Structure of Bimetallic Clusters

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As the name implies, bimetallic clusters are metallic entities comprising atoms of two different metallic elements.[1-3] They are important in catalysis and were conceived originally for this purpose. As a rough guideline, the clusters of interest have sizes smaller than about 100 Å and they are commonly in the size range of 10–50 Å. In some cases, the clusters are so small that virtually every metal atom is a surface atom. Generally, the clusters are dispersed throughout porous particles of a refractory material such as silica or alumina. The refractory material, which is known as a carrier or support, has a very high surface area, frequently in the range of 100–300 m²/g.

Catalysts containing bimetallic clusters can be prepared simply by contacting a suitable carrier such as silica or alumina with an aqueous solution of precursors (e.g., salts) of the two metals of interest. The material is then dried and contacted with a stream of hydrogen at a temperature high enough to accomplish reduction of the metal precursors. The reduction yields bimetallic clusters dispersed on the carrier.

Several types of bimetallic clusters have been of interest in catalysis. One comprises a combination of atoms of a group VIII (8–10)[47] metal and a group IB (11) metal, for example, ruthenium–copper and osmium–copper.[1] In early work on bimetallic catalysts, it was discovered that the activity of a group VIII (8–10) metal for hydrogenolysis reactions of hydrocarbons is decreased markedly by the presence of a Group IB (11) metal.[1,4-9] Inhibition of hydrogenolysis leads to improved selectivity for alkane isomerization reactions[4] and for reactions in which saturated hydrocarbons are converted to aromatic hydrocarbons.[1,5,7] Interest in bimetallic catalysts increased markedly with the discovery of this selectivity phenomenon.

Other interesting types of bimetallic clusters comprise a combination of atoms of two group VIII (8–10) metals, such as platinum–iridium[10-13] and iridium–rhodium,[10,14] or a combination of two group IB (11) metals, e.g., silver–copper or gold–copper.[15] The combination of platinum and rhenium provides an example of still another type, comprising a group VIII (8–10) metal and a metal from group VIIA (7). Platinum–iridium catalysts developed in the Exxon laboratories and platinum–rhenium catalysts developed by the Chevron Co. have been widely used in petroleum refining for the production of aromatic hydrocarbons for automotive fuels.[3]

John H. Sinfelt was born in Munson, PA, in 1931. After receiving his Ph.D. degree from the University of Illinois in 1954, he joined Exxon Research and Engineering Co., where he has conducted research in heterogeneous catalysis for his entire career. He is currently a Senior Scientific Advisor in the Corporate Research Science Laboratories in Annandale, NJ. In the 1960s he began research on bimetallic catalysts. For the past decade his research in this area has emphasized the use of extended X-ray absorption fine structure (EXAFS) for the characterization of the structures of bimetallic clusters. Dr. Sinfelt is the recipient of the 1986 Murphree Award of the American Chemical Society, and this Account is based on his award address.

The initial characterization of bimetallic clusters was limited to chemical probes, e.g., chemisorption of hydrogen and carbon monoxide in conjunction with kinetic studies of a test reaction such as the hydrogenolysis of ethane to methane.[1] The situation changed markedly at a later stage of the research. The change was primarily due to advances in X-ray absorption spectroscopy during the 1970s, especially with regard to extended X-ray absorption fine structure (EXAFS). Advances in methods of analysis of EXAFS data,[16-18] coupled with improvements in methods of obtaining the data with the use of synchrotron radiation,[19] have made EXAFS a valuable tool for obtaining structural information on bimetallic clusters.[20]

Application of EXAFS to Bimetallic Clusters

In an X-ray absorption spectrum of an element, abrupt increases in absorption coefficient (absorption edges) are observed at certain X-ray energies,[21] as illustrated in Figure 1 for the K absorption edge of ruthenium. When X-rays with such an energy are absorbed by atoms of the element, electrons in a particular energy level are ejected from the atoms. A given element will in general have a number of absorption edges corresponding to the different energy levels of the electrons in the atoms.

When X-rays are absorbed by matter other than monatomic gases, a plot of absorption coefficient vs. X-ray energy exhibits oscillations on the high-energy side of an absorption edge. The oscillations constitute the extended X-ray absorption fine structure (EXAFS) which is commonly observed in an X-ray absorption spectrum.[22] The spectrum in Figure 1 was obtained

