

## EXAFS Study of the Influence of Hydrogen Desorption and Oxygen Adsorption on the Structural Properties of Small Iridium Particles Supported on Al<sub>2</sub>O<sub>3</sub>

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Desorption of hydrogen at high temperature leads to a contraction of the Ir-Ir coordination distance of highly dispersed iridium metal particles. The long metal-support oxygen distance (2.55 Å) observed if the metal crystallites are covered with chemisorbed hydrogen disappears after treatment in vacuum at 623 K. Instead, a metal-oxygen coordination in the metal-support interface is now detected with a distance of 2.19 Å. It is concluded that the long metal-oxygen distances found for oxide-supported metal catalysts after reduction in H<sub>2</sub> originate from an M<sup>0</sup>-(OH)<sup>-</sup> interaction or from the presence of chemisorbed hydrogen in the metal-support interface. Admission of O<sub>2</sub> at 77 K does not lead to a corrosive oxidation of the metal particles. The adsorption of O<sub>2</sub> resulted in the same type of Ir-O bonds as present in the metal-support after evacuation.

Structural properties of small metal particles supported on non-interacting substrates (Mylar, rare-gas solids) have been studied extensively with EXAFS.<sup>1-3</sup> The experiments were performed under vacuum showing contractions of the nearest-neighbour distance and a decrease of the Debye temperature of the metal particle due to the softening of the phonon spectrum.<sup>4,5</sup> EXAFS experiments on dispersed metal catalysts supported on interacting substrates, *e.g.*  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, have been carried out after the reduction treatment with the metallic particles covered with chemisorbed hydrogen.<sup>6-10</sup> Under these conditions, contraction of the metal-metal coordination distance has not been observed. Tentative EXAFS results have been reported for Pt/NaY zeolite<sup>11</sup> and Rh/Al<sub>2</sub>O<sub>3</sub><sup>12</sup> catalysts under moderate vacuum conditions showing a contraction of the first-neighbour coordination distance.

Chemisorbed hydrogen influences the electronic properties of the metal, which in turn may change the interaction of the metal particles with the support. The metal-support interaction has been studied with EXAFS for Rh/Al<sub>2</sub>O<sub>3</sub>,<sup>6,7</sup> Rh/TiO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>,<sup>9</sup> and Ir/Al<sub>2</sub>O<sub>3</sub><sup>10</sup> catalysts with the metal particles covered with chemisorbed hydrogen. Long metal-support oxygen bonds (2.55-2.75 Å) with the interfacial metal atoms coordinated by 3 oxygen ions of the support have been observed in all cases. However, in the literature<sup>13-15</sup> EXAFS studies have been reported on metal catalysts which were treated with helium at high temperature after the reduction procedure, resulting in much shorter metal-support bonds 2.1 Å and lower coordination numbers.

Here the results are presented of an EXAFS study of a highly dispersed Ir/Al<sub>2</sub>O<sub>3</sub> catalyst, which was evacuated at high temperature after the reduction process. The influence of the desorption of hydrogen on the structural properties of the small metal particles has been studied. Furthermore, the effect of the evacuation process (removal of chemisorbed hydrogen and hydroxyl groups from the surface of the support) on the structure of the metal-support interface was investigated. Oxygen adsorption at 77 K

was carried out in order to compare the metal–oxygen bonds formed by this adsorption process with the metal–oxygen bonds present at the metal–support interface.

### Experimental

A 0.8 wt % Ir/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetting of the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ketjen type 000-1.5 E, surface area 200 m<sup>2</sup> g<sup>-1</sup> pore volume 0.6 cm<sup>3</sup> g<sup>-1</sup>) with an aqueous solution of IrCl<sub>3</sub> · xH<sub>2</sub>O. Hydrogen chemisorption measurements resulted in H/M = 2.6, indicating highly dispersed metal particles. Further characterization of this catalyst with different physical methods has been described in ref. (16). The treatments of the catalyst prior to the EXAFS experiments were performed in a transmission EXAFS *in situ* cell.<sup>17</sup> The following treatments were carried out: (i) reduction in flowing H<sub>2</sub> at 673 K for 1 h; (ii) evacuation at 623 K for 2 h (vacuum: 10<sup>-5</sup> Pa); (iii) O<sub>2</sub> adsorption (10<sup>5</sup> Pa) at 77 K. EXAFS data were collected after treatments (ii) and (iii) at 77 K. The EXAFS spectra were recorded at the EXAFS station of beamline X-11A of the NSLS at Brookhaven (ring energy 2.5 GeV, ring currents 50–100 mA). The EXAFS data were analysed using phase shifts and backscattering amplitudes obtained from reference compounds.

