Structure and nature of the metal-support interface: characterization of iridium clusters on magnesium oxide by extended x-ray absorption fine structure spectroscopy

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Abstract: X-ray absorption spectroscopy was used to characterize the metal-support interface in catalysts consisting of very small Ir clusters of nearly uniform nuclearity on the surface of MgO powder. $\text{[Ir}_4\text{(CO)}_{12}]$ on MgO was converted in high yield into $\text{[Ir}_4\text{(CO)}_{12}]$ and separately into $\text{[Ir}_6\text{(CO)}_{15}]^{2-}$. Extended X-ray absorption fine structure (EXAFS) data are consistent with the hypothesis that each cluster retained its nuclearity upon decarbonylation. The average Ir-Ir coordination in Ir$_4$/MgO is 2.6 neighbors at a distance of 2.72 Å, and the structure is modeled as a mixture of 40–50% tetrahedra and the remainder four-atom rafts on MgO. The average Ir-Ir coordination in Ir$_6$/MgO is 2.7 neighbors at a distance of 2.72 Å, and the structure is modeled as a mixture of about 25% Ir$_6$ octahedra and the remainder Ir rafts on MgO. Another sample was treated in H$_2$ at 623 K to give a typical supported metal catalyst having a distribution of Ir clusters averaging 10 Å in diameter. The Ir-support interfaces in Ir$_4$/MgO and Ir$_6$/MgO are characterized by single Ir-Mg coordinations at 1.6 Å and fourfold Ir-O coordinations at 2.6 Å; the interface Ir atoms are suggested to be atop Mg ions in the (100) faces of MgO. However, this structural model is simplified, and the Ir-Mg interactions are not fully understood. The results demonstrate that the structurally simple supported Ir clusters are among the simplest supported metals; the metal-oxygen distances of approximately 2.6 Å are quite generally characteristic of metal particles and clusters supported on metal oxides and zeolites; the long distance is attributed to metal atoms interacting with oxygen of the support with hydrogen present at the interface.
has the rock salt structure) exhibits predominantly (100) faces, even in the powder form.13 Thus the surface of MgO is relatively simple and well defined and a good choice for characterization of the metal-support interface. Furthermore, as both the O2- and Mg2+ ions are present in the same surface layers, both the Ir-O and Ir-Mg interactions are expected to be characterized by the EXAFS data. EXAFS evidence of interactions between supported metals and cations of the support has been reported only rarely.6 The results summarized below provide a precise characterization of the metal-support interface. The EXAFS data reduction has been carried out with an improved method, including statistical analysis; the structural parameters are reported with confidence limits determined on the basis of estimates of the noise in the data.

Results

Supported metals prepared from [Ir4(CO)12] and MgO have been prepared in three different ways. The sample designated Ir4/MgO represents that prepared by decarbonylation of [Ir4(CO)12]- on MgO. The sample designated Ir6/MgO represents that prepared by conversion of the tetrairidium carbonyl to [Ir6(CO)14]2- on MgO, which was then decarbonylated. Another sample, designated Ir6/MgO, was treated in hydrogen under more forcing conditions to give larger Ir clusters with a distribution of cluster sizes; it is thus representative of a typically highly dispersed supported metal catalyst of the kind used in industry.

The raw EXAFS data characterizing the three samples are shown in Figure 1A, B, and C. The data quality is high; details are given below in the section entitled EXAFS Data Analysis. A demonstration of the data quality is provided by a Fourier transform (Figure 2), calculated with a $k^3$ weighting ($k$ is the wave vector) and application of a correction for the Ir-Ir phase and backscattering amplitude; data were used from $k = 2.6$ up to $k = 13.5 \text{Å}^{-1}$. For comparison, the Fourier transform of EXAFS data obtained with Ir metal powder (measured at room temperature, thus with more broadened peaks) is also shown.

A preliminary indication of the Ir cluster sizes in the several samples is given by the Fourier transforms of Figure 2. The amplitude of the first-shell Ir-Ir contribution at 2.7 Å (Figure 2) is lower for Ir4/MgO than for the other samples, pointing to Ir4/MgO as the sample with the highest Ir dispersion. The absence of the third and fourth Ir-Ir shells and the very low amplitude of the second shell (at 3.8 Å) also point to the high dispersion of the Ir4/MgO and Ir6/MgO. In contrast, the higher Ir-Ir coordination shells are clearly evident in the data representing the sample that had been treated in hydrogen at a relatively high temperature (Ir6/MgO), showing the lower dispersion of the Ir. However, even in this sample the Ir clusters were still quite small, as indicated by a comparison of the Fourier transforms of EXAFS data characterizing Ir6/MgO and Ir powder; the second, third, and fourth Ir-Ir shells are much more prominent in the Ir powder data than in the others.

The Fourier transforms presented in Figure 2 are $k^3$ weighted and are therefore not appropriate for demonstrating the presence of the low-Z neighbors of Ir in the support (O and Mg). The backscattering amplitude of a low-Z element becomes very small at $k \geq 7 \text{Å}^{-1}$, whereas that of a high-Z scatterer is still significant at higher values of $k$.14 Application of only $k^3$ weighting leads to an underestimation of the contributions of low-Z scatterers, and application of only $k^1$ weighting leads to an underestimation of the contributions of high-Z scatterers. Therefore, both weightings were applied. The presence of low-Z neighbors of Ir is demonstrated in Figure 3, which is a comparison of a $k^1$-weighted


Fourier transform of data characterizing Ir powder and data characterizing the Ir₄/MgO sample (the one with the highest dispersion and the most easily detectable support neighbors). Figure 3 shows both the magnitude (the envelope) and the imaginary part (the oscillations) of the k¹-weighted Fourier transform. The Fourier transform of the EXAFS data characterizing the Ir powder in this figure is scaled to the main peak of the Fourier transform of the EXAFS data characterizing Ir₄/MgO. The peak at the position of the first Ir–Ir shell in Ir powder seems to be split into three peaks; this splitting is caused by the k dependence of the phase shift and backscattering amplitude of the Ir–Ir absorber–backscatterer pair. Application of a Fourier transform that is corrected for the k dependence of the Ir–Ir phase shift and backscattering amplitude shows only one peak for the Ir–Ir contribution (Figure 2). The contrast between the data in the first-shell region for the two samples (Figure 3, both the magnitudes and the imaginary parts of the Fourier transforms) demonstrates the presence of low-Z scatterers in the immediate neighborhood of Ir in the Ir₄/MgO sample; these are inferred to be present in the metal–support interface.