(1) Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308.
(2) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15.
(3) Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts, and Applications*; Wiley: New York, 1983.
(4) Sinfelt, J. H.; Barnett, A. E.; Dembinski, G. W. U.S. Patent 3 442 973, 1969.
(5) Sinfelt, J. H.; Barnett, A. E.; Carter, J. L. U.S. Patent 3 617 518, 1971.
(6) Sinfelt, J. H.; Carter, J. L.; Yates, D. J. C. *J. Catal.* **1972**, *24*, 283.
(7) Sinfelt, J. H.; Lam, Y. L.; Cusumano, J. A.; Barnett, A. E. *J. Catal.* **1976**, *42*, 227.
(8) Ponec, V.; Sachtler, W. M. H. *J. Catal.* **1972**, *24*, 250.
(9) Beelen, J. M.; Ponec, V.; Sachtler, W. M. H. *J. Catal.* **1973**, *28*, 376.
(10) Sinfelt, J. H. U.S. Patent 3 953 368, 1976.
(11) Sinfelt, J. H.; Via, G. H. *J. Catal.* **1979**, *56*, 1.
(12) Garten, R. L.; Sinfelt, J. H. *J. Catal.* **1980**, *62*, 127.
(13) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *J. Chem. Phys.* **1982**, *76*, 2779.
(14) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. *J. Chem. Phys.* **1983**, *78*, 2533.
(15) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. *J. Chem. Phys.* **1985**, *83*, 4793.
(16) Sayers, D. E.; Lytle, F. W.; Stern, E. *Phys. Rev. Lett.* **1971**, *27*, 1204.
(17) Lytle, F. W.; Sayers, D.; Stern, E. *Phys. Rev. B: Solid State* **1975**, *11*, 4825.
(18) Stern, E.; Sayers, D.; Lytle, F. W. *Phys. Rev. B: Solid State* **1975**, *11*, 4836.
(19) Kincaid, B. M.; Eisenberger, P. *Phys. Rev. Lett.* **1975**, *34*, 1361.
(20) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *Catal. Rev.—Sci. Eng.* **1984**, *26*(1), 81.
(21) Stern, E. A. *Sci. Am.* **1976**, *234*(4), 96.
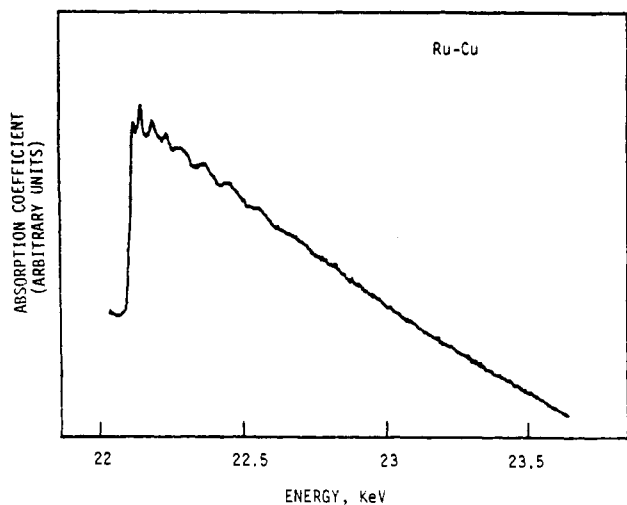
Figure 1. X-ray absorption spectrum of ruthenium–copper clusters at 100 K in the region of the K absorption edge of ruthenium.[23] The abscissa is the energy of the X-ray photons.

Figure 2. Normalized EXAFS data (ruthenium K absorption edge) for ruthenium–copper clusters at 100 K, with associated Fourier transform, filtered transform, and inverse of the filtered transform.[23] The inverse transform isolates the EXAFS due to the nearest-neighbor metal atoms.

at a temperature of 100 K for a catalyst consisting of ruthenium–copper clusters dispersed on silica.[23] The catalyst contained 1 wt % ruthenium and 0.63 wt % copper, corresponding to a copper to ruthenium atomic ratio equal to one. The electrons ejected from the ruthenium atoms are scattered by neighboring ruthenium and copper atoms. The oscillations in the absorption coefficient are attributed to interference between waves associated with the ejected electrons and waves associated with the backscattered electrons.[21]

A photoelectron ejected from an atom as a result of X-ray absorption is characterized by a wave vector K given by the equation

$$K = (2mE)^{1/2}/\hbar \tag{1}$$

where m is the mass of the electron, $\hbar$ is Planck's constant divided by 2π, and E is the kinetic energy of the photoelectron. In the treatment of EXAFS data, the absorption coefficient in the region of the EXAFS is divided into two parts. One part is independent of the environment of the absorber atoms and is identical with the absorption coefficient for the free atom. The other part is the oscillating part which constitutes EXAFS. Division of the latter part by the former normalizes the EXAFS oscillations. The normalized oscillations are represented by the quantity $\chi(K)$, in which K is the photoelectron wave vector. The determination of $\chi(K)$ from experimental EXAFS data has been discussed in detail elsewhere.[17,24,25]

