

STUDY OF THE METAL-SUPPORT INTERFACE  
IN A  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> SUPPORTED,  
REDUCED Ir<sub>4</sub>(CO)<sub>12</sub> CATALYTIC SYSTEM  
BY EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS)

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ABSTRACT

An Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system with small metal particles was synthesized by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Ir<sub>4</sub>(CO)<sub>12</sub> in cyclohexane, followed by reduction. From EXAFS measurements it was concluded that as a result a system with unusually flat metal particles had been obtained in which the metal particles are attached to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface with long Ir-O<sub>support</sub> bonds. The fact that approximately three Ir-O bonds per Iridium atom are present, points to (111) epitaxy.

INTRODUCTION

The bonding of metal particles to the support in metal catalysis is important for catalytic properties as activity, stability, and resistivity against ageing and sintering. For supported Rh (1,2), Pt (3), and Ir (4) catalysts it was found that in fully reduced systems the metal particles are bonded to the support via long (2.6-2.7 Å) M-O<sub>support</sub> bonds. Because of the non-uniform particle size in conventionally (e. g. by pore volume impregnation) prepared catalyst systems, it is difficult to quantify the metal-support bonding with high confidence. Therefore metal-support interfaces in small particles having a uniform particle size are sought. Metal cluster carbonyls adsorbed on a support have been reported as model systems to study the metal-support interface (5,6). These systems have the important advantage that the metal skeleton of the clusters is retained if carefully adsorbed, thus allowing quantification of the cluster-support interaction. Even more important is the fact that after adsorption (contrary to conventional preparation methods) a structurally well-defined system is obtained with small metal clusters which allows us to follow changes in the metal-support bonding during decomposition and reduction. In this study the Ir<sub>4</sub>(CO)<sub>12</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system was

chosen, which makes it possible to compare this system in the reduced state with conventionally prepared, reduced  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  samples.

#### EXPERIMENTAL

$\text{Ir}_4(\text{CO})_{12}$  was obtained from Alfa Products, and used without further purification.  $\gamma\text{-Al}_2\text{O}_3$  (Ketjen, 000-1.5E, surface area  $200\text{ m}^2/\text{g}$ ) was partially dehydroxylated by calcinating in vacuum at 773 K for 8 h. Cyclohexane was dried over a sodium/benzophenone mixture in a  $\text{N}_2$  atmosphere and used freshly distilled. The metal carbonyl was dissolved in the dried cyclohexane and stirred with  $\gamma\text{-Al}_2\text{O}_3$  under  $\text{N}_2$  for 4 h. After filtration and drying overnight in vacuum, the final Ir loading was 0.8 wt%. It was checked by IR and EXAFS that the metal cluster skeleton was still intact after impregnation. The impregnated system was decomposed in vacuum at 473 K for 2 h, and prereduced in flowing  $\text{H}_2$  at 623 K for 15 h.

EXAFS measurements on the  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  sample in  $\text{H}_2$  were performed on Wiggler station 9.2 in Daresbury (U. K.) at the Ir  $L_{\text{III}}$ -edge (11215 eV), at 77 K after in situ reduction at 623 K for 1 h. Also Pt foil and  $\text{Na}_2\text{Pt}(\text{OH})_6$  (to be used as reference compounds) were measured at the Pt  $L_{\text{III}}$ -edge (11564 eV) at 77 K.

#### RESULTS

Data reduction of the EXAFS spectra was performed by background subtraction (pre-edge and cubic spline) and division by the height of the edge according to standard procedures (1). The raw EXAFS of the reduced Ir sample is presented in Figure 1a. Data analysis was performed using Pt foil and  $\text{Na}_2\text{Pt}(\text{OH})_6$  as reference compounds (5), and applying the difference file technique (1). A comparison of experimental and calculated EXAFS in  $k$  and in  $r$  space was used to obtain the best coordination parameters.

First, an estimate for the Ir-Ir contribution was obtained by fitting the high- $k$  data ( $10\text{-}14\text{ \AA}^{-1}$ ) (Figure 2a). This contribution was subsequently subtracted from the experimental data. A clear peak between 2 and  $2.7\text{ \AA}$  was visible in the difference spectrum, and was attributed to low- $Z$  neighbours. It was found that this peak had to be fitted with two low- $Z$  scatterer shells. The shell at the largest distance was assigned to an Ir- $\text{O}_{\text{support}}$  contribution, and the shell at the shortest distance was tentatively assigned to an Ir-C contribution (see Discussion). An Ir-O contribution was calculated using reasonable starting parameters; this contribution was subtracted from the difference spectrum (experimental data minus calculated Ir-Ir shell) and parameters were sought for the remainder (viz. the Ir-C contribution). Then this Ir-C contribution was subtracted from the difference spectrum, and again parameters were sought for the remainder (now representing the Ir-O contribution). The procedure was repeated until no better coordination parameters could be found. Then also the Ir-Ir contribution was included in this recurrent process. The final coordination parameters for the three shells (used to calculate the various contributions in Figure 2) were obtained by a three-shell

fit ( $\Delta k = 3.6\text{-}14.2 \text{ \AA}^{-1}$ ), using as input parameters those obtained in the recurrent procedure. The results are presented in Figure 1 and Table 1.