The final results of the EXAFS data analysis are presented for all three samples in Figures 4–6. Fits obtained by a nonlinear least squares multiple-shell fitting routine are shown in k space and in r (distance) space with k¹ weighting. A statistical justification of the structural parameters and details of the analysis are given in the section entitled EXAFS Data Analysis. The coordination parameters and their standard deviations (calculated from the covariance matrix including the statistical errors of the experimental points), obtained from the nonlinear least squares multiple-shell fitting routine, are given in Table I.

The analysis of the EXAFS data for the Ir₄/MgO sample showed that the second Ir–Ir shell was significant but the third and fourth shells were not detectable. The difference file (obtained by subtracting the sum of the Ir–Ir(1), Ir–Mg, and Ir–O(1) contributions from the primary EXAFS data) provides further evidence of the presence of the second Ir–Ir shell (Figure 7, solid line). The dotted line (Figure 7) represents the second Ir–Ir shell calculated with the parameters obtained from the multiple-shell fit. The coordination parameters characterizing the second shell are included in Table I for comparison with the results of the higher-shell analysis of the data for Ir₄/MgO. The second Ir–Ir shell for Ir₄/MgO was difficult to analyze with the nonlinear least squares fitting routine because other, overlapping higher-shell contributions are present in the data. These weak contributions prevented a reliable analysis of the second Ir–Ir shell with the fitting routine. The data characterizing Ir₄/MgO allow analysis of the second and third Ir–Ir shells.

Figure 4. Results of multiple-shell fitting (dotted line) of the EXAFS data characterizing Ir₄/MgO (solid line): (A) fit in k space (k¹-weighted, Δk = 3.5–12.5 Å⁻¹) and (B) fit in r space (FT: k¹-weighted, Δk = 3.5–12.5 Å⁻¹).

Figure 5. Results of multiple-shell fitting (dotted line) of the EXAFS data characterizing Ir₄/MgO (solid line): (A) fit in k space (k¹-weighted, Δk = 3.5–12.5 Å⁻¹) and (B) fit in r space (FT: k¹-weighted, Δk = 3.5–12.5 Å⁻¹).

Figure 6. Results of multiple-shell fitting (dotted line) of the EXAFS data characterizing Ir₄/MgO (solid line): (A) fit in k space (k¹-weighted, Δk = 3.5–13.5 Å⁻¹) and (B) fit in r space (FT: k¹-weighted, Δk = 3.5–13.5 Å⁻¹).

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Table I. Coordination Parameters

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<tr>
<th>parameters</th>
<th>coordination number, N</th>
<th>Debye-Waller factor, $\Delta s^2 \times 10^3$, $\AA^2$</th>
<th>coordination distance, $R$, $\AA$</th>
<th>inner potential correction, $\Delta E_0$, eV</th>
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<tr>
<td>Ir$_4$</td>
<td>2.6 ± 0.3</td>
<td>0.6 ± 0.7</td>
<td>2.713 ± 0.004</td>
<td>-52 ± 0.7</td>
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<td>Ir$_6$</td>
<td>2.7 ± 0.5</td>
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<td>2.72 ± 0.02</td>
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<td>Ir$_8$</td>
<td>4.6</td>
<td>2.2</td>
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<td>Ir$_4$</td>
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<td>3.8 ± 0.7</td>
<td>2.630 ± 0.007</td>
<td>-0.8 ± 0.6</td>
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<td>7 ± 4</td>
<td>2.65 ± 0.04</td>
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<tr>
<td>Ir$_4$</td>
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<td>13.6 ± 4.3</td>
<td>1.60 ± 0.02</td>
<td>-2 ± 4</td>
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<td>Ir$_6$</td>
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<td>2.5 ± 7.4</td>
<td>1.63 ± 0.06</td>
<td>-9 ± 15</td>
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<td>-0.5 ± 24</td>
<td>2.2 ± 0.2</td>
<td>-5 ± 40</td>
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<td>0.0</td>
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<td>Coordination: Ir-Ir(2) (second shell)</td>
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<tr>
<td>Ir$_4$</td>
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<td>1 ± 4</td>
<td>2.9 ± 0.02</td>
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<tr>
<td>Ir$_6$</td>
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<tr>
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<td>3.85</td>
<td>1.85</td>
<td>-5</td>
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<tr>
<td>Coordination: Ir-Ir(3) (third shell)</td>
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<tr>
<td>Ir$_8$</td>
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</table>

Figure 7. Fourier transform ($k^3$-weighted, $\Delta k = 3.5-12.5 \AA^{-1}$, Ir-Ir phase- and amplitude-corrected) of the difference file (isolated EXAFS minus calculated Ir-Ir(1) + Ir-O(1) + Ir-Mg) (solid line) and calculated Ir-Ir(2) EXAFS function (dotted line) for Ir$_4$/MgO (notation in Table I).

Figure 8. (A) Fourier transform ($k^3$-weighted, $\Delta k = 3.5-12.5 \AA^{-1}$, Ir-Ir-Mg phase-corrected) of difference file (isolated EXAFS minus calculated Ir-Ir(1) + Ir-O(1) (solid line) and calculated Ir-Ir-Mg EXAFS function (dotted line) for Ir$_4$/MgO. (B) Fourier transform ($k^3$-weighted, $\Delta k = 3.5-12.5 \AA^{-1}$, Ir-O phase-corrected) of difference file (isolated EXAFS minus calculated Ir-Ir(1) + Ir-Mg) (solid line) and calculated Ir-O(1) EXAFS function (dotted line) for Ir$_4$/MgO.

The X-ray absorption near edge structure (XANES) provides further evidence of the structures of the supported metal clusters. The normalized $L_{III}$ absorption edge (white line) data for two supported Ir$_4$ samples (Ir$_4$/MgO and Ir$_8$/MgO) and for Ir metal powder are summarized in Figure 10A. The decreasing intensity of the white line with increasing cluster size is consistent with predictions of Hartree–Fock–Slater LCAO calculations characterizing Ir$_4$ and Ir$_{10}$ clusters. However, the intensity of the $L_{III}$ absorption edge characteristic of Ir$_8$/MgO is slightly higher than that of Ir$_4$/MgO (Figure 10B), indicating an effect separate from that of the cluster nuclearity.

