

Structures of supported

Insights into their influence on catalyst performance

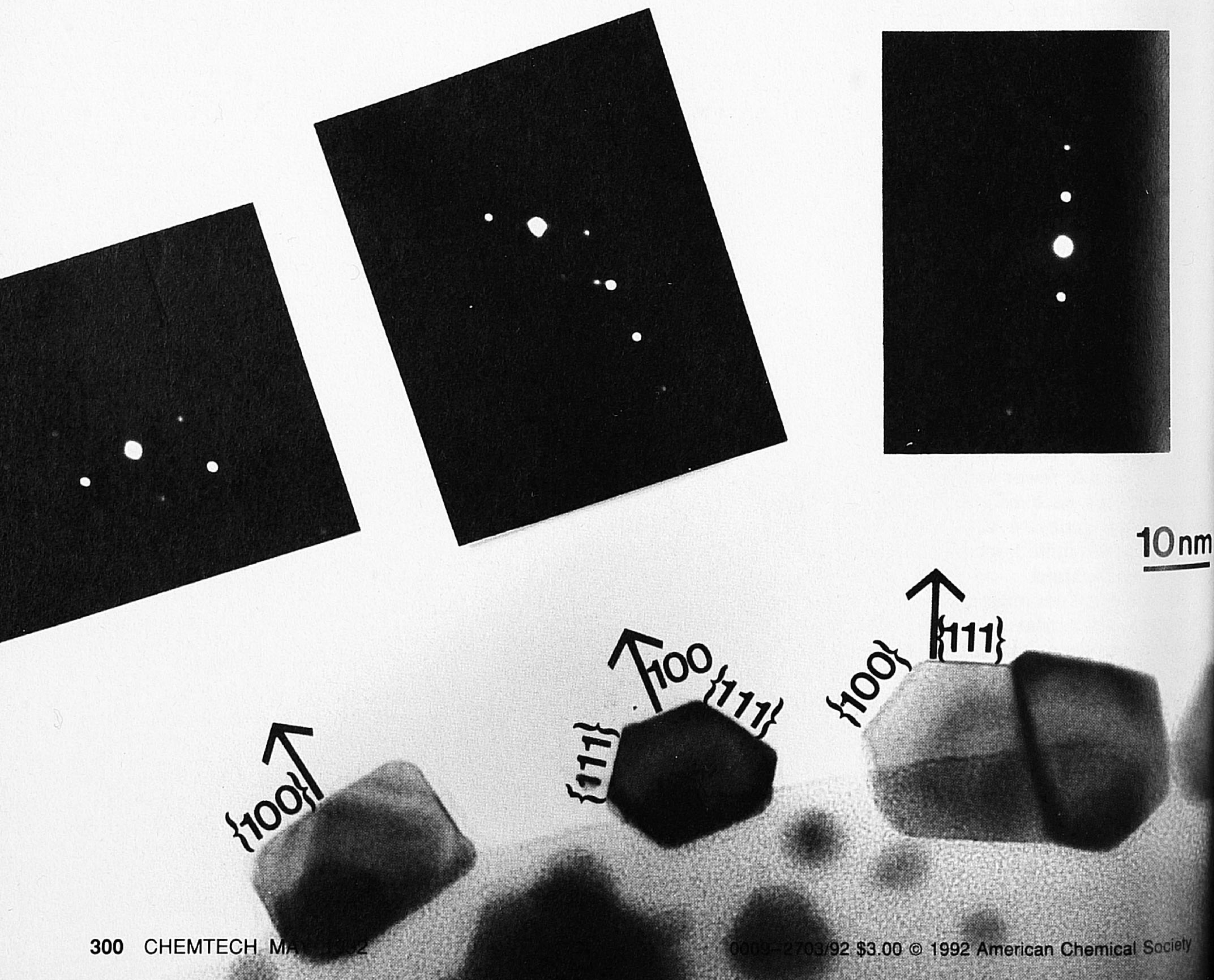
Bruce C. Gates
Diek C. Koningsberger

Metals are ubiquitous in catalysis. Catalysts used commonly in industrial processes such as naphtha reforming and ethylene epoxidation incorporate metal clusters or crystallites dispersed on porous metal oxide metalloenzymes, in which metal complexes are bonded in proteins. These composite materials are typically nonuniform, and their structures are even more difficult to elucidate than those of metalloenzymes, in which metal complexes are bonded in proteins.

Nonetheless, understanding of the structures of supported metals is developing rapidly with the emergence of precise characterization methods and the

toehold offered by structurally simple model catalysts. Our goal here is to summarize advances in this understanding and what they mean for catalysis.

The metals used in many industrial catalysts (such as the silver in ethylene epoxidation catalysts) are supported crystallites (1) that may be as large as a micron or more in diameter. Supported metal crystallites that are more than about 50 Å in diameter can be characterized by established methods, including X-ray diffraction line broadening and transmission electron microscopy and microdiffraction. For example, Figure 1 illustrates the structures of the exposed crystal facets of Pt crystallites supported on SiO₂ (2).



metal clusters

Supported metal crystallites have many of the properties of bulk metals (2): The metal-metal distances are those of the bulk, the surfaces are the ones exposed by large chunks of metal, and the fraction of the surface that exposes a particular surface plane is more or less independent of the particle size. The surface atoms of crystallites of Pt and other noble metals can be titrated accurately by adsorption of hydrogen. These titrations determine the metal surface area, and the catalytic activity for many reactions is proportional to this area.

The supported catalysts used for naphtha reforming and other important processes incorporate metal entities that are only about 10 Å or less in diameter, some of which have 10 or fewer metal atoms; these are referred to as clusters to distinguish them from the larger crystallites. An advantage of these highly dispersed metals is that virtually all atoms are exposed at the surface and are thus accessible to reactants.

Metal clusters on supports have properties that distinguish them from crystallites. For example, because most of the metal atoms in a cluster are in contact with the support, the support may influence the catalytic properties, much as ligands do in molecular catalysts. The strong influence of the support implies that the surface structures and reactivities of clusters are likely to differ from those of bulk metals and crystallites.