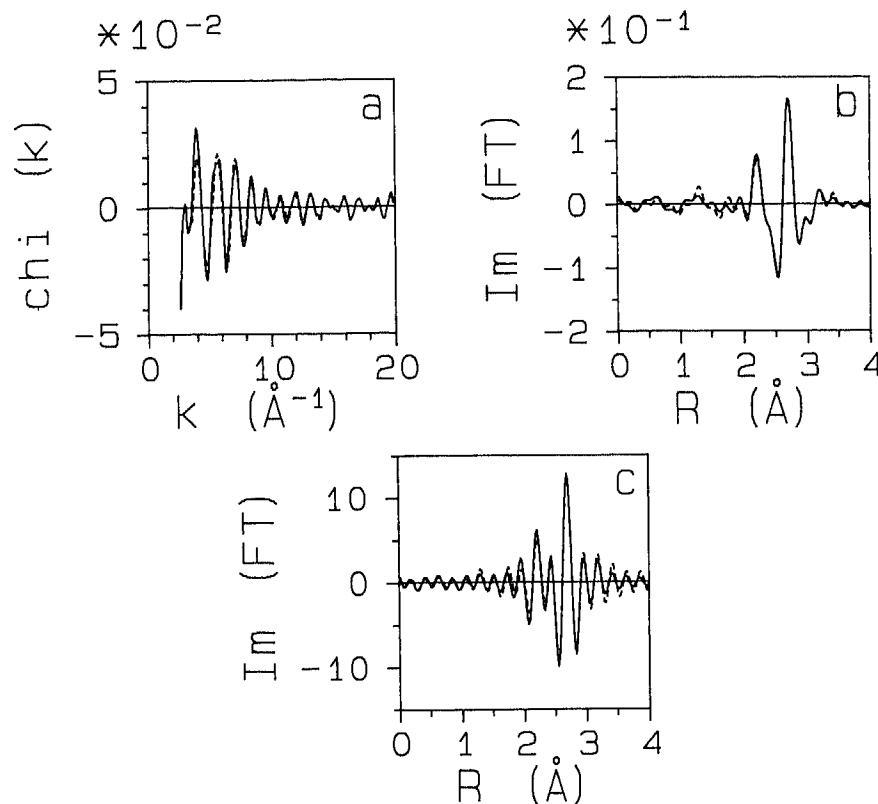


Figure 1. (a) raw EXAFS data of the reduced  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  sample (—) and three-shell fit (---); (b)  $k^1$  Fourier Transform ( $3.6\text{-}14.2 \text{ \AA}^{-1}$ , Ir-Ir phase corrected) of the experimental data (—) and of the corresponding three-shell fit (---); (c)  $k^3$  Fourier Transform ( $3.6\text{-}14.2 \text{ \AA}^{-1}$ , Ir-Ir phase corrected) of the experimental data (—) and of the corresponding three-shell fit (---).

Table 1. Parameters obtained in the three-shell fit of reduced  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$

Shell	N	R (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$V_0$ (eV)	Ref.
Ir-Ir	4.7	2.68	0.0004	4.4	Pt foil
Ir-O	2.4 <sup>a</sup>	2.58	-0.001	-2.0	$\text{Na}_2\text{Pt}(\text{OH})_6$
Ir-C	3.0	2.10	0.0107	2.9	$\text{Na}_2\text{Pt}(\text{OH})_6$

<sup>a</sup>after correction for the electron mean free path:  $N = 2.9$ .

Accuracies:  $N \pm 0.5$ ;  $R \pm 0.02 \text{ \AA}$  (Ir-Ir),  $\pm 0.04 \text{ \AA}$  (Ir-O, Ir-C);  $\Delta\sigma^2 \pm 0.001 \text{ \AA}^2$ .