Discussion

Advantage of Organometallic Precursors. A unique advantage of the organometallic precursors is the opportunity they offer for preparation of extremely small supported metal clusters that are almost optimally suited to precise characterization with EXAFS spectroscopy. The results of this work give evidence that the tetrairidium cluster can be decarbonylated on the support with (16) Ravenek, W.; Jansen, A. P. J.; Van Santen, R. A. J. Phys. Chem. 1989, 93, 6445.
Iridium Clusters on Magnesium Oxide

Figure 9. Magnitude of Fourier transform ($k^2$-weighted, $\Delta k = 3.5-12.5\ \text{Å}^{-1}$) of calculated Ir–Ir and Ir–O(1) EXAFS functions characterizing Ir$_4$/MgO (solid line) and Ir$_4$/MgO (dotted line).

Figure 10. Normalized $L_{III}$ X-ray absorption edge of (A) Ir powder (solid line), Ir$_4$/MgO (dot-dashed line), and Ir$_4$/MgO (dotted line) and (B) Ir$_4$/MgO (dotted line) and Ir$_4$/MgO (dot-dashed line).

little change in nuclearity (Table I). Since the clusters are so small, the EXAFS signal is determined in large measure by the metal–support interactions and not just the metal–metal interactions. Consequently, the EXAFS data offer the prospect of detailed characterization of the structure of the metal–support interface. The samples that usually yield the most explicit structural information from EXAFS analysis are those that are most nearly uniform in structure. Thus an important result of the EXAFS analysis for Ir$_4$/MgO is the evidence that the structure is indeed relatively simple and uniform.

Variations in Cluster Size. The chemistry of the Ir carbonyls on MgO is relatively well defined, being analogous to that occurring in basic solutions.$^{11,12}$ Control of this chemistry allows conversion of the tetrairidium carbonyl precursor in high yield into a hexairidium carbonyl precursor, [Ir$_6$(CO)$_{15}$]$^{2-}.^{12}$ Treatment in He followed by H$_2$ leading to decarbonylation of this cluster gave a supported metal with nearly as high a dispersion as that for the supported metal formed by decarbonylation of the Ir$_4$ cluster on MgO. The high dispersions of these two samples are shown by the extremely small Ir–Ir(1) coordination numbers (Table I). The Ir–Ir(1) coordination number for Ir$_4$/MgO is significantly larger (Table I).

This comparison of coordination numbers is important because it shows that the samples provide a systematic variation of the cluster size and therefore the opportunity for discerning a pattern of changes in the metal–support interface as the fraction of the metal atoms that are in the interface decreases. The data thus offer a unique opportunity to make connections between the relatively precise structural information characteristic of the Ir$_4$ and Ir$_4$ clusters and that representative of the structurally less uniform Ir$_4$/MgO sample, which is more nearly representative of a typical highly dispersed supported metal catalyst.

Structures of the Supported Iridium Clusters. The results of Table I demonstrate that the metal clusters in the Ir$_4$/MgO and Ir$_4$/MgO samples are so small that it is possible to give an accurate characterization of the metal–support interface. The data allow a more detailed structural characterization of supported metals—including the metal–support interface—than any yet reported.

From the EXAFS results in Table I it is concluded that the three samples, representing a range of cluster sizes (as demonstrated by the Ir–Ir(1) coordination numbers, Table I), are much alike insofar as coordination distances are concerned. However, significant differences are observed in the Debye–Waller factors of the interface contributions, and these indicate that with changes in cluster size there are significant changes in the structural detail of the Ir–MgO interface.

Ir$_4$/MgO. The Ir–Ir(1) coordination number characteristic of the sample formed by decarbonylation of [HIr$_4$(CO)$_{11}$]$^{2-}$ on MgO (Table I), namely 2.6, is consistent with the inference that the cluster nuclearity was maintained. However, within the experimental error (Table I), this value is less than 3.0, the value characteristic of the tetrahedron of the metal frame of the precursor [Ir$_4$(CO)$_{12}$] or [H$_2$Ir$_4$(CO)$_{11}$]$^{2-}$, which implies that the tetrahedral frame of the precursor was not retained in all the clusters. It is also evident from the presence of the second-shell Ir–Ir contribution that a simple Ir$_4$ tetrahedron is not consistent with the data (no higher Ir–Ir shells are expected for a tetrahedron). However, the average Ir–Ir coordination number of 2.6 cannot be reconciled with raft-like structures alone either, as the first-shell Ir–Ir coordination number in a square Ir$_4$ raft is 2 and much larger rafts must be assumed to account for $N = 2.6$ (these imply sizeable third and fourth Ir–Ir shells). A small fraction of clusters with nuclearities greater than four may have been present; however, as the third and fourth Ir–Ir shells are almost absent, these must have been rare. There is no conclusive evidence that raft-like structures would be exclusively square; various other arrangements cannot be ruled out.

The EXAFS data have been modeled as simply as possible; they have been found to be consistent with a mixture of Ir$_4$ tetrahedra and square rafts (see Figure 11A). Taking the accuracy of the EXAFS coordination numbers into account, we calculate from the first-shell Ir–Ir coordination number (2.6 ± 0.3) that 40–80% of the clusters consist of tetrahedra. On the
other hand, following the same procedure and using the second Ir–Ir shell \(N = 0.9 \pm 0.4\), a maximum of 50% of the clusters are inferred to be tetrahedra. Combining these results leads to the model that 40–50% of the Ir clusters are tetrahedra and the remainder square rafts.

The metal is depicted as bare atoms on the support, but the samples were investigated in the presence of hydrogen and were therefore likely Ir hydrides, possibly with a \(\text{Ir}^{2+}-\text{H}_6\) charge distribution;\(^{17}\) the available data provide no direct evidence of the locations of the hydrogen atoms in the structure.

\textbf{Ir}/MgO. The coordination number for the first Ir–Ir shell \((2.7)\) and the very small amplitude of the higher Ir–Ir shells in \textit{Ir}/MgO show that there was little coalescence of the original clusters. On the other hand, it is also clear that the original octahedral cluster frame was not maintained in a large fraction of the supported Ir clusters (the first-shell coordination number of an octahedron is 4). The data of Figure 2 show that a significant second Ir–Ir shell was present and, as for \textit{Ir}/MgO, the contribution of the third Ir–Ir shell is negligible. These observations lead to the conclusion that a significant fraction of the Ir atoms in \textit{Ir}/MgO were in two-dimensional structures.