A plot of the function $K\chi(K)$ vs. K is shown in the upper left-hand section of Figure 2 for the ruthenium EXAFS data on ruthenium–copper clusters presented in Figure 1. A Fourier transform of $K\chi(K)$ yields a radial structure function $\phi(R)$, where R is the distance from the absorber atom.[16] It is shown in the upper right-hand section of Figure 2. The prominent peak is associated with scattering of photoelectrons by nearest-neighbor metal atoms about ruthenium absorber
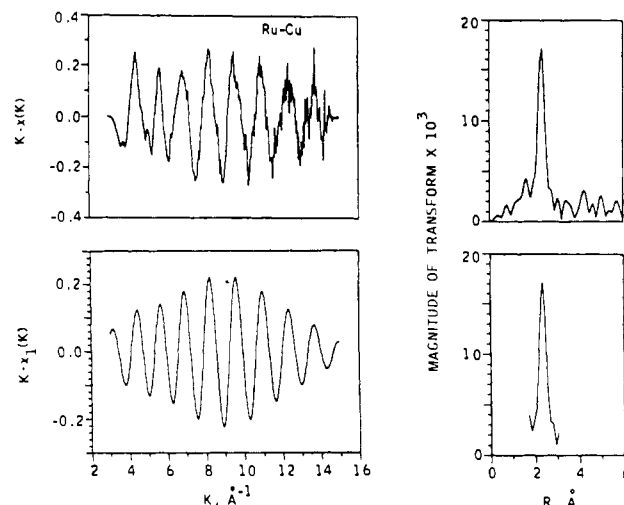
atoms. It is centered at a value of R which is not a true interatomic distance because of phase shifts.[16,18]

In the analysis of EXAFS data, it is useful to invert the Fourier transform over a limited range of R. This procedure determines the contribution to EXAFS arising from shells of atoms within that range of R. In Figure 2, for example, the region of the Fourier transform for values of R between 1.7 and 3.1 Å is isolated in the lower right-hand section of the figure. An inverse transform of this region, which brackets the primary peak, yields the function shown in the lower left-hand section of Figure 2. This function represents the contribution to the EXAFS due to backscattering of electrons by nearest-neighbor metal atoms (ruthenium and copper).

When EXAFS data are obtained on bimetallic clusters, there are two EXAFS functions to consider, one for each component of the clusters.[20,23] The EXAFS function for a given component consists of backscattering contributions from the two types of atoms surrounding absorber atoms of the component. This is illustrated in Figure 3 for osmium–copper clusters dispersed on silica in a catalyst containing 2 wt % osmium and 0.66 wt % copper.[26] The copper to osmium atomic ratio in the catalyst is equal to one. In all three fields of Figure 3, the solid line represents the EXAFS function for the osmium L_{III} edge due to backscattering from nearest-neighbor atoms. The nearest neighbors, of course, include both osmium and copper atoms. The circles in the middle field (field B) represent the contribution to the osmium L_{III} EXAFS due to backscattering from nearest-neighbor copper atoms. The circles in the lower field (field C) represent the contribution from nearest-neighbor osmium atoms. Envelope functions through the maxima and minima in the oscillations represented by the circles have very different shapes in fields B and C, reflecting characteristic differences in the backscattering properties of copper and osmium, which are far apart in atomic number (29 vs. 76). In the upper field (field A) the circles represent the total EXAFS arising from the combined contribu-

(22) Lytle, F. W. In *Physics of Non-Crystalline Solids*; Prins, J. A., Ed.; North-Holland: Amsterdam, 1965; p 12.

(23) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *J. Chem. Phys.* **1980**, *72*, 4832.

(24) Via, G. H.; Sinfelt, J. H.; Lytle, F. W. *J. Chem. Phys.* **1979**, *71*, 690.

(25) Lytle, F. W.; Via, G. H.; Sinfelt, J. H. In *Synchrotron Radiation Research*; Winick, H., Doniach, S., Eds.; Plenum: New York, 1980; pp 401–424.