Supported metal clusters are too small to be characterized by the techniques mentioned above. The clusters are so small that X-ray lines are broadened beyond detection; they are too small to observe with all but the highest resolution electron microscopes, in which they are subject to damage by the electron beam, and they differ from surfaces of bulk metal in their reactivities with hydrogen and CO, so that titration stoichiometries may differ from those for bulk metals and crystallites.

Figure 1. Transmission electron micrograph showing a low-magnification view of a Pt/SiO₂ catalyst that had been heated to 900 °C in H₂ in a quartz reactor.

Microdiffraction patterns from each particle permit determination of exposed crystal facets. The figure shows that just one of the particles in this region exposes only (100) facets. Other particles expose their (111) and (100) surfaces. Transmission electron microscopy of model catalysts such as these provides understanding of the role of adsorbates and supports on the structure of small metal particles. Courtesy of Professor A. Datye, University of New Mexico.

Supported metal clusters are such useful catalysts that extensive effort has been expended to understand them, and improved characterization techniques are beginning to lead to rapid progress. The most incisive technique is EXAFS (extended X-ray absorption fine structure) spectroscopy. The principles of EXAFS and how it is used to determine structures of supported metal clusters are summarized briefly in the accompanying box.

The simpler and more uniform the structures of supported metal clusters, the more that can be learned about them from EXAFS. Thus, some of the best-characterized structures on supports are close analogues of molecular species. In the simplest of these, the metals are not in a metallic state, but rather are present in cationic form in complexes that are bonded to the support. These surface complexes are analogous to soluble metal complexes such as rhodium complexes with triphenyl phosphine ligands (Wilkinson olefin hydrogenation catalyst). The ligands are the groups present on the surface of the metal oxide support, namely, oxygen ions and hydroxyl groups.

A highly dispersed rhodium on γ -Al₂O₃ (Rh/ γ -Al₂O₃) catalyst was prepared conventionally by impregnation with an aqueous solution of RhCl₃ followed by calcining and reduction. Treatment with CO oxidized and fragmented the metal aggregates and gave the structure shown in Figure 2 (3). We have prepared similar

Miller indices

Crystals can be described by the length and mutual angles of three imaginary lines that can be drawn through their centers. These axes are designated x, y, and z, and they may but need not be mutually perpendicular. For example, NaCl crystallizes in the cubic (isometric) system in which all axes are at right angles and are equally long. In sulfur crystals all axes are also mutually perpendicular but are of different length (orthorhombic system). The ratio of the lengths of the crystal axes is a characteristic of the crystal.

The crystal faces are identified by their intercepts with the axes. They are described by Miller indices, which are the reciprocals of the intercepts. Thus a face that intersects the x axis and is parallel to the y and z axes (i.e., intercepts the y and z axes at infinity) is identified as (100). The three faces of a cube have Miller indices of (100), (010), and (001). Octahedral faces that intercept the three axes at unit distance from the origin have Miller indices of (111).

supported metal complexes from organometallic compounds, e.g., $[\text{Os}_3(\text{CO})_{12}]$ on $\gamma\text{-Al}_2\text{O}_3$ (4) and $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ on MgO (5); the latter is also shown in Figure 2. These surface species are metal subcarbonyls; the metals are in low, positive oxidation states, as is the Rh in Wilkinson's hydrogenation catalyst. The carbonyl ligands are good handles for characterization by infrared spectroscopy and by EXAFS. Comparison of the infrared spectra of the surface species with those of molecular analogues gives evidence of the number of carbonyl ligands, the metal oxidation state, and the symmetry of the surface species, which helps to identify the surface groups (ligands) that are bonded to the metal. XANES (X-ray absorption near-edge spectroscopy, which is measured simultaneously with the EXAFS) and XPS (X-ray photoelectron spectroscopy) provide additional evidence of the metal oxidation state. EXAFS spectroscopy characterizes the nature and number of the atoms in the immediate neighborhood of the metal atom, as well as determining quantitative structural data, shown in Figure 2 as bond distances.

EXAFS spectroscopy determines only average distances between atoms, but if the surface species are so uniform that they are almost molecular, then the results indicate bonding distances. The structures shown in Figure 2 are regarded as nearly molecular, because nearly the same symmetries and metal-oxygen, metal-carbon, and carbon-oxygen distances have been found by X-ray diffraction crystallography for analogous transition metal complexes. The metal-oxygen distance of about 2.1 Å is characteristic of compounds of second- and third-row transition metals (Ru, Rh, Re, Os, and Ir) that are present in low positive oxidation states and are singly bonded to oxygen (6). Compounds such as polyoxometallates (metal oxide clusters) with metal subcarbonyls bonded at their surfaces are also characterized by essentially this same metal-oxygen distance (7). We consider these compounds to be good models of the metal-support interface when the metals bear a small positive charge and the complex contains a single metal atom (6).

The structures shown in Figure 2 are rather well understood although the surface planes of the supports to which they are bonded are unknown—and the metals may well be bonded at defect sites. These structures lack metallic character. A step toward a realistic model of a supported metal cluster catalyst resulted from the preparation of $\gamma\text{-Al}_2\text{O}_3$ -supported clusters from a metal carbonyl cluster precursor, $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ (8). EXAFS data characterizing the surface species led to the structural model shown in Figure 3. Here is a structure with neighboring metal centers in a simple, nearly molecular unit, but it also falls short as a model of a supported metal catalyst, because the XANES and XPS data indicate that the Re in the raft-like structure is