### Data Analysis and Results

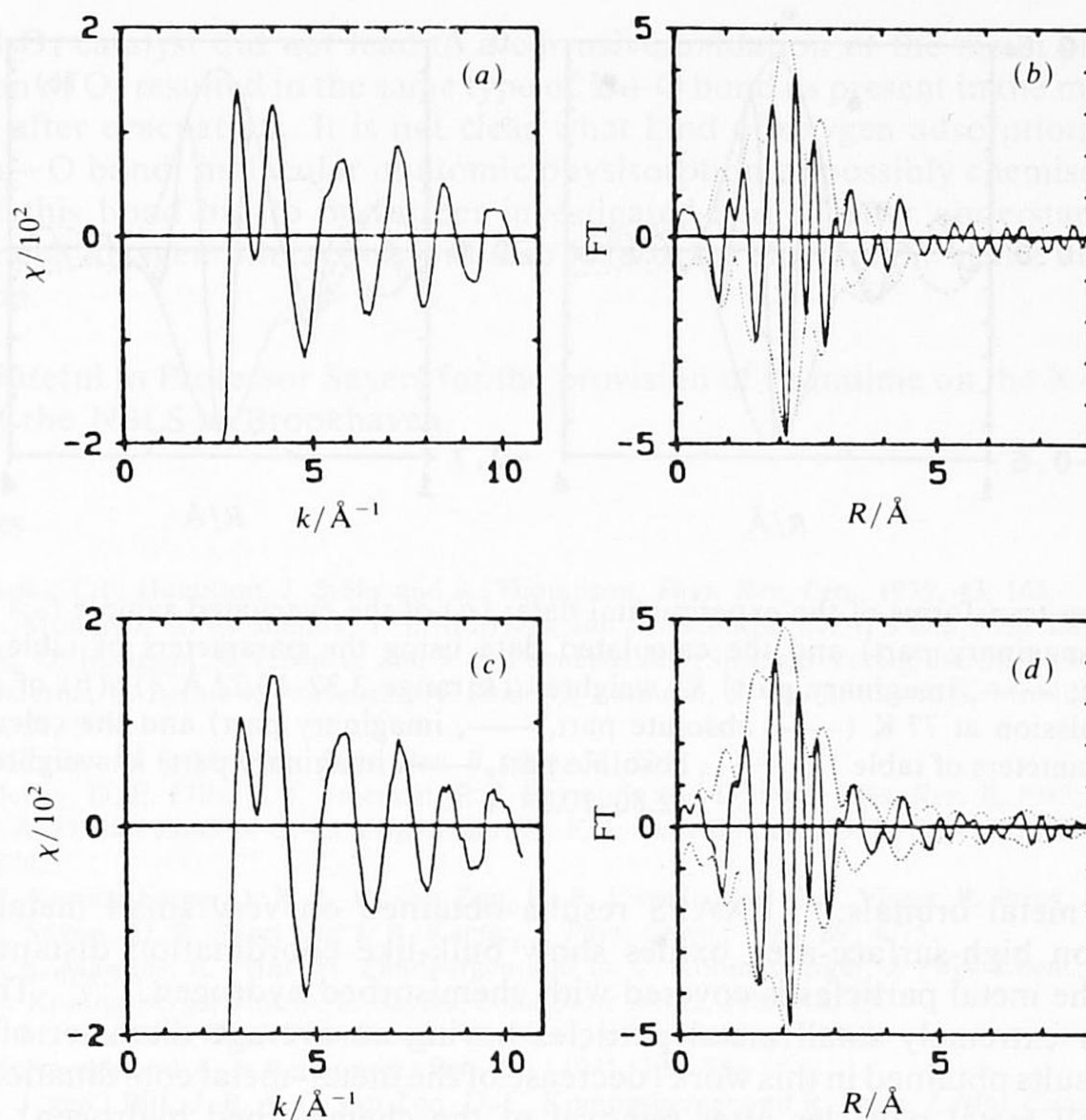
EXAFS oscillations in  $k$  space were obtained from the X-ray absorption spectra by a cubic spline background subtraction and normalization by means of division by the height of the edge. The raw EXAFS data of the samples with their corresponding Fourier transforms are shown in fig. 1. Pt foil was used as reference for the Ir–Ir and Na<sub>2</sub>PtOH<sub>6</sub> for the Ir–O contribution in the EXAFS spectrum. It has been shown theoretically<sup>18</sup> and experimentally<sup>19,20</sup> that platinum references can be used to analyse iridium EXAFS contributions.

