

Heterogeneous Catalysis: Some Recent Developments

Some properties of metal catalysts and recent advances in alloys and bimetallic systems are discussed.

John H. Sinfelt

Catalysis has an important bearing on our everyday lives. Catalytic phenomena are found almost everywhere, ranging from biological processes in living things to large-scale processes for refining petroleum and producing chemicals. In recent years catalysts have been applied extensively in decreasing the pollutants in automobile exhaust gases. There has also been a great deal of interest in catalysts in processes such as coal gasification and liquefaction, which are important for extending our fuel capabilities.

In general, a catalyst is a substance which increases the rate of a chemical reaction without itself being consumed in the process. Catalytic processes are commonly classified as homogeneous or heterogeneous. In homogeneous processes, the reactants and catalyst are present in a single phase, for example, in a solution. In heterogeneous processes, the catalyst is present in a separate phase, as in the case of a solid catalyst in contact with gaseous reactants. In this article I discuss only heterogeneous catalysis, and more specifically catalysis by metals. First, I consider metal catalysts in general, with emphasis on the characterization of the degree of dispersion of the metal. Next, I discuss catalytic specificity by relating the catalytic activity of a metal to its position in the periodic table. Much progress has been made in this area as a result of systematic studies of selected reactions on a variety of metals. Finally, I present some recent devel-

opments in catalysis by alloys and related bimetallic systems. Work in this area has resulted not only in significant advances of a fundamental nature but also in the discovery of new systems of major importance in industrial catalysis.

Dispersion of Metal Catalysts

As applied to a metal catalyst, the term dispersion refers to the ratio of the number of metal atoms in the surface to the total number of metal atoms present (*1*). The dispersion may vary widely, depending on the physical form of the catalyst. For example, Ni-Cu alloys are commonly prepared as powders with surface areas of the order of 1 square meter per gram (*2, 3*), corresponding to dispersions of the order of 0.001. The dispersion of such a catalyst may be estimated from the low-temperature physical adsorption of a gas (*4*). Examples of metal catalysts of much higher dispersion are those consisting of very small metal clusters dispersed on the surface of a carrier. Typically, the carrier is a refractory material with a high surface area such as silica (SiO_2) or alumina (Al_2O_3). Physical adsorption techniques, which give information on the total surface area of a solid, cannot be applied to determine the metal dispersion in such a catalyst, since the unoccupied surface of the carrier commonly constitutes a much larger area than the

metallic component itself. For such supported metal catalysts, one needs to use selective adsorption, in which a gas adsorbs on the metal but not on the carrier. The development during the past 15 years of selective chemisorption methods for determining the degree of dispersion of supported metals on a routine basis represents a major advance in the characterization of catalysts (*5, 6*). Earlier studies by Emmett and Brunauer on Fe catalysts were extremely important in demonstrating the idea of selective chemisorption for the study of multi-component catalysts (*7*).

The application of H_2 chemisorption for determining metal dispersion is illustrated in Fig. 1 for a series of Rh catalysts including an unsupported Rh powder (100 percent Rh) and a number of SiO_2 -supported Rh catalysts with varying Rh concentrations (*1, 8*). Assuming the dissociation of H_2 in chemisorption, I express the data in terms of the quantity H/M, which represents the number of H atoms adsorbed per atom of Rh in the catalyst. This quantity increases continuously with decreasing Rh concentration, which corresponds to increasing dispersion of the Rh. With a stoichiometry of one H atom adsorbed per surface metal atom (*5, 9*), the quantity H/M is a direct measure of the degree of dispersion of the metal. The use of selective chemisorption is especially important for catalysts in which the degree of metal dispersion is extremely high (approaching unity), since it is very difficult or impossible to obtain quantitative information on metal dispersion in any other way. Good examples of such catalysts are the Pt- Al_2O_3 systems used in the reforming of petroleum naphthas for gasoline production (*10*).

Highly dispersed supported metals exhibit certain properties which sharply distinguish them from bulk metals. The magnetic properties of Ni provide a good example of this difference. As shown in Fig. 2, the magnetization of Ni in highly dispersed form in Ni- SiO_2 catalysts is very much lower than that of bulk Ni (*11*). The dependence of the magnetiza-

The author is Scientific Advisor in the Corporate Research Laboratories of Exxon Research and Engineering Company, Linden, New Jersey 07036.

tion on field strength, and also temperature, is not typical of a ferromagnetic metal, and the phenomenon has been termed "superparamagnetism" (12). Data such as those in Fig. 2 are useful in characterizing the dispersion of Ni catalysts.