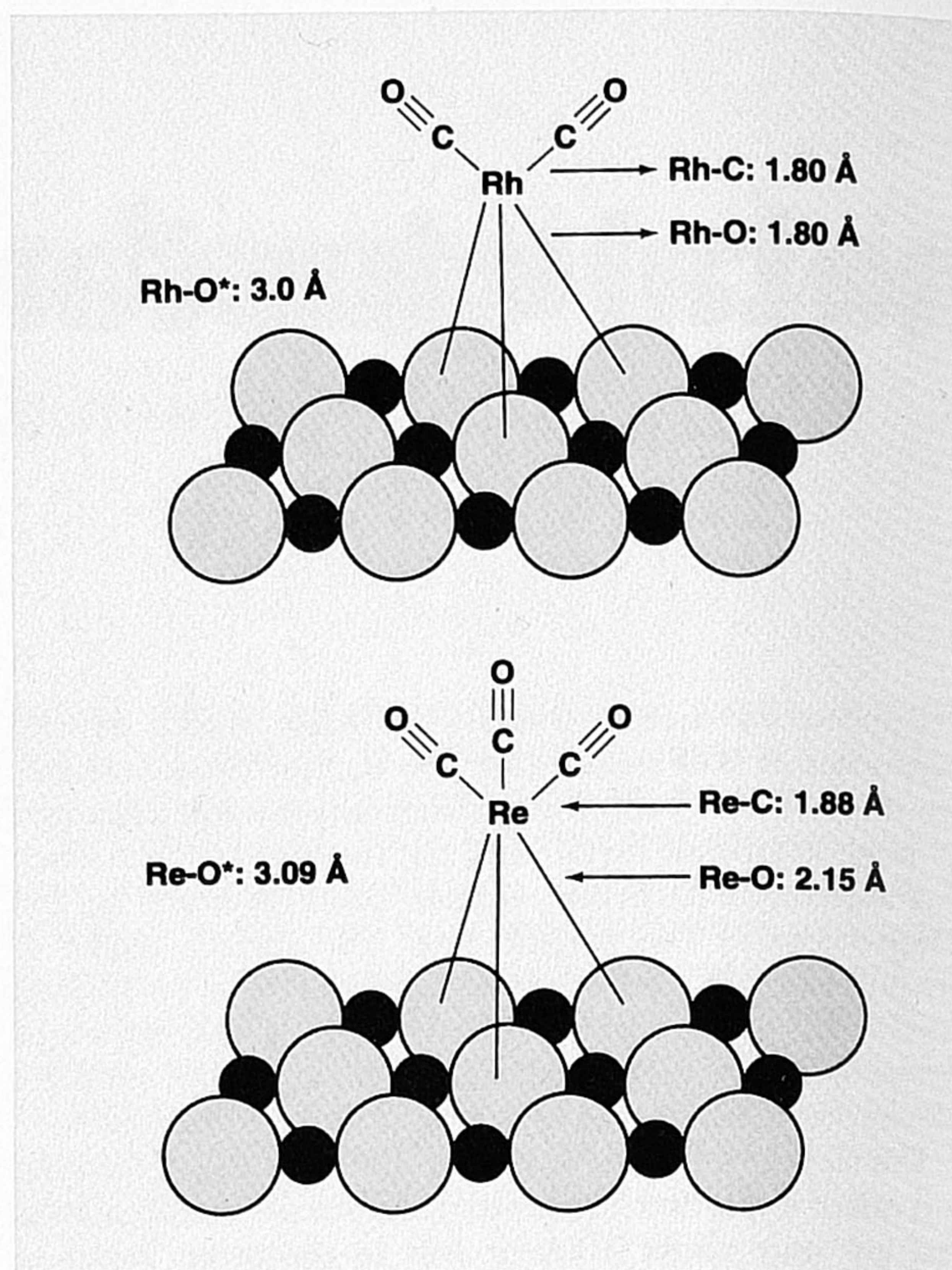


Figure 2. Structures of mononuclear metal carbonyls on metal oxide supports determined by EXAFS spectroscopy. The bond distances and coordination numbers were determined precisely with EXAFS spectroscopy, but the exact structures of the support surfaces remain to be determined. O* refers to carbonyl oxygen.