The main peak of the  $k^1$  Fourier transforms of the data of both samples [fig. 1(a) and 1(b)] shows a complicated structure, arising both from the interference of the Ir–Ir EXAFS with oscillations caused by the presence of metal–oxygen bonds and from the  $k$ -dependent behaviour of the backscattering amplitude and the non-linearities in the phase shift function of the Ir–Ir absorber–backscatterer pair. The effect of the non-linearity of the phase shift and the  $k$ -dependent behaviour of the backscattering amplitude can be eliminated by using a Fourier transform, which is corrected for the Ir–Ir phase shift and backscattering amplitude. The data of the sample after evacuation and after oxygen admission at 77 K have therefore been analysed using phase- and amplitude-corrected Fourier transforms. Final coordination parameters have been obtained by optimizing  $k^1$  and  $k^3$  fits in both  $k$ - and  $r$ -space in order to guarantee a unique set of parameters for the low and high- $Z$  neighbouring scatters.<sup>17</sup> The results for the evacuated sample are listed in table 1. Fig. 2(a) shows the comparison between the experimental data and the model calculated with the parameters listed in table 1.

Admission of O<sub>2</sub> at 77 K changes the EXAFS spectrum at the low  $k$  values [fig. 1(a) and 1(b)]. The low  $R$  side (representing the metal oxygen bonds) of the imaginary parts of both Fourier transforms shows nodes at the same  $R$  values but the amplitude after O<sub>2</sub> adsorption is much higher, implying an increase in the number of metal–oxygen bonds. The high- $k$  part of the EXAFS spectrum (Ir–Ir bonds) does not show any decrease in amplitude, implying a non-corrosive adsorption of oxygen at 77 K. The results of the EXAFS data analysis of the sample after O<sub>2</sub> adsorption at 77 K are presented in table 1 and fig. 2(b).

### Discussion

The EXAFS results obtained for the same Ir/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction in H<sub>2</sub> at high temperature with the metal particles covered with chemisorbed hydrogen have

