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A WELL-DEFINED SUPPORTED METAL CATALYST: Ir_4/MgO

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$[Ir_4(CO)_{12}]$ was used as a precursor for the preparation of a MgO-supported catalyst with a uniquely simple metal structure, Ir_4. The precursor was adsorbed on MgO from hexanes with the metal framework remaining intact, as determined by extended X-ray absorption fine structure (EXAFS) spectra. The surface-bound species was inferred to be predominantly $[HIr_4(CO)_{11}]^-$, which could be extracted from the surface by cation metathesis and identified in solution by infrared spectroscopy. After treatment of the MgO-supported iridium carbonyl in He followed by H_2 at 300 °C, the sample was characterized again by EXAFS spectroscopy; the results provide evidence that the predominant surface species are clusters of four Ir atoms with an average Ir–Ir distance of 2.69 Å.

1. Introduction

Most supported metal catalysts are structurally nonuniform, and attempts to form simpler structures by decomposition of molecular metal clusters on supports have generally been unsuccessful because of cluster fragmentation and aggregation [1,2]. Here we report the preparation of a structurally simple supported metal catalyst, tetrairidium on magnesia (Ir_4/MgO), by controlled decarbonylation of a metal carbonyl precursor formed from $[Ir_4(CO)_{12}]$ on the support. The catalyst at various stages of preparation has been characterized structurally by infrared and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

The iridium carbonyl cluster precursor was chosen because it has a quite stable metal framework, which offers the prospect of remaining intact during chemisorption on the support and subsequent treatments. MgO was chosen as the support

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because it is basic, facilitating the formation of anionic metal carbonyls upon adsorption of $[Ir_4(CO)_{12}]$ [3], and because the powder exposes primarily the simple (100) surface [4].

2. Experimental

The support was prepared by calcination of MgO (MCB, surface area after calcination 75 m^2/g); the powder sample was treated in flowing O_2 at 1 atm as the temperature was ramped from room room temperature to 400 ° C at a rate of 5 ° C/min and then held at 400 ° C for 2 h, after which the sample was evacuated for 14 h and cooled under vacuum to room temperature. The $[Ir_4(CO)_{12}]$ precursor (Strem, used without purification) was slurried with hexanes freshly distilled from sodium benzophenone and brought in contact with the calcined support in the absence of air. The mixture was stirred for 4 h under a N_2 blanket at room temperature and then evacuated for 14 h to remove the solvent.

The sample was characterized by EXAFS spectroscopy at the Synchrotron Radiation Source in Daresbury, U.K., wiggler station 9.2, using a Si (220) crystal monochromator. The sample was pressed into a selfsupporting wafer (calculated to have an absorbance of 2.5) and placed in a controlled-atmosphere cell [5]. The cell was purged with He for 10 min and cooled to liquid nitrogen temperature. Three scans of the sample in He, with a resolution of approximately 3 eV, were made at the Ir L_{III} edge (11215 eV). The monochromator was 50% detuned to minimize the effects of higher harmonics present in the X-ray beam.

The supported iridium carbonyl in a controlled-atmosphere infrared cell was decarbonylated by treatment in flowing He at 1 atm as the temperature was ramped from room temperature to 300 ° C at a rate of 5 ° C/min and then held at 300 ° C for 2 h. The same treatment sequence was carried out with a separate sample in the controlled-atmosphere EXAFS cell. This sample was then cooled to room temperature in flowing He and treated in flowing H_2 as the temperature was ramped from room temperature to 300 ° C and held at 300 ° C for 2 h followed by cooling to room temperature. EXAFS measurements were performed with the sample under H_2 at liquid nitrogen temperature.