As for \textit{Ir}/MgO, we have attempted to model the structures as simply as possible to account for the EXAFS data. Good agreement was obtained with a model consisting of a mixture of octahedra (first Ir–Ir shell coordination number = 4) (Figure 11B) and \(2 \times 3 \times 100\) rafts (first shell Ir–Ir coordination number = 2.3), but we emphasize again that the existence of other raft-like structures cannot be ruled out. On the basis of the overall first-shell Ir–Ir coordination number determined by EXAFS spectroscopy (2.7), it is estimated that about 25% of the Ir clusters were octahedral.

\textbf{Ir}/MgO. The EXAFS data characterizing the conventional supported metal catalyst symbolized as \textit{Ir}/MgO (Table I) give an average Ir–Ir distance of 2.72 Å; this is consistent with the inference that the structure is metallic and reduction is almost complete (no evidence is found for the presence of iridium oxide, which would show in an Ir–O contribution with \(R \approx 1.95\) Å). The metal clusters in such a catalyst are usually three-dimensional, sometimes approximated as hemispherical.\(^{3}\) The higher-shell EXAFS data, represented by the spectrum in \(r\)-space (Figure 2), confirm that the Ir particles in \textit{Ir}/MgO are three-dimensional; both second and third metal–metal shells are present.\(^{18}\)

The \textit{Ir}/MgO sample, in contrast to the others, is characterized by a distribution of metal cluster sizes (and probably shapes), as its preparation was carried out under severe conditions that led to cluster fragmentation and metal aggregation. An average Ir cluster diameter of 10 Å was estimated from the Ir–Ir coordination number determined with EXAFS spectroscopy (the clusters were assumed to be hemispheres with the fcc structure).\(^{5}\) This estimate implies that on average there were approximately 14 Ir atoms per cluster. Thus, even after the severe treatment, a few Ir clusters are still present in typical highly dispersed Pt/Al\(_2\)O\(_3\) catalysts.\(^{19}\)

A comparison of the relative magnitudes of the higher Ir–Ir shells in \textit{Ir}/MgO and Ir powder (Figure 2) might at first seem to suggest that the Ir particles in \textit{Ir}/MgO are not well approximated as hemispheres. The high amplitude of the second Ir–Ir shell would be consistent with flatter structures. However, calculations for small fcc model clusters having a \((100)\) basal plane showed that a high amplitude of the second metal–metal shell is consistent with approximately hemispherical clusters.

\begin{equation*}
N(i) = \frac{3.4}{X} + \frac{0.75}{X} \times N(i)_{\text{tet}}
\end{equation*}

\begin{equation*}
N(i)_{\text{tet}} = \frac{3.4}{X} + \frac{0.5}{X} \times N(i)_{\text{tet}}
\end{equation*}

\begin{equation*}
N(i)_{\text{tet}} = \frac{3.4}{X} + \frac{0.5}{X} \times N(i)_{\text{tet}} = 3.4, \text{ resulting in } N(i) = 3.9.
\end{equation*}

Taking into account the experimental errors in the EXAFS data (Table 1), we might therefore suggest that the Ir–MgO interface could be modeled with an Ir–O coordination number of 4; a fourfold Ir–O coordination can be visualized on the \((100)\) face of MgO. This is the predominant face.\(^{13}\) However, it is not appropriate to rule out clusters on other fourfold sites, on other faces, and at imperfections on the MgO surface where the coordination is less; the data are not sufficient to distinguish these possibilities.

In \textit{Ir}/MgO, in addition to the interface contributions characterized by an Ir–O(1) distance of 2.65 Å and an Ir–Mg distance at 1.63 Å, there is an Ir–O(2) shell at 2.2 Å that is not found in the EXAFS data for \textit{Ir}/MgO. The identification of this Ir–O(2) contribution is not obvious; we suggest that it may be an indication that some of the clusters are positioned at surface.

\begin{equation*}
\frac{2.7}{X} \times N(i)_{\text{tet}} + \frac{2.7}{X} \times N(i)_{\text{tet}} = 3.4, \text{ resulting in } N(i) = 3.9.
\end{equation*}

\(X\) the distance to the next shell in the \((100)\) face of MgO.

\(X\) the distance to the next shell in the \((100)\) face of MgO.

\textbf{Acknowledgments}. The authors would like to acknowledge financial support from the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Iridium Clusters on Magnesium Oxide defects such as Mg cation vacancies. For example, a structure such as that suggested in Figure 11B (with one atom of the octahedron located at a cation vacancy) could account for anchoring of the octahedron to the support. Replacement of the Mg cation for Ir results in an Ir–O coordination distance of 2.11 Å if that Ir atom takes the exact Mg cation position, close enough to the observed Ir–O(2) distance of 2.2 Å. A relatively rigid structure such as this would account for the small Debye-Waller factor observed (Table I) for the Ir–Mg contribution at 1.63 Å and the Ir–O(2) shell at 2.2 Å. Such a structure also provides an explanation for the large Debye–Waller factor observed for the Ir–O(1) contribution at 2.65 Å: Four of the octahedral Ir atoms are suggested to be positioned on the MgO surface, but there would be a large variation in the Ir–O distances associated with these Ir atoms because of the lattice mismatch with MgO.

The coordination numbers calculated for the Ir–O contributions in this model agree well with those obtained from EXAFS analysis. In the raft, all the Ir atoms contribute to the Ir–O(1) shell at 2.65 Å (with \(N(\text{Ir}-\text{O}(1)) = 4\)) and there is no Ir–O(2) contribution \((N(\text{Ir}-\text{O}(2)) = 0)\). In the octahedron, only one Ir atom out of the six (the anchoring atom) contributes to the Ir–O(2) shell, and this one has four Ir–O(2) interactions; the overall octahedral coordination number is \(N(\text{Ir}-\text{O}(2)) = 4/6\). Four of the octahedral Ir atoms contribute to the Ir–O(1) shell at 2.65 Å (fourfold bonding); thus the overall octahedral coordination number for this shell is \(N(\text{Ir}-\text{O}(1)) = 16/6\). For a comparison with the EXAFS results for Ir\(_4\)/MgO, the coordination numbers calculated above have to be weighted according to the occurrence of the rafts and octahedra: \(N(\text{EXAFS}) = 0.75N(\text{raft}) + 0.25N(\text{oct})\). In this way, \(N(\text{Ir}-\text{O}(2)) = 0.17\) is calculated (the corresponding value determined in the EXAFS analysis, \(N(\text{Ir}-\text{O}(2)) = 0.2\), Table I), and similarly, \(N(\text{Ir}-\text{O}(1)) = 3.67\) (vs 3.7 from the EXAFS analysis).

