ment, and what we have to do is find out how the genes get hold of the cell. That is just another way of saying that the molecular biology of development is the molecular biology of the cell."

In principle any mutant that affects development might yield some insight into the grammar that lies between the genetic space and the organismic space. "The name of the game now is gene products: the ability to do inside-out biology." There are, for instance, mutants that cause a particular cell division cascade to reiterate. "Find out what the product of that gene is, what cells it operates in, what it does: and then you might know something about the control of these reiterative divisions." After a moment's reflection Brenner adds, "Of course, it might tell you nothing at all."

It has become clear from the *C. elegans* that there is not a simple set of obvious rules that governs development, and some critics have said that Brenner and his associates are no nearer understanding the process, that all they have done is describe what happens. "I'm not sure that there necessarily is anything more to understand than what it is," he responds. "That is a possibility for this level of complexity." Perhaps because organisms are the products of evolutionary change within certain biological and architectural constraints, simple description of how they are put together is going to yield the most profound insights. In which case, the choice of *C. elegans* has been apposite, as anything bigger would be intractable to description in the detail that is necessary.

Other critics say that the project is just too difficult, at which point Brenner's molecular biology macho comes to the fore: "I don't accept that. Peter Medawar has written that science is the art of the soluble. My reply is that molecular biology is the art of the inevitable. If you do it, it's inevitable you will find out how it works—in the end. Maybe it won't be until you are able to put the last period on the page, when you know everything, that you will be able to say, aha, now I understand! But you will get there in the end."—**ROGER LEWIN**

Unusual Bimetallic Catalyst Synthesized

A manganese-cobalt catalyst prepared by solvated metal atom dispersion has some unusual catalytic properties

What appears to be the first known case in which one metal activates a second metal for heterogeneous catalysis has been reported by Kenneth J. Klabunde and Yuzo Imizu of Kansas State University. These investigators have found that small pseudo-organometallic particles containing manganese and cobalt have activities for catalytic hydrogenation of alkenes that are much higher than those of similar particles containing only cobalt. The new particles also have much higher activity than commercial catalysts or similar particles containing other metals. Manganese, however, has very little catalytic activity for the reaction, indicating that the activation is somehow effected by its interaction with the cobalt.

The new Mn-Co catalyst, reported in the *Journal of the American Chemical Society* [**106**, 2721 (1984)], is but the most recent in a series of unusual catalysts produced by Klabunde and his coworkers using a technique known as solvated metal atom dispersion (SMAD). The technique, he says, was designed to take advantage of the fact that small clusters of metal atoms "are fundamentally different and more reactive than clean metal surfaces." * SMAD catalysts are typically more reactive than conventional catalysts and, in many cases, show unusual specificity.

The SMAD catalysts are prepared in a vacuum flask whose walls are cooled to −196°C by liquid nitrogen. The metal to be studied is vaporized in a small electric crucible in the center of the flask. At the same time, small quantities of a solvent are also admitted to the flask. The solvent vaporizes rapidly, then condenses on the walls of the flask along with the metal atoms. Varying heating rate and the relative proportions of metal and solvent make it possible to regulate the size of the metal clusters that are formed.

The nature of the solvent is important. It must be only weakly solvating and relatively inert to oxidative addition, abstraction, or electron transfer processes. Among the best solvents are hydrocarbons such as pentane, hexane, toluene, and tetrahydrofuran; many of the best catalysts, including the Mn-Co particles, are made with toluene as the solvent.

These "bare" metal clusters—called bare because there are no covalent metal-carbon or metal-hydrogen bonds—can be quite reactive. Aluminum atoms, for example, react with methane at 10 K; this phenomenon has not been observed for single atoms of any other metal, and Klabunde attributes the reactivity to the ^2P electronic state of aluminum, which gives it a "free-radical-like" character. Other single metal atoms react with methane at 10 K only if they have been excited by light.

Nickel clusters of unknown size react vigorously with pentane at 140 K. In fact, the nickel clusters react so extensively with pentane that pseudo-organometallic particles precipitate as a stable powder. (Klabunde calls these powders pseudo-organometallic because, even though there are extensive metal-carbon and metal-hydrogen bonds, they do not have a fixed composition and they are not soluble.) In most cases, single metal atoms are more reactive with alkanes than are clusters. Klabunde has some evidence, however, that methyl bromide reacts with clusters of magnesium but not with single atoms. If this finding is confirmed, he says, "this would be the first concrete example of an atom being less reactive than a cluster."

Catalysts can be prepared from the frozen matrix by either of two methods. In each case, the matrix is allowed to melt to form a frozen slurry. If warming is allowed to continue, the solvated metal atoms will react to form pseudo-organometallic powders, with the temperature of formation depending on the individual metal involved. The size of the particles can be controlled, at least in part, by regulating the rate of warming. Alternatively, the solvent can be allowed to permeate a support (such as zeolites, aluminas, or silicas) before the warming is completed. The same type of reaction with solvent occurs upon warming, but in this case, the pseudo-organometallic particles are deposited on the surface of the support.