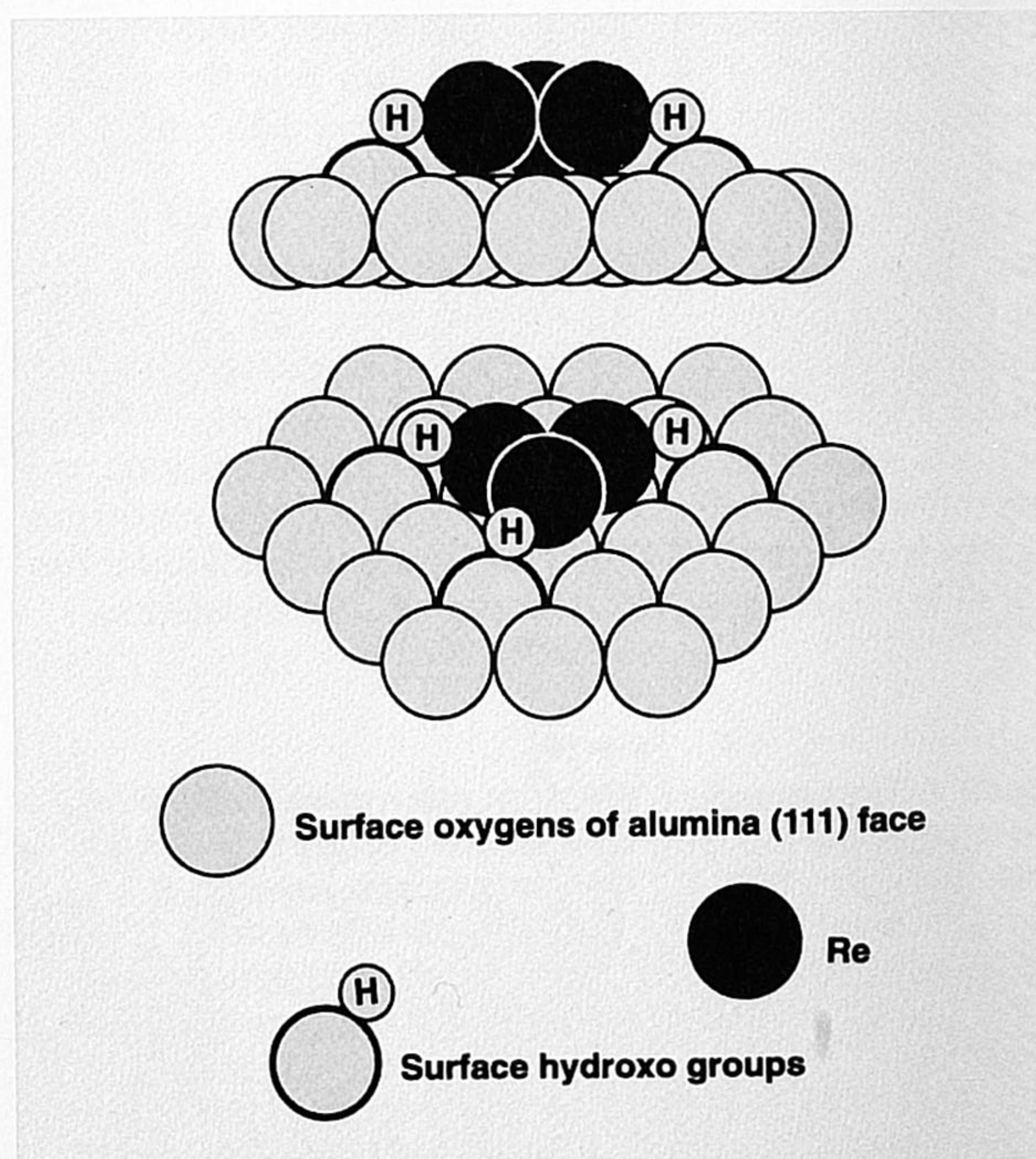


Figure 3. Structural model of a highly dispersed supported trirhenium raft, $\text{Re}_3/\gamma\text{-Al}_2\text{O}_3$ determined by EXAFS spectroscopy (8).

EXAFS spectroscopy

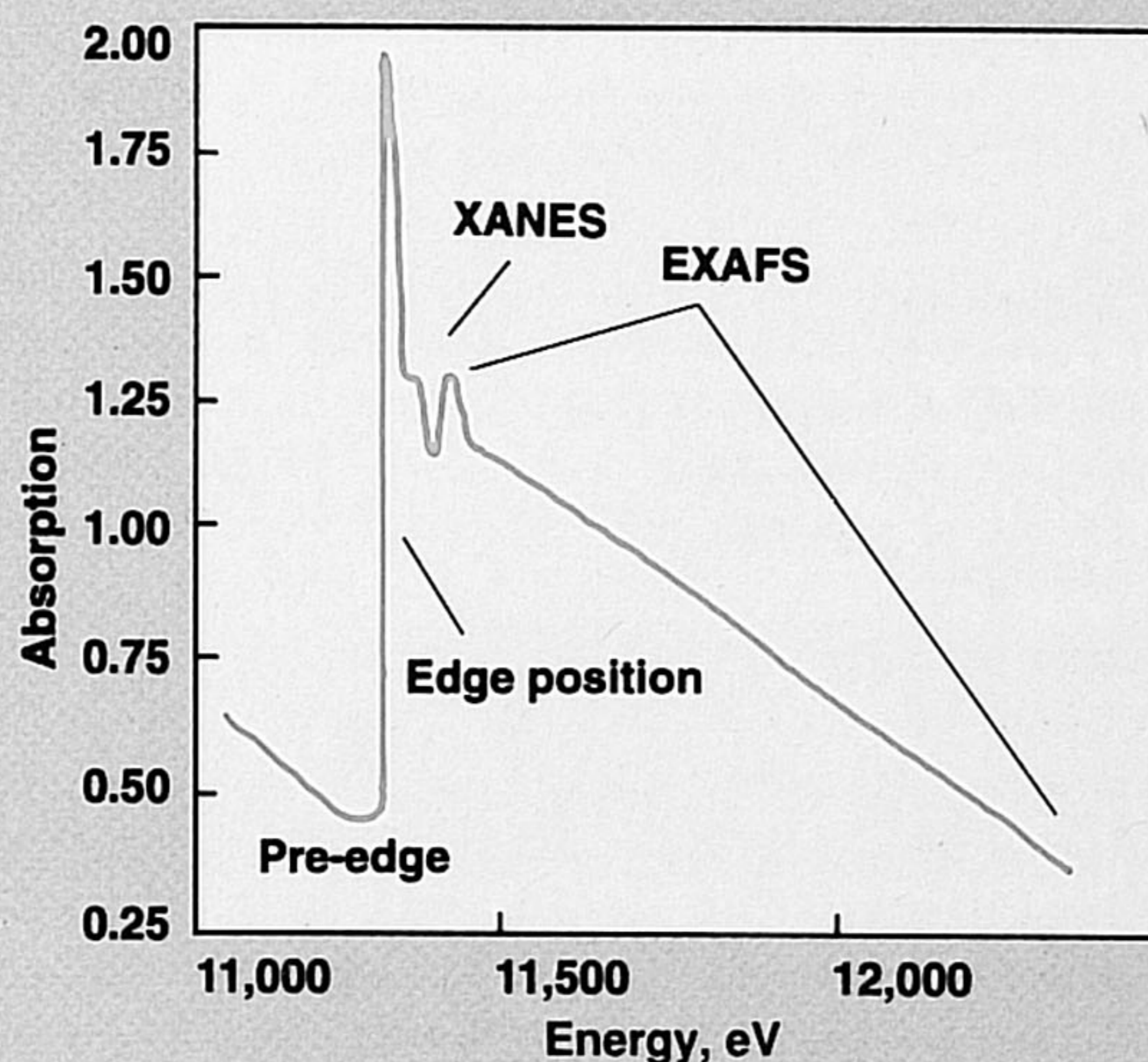
In an X-ray absorption spectroscopy experiment, a solid sample is pressed into a wafer and placed in a controlled-atmosphere cell. An intense beam of X-rays, usually from a synchrotron source, passes through the sample. The absorption of the X-rays for the most part changes only gradually as the energy (wavelength) is increased, but when the energy increases to a critical minimum, the photon ejects an electron from the core of an atom called the absorber atom. Absorption then rises sharply, creating an absorption edge. The absorption of the radiation is measured as a function of wavelength in the region of the absorption edge of a heavy absorber atom. The absorption spectrum in the region of the absorption edge is analyzed in X-ray absorption near-edge spectroscopy (XANES) and provides, among other things, information about the oxidation state of the absorber metal atom.