The suggestion that most of the Ir clusters are present on the (100) faces of MgO is supported by the relative magnitudes of the Ir–Ir shells. The large amplitude of the second shell with respect to the third (Figure 2) points to Ir rafts as a substantial contribution to the metal structures in Ir\(_4\)/MgO and Ir\(_6\)/MgO and indicates the relatively large contribution of the basal plane of the clusters in Ir\(_4\)/MgO. Ir rafts with the (100) arrangement might be expected to provide the best (epitaxial) fit on the MgO surface of the Ir–Ir(1) shell at 2.65 Å (100) face, as has been assumed in the models mentioned above. The assumption of rafts with this structure on the MgO (100) plane accounts for the large differences in the Debye-Waller factor \((\Delta r^2)\) observed for the Ir–Mg contributions (Table I). The largest Debye-Waller factor (indicating the largest distribution of Ir–O and Ir–Mg distances) would be expected for the sample with the largest interfacial area \((A_{\text{facet}})\), corresponding to the lattice mismatch of 9% (the Ir–Ir distance is 2.72 Å and the MgO lattice constant is 2.98 Å). However, the largest value of \(\Delta r^2\) was observed for Ir\(_4\)/MgO, the sample with the smallest clusters. This result might be taken as an indication that a significant fraction of the Ir clusters were present at surface defects. Alternatively, if it is correct to assume that the Ir clusters were largely present on the (100) plane, then the value of the Debye–Waller factor can be explained as follows: A large fraction of the Ir clusters is calculated to be present as tetrahedra, and these clusters expose a trigonal basal plane, which does not conform to the square (100) face of MgO (Figure 11A).

**Nature of the Metal–Support Interface.** The EXAFS observations raise fundamental questions about the nature of the interactions at metal–support interfaces. It has been suggested that the long metal–oxygen distances (2.6–2.8 Å) observed in this work and for numerous other samples, as stated in the introduction, may indicate the presence of hydrogen in the metal–support interface or, alternatively, interactions of metal atoms with hydroxyl groups of the surface.\(^{(22)}\)

![Figure 12](image-url) Structural models of the Ir–MgO interface. (A) Ir metal atom on a partially hydroxylated MgO (100) surface with hydrogen in the metal–oxygen interface. (B) Ir metal atom on a fully hydroxylated MgO (100) surface.

The suggestion that the metal atoms of the clusters were in contact with hydroxyl groups of the support has been tested in experiments with a reduced Ir/γ-Al\(_2\)O\(_3\) sample evacuated at a high temperature (623 K); EXAFS results demonstrated that the evacuation led to the disappearance of the long metal–oxygen distance.\(^{(24)}\) Instead, a metal–oxygen distance of about 2.2 Å was detected. The evacuation of the sample is expected to have led to a dehydroxylation of the support, which in turn may have removed OH groups from the metal–support interface. This shorter metal–oxygen distance might be interpreted as evidence that a new kind of interaction resulted as the surface OH groups were converted into surface O\(^2\) ions in contact with the metal. However, evacuation also leads to removal of chemisorbed hydrogen from the surface of the metal and possibly from the metal–support interface. Therefore, it is also possible that the observed long metal–oxygen distance is a consequence of the presence of hydrogen at the metal–support interface.\(^{(22)}\) Furthermore, evacuation also leads to changes in the morphology of the supported clusters, producing more raft-like structures that may be more polarized; thus the relatively short metal–oxygen distances of 2.1–2.2 Å may be explained by the interaction of metal atoms with small positive charges with oxygen of the interface.\(^{(22,25)}\)

The present results are not sufficient to resolve these issues, but they do help to distinguish between two of the possibilities, as follows. As outlined above, the Ir at the interface is inferred to be coordinated principally to four oxygens. The oxygens on the surface of partially hydroxylated MgO include O\(^2\) as well as oxygen of OH\(^-\) groups of more than one kind, including protonated O\(^2\) ions terminating the MgO lattice and OH groups bonded to Mg\(^{2+}\) ions terminating the lattice.\(^{(26)}\) This results in two limiting cases for the Ir atoms at the MgO surface (Figure 12A and B).

The two simple models can be described as follows: (1) If the support surface has no hydroxyl groups in contact with the clusters, individual Ir atoms on the MgO (100) face are positioned between the oxygens and directly above the Mg\(^{2+}\) ions (Figure 12A). From the MgO crystallographic distances\(^{(13)}\) and an Ir–O coordination distance of 2.6 Å (Table I), an Ir–Mg distance of 1.5–1.6 Å is expected. (2) If the MgO (100) face is fully hydroxylated, then the Mg\(^{2+}\) ions are covered by OH groups. Ir atoms on this surface that have an Ir–O coordination number of 4 would have


to be placed between four OH groups, each positioned on top of a Mg$_2$O$_2$ surface ion (Figure 12B). Using the same coordination distances as in the former model and a Mg–OH distance of 2.106 Å (equal to the Mg–O distance in MgO), an Ir–Mg distance of 4.1–4.2 Å is calculated. The Ir–Mg distances indicated by EXAFS (1.6–1.7 Å, Table I) are in agreement with the first but not the second of these limiting-case models.