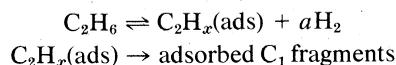
The types of sites present in the surface of a metal are a function of the degree of dispersion of the metal. In large metal crystals, only a very small fraction of the surface atoms is present at edges and corners. As the crystal size is decreased, this fraction increases and approaches a value of the order of unity for extremely small crystals (or clusters) containing only a few atoms. The coordination numbers of atoms at edge and corner sites are lower than those of other atoms in exposed crystal faces. As a result, one might well expect the state of dispersion of a metal to affect its specific catalytic activity, that is, the activity per unit surface area. This dependence of specific catalytic activity on dispersion has indeed been demonstrated for certain reactions which have been designated as "structure-sensitive" reactions (8, 13). Interestingly, however, there are "structure-insensitive" reactions for which the specific activity of a metal is virtually independent of the state of dispersion (13). The elucidation of structure sensitivity is the objective of much current research in heterogeneous catalysis.

Catalytic Specificity of Metals

An extremely important feature of heterogeneous catalysis is specificity in relation to the chemical constitution of a surface (14, 15). The hydrogenolysis of alkanes provides an excellent example of specificity in catalysis by metals. In this type of reaction C-C bonds rupture and C-H bonds form. The simplest hydrogenolysis reaction of a hydrocarbon is the conversion of ethane (C₂H₆) to methane (CH₄):



This reaction has been studied in detail over a number of metals (15, 16). The reaction may be dissected into two separate steps, the symbol (ads) signifying an adsorbed species:



The quantity a is equal to $(6 - x)/2$. The first step is chemisorption of C₂H₆ with the dissociation of C-H bonds, ultimately yielding a hydrogen-deficient surface species, C₂H _{x} . This species then under-

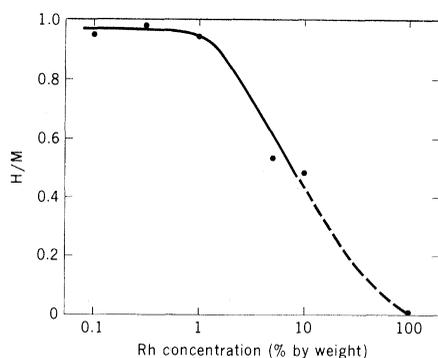


Fig. 1. Chemisorption of H₂ on a series of Rh catalysts of varying concentration. The catalysts containing 0.1 to 10 percent Rh are SiO₂-supported catalysts. The quantity H/M refers to the number of H atoms adsorbed per atom of Rh metal in the catalyst. All of the catalysts were reduced in H₂ at 450°C in their preparation. The chemisorption data were obtained at room temperature (1, 8).

goes C-C scission to yield adsorbed C₁ fragments which are subsequently hydrogenated to CH₄.

Specific catalytic activities of all of the metals of group VIII and of Re in group VII A for C₂H₆ hydrogenolysis are given in Fig. 3, which is divided into three sections representing the metals of the first, second, and third transition series. The group I B metals (Cu, Ag, and Au), for which data are not shown, are much less active than the least active group VIII metals (15). The most complete data are available for the metals of the third transition series, in which the hydrogenolysis activity attains a maximum value at Os. From Os to Pt, the activity decreases by seven orders of magnitude. A similar variation is observed from Ru

to Pd in the second transition series, and Ru is probably the most active metal in the series. This conclusion is supported by data indicating that the hydrogenolysis activity of Mo (group VI A) is very low compared to that of Ru (17). The pattern of variation of hydrogenolysis activity in the first transition series is different, the maximum activity being found in the third rather than the first subgroup within group VIII. This difference in detail is somewhat analogous to known chemical differences between elements of the first transition series on the one hand and the corresponding elements of the second and third transition series on the other (18).

Included with the plots of hydrogenolysis activities of the metals in Fig. 3 are plots of the percentage d -character of the metallic bond, a quantity introduced by Pauling (19) as a measure of the extent of participation of d -orbitals in the bonding between atoms in a metal lattice. For the metals within a given transition series, the patterns of variation of hydrogenolysis activity and percentage d -character from one metal to another are similar. However, the hydrogenolysis activities of Fe, Co, and Ni in the first transition series are comparable to those of metals with significantly higher d -character in the second and third transition series. Thus, the percentage d -character alone is not sufficient to characterize the catalytic activity of transition metals for hydrogenolysis (15).

For a number of other reactions catalyzed by metals, maximum catalytic activity is also found among the metals of group VIII. Examples of reactions that have been extensively investigated are the hydrogenation of ethylene (C₂H₄) to C₂H₆ and of benzene (C₆H₆) to cyclohexane (C₆H₁₂) (20). Within group VIII, however, there are major differences in the relative catalytic activities of the metals for hydrogenation and hydrogenolysis reactions. Thus Pt, which is less active by five orders of magnitude than Ir for C₂H₆ hydrogenolysis, is actually more active for C₂H₄ hydrogenation.