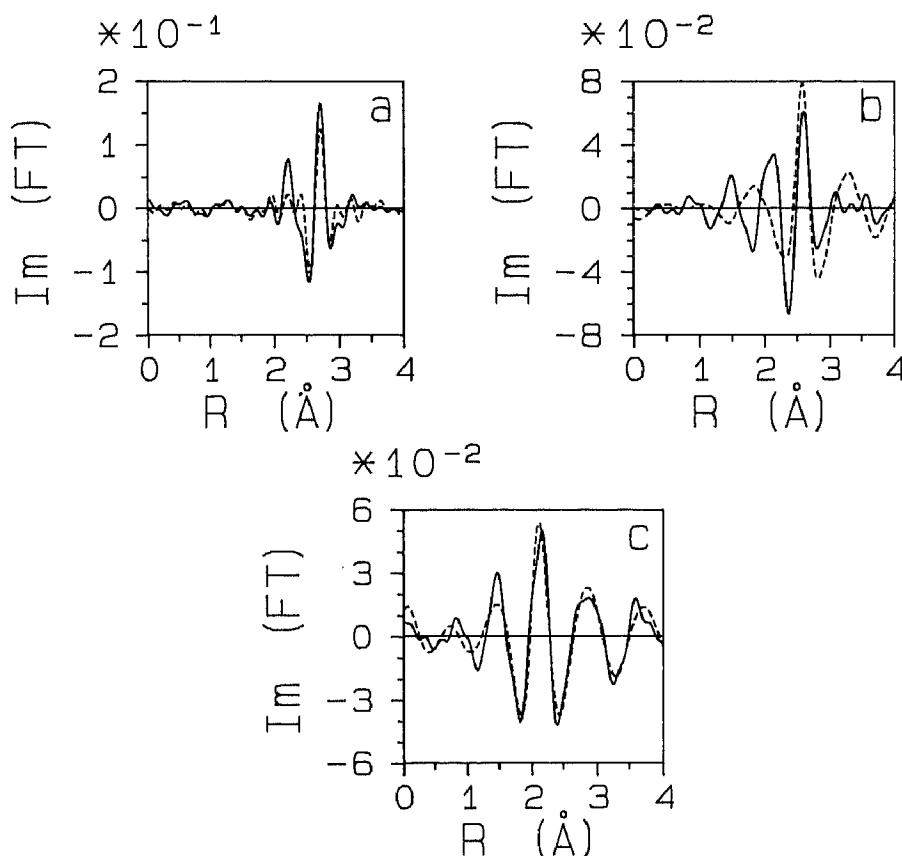


Figure 2. (a)  $k^1$  Fourier Transform ( $3.6\text{-}14.2 \text{ \AA}^{-1}$ , Ir-Ir phase corrected) of the experimental data (—) and of the calculated Ir-Ir contribution (---); (b)  $k^1$  Fourier Transform ( $3.6\text{-}14.2 \text{ \AA}^{-1}$ , Ir-O phase corrected) of the difference between experimental data and Ir-Ir contribution (—) and the calculated Ir-O<sub>support</sub> contribution (---); (c)  $k^1$  Fourier Transform ( $3.6\text{-}14.2 \text{ \AA}^{-1}$ , Ir-O phase corrected) of the difference between the experimental data, and Ir-Ir plus Ir-O<sub>support</sub> contributions (—) and the calculated Ir-C contribution (---).

#### DISCUSSION

The Ir-Ir first shell coordination number indicates that very small particles have been formed, although the original cluster size ( $N = 3$ ) was not retained. A significant contribution of Ir-O bonds at  $2.58 \text{ \AA}$  was detected. This relatively large contribution of the metal-support interface (large Ir-O coordination number) indicates that the metal particles are disc-like rather than half-spherical in shape (as was observed for conventionally prepared samples) (1). The coordination shell at  $2.10 \text{ \AA}$  is tentatively assigned to an Ir-C contribution, and not to an (oxidic) Ir-O contribution, because (i) carbon can be present on the metal surface as a residue from CO ligands or cyclohexane; (ii) no

Ir-Ir contribution from Iridium oxide ( $R \sim 3 \text{ \AA}$ ) is observed, which should be present if part of the Iridium is in the oxidic state.

The existence of a metal-support contribution at a coordination distance significantly larger than the oxidic metal-oxygen distance has been observed before (1-4). Recent results obtained with a reduced  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  catalyst measured in  $\text{H}_2$  and in vacuum show that the  $\text{Ir-O}_{\text{support}}$  coordination distance shrinks upon evacuation (4). Because no evidence is found that oxidation of the Iridium metal particles has occurred, we infer that the large Ir-O coordination distance results from an  $\text{Ir}^0\text{-HO}_{\text{support}}^{1-}$  contribution rather than from an  $\text{Ir}^0\text{-O}_{\text{support}}^{2-}$  contribution, and thus the shortening is caused by dehydroxylation of the metal-support interface. Although the mean radii of the  $\text{O}^{2-}$  and  $\text{OH}^{1-}$  surface groups do not differ very much, we think that in the case of  $\text{O}^{2-}$  the Ir-O bond is much easier polarized, which causes the observed shortening upon evacuation.

#### CONCLUSIONS

Reduction of  $\text{Ir}_4(\text{CO})_{12}$  adsorbed on  $\gamma\text{-Al}_2\text{O}_3$  yields a good model system to study the metal-support interactions. The original nuclearity of four is not retained in the reduced state, but a system is obtained with small metal particles which have a very special, flat particle form, in which as a consequence the number of  $\text{M-O}_{\text{support}}$  bonds per metal atom can be determined with high accuracy. The metal-support interface consists of long  $\text{Ir-O}_{\text{support}}$  bonds, that might be better described as an  $\text{Ir}^0\text{-HO}_{\text{support}}^{1-}$  interaction. Within the limits of accuracy, each Ir atom is bonded to the support by three Ir-O bonds, which strongly points to (111) epitaxy.

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