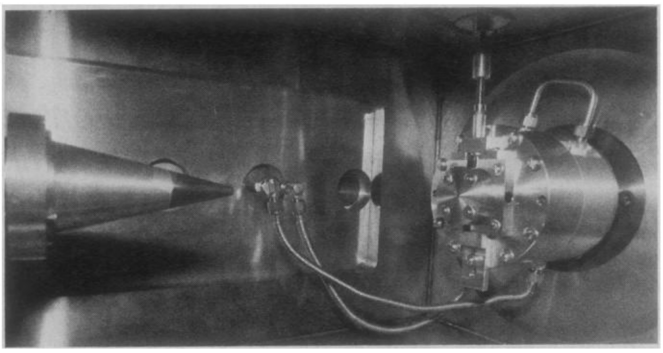
The two investigators have independently measured structures and vibrations for small particles and ionization potentials and electronic properties for some larger ones. "We have seen," says Kaldor, "some very interesting effects that suggest, first, that the movement of this electronic behavior is not monotonic, but is sensitive to the number of atoms in the cluster." Their results for copper and silver, for example, agree fairly well with theoretical calculations by Baetzold and Roald Hoffman of Cornell University. This theory predicts, for example, that the ionization potentials of clusters decrease relatively sharply for clusters containing two to about 10 atoms, and then fall more gradually until the bulk value is reached at about 80 atoms.

In general, however, clusters with odd numbers of atoms have lower ionization potentials than the even-numbered clusters on either side. In the even-numbered clusters, says Smalley, the valence electrons are tightly bound, and the ionic structure obtained when an electron is removed is different from the molecular structure. In the odd-numbered clusters, the electron is removed, in effect, from an antibonding orbital and is given up more freely. Measurements of photoemission signals for clusters ranging from single metal atoms to bulk film by Gary Mason, Gustav R. Apai, and Shuittong Lee of Eastman Kodak Company have also shown that the onset of bulk properties occurs at sizes greater than 100 atoms.

Their results have not all supported theory, however. Some calculations had indicated that the atoms in a chromium dimer, for example, are "hardly bonded at all," and that the bond length should be about 3 angstroms. "Theorists had assumed that bonding would be mostly by *s* orbitals, which extend out farther, and that *d* orbitals would make little contribution." However, Smalley has observed recently that the actual bond length is 1.68 angstroms—"the tightest bond known to man"—and that the bonding is almost entirely by *d* orbitals with little *s* participation at all. The bond length, in fact, is only two-thirds of the bond distance in bulk chromium. They have recently found a similar, less dramatic, effect for molybdenum dimers.

Kaldor has also observed that the ionization potentials for iron clusters containing three to five atoms are higher than that for a cluster containing two atoms, while the potentials for clusters containing 13 to 17 atoms are higher than that for a cluster of 12 atoms—a situation not predicted by theory. A similar inversion of the monotonic curve for ionization potentials occurs for nickel clusters containing six atoms. "A lot of theoretical calculations are going to have to be redone now," concludes Smalley.

Ozin, in contrast, has worked on the nucleation of metal atoms at very low temperatures to produce small clusters. Gaseous metal atoms are mixed with relatively large amounts of inert gases and cooled to the range of 10 to 20 K. The metal atoms are then entrapped in a growing film of inert gas, either singly or



Exxon Research and Engineering Company

A close-up of the interior of the main chamber of the supersonic metal cluster beam apparatus. The laser beam enters from the right to strike the target rod contained in the metal cluster faceplate. The conical skimmer at the left is the first of two that collimate the beam.

in very small clusters. Larger clusters can be generated in a controlled fashion in three ways: the metal concentration in the gas can be increased; the temperature of deposition can be increased or the inert gas film annealed (heated); or the metals can undergo photoaggregation by a technique developed at the University of Toronto. In photoaggregation, the entrapped metal atoms are excited at certain atomic resonance transition frequencies with light; nonradiative relaxation processes cause the atoms to migrate, forming clusters. The technique, says Ozin, "gives us a nice, controlled way to build clusters of 2, 3, 4, 5, or 6 atoms, moving only single atoms, not clusters." Before the advent of the work of Smalley and Kaldor in the last year or so, the low-temperature techniques developed by Ozin and by Martin Moscovits of the University of Toronto were the only way to generate the clusters of interest in catalysis.

Baetzold describes Ozin's and Moscovits' studies as "very important work" because they make it possible to study the detailed structure and properties of small metal clusters in different supports "at your leisure." Because the structure of the inert gas film is highly regular (isotropic)—as opposed to the irregular (anisotropic) surface of a conventional support—spectroscopic interference is minimized and it is possible, Ozin says, to use "virtually every spectroscopic technique that is used in studying metal surfaces."