In the hydrogenolysis of saturated hydrocarbons with a number of non-identical C-C bonds, there may be different rates of scission at different locations in the molecule. A classical example of catalytic specificity is the highly selective attack of Ni catalysts on the terminal C-C bonds in alkanes (21). Thus, in the hydrogenolysis of n -hexane on Ni at 180°C the only products at low conversion are CH₄ and n -pentane, formed in equimolar amounts (22). With Pt catalysts, however, the rupture of non-

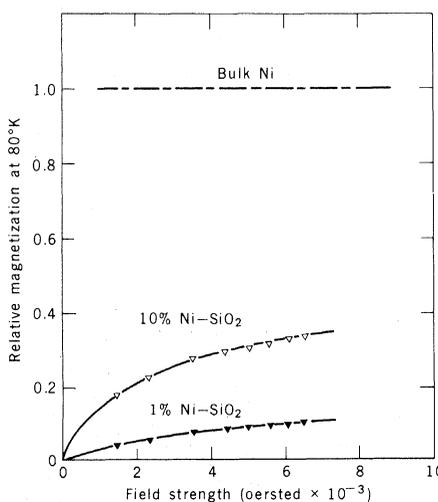


Fig. 2. Comparison of the magnetization of SiO₂-supported Ni catalysts with that of bulk Ni. The catalysts were reduced in H₂ at 370°C in their preparation, and the systems were subsequently evacuated at 370°C prior to magnetic measurements (11).

identical C-C bonds is nonselective, giving a spectrum of primary products. There is also extensive variation among the group VIII metals of the second and third transition series in the pattern of rupture of C-C bonds in *n*-heptane hydrogenolysis (23).

In the hydrogenolysis of alkanes on the group VIII metals of the first transition series (that is, Fe, Co, and Ni) the mode of C-C scission is consistent with a reaction scheme involving successive demethylation of the hydrocarbon chain (22, 24). According to this scheme, scission occurs only at terminal C-C bonds. Thus one of the fragments is always a C₁ species which is then hydrogenated to form CH₄. The other fragment can undergo further scission at the terminal C-C bond to produce additional CH₄, or it can be hydrogenated and desorbed into the gas phase. On Fe, the primary product consists almost entirely of CH₄; this result suggests that desorption of products is strongly limiting. The successive demethylation scheme of hydrogenolysis does not apply to the group VIII metals of the second and third transition series, another indication that these metals behave very differently from those of the first transition series in the catalytic hydrogenolysis of hydrocarbons.

Catalysis by Alloys

Bimetallic catalysts have long been used to investigate the relationship between the catalytic activity of a metal and its electronic structure (25). The original ideas were based on the electronic structure of a metal crystal as a whole rather than on the localized electronic structures of individual surface atoms. As experimental data on chemisorption and catalysis on alloys have accumulated, however, it has become increasingly clear that localized properties of surface atoms are very important. In the case of a Ni-Cu alloy, for example, the atoms of the two metals retain their inherent chemical differences, although bonding properties of the atoms are probably altered to some degree. The electronic factor in catalysis by alloys is currently being pursued from this point of view (26).

A complicating feature in catalytic studies on metal alloys is the possibility of a difference between surface and bulk compositions. Evidence for such a difference in the case of Ni-Cu alloys is based on the observation that strong H₂ chemisorption does not occur on Cu. The addition of only a few percent of Cu to Ni decreases the amount of strongly

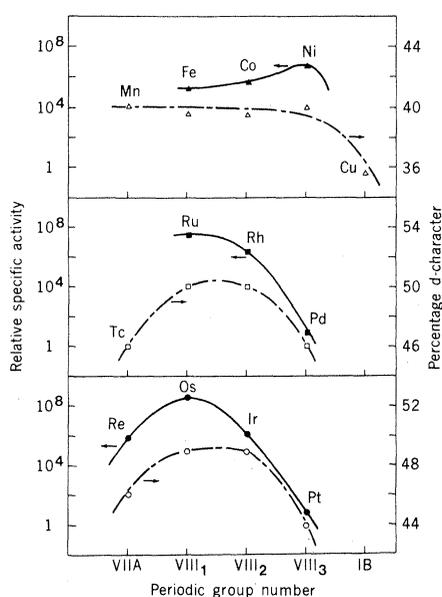


Fig. 3. Catalytic activities of metals for C₂H₆ hydrogenolysis in relation to the percentage *d*-character of the metallic bond. The closed points represent specific activities compared at a temperature of 205°C and C₂H₆ and H₂ pressures of 0.030 and 0.20 atmosphere, respectively; the open points represent the percentage *d*-character. Three sections are shown to distinguish the metals in the different long periods of the periodic table (15).

chemisorbed H₂ severalfold, an indication that the concentration of Cu in the surface is much greater than in the bulk. Similar results have been obtained by several different groups of investigators (3, 27), and the findings are consistent with the results of studies of surface composition by Auger spectroscopy