(26) Sinfelt, J. H.; Via, G. H.; Lytle, F. W.; Greegor, R. B. *J. Chem. Phys.* **1981**, *75*, 5527.
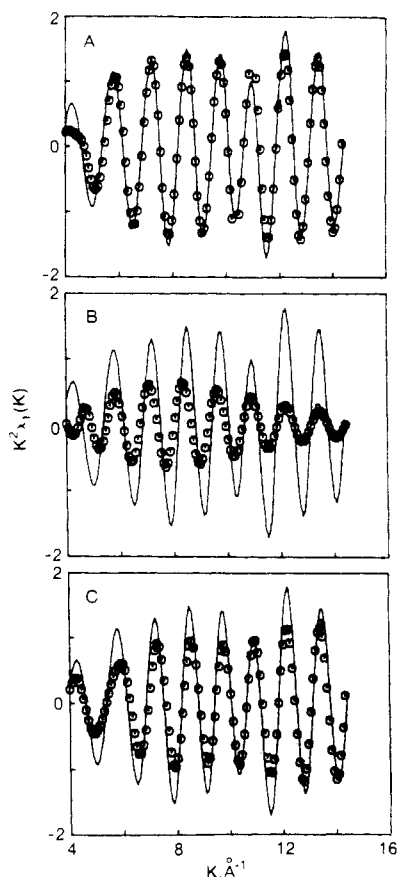
Figure 3. Contributions of nearest-neighbor copper and osmium backscattering atoms (circles in fields B and C, respectively) to the EXAFS associated with the osmium L_{III} absorption edge of osmium–copper clusters. The circles in field A show how the individual contributions combine to describe the experimental EXAFS represented by the solid line.[26]

tion of nearest-neighbor osmium and copper atoms, as determined by the data-fitting analysis. Comparison of the points with the solid line in the upper field provides a measure of the quality of fit obtained in a quantitative analysis of this type. Precisely the same type of analysis has also been made of the EXAFS associated with the K absorption edge of the copper in the osmium–copper clusters.[26] Details of the quantitative analysis of EXAFS data on bimetallic clusters, including the use of data on appropriate reference materials, can be found in our early papers.[23,26] An important part of the analysis is concerned with phase shift functions. Published work of scientists at Bell Laboratories[27,28] has been very helpful in this aspect of the analysis.

Structural Features of Bimetallic Clusters

Systems of Miscible Components. If two metals A and B fulfill certain conditions,[29] they will form solid solutions over the whole range of compositions from pure A to pure B. A bimetallic cluster of A and B may then be regarded simply as a small aggregate consisting of a solid solution of atoms of the two metals. Examples include Ir–Rh,[14] Au–Cu,[15] and Pt–Cu[30] clusters, for

which structural information has in all cases been obtained from EXAFS data.

For catalysts containing Ir–Rh clusters, it has been concluded from EXAFS studies that the surface sites in the clusters are preferentially occupied by rhodium atoms.[14] The analysis of the EXAFS data shows that the average number of nearest-neighbor metal atoms about a rhodium atom is lower than the number about an iridium atom. Since the coordination number of a surface atom in a cluster is lower than that of an interior atom, one concludes that rhodium concentrates in the surface of the clusters. Thus, the EXAFS data provide evidence of a partial segregation of the rhodium from the iridium.

Some degree of segregation of the components is also observed in Au–Cu clusters, and again there is an indication that one of the components may concentrate in the surface.[15] This finding could have been anticipated from earlier work indicating a difference between the surface and bulk compositions of massive Au–Cu alloys.[31-33] There is some evidence that the surface composition of Au–Cu clusters may be influenced by the gaseous atmosphere in contact with the clusters.[15] Such a phenomenon is well-known for metal alloys.[34,35]

The phenomenon of ordering, in which atoms of one component are preferentially coordinated to atoms of the other, is not evident in the bimetallic clusters considered here. In this respect, Au–Cu and Pt–Cu clusters with 1:1 atomic ratios of the components differ significantly from the corresponding bulk alloys, which are well-known examples of ordered solid solutions.[36,37]

Systems of Limited Miscibility. Systems of interest as bimetallic clusters are not limited to combinations of metallic elements which form solid solutions in the bulk. Experiments on the chemisorption and catalytic properties of materials containing copper and either ruthenium or osmium led to the discovery of Ru–Cu and Os–Cu bimetallic clusters,[1] the components of which are completely immiscible with one another.[38] It was concluded that the copper was present on the surface of the ruthenium or osmium, analogous to an adsorption layer.[2,7]

Results of EXAFS experiments on silica-supported Ru–Cu clusters with a diameter of approximately 30 Å and a 1:1 stoichiometry of copper to ruthenium are in excellent agreement with this model.[23] In these clusters the surface atoms constitute about half of the total atoms. Therefore, the surface can consist entirely of copper, in the form of a monolayer covering an internal core of ruthenium. In the ruthenium core, Ru–Ru bonds would then represent a very high fraction of the bonds involving ruthenium atoms. Consequently, the average environment about a ruthenium atom in the Ru–Cu clusters would not be very different from that in the pure ruthenium clusters. When measurements of the EXAFS associated with the K absorption edge

(27) Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Phys. Rev. Lett.* 1976, *36*, 1346.

(28) Teo, B. K.; Lee, P. A. *J. Am. Chem. Soc.* 1979, *101*, 2815.

(29) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold: New York, 1950; p 335.

(30) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. *J. Chem. Phys.* 1985, *83*, 353.

(31) Potter, H. C.; Blakely, J. M. *J. Vac. Sci. Technol.* 1975, *12*, 635.