Ozin has found that small metal clusters in low-temperature supports can have unusual shapes. Silver trimers, for example, can form triangles, a shape that is not seen in the bulk metal. These clusters, moreover, are very easily deformed and geometric isomers can be trapped at low temperatures and interconverted photochemically or thermally. Bond lengths are also not the same as in the bulk metal: in general, the smaller the cluster the longer the bond. Conduction bands in the clusters show discrete levels, whereas there is a continuum in the conduction bands of bulk solids.

How important are these differences? "That depends on whether you are a chemist or a physicist," says Ozin. "A physicist is concerned with ionization potentials, Fermi energies, and the like, and for these properties the transition to bulk character occurs for clusters of roughly 100 atoms. But if you are a chemist, as I am, the differences may not be so important. If you are comparing a Ni_6 cluster to a Ni_{100} cluster, you have to look at how the reacting molecule 'sees' the cluster. Carbon monoxide, for example, can bond only to a maximum of four atoms, and generally it bonds only to one or two. Then you have to consider whether the bonding and chemistry are localized or delocalized. It appears that you need only a few atoms to describe the main features of chemisorption. . . . With larger clusters, the principal effects you see are lateral interactions with nearby carbonyls. So the chemistry is not much different. For chemistry, the transition from molecules to bulk-like properties seems to occur in the region of about 13 atoms."

The debate over where the transition to bulk properties occurs is obviously not resolved. That does not mean, however, that useful catalytic reactions cannot be obtained with small clusters. Ozin, for example, has used his low-temperature techniques to "deposit" single metal atoms into anhydrous organic solvents at low temperatures. Below about −70°C, these atoms are solvated weakly and remain in solution. If the solvated atoms are brought into contact with a support and the solution is warmed to about −50°C, the metal atoms are desolvated and deposited on the support in the form of very small clusters.

Ozin has been using a Faujesite zeolite, a porous aluminosilicate that has cavities as large as 12.4 angstroms in diameter and windows or entrances about 7.4 angstroms in diameter. When *bis*-toluene iron or cobalt are used to prepare the catalyst, the metal is deposited in the cavities in clusters ranging in size from 4 to 12 angstroms in diameter. The microcrystallites are very stable, and the combination of small pore size and small particle size give great selectivity. When Ozin performed Fischer-Tropsch chemistry with these catalysts at the low pressure of 1 atmosphere, a temperature of 240°C, and a hydrogen to carbon monoxide ratio of 2:1, he obtained 85 weight percent of butenes in the product, an "extraordinary" selectivity that had not even been contemplated in the past. Several companies are examining the catalyst with great interest.

A unique approach to slightly larger crystallites has been taken by Robert L. Burwell, Jr., of Northwestern University. Burwell decomposes a molybdenum carbonyl, $Mo(CO)_6$, on the surface of alumina. Other investigators have tried this and found that the hexavalent molybdenum can be reduced only to a tetravalent state because of interactions with hydroxyls on the surface of the support. Burwell and Alan Brenner of Wayne State University had earlier found that divalent molybdenum could be prepared if the support were first partially dehydroxylated by heating at 450°C. Now Burwell has completely dehydroxylated the alumina by heating it to 950°C in a fused silica reactor. On this support, it is possible to reduce the metal to the zerovalent state, giving what Burwell calls "the first supported metallic molybdenum catalyst."

This catalyst, he says, has "extraordinary activity." It is more reactive than supported platinum for hydrogenation of olefins—so reactive that the reaction must be studied at −46°C. It is somewhat less reactive than nickel for hydrogenation of carbon monoxide to hydrocarbons, but it can be used at higher temperatures, a practical advantage. Burwell also says that it is "the most active supported catalyst known for the activation of aliphatic carbon-hydrogen bonds" and "the most active catalyst known for hydrogenolysis of alkanes."

The study of naked metal clusters is still in its infancy. "In the next 10 years," says Ozin, "we will have a fairly comprehensive picture of the properties of small metal clusters, going from atoms to molecules to bulk metal. This will ultimately provide a better understanding of the interaction between the catalyst and its support, a vital but poorly understood aspect of heterogeneous catalysis. What's held back the field has been the difficulty of synthesizing and identifying the clusters." Now, adds Smalley, "we have the ability to make virtually any cluster we desire," and progress should be much more rapid.

—**Thomas H. Maugh II**