At energies slightly higher than the edge energy, there are oscillations in the absorption (the fine structure) that are characteristic of the backscattering of radiation associated with the ejected electrons by the atoms in the immediate neighborhood of the absorbing atom. The EXAFS function (χ function) is determined from this fine structure by background subtraction. When the Fourier transform of the EXAFS function is plotted as a function of the distance from the absorbing atom, it shows peaks at approximately the distances of the neighboring backscatterers. In data analysis, the parameters determining the coordination numbers and average distances of the backscatterers from the absorbing atom are estimated by fitting of the data.

If a supported metal catalyst has nearly uniform metal structures on the scale of a few Angstrom units, then the fine structure provides information about the nature of the neighboring atoms and determines the number of near-neighbor atoms of each kind and their distances from the absorbing atom. The sample need not be structurally regular on a larger scale, as is required for X-ray diffraction; thus liquids, enzymes, and amorphous materials such as supported metals can be characterized by EXAFS spectroscopy. If more than a few phases are present in the sample or if the size distribution of the metal clusters or crystallites is nonuniform, however, then little precise structural information can be obtained because the method determines an average for the whole sample.

Details of the structure of the metal-support interface can be obtained by EXAFS spectroscopy only if the supported metal clusters are smaller than about 15 Å, because only then do the support atoms contribute a large enough fraction of the total EXAFS function. EXAFS characterizations of the metal-support interface have emerged only recently; successful quantitative characterization of the interface structure requires high-quality data obtained for small metal clusters on supports and a data

analysis that takes account of the backscattering of low atomic weight elements (typically oxygen) at the interface. The EXAFS function at high values of the wavenumber k (the energy beyond the absorption edge) is determined primarily by the heavy backscatterers. The EXAFS function at low values of k is determined primarily by the light backscatterers. Thus by using a k^3 weighting in the Fourier transformation of the EXAFS function, a higher weight is placed on the contribution made by the heavy neighboring metals. On the other hand, use of k^1 weighting puts a higher value on the contributions of neighboring oxygen atoms. Analyses that emphasize the metal-metal interactions lead to an underestimation of the contributions of the low atomic weight scatterers. A preferred method of analysis takes account of both the metal-metal interactions (with a k^3 -weighted Fourier transform) and the metal-oxygen interactions (with a k^1 -weighted Fourier transform). The structure parameters are determined in a nonlinear multiple shell fit in energy space, together with an optimization of the parameters in distance space. The optimization of the fits in energy space and in distance space with both the k^3 - and k^1 -weighted Fourier transforms of the EXAFS function is necessary for accurate determination of both the metal-metal and metal-oxygen interactions. Details are given in reference 9. (Also see Kelley, M. CHEMTECH, March 1987, p. 170.)



Results of an EXAFS experiment characterizing tetrairidium carbonyl clusters, $[\text{Ir}_4(\text{CO})_{12}]$ (23). With increasing wavelength of the X-rays, the absorption decreases until the Ir L_{III} absorption edge is reached, whereupon there is a sharp increase; at higher energies, there are oscillations referred to as the fine structure.

cationic, with the EXAFS data indicating an average Re-Re distance that is markedly shorter than that in bulk Re metal; the short distance implies multiple metal-metal bonds in the supported trirhenium. Re is evidently too oxophilic to mimic the noble metals like Pt that are typical of industrial catalysts.

In a further step toward a representative model of a supported metal cluster catalyst we examined various noble metal (iridium) clusters that were supported on MgO (Table 1) (9). Our carbonyl cluster $\text{Ir}_4(\text{CO})_{12}$ reacted with the basic hydroxyl groups of the MgO surface to give predominantly the anionic cluster $[\text{HIr}_4(\text{CO})_{11}]^-$ (10), which, upon decarbonylation in He

followed by treatment in H_2 at 300 °C, gave structures characterized by the EXAFS data of Table 1. These data are consistent with the retention of Ir_4 clusters in the supported metal species. The indications from EXAFS are that the clusters are metal-like; the average Ir-Ir distance is 2.71 Å, and that in bulk Ir metal is 2.72 Å. The EXAFS data indicate that there is not just one structure of the Ir cluster; if all four Ir atoms were in a tetrahedral cluster the absorbing atom would have three nearest neighbors, i.e., the first-shell Ir-Ir coordination number would be 3. Instead, it is 2.6 ± 0.3 , which indicates that some backscatterers are farther away. This is confirmed by the coordination number of the second Ir-Ir shell

Table 1. Structural data determined by EXAFS spectroscopy for three different samples of MgO-supported Ir clusters

Parameters	Coordination number ^a	$10^3 \times$ Debye-Waller factor $\Delta\sigma^2$, Å ^{2e-} b	Average absorber-backscatterer distance, R, Å	Inner potential correction, ΔE_0 , eV ^c
Coordination: Ir-Ir (first shell) ^d				
Ir_4	2.6 ± 0.3	0.6 ± 0.7	2.713 ± 0.004	-5.2 ± 0.7
Ir_6	2.7 ± 0.5	0.4 ± 1.0	2.72 ± 0.02	-4.5 ± 2.1
Ir aggregates ^e	4.6	2.2	2.72	-5.8
Coordination: Ir-Ir (second shell) ^d				
Ir_4	0.9 ± 0.4	1 ± 4	3.86 ± 0.02	-6 ± 2
Ir_6	—	—	—	—
Ir aggregates ^e	3.1	2.1	3.85	-5
Coordination: Ir-Ir (third shell) ^d				
Ir_4	—	—	—	—
Ir_6	—	—	—	—
Ir aggregates ^e	4.5	3.0	4.7	-0.2
Coordination: Ir-O ₁ ^f				
Ir_4	3.4 ± 0.1	3.8 ± 0.7	2.630 ± 0.007	-0.8 ± 0.6
Ir_6	3.7 ± 1.1	7 ± 4	2.65 ± 0.04	-2 ± 5
Ir aggregates ^e	2.2	3.9	2.60	0.6
Coordination: Ir-O ₂ ^g				
Ir_4	—	—	—	—
Ir_6	0.2 ± 0.6	-0.5 ± 24	2.2 ± 0.2	-5 ± 40
Ir aggregates ^e	0.3	0.0	2.1	-2.2
Coordination: Ir-Mg				
Ir_4	0.3 ± 0.1	13.6 ± 4.3	1.60 ± 0.02	-2 ± 4
Ir_6	0.2 ± 0.2	2.5 ± 7.4	1.63 ± 0.06	-9 ± 15
Ir aggregates ^e	0.4	15.5	1.65	-5

^a The number of nearest neighbor backscatterers near the absorbing Ir atom.