(32) McDavid, J. M.; Fain, S. C., Jr. *Surf. Sci.* 1975, *52*, 161.

(33) van Santen, R. A.; Toneman, L. H.; Bouwman, R. *Surf. Sci.* 1975, *47*, 64.
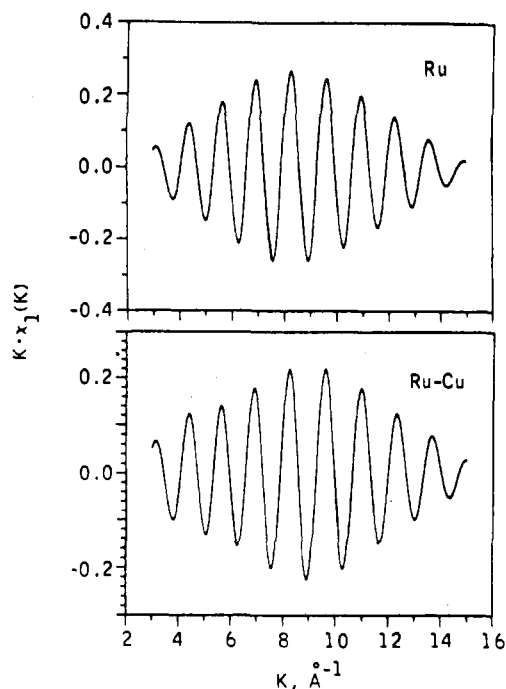
(34) Williams, F. L.; Boudart, M. *J. Catal.* 1973, *30*, 438.

(35) Bouwman, R.; Lippits, G. J. M.; Sachtler, W. M. H. *J. Catal.* 1972, *25*, 350.

(36) Cullity, B. D. *Elements of X-ray Diffraction*; Addison-Wesley: Reading, MA, 1956; pp 370–372.

(37) Schneider, A.; Esch, U. *Z. Elektrochem.* 1944, *50*, 290.

(38) Hansen, M. *Constitution of Binary Alloys*, 2nd ed.; McGraw-Hill: New York, 1958; pp 607, 619, 620.

Figure 4. Comparison of the ruthenium EXAFS (K absorption edge) of ruthenium and ruthenium–copper clusters at 100 K. The EXAFS shown is the part due to nearest-neighbor metal atoms.[23]

Figure 5. Comparison of the copper EXAFS (K absorption edge) of copper and ruthenium–copper clusters at 100 K. The EXAFS shown is the part due to nearest-neighbor metal atoms.[23]

of ruthenium are compared for ruthenium–copper and ruthenium clusters (Figure 4), the results are therefore not very different. For the copper monolayer at the surface, however, Cu–Ru bonds represent a substantial fraction of the total bonds in which the copper atoms participate, since all of the copper atoms in a monolayer would be coordinated to ruthenium atoms underneath. Thus, the environment of the copper atoms in the Ru–Cu clusters would be very different from that in pure copper clusters. This difference is clearly seen in measurements of the EXAFS associated with the K absorption edge of copper in the two types of clusters (Figure 5). The EXAFS functions in Figure 5 differ in both shape and magnitude, which is indicative of the different environment of the copper in the two types of clusters. Because of the marked differences in the backscattering properties of ruthenium and copper atoms, it is an easy matter to distinguish nearest-neighbor atoms of these elements in the analysis of EXAFS data. In both Figures 4 and 5, the EXAFS functions represent the contributions due to nearest-neighbor metal atoms. They were obtained by inversion of Fourier transforms of EXAFS data over a range of distances chosen to isolate these contributions.

The ruthenium–copper system represents an extreme case in view of the very limited miscibility of ruthenium with copper. A system which is less extreme in this respect is the rhodium–copper system, since the components both possess the face-centered-cubic structure and are slightly miscible at conditions of interest in catalysis.[38] Results of EXAFS studies on rhodium–copper clusters[39] are similar to the results on ruthenium–copper clusters, in that the rhodium atoms are coordinated predominantly to other rhodium atoms while the copper atoms are coordinated extensively to
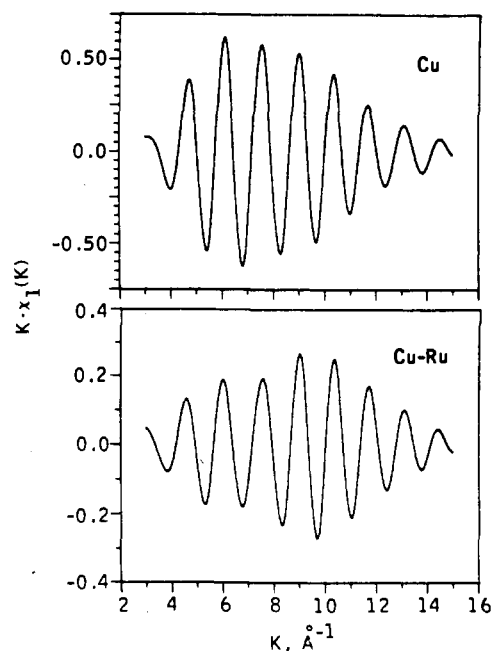
both copper and rhodium atoms.