Although the Ir–Mg distances obtained from EXAFS analysis agree with the interface model depicted in Figure 12A, the low value of the Ir–Mg distance raises questions about the chemical state of the Ir in the samples. The Ir–Ir coordination distance (2.72 Å) suggests that the Ir is in the zerovalent state. In that case, simple addition of the radii of Mg$^2+$ (0.66 Å) and Ir$^0$ (1.36 Å) results in an expected Ir–Mg distance of approximately 2 Å. An Ir–Mg distance of 1.5–1.6 Å would be expected on the basis of geometrical considerations as argued above, but clearly then not all Ir can be in the zerovalent state. The observed Ir–Mg distance (1.6–1.7 Å) is somewhat larger than that expected for Ir on undistorted MgO. We suggest that the Mg ion may move slightly away from the interface Ir atom (Figure 12A), which is as expected if some Ir atoms bear a small positive charge. We thus suggest that at least some of the Ir atoms present in the metal–support interface should be regarded not as Ir$^0$ but instead as Ir$^+$. As mentioned before the Ir clusters were investigated in the presence of hydrogen and were therefore hydrides with possibly a Ir$^+$–H$^+$ charge distribution. The removal of these hydride ligands (e.g. by evacuation or by high-temperature reduction) may lead to a direct Ir$^0$–O$^2-$ interaction with a higher degree of polarization, as suggested for the Ir hydrides. This direct Ir$^0$–O$^2-$ interaction implies the existence of relatively short (ca. 2.2 Å) metal–oxygen distances. Such short distances are characteristic of metal subcarbonyls on metal oxides, and the existence of such short distances in oxide-supported metals has been suggested to be an indication that some of the interface metal atoms bear small positive charges. This metal–oxygen distance is about the same as the short Ir–O(2) distance (about 2.2 Å) that occurs in Ir$_4$/MgO and Ir$_6$/MgO, and also here it is suggested to be attributable to the Ir–O (viz. Ir$^4$–O) bonds of the anchoring Ir atom in the octahedral Ir$_6$ clusters in direct contact with the support oxygen (Figure 11B).

In summary, on the basis of the observed Ir–Mg distances, we conclude that some Ir in the interface must bear small positive charges. We also conclude that Ir was not present on sites where the surface was fully hydroxylated; it must have been present on sites that were dehydroxylated or partially hydroxylated. The surface ligands are thus inferred to include O$^2-$ and/or OH$^-$ (originating from H$^+$ interacting with O$^2-$, as shown in the side view of Figure 12A). The Ir–O distance of about 2.6 Å has been similarly observed for a number of conventional supported metals on various metal oxides and zeolites. This distance was found only with samples characterized by EXAFS spectroscopy in the presence of H$_2$. This metal–oxygen distance thus may be characteristic of interfaces in which hydrogen is present between metal atoms and oxygen ions of metal oxide supports, including zeolites. The observations refer to the following metals: Rh,$^{3,4}$ Pd,$^{27}$ Re,$^{28}$ Os,$^{29}$ Ir$^{15,24}$ (also this work), and Pt.$^{18,19,20}$ The nature of hydrogen at the interface remains to be elucidated; in one limiting case, it might be protonic and associated primarily with the oxygen, and in another limiting case it might be hydridic and associated primarily with the metal. Removal

of the hydrogen from the interface is accompanied by structural rearrangement of the metal–support interface, which is expected to influence the electronic structure of the metal clusters and thereby the catalytic properties of the supported metals.

### Experimental Section

#### Catalyst Preparation

**A. Ir$_4$/MgO.** The sample was prepared by chemisorption of [Ir$_4$(CO)$_{12}$] on MgO, as communicated previously, followed by decarbonylation. All the steps were carried out in the near absence of air on Schlenk lines and in nitrogen-filled dryboxes; details are given below.

[Ir$_4$(CO)$_{12}$] (Strem) was used without further purification. Reagent-grade hexanes were dried by refluxing over sodium benzophenone ketyl. Nitrogen (99.999%) (Matheson) was purified by passage through traps containing CuO and activated molecular sieves to remove traces of oxygen and moisture, respectively. The partially dehydroxylated MgO powder (MCB) was prepared by treatment in flowing oxygen as the temperature was ramped from room temperature to 673 K; this temperature was held for 2 h, and the sample was evacuated and held for a further 14 h at this temperature. The MgO was cooled under vacuum to room temperature and removed in the drybox. The surface area of the powder was approximately 75 m$^2$/g as determined by N$_2$ adsorption.

The MgO-supported sample was prepared by slurring [Ir$_4$(CO)$_{12}$] (0.029 g) in freshly distilled hexanes (50 mL) in a Schlenk flask under N$_2$. The MgO (2.0 g) was added to the slurry, which was stirred for 4 h at room temperature. The solid sample was dried by evacuation for 14 h at room temperature.

The resulting sample was treated in flowing helium while being heated to 573 K at a rate of 5 K/min, held at this temperature for 2 h, cooled in flowing helium, and then treated in flowing H$_2$ as it was heated at 5 K/min to 573 K. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used to characterize the sample at various stages of the preparation; the spectrometer was a Nicolet 7199; the cell and methods are described in a thesis. The spectra demonstrate that the Ir was fully decarbonylated after the treatment described above. Results presented elsewhere provide evidence that the intermediate surface structure formed upon adsorption of the [Ir$_4$(CO)$_{12}$] was predominantly [HIr$_4$(CO)$_{11}$]; this was extracted from the surface and identified in solution.

**B. Ir$_6$/MgO.** The sample was prepared by conversion of the intermediate [HIr$_4$(CO)$_{11}$] on the MgO surface to predominantly [Ir$_6$(CO)$_{14}$], which could be extracted from the surface with a solution of [PPN][Cl] in acetone, as described elsewhere. The surface reaction giving the hexairidium cluster anion took place as the sample was treated in flowing CO at atmospheric pressure as the temperature was ramped at 5 K/min to 473 K and held for 8 h. This sample was decarbonylated by treatment in flowing He at 573 K for 2 h followed by treatment in flowing H$_2$ as it was heated at 5 K/min to 573 K and held for 2 h before cooling to room temperature in flowing H$_2$. The decarbonylation was followed by infrared spectroscopy.

**C. Ir$_4$/MgO.** An Ir$_4$/MgO sample that is a typically highly dispersed supported metal catalyst was prepared by impregnation of MgO with a solution of [Ir$_4$(CO)$_{12}$] in cyclohexane. The MgO was prepared as follows: 88 g of Mg(NO$_3$)$_2$·6H$_2$O was dissolved in 400 mL of distilled water. This solution was added dropwise with vigorous stirring to a 1000-mL water/ice mixture in which 200 mL of concentrated ammonia had been dissolved. After all the Mg(NO$_3$)$_2$ solution had been added and the ice melted, the precipitate was filtered, suspended in 75 mL of water/ice mixture, and filtered again. This procedure was repeated until the pH of the suspension was 7. After the last filtration, the precipitate was dried overnight at 393 K and ground to a white powder, which was calcined in nitrogen at 473 K for 2 h (heating rate, 5 K/min) to remove nitrogen-containing residues. The resulting MgO powder had a surface area of 119 m$^2$/g (determined by N$_2$ adsorption). The MgO was partially dehydroxylated by calcining the vacuum at 873 K for 8 h (heating rate, 5 K/min). [Ir$_4$(CO)$_{12}$] (Alfa, used without further purification) and cyclohexane (dried over sodium benzophenone ketyl) was used immediately.