^b A measure of disorder of the sample; our data illustrate the relative imprecision of this parameter in comparison to the precision of the absorber-backscatterer distance, R.

^c An adjustable parameter in the EXAFS analysis.

^d The nearest backscatterers of a particular element are said to be in the first shell; those at the next nearest distance are said to be in the second shell, etc.

^e Structurally nonuniform sample prepared by treatment in H_2 to sinter Ir clusters.

^f Longer Ir-O distance.

^g Shorter Ir-O distance.

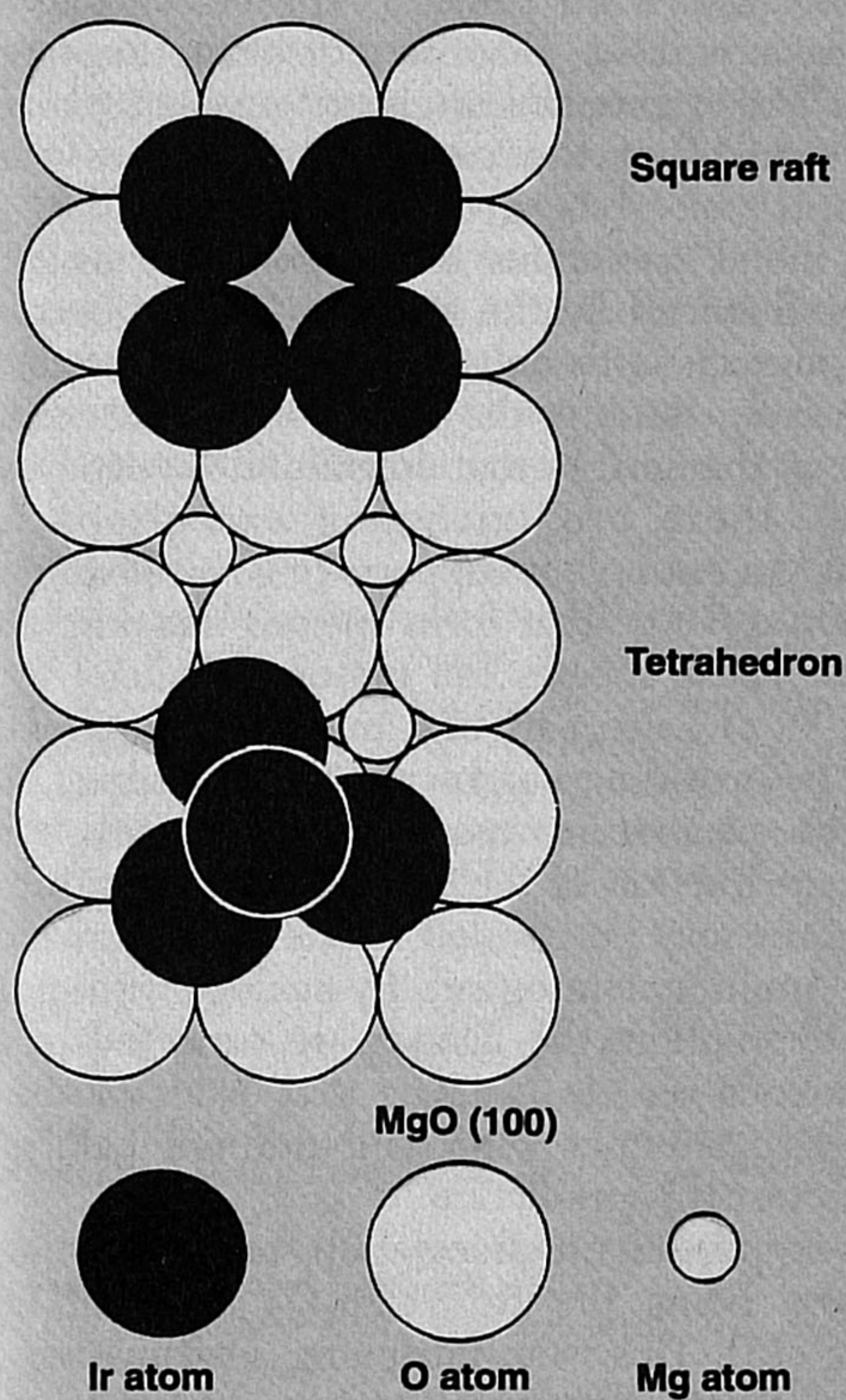


Figure 4. Structural models of MgO-supported tetrairidium clusters determined by EXAFS spectroscopy (9).

(0.9 ± 0.4) (Table 1). This value indicates that there are iridium atom backscatterers farther removed from the absorber atom. Thus, the data model well as a mixture, with 40–50% of the Ir being in four-atom tetrahedra (as in the precursor iridium carbonyl) and the remainder being in four-atom rafts lying flat on the support surface (Figure 4).

Similarly, we prepared $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ as the precursor on the MgO surface (9). When this cluster was decarbonylated, relatively simple surface structures formed, as characterized by EXAFS spectroscopy (Table 1). The data indicate structures that are more complex than those formed from the tetrairidium precursor. The higher-shell Ir–Ir data show that there are Ir atoms at distances greater than the Ir–Ir bonding distance of about 2.72 Å. The data are consistent with the postulate of some octahedral six-atom clusters, but other species are present also, including some with longer metal–metal distances that are best modeled as rafts. The structures get complicated rather fast as the number of metal atoms in them increases beyond four.

When small Ir clusters such as these on the surface

were subjected to high-temperature H_2 , the metal sintered to give larger, less uniform clusters, as discussed below.

Supported metal clusters with nonuniform structures

EXAFS spectroscopy has been used to characterize many supported metal catalysts prepared conventionally, e.g., by impregnation of the support with an aqueous solution of a metal salt, followed by calcination and reduction in hydrogen. Some of these catalysts incorporate metal clusters consisting of about 10 atoms each, but the structures are usually highly nonuniform.