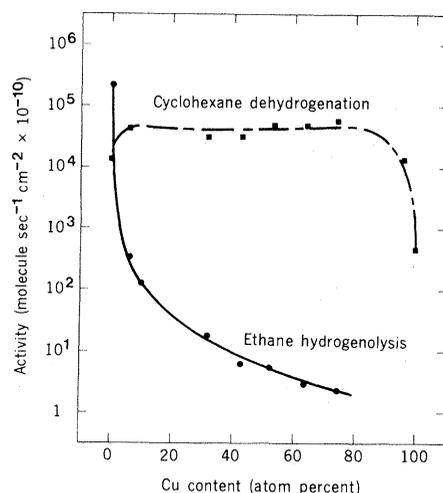


Fig. 4. Activities of Ni-Cu alloy catalysts for the hydrogenolysis of C₂H₆ to CH₄ and the dehydrogenation of C₆H₁₂ to C₆H₆. The activities refer to reaction rates at 316°C. The C₂H₆ hydrogenolysis activities were obtained at C₂H₆ and H₂ pressures of 0.030 and 0.20 atmosphere, respectively. The C₆H₁₂ dehydrogenation activities were obtained at C₆H₁₂ and H₂ pressures of 0.17 and 0.83 atmosphere, respectively (3).

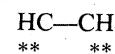
(28). An important factor in determining surface composition is the nature of the gas in contact with the surface of an alloy. Thus, for Ni-Au alloys, Au concentrates in the surface in an inert atmosphere, whereas Ni is the predominant surface component in the presence of O₂ (29). If the interaction of a gas with one of the components is sufficiently strong and selective, the surface tends to be enriched in that particular component.

The emphasis in early studies on alloy catalysts was on the activity for a particular reaction, often a simple hydrogenation reaction of an unsaturated hydrocarbon. The possibility that the effect of alloying depends on the type of reaction has only recently received any attention. A striking example of specificity with regard to the type of reaction is provided by recent work on Ni-Cu alloy catalysts in which two different reactions were investigated, the hydrogenolysis of C₂H₆ to CH₄ and the dehydrogenation of cyclohexane (C₆H₁₂) to benzene (C₆H₆) (3). The latter reaction, represented by the equation



is an important reaction in the production of gasoline components in the petroleum industry (10). The effect of Cu on the catalytic activity of Ni for this reaction is very different from that found for C₂H₆ hydrogenolysis, as shown by the data on a series of Ni-Cu alloys in Fig. 4. In the case of C₂H₆ hydrogenolysis, adding only 5 atom percent Cu to Ni decreases the catalytic activity by three orders of magnitude. With further addition of Cu, the activity continues to decrease. However, the activity of Ni for the dehydrogenation of C₆H₁₂ is affected very little over a wide range of Ni-Cu alloy composition and actually increases on the addition of the first increments of Cu to Ni. Only as the catalyst composition approaches pure Cu is a marked decline in activity for this reaction observed.

In interpreting the C₂H₆ hydrogenolysis data, it is necessary to recall the hypothesis of a hydrogen-deficient surface intermediate, C₂H_{*x*}, which is bonded to more than one metal atom in the surface. If the composition of the intermediate corresponds to C₂H₂, we might visualize a structure of the form



where the asterisks represent bonds between the C atoms and active metal surface atoms. Such an intermediate would require sites comprising "multiplets" of