The catalyst was prepared by treatment of the MgO in flowing H$_2$ at 573 K for 2 h (heating rate, 5 K/min) and passivated in air at room temperature. The solid was then dehydroxylated by calcining the sample at 873 K for 8 h (heating rate, 5 K/min). The sample was transferred in flowing H$_2$ at a rate of 5 K/min, held at this temperature for 2 h, and then treated in flowing H$_2$ as it was heated at 5 K/min to 573 K. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used to characterize the sample at various stages of the preparation; the spectrometer was a Nicolet 7199; the cell and methods are described in a thesis. The spectra demonstrate that the Ir was fully decarbonylated after the treatment described above.

Results presented elsewhere provide evidence that the intermediate surface structure formed upon adsorption of the [Ir$_4$(CO)$_{12}$] was predominantly [HIr$_4$(CO)$_{11}$]; this was extracted from the surface and identified in solution.

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EXAFS Measurements. EXAFS measurements of the supported iridium catalysts were performed at EXAFS station 9.2 of the Wiggler beamline of the synchrotron radiation source (SRS) at Daresbury, U.K. The station was operated with a double crystal monochromator, Si(220), detuned to 30% intensity to minimize the presence of higher harmonics in the beam. The estimated resolution was 3 eV at the Pt LIII edge (11.564 eV). The measurements were carried out in the transmission mode with optimized ion chambers to measure the radiation intensity. Data were collected at each energy for 1 s, and results from several scans (Ir/MgO, 4 scans; Ir3/MgO, 2 scans; Ir6/MgO, 6 scans) were averaged to minimize high- and low-frequency noise.

The supported Ir samples were pressed into thin self-supporting wafers (each with an absorbance of approximately 2.5) and mounted in an in-situ EXAFS cell.32 The Ir3/MgO sample had been prepared at the University of Delaware and sealed inside three layers of glass vials, each individually sealed with parafilm, the vial cap, and electrical tape. The sample was transported to Daresbury and loaded into the EXAFS cell at the synchrotron under N2 in a drybox. Data were collected with the sample in the presence of H2 at approximately liquid nitrogen temperature. A fraction of the precursor ([H4Ir(CO)11]− supported on MgO), handled in the same way as the samples characterized with EXAFS spectroscopy, was resealed and returned to Delaware, where it was characterized by infrared spectroscopy and found to be essentially unchanged. These results confirm the lack of contamination of the samples.

The sample consisting predominantly of [Ir6(O)6]− on MgO was prepared from the sample consisting predominantly of [H4Ir(CO)11]− on MgO and then decarbonylated, as described above, with the work done in Delaware. The sample transport and handling and the EXAFS measurements were carried out as described above for the sample prepared by decarbonylation of the MgO-supported [H4Ir(CO)11]−. The Ir3/MgO sample was re-reduced as it was heated in flowing H2 to 623 K. Pt LIII edge (1.564 eV) and Ir4/MgO data were made with the sample in a H2 atmosphere; details are given as above for the other samples.

EXAFS data were also collected to characterize the reference materials: The Pt LIII edge (11.564 eV) of Pt foil and Na3Pt(OH)6, and the Ir LIII edge of IrAl alloy were measured at liquid nitrogen temperature.61 Ir powder was measured as received at room temperature in the beam. The estimated resolution was 1 eV. The measurements were made with optimized ion chambers to measure the radiation intensity. Data were collected at each energy for 1 s, and results from several scans (Ir6/MgO, 4 scans; Ir3/MgO, 2 scans; Ir6/MgO, 6 scans) were averaged to minimize high- and low-frequency noise.

C. Fits in k space and in r space: Use of Both k- and k2-Weighted Fourier Transforms. The EXAFS data analysis was performed with the experimentally determined phase shifts and backscattering amplitudes for the Ir–Ir and Ir–O contributions, and the theoretical reference for the Ir–Al contribution. A nonlinear least squares multiple-shell fitting routine was used to fit the data in k space (with k weighting). The program allowed simultaneous monitoring of the unweighted fits in k space as well as the sum of the squares of the residuals between the fit and the data for the k2-weighted function and the sum of the squares of the residuals between the fit and the data for both the magnitude and the imaginary parts of the Fourier transforms. The difference file technique was applied together with phase-corrected Fourier transforms to identify the different contributions in the EXAFS data.3 To determine reliably the parameters characterizing the high-Z (Ir and O) and low-Z (O and Mg) contributions, multiple-shell fits were made in k space (simultaneously monitoring the fit in r space) was done with application of both k and k2 weighting; use of both is a prerequisite as the dependence on k of the backscattering amplitude of low-Z elements (such as O and Mg) is different from that of high-Z elements (such as Ir); the backscattering amplitude of a low-Z element becomes very small at k > 7 Å−1, whereas that of a high-Z scatterer is still significant at higher values of k.26,31 Application of only k weighting leads to an underestimation of the contributions of low-Z scatterers, and application of only k2 weighting leads to an overestimation of the contributions of high-Z scatterers.

Optimization of both the k- and k2-weighted fits in both k space and r space results in a better decoupling of the EXAFS parameters (N, Δe, R, and ΔEg) than could be realized if only more restricted criteria (using only k or k2) were applied in the fitting; this fitting procedure therefore gives a more reliable set of parameters than could be estimated with the more restricted criteria.36

In some cases the EXAFS coordination numbers N obtained in the data analysis had to be corrected for the difference in distance between the absorber–backscatterer pair of the reference shell and that of the shell to be analyzed. This correction is required because the factor exp(−2R/λ) in the EXAFS formula is not negligible.41 The correct coordination number N is therefore N/ exp[−2(R − Rref)/λ] was taken to be equal to 6 Å, which is a reasonable approximation for values of k > 3 Å−1.