However, when we compare EXAFS results on rhodium–copper and ruthenium–copper catalysts in which the Cu/Rh and Cu/Ru atomic ratios are both equal to one, we find some differences which can be related to the differences in miscibility of copper with ruthenium and rhodium. The extent of concentration of copper at the surface appears to be lower for the rhodium–copper clusters than for the ruthenium–copper clusters, as evidenced by the fact that rhodium exhibits a greater tendency than ruthenium to be coordinated to copper atoms in such clusters. The rhodium–copper clusters presumably contain some of the copper atoms in the interior of the clusters.

On moving further right in the periodic table from rhodium to silver, one again observes only limited miscibility of this metal with copper.[40] Measurements of the EXAFS associated with the K absorption edges of silver and copper in a catalyst containing silver–copper clusters on silica (Ag/Cu atomic ratio 0.9) reveal extensive segregation of the components.[15] The results are similar to those obtained for ruthenium–copper and rhodium–copper clusters in this respect but are different in another. For the silver–copper clusters, the EXAFS results indicate that the surface consists predominantly of silver rather than copper, since the silver has an average coordination number significantly lower than that of the copper. The conclusion is in agreement with that reported in studies of bulk alloys of silver and copper by other investigators.[41]

Thus, for bimetallic clusters of copper with the metals ruthenium, rhodium, and silver of the second long period of the periodic table, there is extensive segregation of the components from each other in all cases, as would be expected on the basis of the limited miscibilities of the components. In all cases, the component with the lower cohesive energy density (i.e., lower ratio of heat

(39) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. *J. Chem. Phys.* **1983**, *78*, 882.

(40) Stockdale, D. *J. Inst. Met.* **1930**, *43*, 193.

(41) Betz, G.; Arias, M.; Braun, P. *Nucl. Instrum. Methods* **1980**, *170*, 347.

of sublimation to molar volume) appears to concentrate at the surface, at least in an atmosphere of hydrogen or inert gas.

Bimetallic clusters of copper with the metals rhenium, osmium, and iridium of the third long period of the periodic table provide another interesting series in which the components exhibit very limited miscibility in the bulk.[30] The bimetallic systems Os–Cu and Re–Cu may be regarded as completely immiscible.[38,42] The Ir–Cu system is a less extreme case, but the miscibility is still very limited.[43] Despite the limited bulk miscibility of the components, bimetallic clusters are again observed. These systems are similar to Ru–Cu, in that copper is the component which is expected to be present at the surface. However, the clusters actually investigated were smaller than the Ru–Cu clusters already discussed. The diameters were 15 Å or lower, so that surface atoms constituted more than 70% of the total metal atoms present in the clusters. Consequently, with a 1:1 atomic ratio of copper to the other component, the surface cannot consist solely of copper. Moreover, EXAFS data indicated that the rhenium, osmium, and iridium atoms were on the average coordinated more extensively to copper atoms than were the ruthenium atoms in the Ru–Cu clusters. The Re–Cu clusters presented an extreme case in which the average coordination number of the atoms was only four. Such a low value implies that the clusters are extremely small, and one can readily visualize structures in which all of the atoms are surface atoms. The EXAFS data also indicated that the environment about the rhenium atoms was on the average not very different from that about the copper atoms, in marked contrast to the Ru–Cu clusters. Thus, the average environment about a given type of atom in very small bimetallic clusters may be very different from that in substantially larger clusters.

Bimetallic Clusters in Reforming Catalysts

Two bimetallic systems which have had a major impact in industrial catalysis since the early 1970s are platinum–iridium and platinum–rhenium. The impact has been in the area of petroleum refining, where they have been a key factor in making unleaded gasoline feasible. These systems are treated separately from the other bimetallic systems because of some special considerations in the application of EXAFS to them.