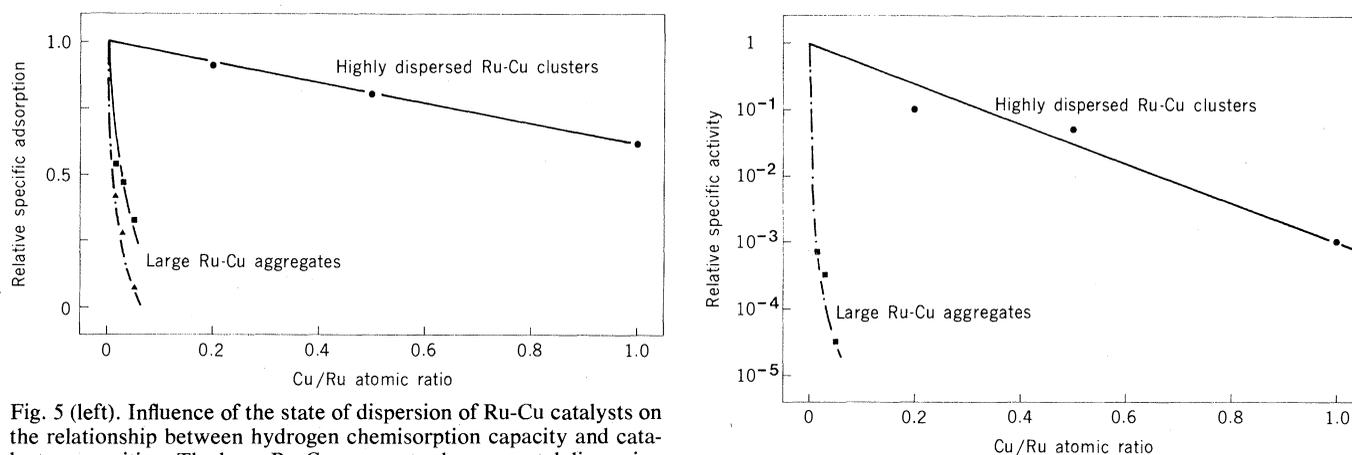


Fig. 5 (left). Influence of the state of dispersion of Ru-Cu catalysts on the relationship between hydrogen chemisorption capacity and catalyst composition. The large Ru-Cu aggregates have a metal dispersion of the order of 1 percent, whereas the highly dispersed Ru-Cu clusters have a metal dispersion of the order of 50 percent. The latter were supported on SiO₂. In the case of the large Ru-Cu aggregates, the square points represent total H₂ chemisorption and the triangular points represent strongly chemisorbed H₂, that is, H₂ that cannot be removed by evacuation at room temperature (31). Fig. 6 (right). Influence of the state of dispersion of Ru-Cu catalysts on the relationship between C₂H₆ hydrogenolysis activity and catalyst composition. The catalysts are the same as in Fig. 5 (31).

adjacent active metal atoms. [The term multiplet is taken from the work of Balandin (30).]

If the active metal atoms are diluted with inactive metal atoms in the surface, the concentration of active multiplets will decline sharply. For the Ni-Cu alloy system, in which the inactive Cu atoms concentrate strongly in the surface, the addition of only a few percent of Cu to Ni will result in a markedly lower concentration of multiplet Ni atom sites. Although such a geometric argument can account for a large inhibiting effect of Cu on the hydrogenolysis activity of Ni, it is difficult to dismiss the possibility that electronic interaction between Cu and Ni may also affect the catalysis. In view of the low ability of Cu relative to Ni to chemisorb a variety of hydrocarbons, one might reasonably expect that the addition of Cu to Ni in an alloy would decrease the strength of adsorption of hydrocarbon species on the surface. In C₂H₆ hydrogenolysis, the strength of bonding between the two C atoms in the chemisorbed intermediate might be expected to vary in an inverse manner with the strength of bonding of the C atoms to the metal. One would then conclude that rupture of the C-C bond would be inhibited by a decrease in the strength of adsorption accompanying the addition of Cu to Ni. If C-C rupture is rate-limiting, the rate of hydrogenolysis should then decrease.

The C₆H₁₂ dehydrogenation reaction may not require a site consisting of a multiplet of active Ni atoms. Although this lack of a multiplet site requirement would account for the absence of a steep decline in activity as Cu is added to Ni, it does not explain why Cu-rich alloys have dehydrogenation activities as high or

higher than that of pure Ni. However, if the activity is controlled by a step whose rate is inversely related to the strength of adsorption (for example, desorption of the C₆H₆ product), the addition of Cu to Ni could increase the activity of a catalytic site and compensate for a decrease in the number of such sites. Over the range of composition from pure Ni to pure Cu, however, it is likely that the rate-determining step changes. For pure Cu, the chemisorption of the C₆H₁₂ itself may be limiting.

The Ni-Cu alloys that I have discussed were prepared under conditions of complete miscibility of the two components. At this point it is pertinent to consider a system such as Ru-Cu, the components of which are essentially completely immiscible in the bulk. The crystal structures of the two metals are different, Ru having a hexagonal close-packed structure and Cu a face-centered cubic structure. Although the Ru-Cu system can hardly be considered as an alloy-forming system, bimetallic Ru-Cu aggregates can be prepared which are similar to alloys such as Ni-Cu in their catalytic behavior. In such aggregates, the Cu tends to cover the surface of the Ru (31). Evidence for this structure comes from studies of H₂ chemisorption capacity and C₂H₆ hydrogenolysis activity, both of which are markedly suppressed when even small amounts of Cu are present with the Ru. The interaction between the two components may be considered analogous to that which would exist in the chemisorption of Cu on Ru. The behavior of the Ru-Cu system for C₂H₆ hydrogenolysis is similar to that observed for Ni-Cu. In C₆H₁₂ dehydrogenation to C₆H₆, the two systems also behave similarly, in that Cu has only a small effect

on dehydrogenation activity. However, pure Ru exhibits extensive hydrogenolysis of C₆H₁₂ to alkanes of lower carbon number (mostly CH₄) in addition to dehydrogenation to C₆H₆. Addition of Cu to Ru suppresses hydrogenolysis strongly relative to dehydrogenation, so that a marked increase in the selectivity to C₆H₆ is observed. The chemisorbed intermediates are probably different in the dehydrogenation and hydrogenolysis reactions. As in the case of C₂H₆ hydrogenolysis, the intermediate in C₆H₁₂ hydrogenolysis is probably a hydrogen-deficient surface residue which forms bonds with more than one surface metal atom.

In general, the addition of a group I B metal to a group VIII metal decreases hydrogenolysis activity markedly but has a much smaller effect on such other reactions as dehydrogenation, hydrogenation, and isomerization of hydrocarbons (3, 31-33). Selectivity is therefore an important aspect of hydrocarbon conversion on bimetallic catalysts of this type.