D. Analysis of the EXAFS Data for the MgO-Supported Ir Samples. Analysis of the EXAFS data for each sample was performed in an isolated part of the spectrum. The data were Fourier transformed (k weighting) followed by an inverse Fourier transformation with a window ΔR (Ir/MgO, 2.6 Å < R < 15.0 Å; 0.7 Å < r < 4.0 Å; Ir3/MgO, 2.6 Å < r < 13.6 Å; 0.5 Å < r < 3.3 Å; and Ir6/MgO, 2.6 Å < r < 16.2 Å, 0.8 Å < r < 4.8 Å). These isolated EXAFS functions are now referred to as the "primary EXAFS".

The Ir–Ir(1) contribution was estimated first, as it is the largest component in the EXAFS spectrum; it was estimated in k space by applying a fit determined with k2 weighting of the data with k > 6 Å−1. The contribution of the low-Z scatterers present in the data is largely suppressed by this procedure. An Ir–Ir EXAFS function was then calculated with the first guess parameters obtained from the provisional fit. This Ir–Ir(1) contribution was subtracted from the primary EXAFS, and the resulting difference file was analyzed further for Ir–O contributions by

determining the Ir–O(1) contribution that agreed best with the difference file in a $k^2$-weighted Ir–O phase-corrected Fourier transform.

The estimates of the Ir–Ir(1) and Ir–O(1) contributions were further optimized by performing multiple-shell fits in $k$ space and in $r$ space with both $k^1$ and $k^2$ weighting. Small but significant deviations still remained in the range $1.5 < r < 2.2 \text{ Å}$. Further analysis showed that this deviation was associated with the contribution of another low-Z scatterer. The plausible candidates for the third scatterer are carbon contaminants or Mg cations of the MgO support. With the aid of phase-corrected Fourier transforms, it was established that an Ir–Mg contribution was present. Finally, for Ir$_4$/MgO and Ir$_6$/MgO it was necessary to include an Ir–O(2) contribution in the same way. Likewise, Ir–Ir(2) contributions were added for Ir$_4$/MgO and Ir$_6$/MgO, and also Ir–Ir(3) for Ir$_6$/MgO. The final coordination parameters were then obtained as described above by determining multiple-shell fits in $k$ space and in $r$ space with $k^1$ and $k^2$ weighting.

The resulting coordination parameters are given in Table I. The standard deviations given for the Ir$_4$/MgO and the Ir$_6$/MgO samples are calculated from the covariance matrix including the actual noise obtained for the Fourier filtered EXAFS function as outlined above. The value of the goodness of fit ($\chi^2$) as defined in the Report on Standards and Criteria in EXAFS Spectroscopy for Ir$_4$/MgO was $\chi^2 = 1.3$ with 16 fit parameters and 3.8 degrees of freedom. The weakest contribution to this fit was the Ir–Mg coordination. The confidence limit of this contribution was calculated by first determining the $\chi^2$ value for the goodness of fit incorporating only three shells: Ir–Ir(1), Ir–O(1), and Ir–Ir(2). $\chi^2 = 5.3$ was obtained, with 12 fit parameters and 7.8 degrees of freedom. Using these values for $\chi^2$, the F-test was applied and it showed, at an 85% confidence level, that the Ir–Mg contribution is present. Thus, we feel confident that the data for Ir$_4$/MgO are best represented by a four-shell fit. For Ir$_6$/MgO, $\chi^2 = 2.1$ (with 16 fit parameters and 1 degree of freedom) was obtained. Our analysis package is not yet able to perform a statistical analysis with 24 fit parameters as is necessary for the analysis of the Ir$_6$/MgO sample. No errors are given for this sample in Table I. The estimated errors for the coordination numbers vary from 10% for the dominant Ir–Ir(1) shell to 30% for the higher shells. The standard deviation of the coordination distances ranges from 0.01 for the Ir–Ir(1) shell to 0.03 for the higher shells.

Conclusions

Ir/MgO catalysts with various nuclearities have been characterized with EXAFS spectroscopy to elucidate the structure of the metal–support interface. Beginning with the precursor $\text{[Ir}_4\text{(CO)}_{12}]$ supported on MgO, Ir$_4$/MgO was prepared via $\text{[Ir}_4\text{(CO)}_{12}]$. With EXAFS spectroscopy, it has been shown that upon careful decarbonylation, the cluster nuclearity of the intermediate is maintained in the final product. More severe treatment in $H_2$ of $\text{[Ir}_4\text{(CO)}_{12}]$ on MgO results in an Ir$_4$/MgO catalyst with larger, structurally nonuniform Ir clusters.

EXAFS analysis of the first and higher Ir–Ir shells and model calculations show that the Ir$_4$/MgO sample can be modeled as a mixture of Ir$_4$ tetrahedra and square rafts. The EXAFS data characterizing Ir$_6$/MgO are well represented by a mixture of Ir$_6$ octahedra and (100) rafts, and the data characterizing Ir$_6$/MgO lead to a model consisting of Ir metal clusters, approximately hemispherical and averaging 10 Å in diameter, with a (100) basal plane in contact with the MgO support.

Ir–O contributions with a coordination distance of 2.6 Å and associated with the metal–support interaction are large in all three samples. The Ir atoms at the interface are approximately fourfold coordinated to oxygen, and it is suggested that the Ir clusters are predominantly present on the (100) faces of MgO, where a fourfold coordination is most easily pictured. The EXAFS data indicate an Ir–Mg contribution at 1.7 Å, which implies that Ir atoms at the interface are positioned at surface Mg ions on (partially) dehydroxylated parts of the MgO faces. Relatively long (2.5–2.7 Å) metal–oxygen distances are found in supported metals only when they are characterized in a $H_2$ atmosphere, and it is postulated that this distance characterizes the interaction between reduced metal atoms and surface oxygen atoms or the interaction between these interfacial metal atoms and oxygen atoms with hydrogen present in the metal–support interface.

Small Ir–O contributions with a coordination distance of 2.2 Å, found to be characteristic of Ir$_4$/MgO and Ir$_6$/MgO samples, but not Ir$_6$/MgO, are not ascribed to an oxidic fraction of the Ir but instead are thought to be an indication of the metal–support interface where positively charged metal atoms interact with oxygen at the interface. Some of these Ir atoms at the interface may penetrate into Mg vacancies.

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