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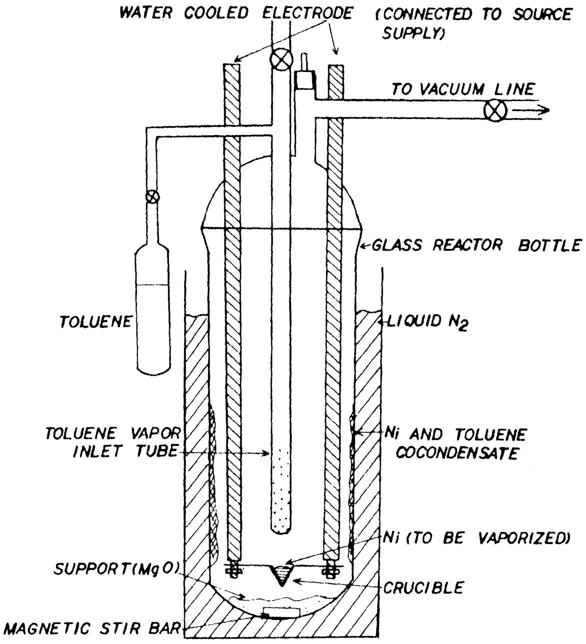
*For a review of the significance of particle size in catalysis, see *Science*, 3 June 1983, p. 1032.

In addition to regulating the size of the particles, this method serves two other purposes. The layer of organic material surrounding the metal atoms provides insulation from electronic interactions with the support, which are often observed for conventionally prepared catalysts. The organic layer also anchors the particle to the support through some still unknown mechanism. Ron Andres of Purdue University has used related techniques to attach bare metal clusters to supports, but has found that the bare clusters are very mobile, and sinter (agglomerate into much larger particles) at relatively low temperatures. In contrast, Klabunde has found that one nickel catalyst on alumina, for example, does not begin to sinter until the temperature rises to about 600°C.



SMAD reactor

Cross section of the device used by Klabunde to prepare SMAD catalysts. The support on which the catalyst is to be deposited is placed in the device before the clusters are formed. [Source: Kenneth Klabunde]

Many SMAD catalysts have potentially useful properties. The powder that results from nickel-hexane slurries, for example, is a very active hydrogenation catalyst for benzene and cyclohexene—more active than the conventional Raney nickel. It is also very reactive with alkyl halides. A nickel-tetrahydrofuran powder is a very good catalyst for disproportionation of cyclohexene to benzene and cyclohexane. Slurries of lead in tetrahydrofuran react with methyl iodide to give $(CH_3)_3PbI$, the first example of a direct lead-alkyl halide reaction.

Supported SMAD catalysts are also potentially useful. For example, highly dispersed, supported nickel catalysts are more active than conventional catalysts for hydrogenolysis of methylcyclopentane, hydrogenation of toluene, dehydrogenation of isopropyl alcohol, and conversion of carbon monoxide to methane. In the first three of these cases, the catalytic activity is independent of the support; for the conventional catalysts, in contrast, the catalytic activity in these same reactions is very sensitive to the nature of the support. Klabunde attributes the higher activity of the SMAD catalysts to their having higher nickel surface areas (smaller particles) and a greater proportion of nickel in the catalytically active zero-valent state.

The methanation of carbon monoxide, however, is sensitive to the support, with MgO providing the greatest activity. Klabunde says this is not an effect of interaction between the catalyst and the support. Rather, carbon monoxide can be adsorbed readily on MgO and this apparently aids in the initial carbon monoxide reduction step.

The new Mn-Co system is supported on silica. "The remarkable finding," Klabunde says, "is that addition of manganese, itself an almost inactive catalyst, substantially increases the catalytic activity of the cobalt-silica system." Only 2.5 atom-percent of manganese increases the activity for 1-butene hydrogenation by a factor of 100. Even higher activities are obtained by adding more manganese, up to 51 atom-percent, where the hydrogenation rate at −60°C is controlled by diffusion. Addition of iron to cobalt also increases the hydrogenation rate, but by a much smaller amount. The addition of chromium is detrimental, however.

Klabunde's discovery is of particular importance because there has been a great deal of interest recently in the production of catalysts containing both "early" and "late" transition metals—that is, those at the beginning and end of the row in the periodic table. Those interested in both heterogeneous and homogeneous reactivity hope that such combinations might lead to unusual selectivity in Fischer-Tropsch chemistry, the reactions of hydrogen and carbon monoxide. Some investigators, such as John Sinfelt of Exxon Research and Engineering Company, have shown that a second metal can in fact change the selectivity of a catalyst. There has, however, been no previous demonstration of substantial activation of one metal by a second, and this observation thus suggests that some unusual chemistry may be found in "early-late" complexes.

In a longer paper now in press in the *Proceedings of the Organic Reactions Catalysis Society*, Klabunde and Imizu have examined the system in more detail. They have found that manganese also provides a similar increase in the cataytic hydrogenolysis of cyclopropane by cobalt. For both reactions, the Mn-Co catalyst is more active than commercial platinum and cobalt catalysts by a factor of 10 to 100.

Part of the increased activity may be attributed to increased dispersion of the cobalt; in a SMAD cobalt catalyst, about half of the cobalt atoms are on the surface of particles and exposed to the reactants. In the Mn-Co particles, between 80 and 90 percent of the cobalt atoms are on the surface. Nonetheless, Klabunde argues that the most important catalytic effect of adding manganese is probably an increase in electron density at the cobalt atoms.

Despite the potential of the SMAD catalysts, there has been very little commercial interest—although Phillips Petroleum Company has supported part of Klabunde's research. He has provided small quantities of catalysts to several industrial research laboratories, "but most of them require substantially larger quantities for an effective evaluation and no one has been willing to take the initial step of scaling the technique up to a pilot plant stage. It is unlikely that any group has conducted its own studies, because preparation of the catalysts requires a certain amount of technique and skill and I don't think they would be able to do it without the involvement of either myself or one of my students." Several venture capital firms have expressed some interest in the catalysts, however, and there is a possibility that Klabunde may start his own company. "If the biotech people can do it," he concludes, "there is no reason why chemists shouldn't also."

—**Thomas H. Maugh II**