Some of the most nearly uniform of the conventionally prepared catalysts are supported in zeolites. Zeolites are aluminosilicates that have uniform molecular-scale pores as part of their crystalline structures, and the uniformity of the pores may contribute to the uniformity of the metal clusters formed in them. Catalysts consisting of Pt clusters in zeolite L containing Ba and/or K as the exchangeable ions are active and selective for conversion of straight-chain paraffins into aromatics (11). Transmission electron microscopy shows that when the catalyst is properly prepared, it consists of extremely small clusters of platinum in the zeolite pores, with almost no metal outside the pores (12). EXAFS spectra characterizing this catalyst show Pt clusters of only five or six atoms each, on average.

Catalysts prepared conventionally on amorphous metal oxide supports such as $\gamma\text{-Al}_2\text{O}_3$ are not nearly so uniform as the Pt in zeolite L, but the metal clusters may still be so small that they can be characterized rather precisely with EXAFS spectroscopy. An average structure determined for Rh/ $\gamma\text{-Al}_2\text{O}_3$ is shown in Figure 5; the cluster has seven Rh atoms. The Ir clusters in the sintered catalyst mentioned above are larger, as indicated by the higher-shell Ir–Ir data determined by EXAFS spectroscopy (Table 1). The average Ir cluster contains about 10 atoms.

One of the striking results to emerge from EXAFS data measured for a variety of conventionally made supported metal clusters (Rh/ $\gamma\text{-Al}_2\text{O}_3$ [3], Rh/ TiO_2 [13], Pt/ $\gamma\text{-Al}_2\text{O}_3$ [14], Pd/zeolite X [15], Os/MgO [16], and Ir/ $\gamma\text{-Al}_2\text{O}_3$ [17]) is that the metal–metal oxide interface is characterized by both a short metal–oxygen distance (about 2.1 Å) and a long distance (2.5–2.7 Å); the pattern holds for the whole group of metals on a variety of metaloxide supports. The longer distance is observed only when hydrogen is present on the surface.

What do these results tell us about the structures of highly dispersed supported metals? The shorter metal–oxygen distance is approximately the same as that characteristic of the polar bonds between oxygen and metal ions in low positive oxidation states (Figure 2). This comparison suggests that metal atoms in clusters at the

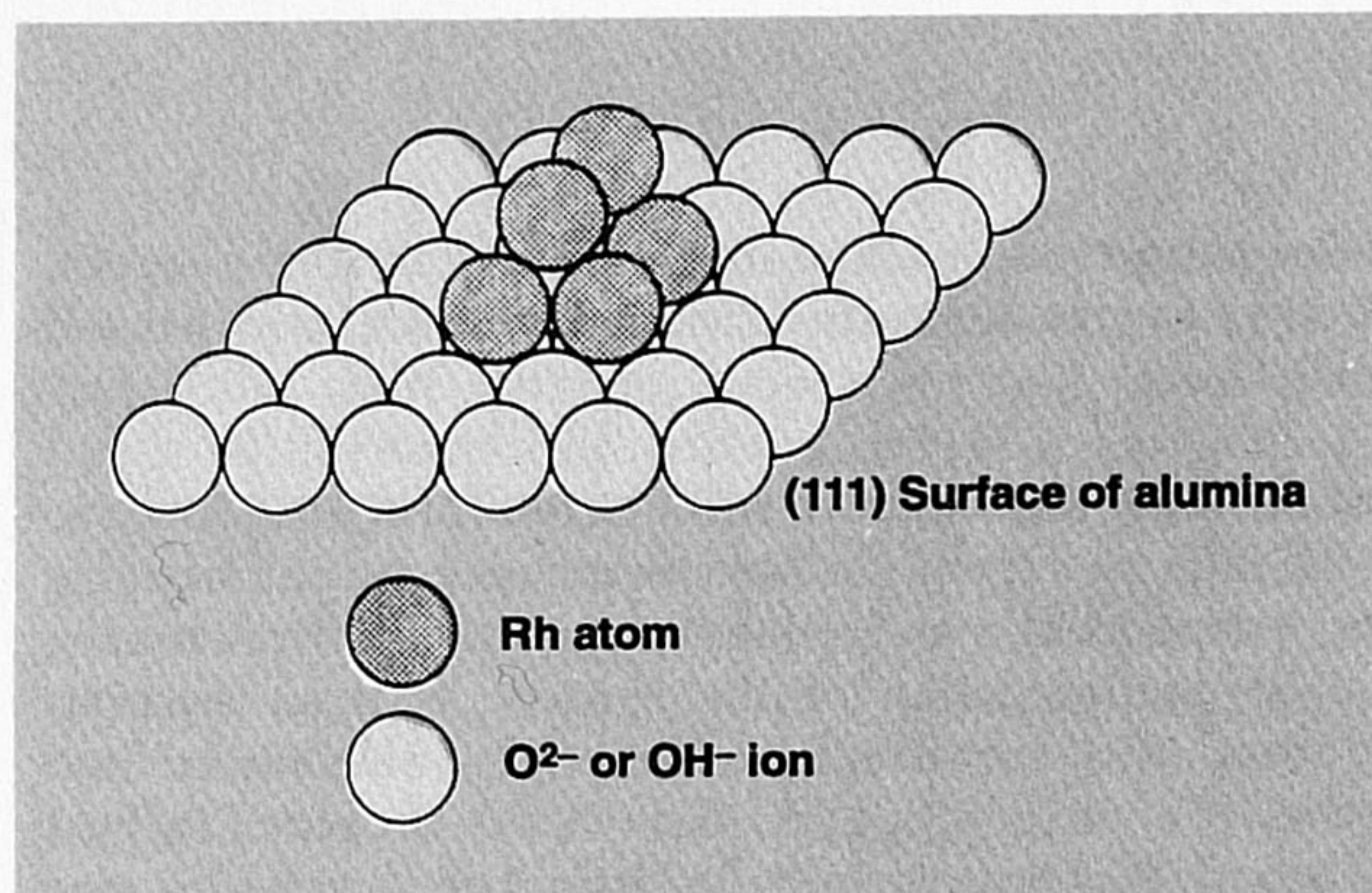


Figure 5. Model of a representative structure in highly dispersed Rh/ γ -Al₂O₃, inferred from EXAFS and other data (3).

metal-metal oxide interface are polarized, bear at least a partial positive charge, and interact with oxygen of the support much as the metal subcarbonyls of Figure 2 do (6). The longer metal-oxygen distance may indicate metal-oxygen interfaces with zerovalent metal atoms interacting with oxygen ions at the surface. Alternatively, it may indicate metal-oxygen interfaces with hydrogen atoms between the oxygen and metal atoms; evacuation of the samples to remove hydrogen leads to disappearance of this longer distance, and readsorption of hydrogen leads to its reappearance (18). Whether the hydrogen has more of the character of protons in -OH groups or more of the character of hydrides bonded to the metal remains to be determined.