X-ray absorption spectra at 100 K for platinum–iridium and platinum–rhenium catalysts in the region of the L absorption edges of the components are given in Figures 6 and 7. The different energies characteristic of the various edges for platinum, iridium, and rhenium in Figures 6 and 7 provide a vivid demonstration of the element specificity of X-ray absorption spectroscopy, which is the key feature in its use as a structural probe. The spectra are for a platinum–iridium catalyst containing 10 wt % each of platinum and iridium[13] and a platinum–rhenium catalyst[44] containing 1 wt % of each of the metals. The spectrum for the platinum–iridium catalyst was obtained from measurements of the intensity of the X-rays transmitted through a sample of
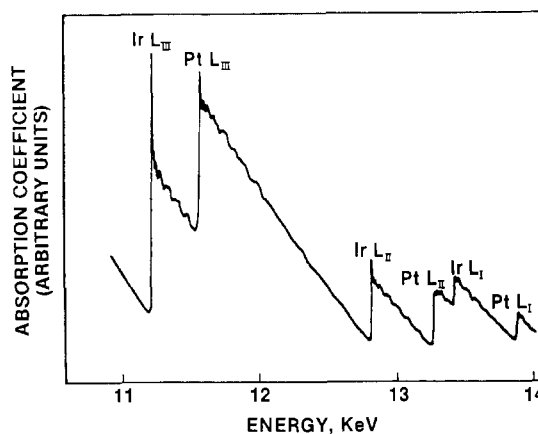
(42) Knook, B.; Star, W. M.; van Rongen, H. J. M.; van den Berg, G. J. *Physica (Amsterdam)* **1964**, *30*, 1124.
(43) Raube, E.; Roschel, E. *Z. Metallkd.* **1969**, *60*, 142.
(44) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H., data obtained at Stanford Synchrotron Radiation Laboratory.

Figure 6. X-ray absorption spectrum of platinum–iridium clusters at 100 K in the region of the L absorption edges of iridium and platinum.[13]

the catalyst. In the case of the platinum–rhenium catalyst, the intensity of fluorescent X-rays was measured. In Figure 6, the ordinate is proportional to the logarithm of I_0/I_t, where I_0 and I_t are the intensities of incident and transmitted X-rays, respectively. In the upper field of Figure 7 the ordinate is the ratio I_f/I_0, where I_f is the intensity of fluorescent X-rays. The use of both transmission and fluorescence experiments in EXAFS studies is now common practice. A discussion of the considerations in choosing one as opposed to the other is given elsewhere.[45] In the spectrum for the platinum–rhenium catalyst in the upper field of Figure 7, the EXAFS oscillations are not apparent on the scale of the plot. In the lower field of Figure 7 the oscillations are shown on a greatly expanded scale after removal of background absorption. The ordinate $\Delta(I_f/I_0)$ is the difference between an instantaneous value of I_f/I_0 and a background value at the same energy from the upper field of Figure 7.

The catalysts for which X-ray absorption spectra are given in Figures 6 and 7 have higher metal contents than commercial reforming catalysts. The latter typically have total metal contents (platinum plus iridium or rhenium) of about 1 wt % or lower, and alumina is used as the carrier.

The analysis of EXAFS data on platinum–iridium and platinum–rhenium catalysts has the limitation that the backscattering properties of the components are not very different (since the atomic numbers are so close together). As a consequence, distinguishing the contributions of different types of nearest neighbors to EXAFS is more difficult than for the bimetallic systems discussed earlier in this article, since for all of those systems the atomic numbers of the components were very different.

In an analysis of EXAFS data (L_{III} absorption edges) on platinum–iridium clusters, including data on catalysts with platinum and iridium contents ranging from 1 to 10 wt % of each component,[13] no attempt was made to distinguish between platinum and iridium neighbors. Emphasis was placed on the determination of interatomic distances, and conclusions regarding structural features were based entirely on such information. It was possible to determine the distances very reliably, since the phase shift functions for the relevant

(45) Teo, B. K. In *EXAFS Spectroscopy: Techniques and Applications*; Teo, B. K., Joy, D. C., Eds.; Plenum: New York, 1981; pp 38–43.
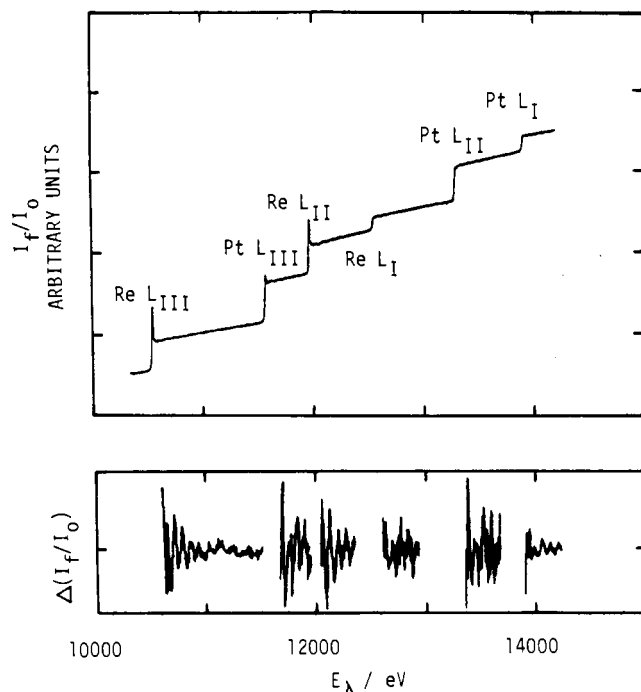
Figure 7. X-ray absorption spectrum of platinum–rhenium clusters at 100 K in the region of the L absorption edges of platinum and rhenium (upper field of figure), as determined from measurements of the intensity of fluorescent radiation.[44] The EXAFS oscillations, which are not apparent in the upper field of the figure, are shown on a greatly expanded scale in the lower field after removal of background absorption.