"Bimetallic Cluster" Catalysts

Bimetallic systems of the type considered in the previous section have surface areas that are too low, by about two orders of magnitude, for use as industrial catalysts. One method of increasing the surface area of a metal is to disperse it on a carrier such as SiO₂ or Al₂O₃. The carrier itself has a high surface area, commonly in the range of 100 to 300 square meters per gram. One can prepare a supported bimetallic catalyst by impregnating a carrier with an aqueous solution of salts of the two metals of

interest. The material is dried and then brought in contact with a stream of H_2 at elevated temperature to reduce the metal salts. This procedure results in the formation of very small metal clusters dispersed on the surface of the carrier. The nature of these clusters is the question of interest. Will the individual clusters be monometallic, or will they contain atoms of both metals and therefore be bimetallic? On purely statistical grounds one might expect that the individual clusters would contain atoms of both metals. This expectation is supported by experiment, even for cases in which the individual metal components exhibit very low miscibility in the bulk (33, 34). Examples of such metal clusters which have been investigated are Ru-Cu and Os-Cu supported on SiO_2 , in which the metal clusters cover about 1 percent of the surface of the SiO_2 (33). The metal dispersion, expressed as the percentage of metal atoms present in the surface, is in the range of 50 to 100 percent in these systems.

Although direct experimental verification of bimetallic clusters in such highly dispersed systems is difficult, a catalytic reaction can serve as a sensitive probe to obtain evidence of interaction between the atoms of the two metallic components. For supported bimetallic combinations of a group VIII and a group I B metal, the hydrogenolysis of C_2H_6 to CH_4 is a very useful reaction for this purpose. In unsupported bimetallic systems of this type, the interaction between the group VIII metal and the group I B metal markedly decreases the hydrogenolysis activity of the group VIII metal. In applying C_2H_6 hydrogenolysis as a probe to establish interaction between Cu and either Ru or Os on a carrier, one looks for a marked suppression of the hydrogenolysis activity of the group VIII metal when Cu is present. Experiments of this type have demonstrated clearly that the metal components are not isolated from each other on the carrier and therefore provide evidence for the existence of bimetallic clusters (33). Chemisorption of H_2 can be employed in a similar manner as a probe, in which case interaction of Cu with either Ru or Os is indicated by a suppression of chemisorption capacity. The utilization of H_2 chemisorption and C_2H_6 hydrogenolysis as probes to detect bimetallic clusters is illustrated by the data on highly dispersed Ru-Cu clusters in Figs. 5 and 6.

It is interesting to consider how the state of dispersion of Ru-Cu catalysts affects the relationship between H_2 chemisorption capacity or C_2H_6 hydro-

genolysis activity and catalyst composition (31). Data comparing large Ru-Cu aggregates with highly dispersed Ru-Cu clusters are given in Figs. 5 and 6. The highly dispersed clusters require a much higher atomic ratio of Cu to Ru than the large aggregates to achieve a given degree of inhibition of H_2 chemisorption or C_2H_6 hydrogenolysis. The required ratios differ by a factor approximately equal to the ratio of the metal dispersions of the catalysts. This result indicates that the Cu in a Ru-Cu aggregate is confined to the surface, which is consistent with the extremely low miscibility of the two metals in the bulk state. If one envisions a series of Ru-Cu aggregates of varying size, each containing a monolayer of Cu on the surface, the atomic ratio of Cu to Ru in an aggregate will increase with decreasing aggregate size. When the aggregates become small enough, the atomic ratio of Cu to Ru attains a value of the order of unity. The resulting Ru-Cu entity is a model of a highly dispersed bimetallic cluster. Consequently, a highly dispersed bimetallic cluster may have compositions far outside the range of those possible in a bulk solid solution of the two metals.

As Cu is incorporated with Ru or Os in bimetallic clusters, the selectivity for conversion of C_6H_{12} to C_6H_6 is improved greatly (33); hydrogenolysis to alkanes is inhibited markedly, whereas dehydrogenation to C_6H_6 is relatively unaffected. The behavior is similar to that described for unsupported Ru-Cu aggregates earlier and therefore provides further evidence for the interaction between Cu and the group VIII metal on the carrier.

The bimetallic clusters considered up to this point have been combinations of a group VIII and a group I B metal. These systems have been discussed because they are good model systems in which chemisorption and catalysis can be used as probes in investigating the bimetallic cluster concept. From the viewpoint of practical catalysis the obvious interest in this type of system is the improved selectivity for certain reactions, as a result of the inhibition of hydrogenolysis. Another type of bimetallic cluster of interest is a combination of atoms of two group VIII metals, for example, Pt-Pd, Pt-Rh, or Pt-Ir (35).