Influence of structure on catalyst performance

Now it is fair to ask what bearing these structural details have on the catalytic performance of supported metal clusters. Research is still in an early stage, and thus the discussion is supported with only a few examples.

A metal-catalyzed reaction is classed as structure-insensitive if it proceeds at a rate that is independent of the metal crystal face doing the catalysis or the size of the cluster doing the catalysis (1, 13). Such reactions are believed to require only a single metal center on the surface. An example is olefin hydrogenation; it is not difficult to believe that only a single metal center is required as a catalytic site, as the Wilkinson catalyst has a single metal atom.

Reactions that occur at different rates on different faces of a metal crystal or on clusters of different sizes are called structure-sensitive (1, 13). The catalytic sites are inferred to be ensembles of metal atoms, and the rate depends on their structures. Examples of structure-sensitive reactions are paraffin hydrogenolysis and ammonia synthesis. The identities of the catalytic sites are not precisely known. The catalytic properties of metal clusters are expected to be most sensitive to structure

when the clusters are smallest; clusters smaller than a critical size will be inactive for structure-sensitive reactions. Precise control of cluster nuclearity may allow precise control of the catalytic properties for such reactions.

Large metal crystallites on supports are usually only scarcely influenced by the support. That is because the support interacts with only a small fraction of the metal atoms, namely, those at the metal-support interface and not those at the surface that constitute the catalytic sites. However, there are intriguing exceptions to this statement. An example is supports (e.g., a reducible metal oxide such as TiO₂) that form species that migrate onto the metal. These species can poison the metal by partly covering it or, alternatively, make it more active or selective by providing nearby promoter groups (14).

When the catalyst incorporates small clusters, however, a significant fraction of the metal atoms constituting the catalytic sites may be bonded to the support, which acts as a large multidentate ligand. By analogy with molecular catalysis in solution, the ligands are expected to have a large influence on the catalytic properties of the metal centers. Experiments with well-defined catalysts are needed to test this prediction.

Many supported metal catalysts are bimetallics, the best known being the Re-Pt/Al₂O₃ used for naphtha reforming (15). This is an intriguing combination, as the group 7 metal Re is oxophilic and tends to be present in a cationic form at the surface of a metal oxide support, whereas the group 8 metal Pt is noble and tends to be present in a zerovalent form. The structures of Re-Pt catalysts are vigorously debated; catalysts have been made and characterized by EXAFS spectroscopy and found to contain the two metals in intimate contact in alloy-like bimetallic clusters (16). In contrast, samples have been made in which the metals appear to be segregated, and the Re may be cationic (17). A catalyst has been made from [Re₂Pt(CO)₁₂] on Al₂O₃, and the EXAFS characterization (19) suggests that the metal is present in a bilayer structure, with cationic Re bonded to the oxygen of the support providing a platform for clusters of a few Pt atoms, which are not in direct contact with the support. The Re may play a role in stabilizing the dispersion of the Pt.

Hydrogen at the metal-support interface, indicated by the relatively long metal-oxygen distance of about 2.7 Å, is expected to influence the properties of supported metal clusters. There is indirect evidence that it does (18). For example, Al₂O₃-supported Pt catalysts for hydrogenolysis of *n*-hexane are much more active when reduced in H₂ at low temperatures than when reduced in H₂ at high temperatures (20, 21). And the long Pt-O distance was not present after high-temperature reduction (18). Similarly, the selectivity for *n*-hexane conversion to

aromatics catalyzed by Pt/Al₂O₃ decreased when the temperature of pretreatment in H₂ was increased (22). These results are consistent with the suggestion that the presence of hydrogen at the metal-support interface has a strong influence on the activity and selectivity of the metal clusters for hydrocarbon conversion.

Details of these phenomena remain to be elucidated, but with continuing improvement in the techniques for determining structures of catalyst surfaces, understanding may emerge that will allow design of the catalytic sites.

Acknowledgments

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Bruce Gates is the H. Rodney Sharp Professor of Chemical Engineering and Professor of Chemistry at the University of Delaware (Center for Catalytic Science and Technology, Dept. of Chemical Engineering, University of Delaware, Newark, DE 19716; 302-831-2347). He was recently a Deutsche Forschungsgemeinschaft Professor at the Institute of Physical Chemistry of the University of Munich. His textbook *Catalytic Chemistry* has just been published by John Wiley & Sons.



Diik Koningsberger is Professor at the University of Utrecht and a faculty member of the Eindhoven University of Technology. His research focuses on the structural and catalytic properties of supported metals, and his group has developed computer programs with a new method of EXAFS data analysis. He is co-editor of *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*; Wiley, 1988.

HONEY

Beekeeping was recorded as early as Egyptian times. Until 400 years ago honey and fruit were the only known sweeteners. Honey, intensely sweet and immune to spoilage, was no less than a miracle to early humans. Honeybees turn nectar into honey by adding an enzyme (invertase) that converts the sugars to a chemical form that bacteria and many molds cannot metabolize. Worker bees fan the nectar in honeycomb cells until it is so viscous that

bacterial motility is inhibited and so dry (less than 20% water) that it dehydrates and kills yeasts and other microorganisms. Also, bees add another class of enzymes (oxidases) that convert some of the sugar into hydrogen peroxide, a potent antibiotic. All these processes work together to make honey free from spoilage.

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