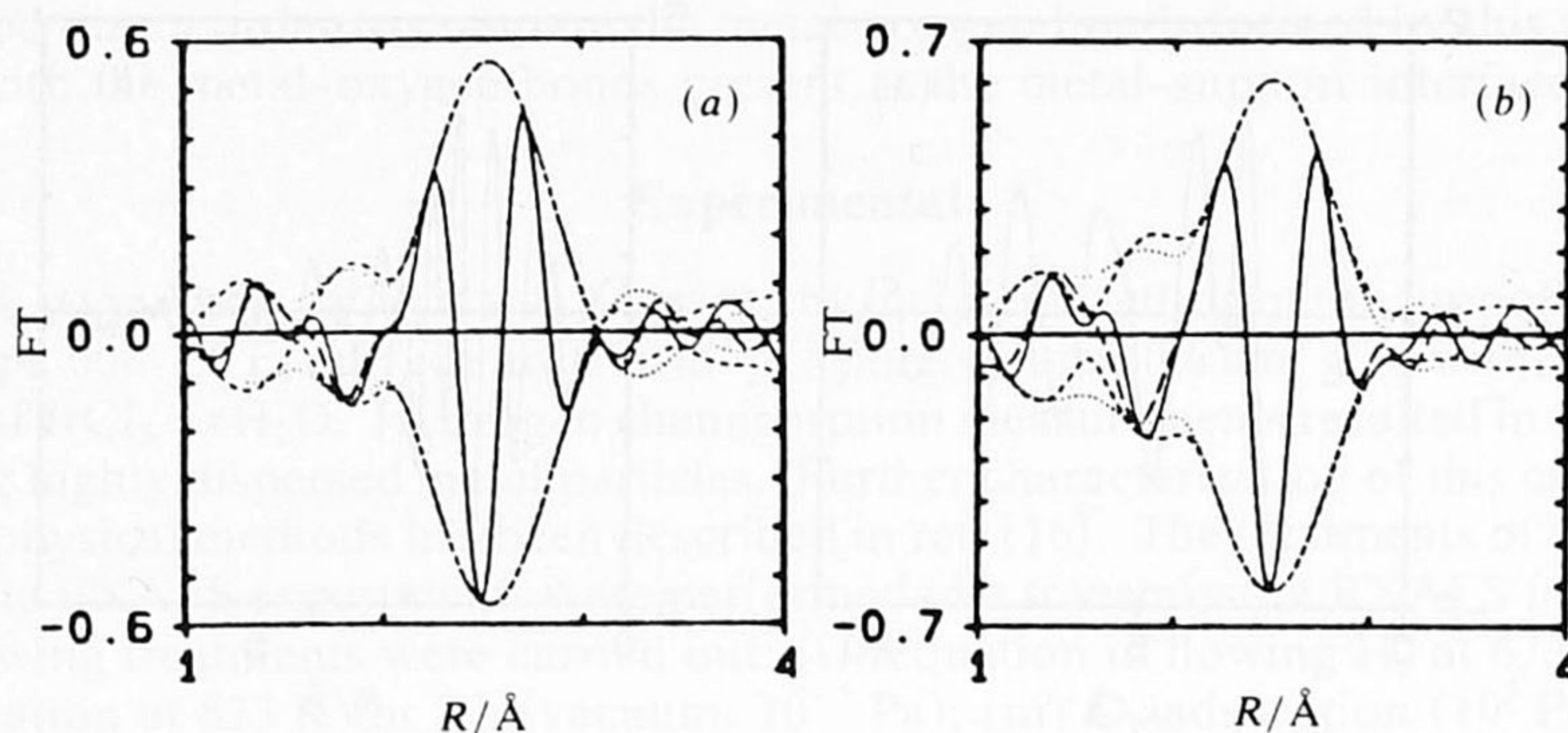


**Fig. 1.** EXAFS spectra of the sample after re-reduction and evacuation (a) and after admission of oxygen at 77 K (c) with their  $k^1$ -weighted Fourier transforms (b) ( $k$  range 2.81–10.22  $\text{\AA}^{-1}$ ) and (d) ( $k$  range 2.80–10.24  $\text{\AA}^{-1}$ ), respectively ( $\cdots$ , magnitude and —, imaginary part).

**Table 1.** Coordination parameters

treatment	$\text{Ir}^0-\text{Ir}^0$			$\text{Ir}^0-\text{O}_s^{2-}$		
	$N$	$R/\text{\AA}$	$\Delta\sigma^2 \times 10^3 \text{\AA}^2$	$N$	$R/\text{\AA}$	$\Delta\sigma^2 \times 10^3 \text{\AA}^2$
reduction (427 K)	4.9	2.71	2.0	1.8	2.55	5.0
evacuation (650 K)	4.0	2.64	2.8	0.7	2.19	3.5
$\text{O}_2$ at 77 K	5.5	2.64	5.5	1.1	2.21	9.0

been reported by van Zon<sup>10</sup> and are included in table 1. It was concluded that the particle morphology is hemispherical with a diameter of 9  $\text{\AA}$  consisting of about 12 atoms. By comparing the results of van Zon<sup>10</sup> with the results presented here it can be seen that the coordination number of the Ir—Ir shell was decreased by the evacuation. It must therefore be concluded that the particle morphology changed during evacuation from hemispherical to (almost) flat. The Ir—Ir coordination distance was decreased by 0.07  $\text{\AA}$  by removal of chemisorbed hydrogen. A decrease of the metal—metal coordination distance can normally be expected when going from bulk metal to very small metal particles, owing to a softening of the phonon spectrum caused by the dehybridisation