Our present knowledge of bimetallic clusters is derived largely from studies of their chemisorption and catalytic properties. X-ray diffraction has provided direct evidence for the existence of Pt-Ir clusters in the approximate size range of 25 to 50 angstroms (35). However, it becomes increasingly difficult to charac-

terize such systems by conventional physical methods as the metal dispersion increases. In recent years, there have been advances in x-ray absorption spectroscopy which hold much promise for this purpose. It has been shown that extended x-ray absorption fine structure (EXAFS) gives structural information on noncrystalline materials (36). The application of EXAFS to bimetallic catalysts is currently being investigated by Sinfelt and his collaborators (37).

The concept of bimetallic clusters may be generalized to polymetallic clusters. Polymetallic clusters are clusters containing atoms of two or more metals and thus include bimetallic clusters as a special case (35). Polymetallic clusters make possible great flexibility in the design of metal catalysts. Virtually any property of a metal catalyst, including activity, selectivity, or surface stability, may be influenced if the metal is combined with one or more other metals in the form of polymetallic clusters. Such materials have been shown to have practical industrial use. Research in this area at the Exxon Corporate Research Laboratories has recently led to a new catalyst for use in the reforming of petroleum naphthas (38), which has been applied extensively in commercial operations.

Summary

In recent years major progress has been made in the area of heterogeneous catalysis by metals. Much has been learned about the nature of metal catalysts and of catalytic phenomena on metals. Characteristic patterns of catalytic behavior among the metallic elements have been established for certain classes of reactions, and these patterns provide a first step toward a more comprehensive understanding of catalytic specificity. Studies on metal alloys and related bimetallic catalysts have revived interest in a geometric factor in surface catalysis to complement the traditional electronic factor. Closely related to this geometric factor is the discovery that selectivity, rather than activity alone, is a major factor in reactions on bimetallic catalysts.

Concurrent with progress in understanding how catalysts work, advances are also being made in the development of new catalyst systems, examples of which are the bimetallic (or polymetallic) cluster catalysts. Research in this area provides an example of how advances in catalyst technology can be realized within a framework of fundamental research on catalytic phenomena (38).

References and Notes

- J. H. Sinfelt, *Annu. Rev. Mater. Sci.* **2**, 641 (1972).
- W. K. Hall and P. H. Emmett, *J. Phys. Chem.* **62**, 816 (1958).
- J. H. Sinfelt, J. L. Carter, D. J. C. Yates, *J. Catal.* **24**, 283 (1972).
- S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
- J. H. Sinfelt, W. F. Taylor, D. J. C. Yates, *J. Phys. Chem.* **69**, 95 (1965); J. H. Sinfelt and D. J. C. Yates, *J. Catal.* **8**, 82 (1967); L. Spenadel and M. Boudart, *J. Phys. Chem.* **64**, 204 (1960).
- J. E. Benson and M. Boudart, *J. Catal.* **4**, 704 (1965).
- P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.* **59**, 310 (1937).
- D. J. C. Yates and J. H. Sinfelt, *J. Catal.* **8**, 348 (1967).
- M. A. Vannice, J. E. Benson, M. Boudart, *ibid.* **16**, 348 (1970); G. R. Wilson and W. K. Hall, *ibid.* **17**, 190 (1970).
- J. H. Sinfelt, *Adv. Chem. Eng.* **5**, 37 (1964).
- J. L. Carter and J. H. Sinfelt, *J. Phys. Chem.* **70**, 3003 (1966); J. H. Sinfelt, *Catal. Rev.* **3** (No. 2), 175 (1969).
- C. P. Bean and J. D. Livingston, *J. Appl. Phys.* **30**, 120S (1959); P. W. Selwood, *Adsorption and Collective Paramagnetism* (Academic Press, New York, 1962), pp. 35-50.
- M. Boudart *et al.*, *J. Catal.* **11**, 35 (1968).
- J. H. Sinfelt, *AIChE J.* **19**, 673 (1973); *Prog. Solid State Chem.* **10** (No. 2), 55 (1975).
- _____, *Adv. Catal.* **23**, 91 (1973).
- _____, *Catal. Rev.* **9** (No. 1), 147 (1974).
- _____, and D. J. C. Yates, *Nature (London) Phys. Sci.* **229**, 27 (1971).
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience, New York, 1962), pp. 661 and 760.
- L. Pauling, *Proc. R. Soc. London Ser. A* **196**, 343 (1949).
- G. C. A. Schuit and L. L. van Reijen, *Adv. Catal.* **10**, 242 (1958).
- V. Haensel and V. N. Ipatieff, *J. Am. Chem. Soc.* **68**, 345 (1946).
- H. Matsumoto, Y. Saito, Y. Yoneda, *J. Catal.* **19**, 101 (1970).
- J. L. Carter, J. A. Cusumano, J. H. Sinfelt, *ibid.* **20**, 223 (1971).
- H. Matsumoto, Y. Saito, Y. Yoneda, *ibid.* **22**, 182 (1971).
- G. M. Schwab, *Discuss. Faraday Soc.* **8**, 166 (1950); D. A. Dowden, *J. Chem. Soc.* **1950**, 242 (1950).
- W. M. H. Sachtler and P. van der Plank, *Surf. Sci.* **18**, 62 (1969).
- P. van der Plank and W. M. H. Sachtler, *J. Catal.* **7**, 300 (1967); D. A. Cadenhead and N. J. Wagner, *J. Phys. Chem.* **72**, 2775 (1968).
- C. R. Helms, *J. Catal.* **36**, 114 (1975).
- F. L. Williams and M. Boudart, *ibid.* **30**, 438 (1973).
- A. A. Balandin, *Adv. Catal.* **10**, 96 (1958).
- J. H. Sinfelt, Y. L. Lam, J. A. Cusumano, A. E. Barnett, *J. Catal.* **42**, 227 (1976).
- J. H. Sinfelt, A. E. Barnett, J. L. Carter, U.S. Patent 3,617,518 (1971); V. Ponc and W. M. H. Sachtler, *J. Catal.* **24**, 250 (1972); J. M. Beelen, V. Ponc, W. M. H. Sachtler, *ibid.* **28**, 376 (1973); V. Ponc and W. M. H. Sachtler, in *Proceedings of the 5th International Congress on Catalysis*, J. W. Hightower, Ed. (North-Holland, Amsterdam, 1973), p. 645.
- J. H. Sinfelt, *J. Catal.* **29**, 308 (1973).
- _____, in *Proceedings of the 5th International Congress on Catalysis*, J. W. Hightower, Ed. (North-Holland, Amsterdam, 1973), p. 653.
- _____, U.S. Patent 3,953,368 (1976).
- D. E. Sayers, F. W. Lytle, E. A. Stern, *Phys. Rev. Lett.* **27**, 1204 (1971).
- F. W. Lytle, G. H. Via, J. H. Sinfelt, *Preprints Div. Petrol. Chem. Am. Chem. Soc.* **21** (No. 2), 366 (1976).
- J. H. Sinfelt, *Chem. Eng. News* **50**, 18 (3 July 1972).