3. Data analysis and results

The yellow-orange supported sample prepared from $[Ir_4(CO)_{12}]$ had the infrared spectrum $\nu_{CO} = 2071$ w, 2037 s, 1988 s, br cm^{-1}. For comparison, the spectrum of $[Ir_4(CO)_{12}]$ in THF is 2068 vs, 2027 m cm^{-1}. A comparison of these spectra indicates that the cluster carbonyl was not physisorbed, but instead reacted with the basic MgO surface. In basic solution, $[Ir_4(CO)_{12}]$ is converted to the yellow $[HIr_4(CO)_{11}]^-$ [6], and this anion is therefore a candidate surface species.

The surface organometallic species was extracted by bringing the sample in contact with a solution of bis(triphenylphosranylidene) ammonium chloride, [PPN]Cl, in THF. The resulting yellow extract solution had the following infrared spectrum: $\nu_{CO} = 2015$ s, 1986 m, 1964 s, 1895 w cm^{-1}. The first and third peaks suggest the presence of the anion $[HIr_4(CO)_{11}]^-\{\nu_{CO}(THF) = 2065$ sh, 2015 s, 1965 s cm^{-1} [5]}, possibly with some other iridium carbonyls; the 1895 cm^{-1} peak suggests a mononuclear species, $[Ir(CO)_4]^-\{\nu_{CO}(THF) = 2000$ w, 1898 s, 1868 sh cm^{-1} [6]}. This mononuclear species is formed in basic solution from $[HIr_4(CO)_{11}]^-$[6], and we infer that the basic MgO might have assisted in its formation in the extract solution; there is no evidence that this mononuclear iridium carbonyl had been present on the surface of the MgO.

The results, therefore, are consistent with the hypothesis that the $[Ir_4(CO)_{12}]$ had been chemisorbed with the metal frame intact. The differences between the infrared spectrum of the surface-bound iridium carbonyl and that of $[HIr_4(CO)_{11}]^-$ in solution, however, leave some doubt about the exact identity of the surface species. Therefore, further characterization of the surface species was carried out with EXAFS spectroscopy.

The raw EXAFS signal for the sample formed by chemisorption of $[Ir_4(CO)_{12}]$ (fig. 1A) has a signal to noise ratio estimated to be 40/1. The EXAFS function shows oscillations to a value of k, the wave vector, of about 15 $Å^{-1}$, indicating the presence of near-neighbor metal scatterers. The data were analyzed as follows: standard procedures [7] were used to extract the EXAFS function from the absorption spectrum, and then the difference file technique [8,9] was used with experimentally determined reference files obtained from EXAFS measurements of $[Ir_4(CO)_{12}]$ and Pt foil [10]. Final fitting in k space and optimization in r space, both with k^1 and k^3 weighting, was needed to obtain a unique set of coordination parameters [11]. The $[Ir_4(CO)_{12}]$ data were used for both the Ir–C and the Ir–O interactions, whereby the effects of multiple scattering were accounted for [12]. The Pt data were used to represent the Ir–Ir interaction, since Ir and Pt are near neighbors in the periodic table and, therefore, characterized by virtually the same backscattering functions [13,14].

The data were Fourier transformed over the useful range (2.74–15.12 Å) with k^3 weighting and no phase correction. The major contributions were isolated by inverse transformation from 1.02–3.78 Å. The isolated data were analyzed for metal contributions by fitting over the high-k range using the Pt foil reference file. Subtraction of the metal contribution resulted in an EXAFS function which was fitted with contributions representing C and O*, where O* represents O of the carbonyl.