**Fig. 2.** Fourier transforms of the experimental data: (a) of the evacuated sample (---, absolute part; —, imaginary part) and the calculated data using the parameters of table 1 (·····, absolute part; —, imaginary part)  $k^1$  weighted ( $k$  range 3.32–10.22 Å<sup>-1</sup>); (b) of the sample after O<sub>2</sub> admission at 77 K (---, absolute part, —, imaginary part) and the calculated data using the parameters of table 1 (·····, absolute part, —, imaginary part)  $k^1$  weighted ( $k$  range 2.80–10.24 Å<sup>-1</sup>).

of the spd metal orbitals.<sup>4,5</sup> EXAFS results obtained on very small metal particles supported on high-surface-area oxides show bulk-like coordination distances, if the surface of the metal particles is covered with chemisorbed hydrogen.<sup>6,7,9,10</sup> This is even the case for extremely small metal particles having an average diameter of *ca.* 5 Å.<sup>8</sup> From the results obtained in this work (decrease of the metal–metal coordination distance in very small metal particles after removal of the chemisorbed hydrogen) it may be concluded that the chemisorption of hydrogen tends to cancel the effect of the dehybridisation of the spd orbitals when going to smaller particle sizes.

The results of the analysis of the sample after oxygen admission at 77 K show no corrosive oxidation of the metal particles and an increase in the coordination number of the Ir–Ir shell. This can indicate formation of large particles but it is more likely that adsorption of oxygen at 77 K has resulted in a change in the particle shape from flat to spherical. The fact that the Ir–Ir coordination distance is exactly the same as in the evacuated sample suggests that the effect of oxygen adsorption on the of the orbitals is different from the effect of hydrogen chemisorption.

An Ir–O coordination with a distance of 2.19 Å is observed after evacuation. This distance is significantly larger than the distance of 1.95 Å found for the Ir–O bond in samples that were totally oxidized. It must therefore be concluded that in the evacuated sample this bond originates from the interaction of the particle with the support. The detection of metal–support oxygen bonds has been reported by several investigators.<sup>6–10,13–16</sup> Metal–support bonds with distances in the range 2.5–2.7 Å have been found for supported rhodium and platinum catalysts measured after reduction with 10<sup>5</sup> Pa H<sub>2</sub> present in the *in situ* EXAFS cell.<sup>6,9</sup> The metal–support–oxygen bond with a distance of 2.55 Å found for the same Ir/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction<sup>10</sup> is completely absent after evacuation at high temperature. Instead, a considerably shorter metal–support bond is detected. The evacuation procedure not only removes the chemisorbed hydrogen, but also leads to a dehydroxylation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The Ir–O coordination has a distance of 2.19 Å, with a coordination number much lower than that found with the supporting surface covered with OH groups. This may lead to the conclusion that the long metal–oxygen distances found for oxide-supported metal catalysts after reduction originate from an M<sup>0</sup>–(OH)<sup>-</sup> interaction or from the presence of chemisorbed hydrogen in the metal–support interface. Admission of O<sub>2</sub> at 77 K onto

the Ir/Al<sub>2</sub>O<sub>3</sub> catalyst did not lead to a corrosive oxidation of the metal particles. The adsorption of O<sub>2</sub> resulted in the same type of Ir—O bond as present in the metal-support interface after evacuation. It is not clear what kind of oxygen adsorption created this type of Ir—O bond: molecular or atomic physisorption or possibly chemisorption. The nature of this bond has to be further investigated and a better understanding of this type of metal-oxygen interaction will also lead to an elucidation of the metal-support interaction.

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