Norepinephrine-Dopamine Interactions and Behavior

A new hypothesis of stress-related interactions between brain norepinephrine and dopamine is proposed.

Seymour M. Antelman and Anthony R. Caggiula

Of the many transmitter candidates known to exist in the central nervous system, the catecholamines dopamine (DA) and norepinephrine (NE) have been most often linked to the behavioral pathology of a number of neurological and psychiatric disorders. Among these disorders are Parkinson's disease (1), Huntington's and hyperthyroid chorea (2), Gilles de la Tourette's syndrome (3), and the schizophrenias (4). It has also been suggested that catecholamines may play a role in affective disorders (5).

Work with animals similarly suggests that NE- or DA-containing neural pathways, or both, may play critical roles in numerous basic survival-related activities such as eating (and food-oriented activities such as licking and gnawing) (6-8) as well as reproductive behavior (9, 10), stress-related aggression (11, 12),

Dr. Antelman is assistant professor in the departments of psychiatry and psychology, and Dr. Caggiula is associate professor in the departments of psychology and pharmacology, at the University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

and electrical self-stimulation of the brain (13, 14). The seemingly ubiquitous nature of catecholamine involvement across a wide spectrum of behaviors and the remarkable adaptive capacity of catecholamines to maintain relatively normal function even in cases of severe damage (1), suggests that catecholamine systems may play a very fundamental role in mediating the interaction between the organism and its environment.

In recent years, there has been a considerable shift of opinion regarding the relative importance of NE and DA in the mediation of many behaviors. In stark contrast to the ever-growing number of activities in which DA appears to be implicated, the list of behaviors in which a role for NE is seriously considered appears to be declining. Indeed, in summarizing a recent symposium on monoamines, Lipton (15) was prompted to remark that "So much of the behavior previously attributed to NE now has been found to be mediated by DA that

questions arise about the role of NE." We believe that these questions may be the unfortunate result of the traditional NE versus DA approach which has characterized catecholamine research in psychopharmacology for so long.

As an alternative to an either-or approach, it may be more profitable to study the possible interactions between these catecholamines. Although very little work has been deliberately devoted to examining possible interactions between NE and DA (16), there is substantial support for the existence of an important relationship between these amines. Moreover, the implications stemming from this relationship may help in the resolution of long-standing controversies dealing, for example, with the relative importance of brain NE and DA systems in reward behavior, and may have far-reaching importance for the better understanding of disorders such as Parkinson's disease and schizophrenia.

Statement of Hypothesis

There is much evidence that suggests that interference with brain NE-containing systems will, under some circumstances, potentiate a variety of behaviors while, under other conditions, the identical manipulations may depress the very same behaviors. We believe that these apparently contradictory findings can be explained or resolved by the consideration of three key factors: (i) the behaviors in question are critically dependent on the normal functioning of brain DA-containing systems, (ii) the potentiation or depression of an organism's behavior relates to the activational features of the environment, and (iii) the behavioral out-