pairs of absorber and backscattering atoms were very well-known. There is the complication of overlap of the EXAFS associated with the L_{III} absorption edges of iridium and platinum, since the edges are not very far apart in energy (348.5 eV). Separating the iridium EXAFS from the platinum EXAFS in the region of overlap is therefore necessary.[13]

In the analysis of the EXAFS data, two interatomic distances were obtained, one characteristic of platinum EXAFS and the other of iridium EXAFS. If the average environment about a platinum atom in the clusters was the same as that about an iridium atom, one would have expected these two distances to be equal. However, the distance characteristic of platinum EXAFS was greater than that characteristic of iridium EXAFS, indicating that the clusters contained platinum-rich and iridium-rich regions. From surface energy considerations, it was concluded that the platinum-rich region would be present at the surface or boundary of a cluster.

From an analysis of the EXAFS data in Figure 7 for the platinum–rhenium catalyst and of EXAFS data obtained on a palladium–rhenium catalyst, it has been concluded that rhenium forms bimetallic clusters with both platinum and palladium.[46] As with the platinum–iridium clusters, however, the clusters have regions rich in rhenium and other regions that are rich in platinum or palladium.

(46) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H., to be submitted for publication.
(47) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is usually preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

The metal clusters in petroleum reforming catalysts are characterized by a very high dispersion, defined as the ratio of surface atoms to total atoms in the clusters. One explanation for an advantage of both Pt–Ir and Pt–Re clusters over pure Pt clusters is a better maintenance of dispersion in the reducing atmosphere in which reforming reactions occur, with a corresponding improvement in the activity maintenance of the catalyst over a period of time.

The presence of iridium also limits the buildup of carbonaceous residues in catalysts containing Pt–Ir clusters, presumably because of the high hydrogenolysis activity of iridium. Since carbonaceous residues decrease catalytic activity, the lower rate of accumulation leads to improved activity maintenance.[3] Although the increased hydrogenolysis activity resulting from the presence of iridium also means that C_6–C_{10} alkanes in the feed stream are converted at a higher rate to C_1–C_4 alkanes, the rate of conversion to more valuable aromatic hydrocarbons increases simultaneously. The fraction of methane in the C_1–C_4 products also increases. The overall result of replacing Pt clusters with Pt–Ir clusters is a catalyst with a much higher activity for reforming, which can be operated for a longer period of time before regeneration to remove carbonaceous residues is required. The interaction between platinum and iridium in the bimetallic clusters is important, since the hydrogenolysis activity of pure Ir clusters is too high to give a satisfactory product distribution.

Both Pt–Ir and Pt–Re catalysts are exposed to sulfur in situ prior to use in reforming. This treatment moderates the hydrogenolysis activity, which poses a problem during the start-up of a reformer. Iridium and rhenium both are much more active for hydrogenolysis than platinum. The sulfur associated with Pt–Ir clusters largely desorbs during the early part of a reforming run. With Pt–Re clusters, however, the sulfur is strongly bound to the rhenium and is therefore retained. The marked suppression of the hydrogenolysis activity of the rhenium by sulfur has the consequence that the yield of liquid product with a given octane number is usually about 1% higher for a Pt–Re catalyst than it is for a Pt–Ir catalyst. However, a Pt–Re catalyst is only about half as active as a Pt–Ir catalyst in a typical reforming operation. It is also interesting to note that the accumulation of carbonaceous residues on a Pt–Re catalyst is substantially higher.[3]

Concluding Remarks

Results of EXAFS studies on various supported bimetallic catalysts have provided excellent confirmation of earlier conclusions[1,2,10–12] regarding the existence of bimetallic clusters in such catalysts. Major structural features of bimetallic clusters deduced from chemisorption and catalytic data, or anticipated from considerations of the miscibility or surface energies of the components, have received additional support from EXAFS data. This application of EXAFS has been very timely, in view of the enormous interest in bimetallic systems in both catalytic science and technology. Moreover, it has provided a crucial test of the EXAFS method for investigations of catalyst structure.