Fitting with these three contributions failed to provide an adequate representation of the data in the region of approximately 2.1 Å. Therefore, a fourth contribution was included, representing a possible bridging carbonyl ligand. The

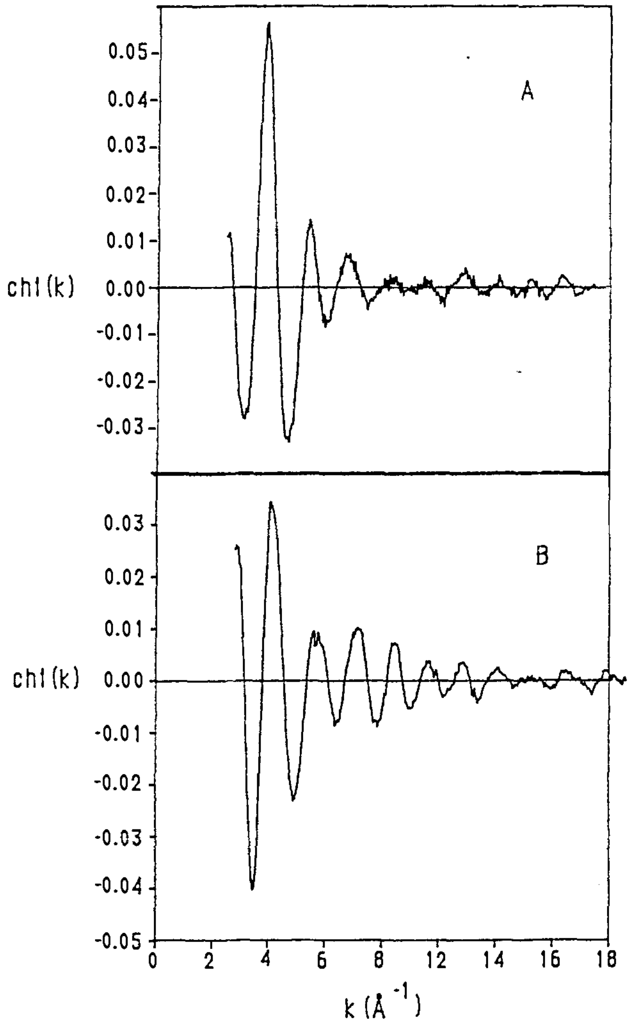

Fig. 1. Raw EXAFS data characterizing (A) sample prepared by bringing $[Ir_4(CO)_{12}]$ in contact with MgO and (B) sample after treatment with He followed by H_2 at 300 ° C for 2 h.

final results including four contributions and giving the best agreement with the data in k and in r space are shown in fig. 2. The structural parameters obtained from the data analysis are summarized in table 1. The results show an average Ir–Ir coordination number of approximately 3, consistent with the retention of the Ir_4 framework in the supported organometallic species. The Ir–Ir distance of 2.71 Å is similar to that in crystalline $[Ir_4(CO)_{12}]$, 2.69 Å [15] and that in crystalline $[P(CH_2C_6H_3)(C_6H_5)_3][HIr_4(CO)_{11}]$, 2.73 Å [16]. The Ir–C interactions detected at distances of 1.86 and 2.10 Å are inferred to be evidence of terminal and bridging carbonyl ligands. For comparison, the crystal structure of $[CH_2PhPh_3P][HIr_4(CO)_{11}]$ indicates an average Ir to terminal carbon distance of

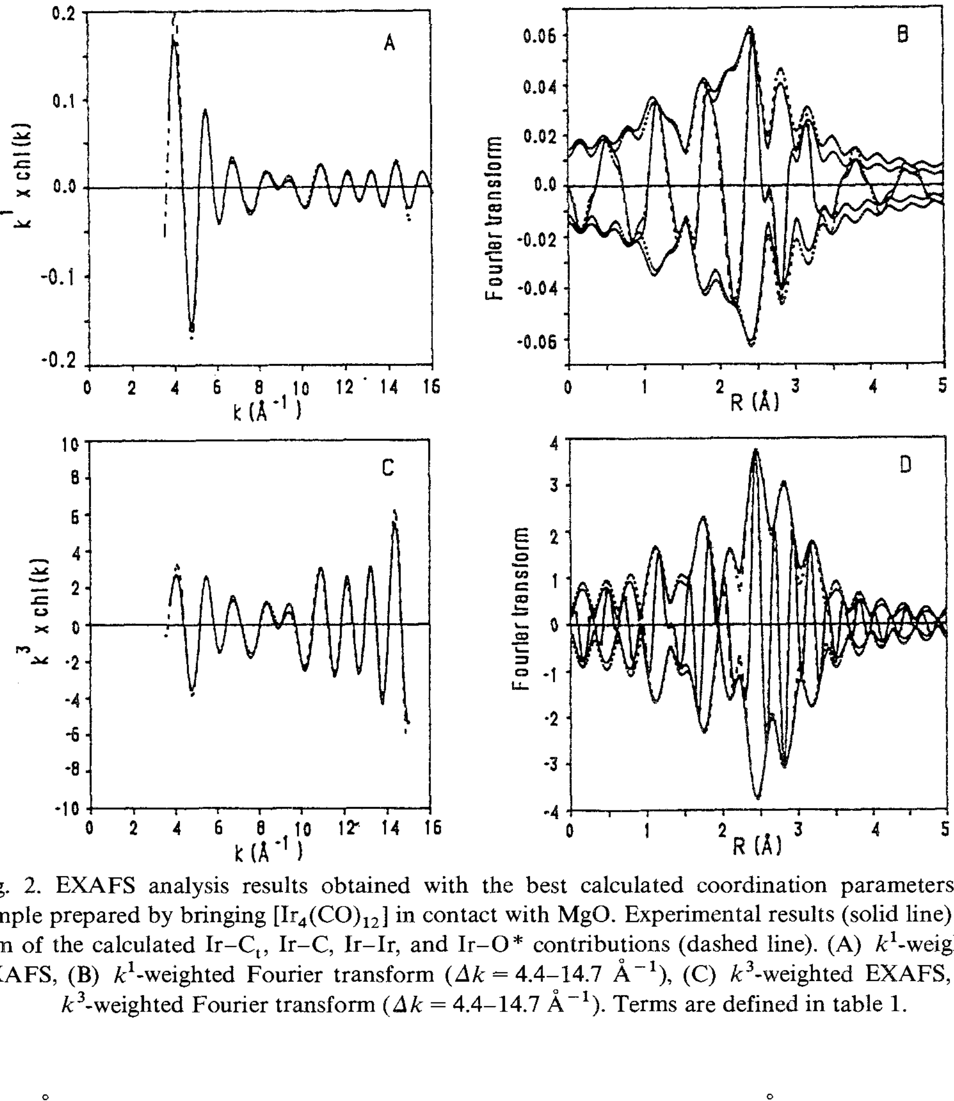

Fig. 2. EXAFS analysis results obtained with the best calculated coordination parameters for sample prepared by bringing [$Ir_4(CO)_{12}$] in contact with MgO. Experimental results (solid line) and sum of the calculated Ir–C_t, Ir–C, Ir–Ir, and Ir–O* contributions (dashed line). (A) k^1-weighted EXAFS, (B) k^1-weighted Fourier transform ($\Delta k = 4.4$–14.7 Å^{-1}), (C) k^3-weighted EXAFS, (D) k^3-weighted Fourier transform ($\Delta k = 4.4$–14.7 Å^{-1}). Terms are defined in table 1.

1.84 Å and Ir to bridging carbon distances of 1.98 and 2.18 Å. The Ir–C_{bridging} distance of 2.10 Å determinated by EXAFS represents an average of the bridging carbon distances. A contribution resulting from the Ir–O* interaction was observed at a distance of 3.04 Å, in agreement with the value found by X-ray diffraction for the anion. A more detailed analysis of the EXAFS data for this and related samples is to be published elsewhere.

The infrared spectrum of the sample after it had been treated in He at 300 °C indicated that it had been fully decarbonylated. The EXAFS spectrum of this sample, following treatment in He at 300 °C, is shown in fig. 1B. The signal to noise ratio of these raw data in high, estimated to be 70/1. The data give evidence of the Ir–Ir interaction, but a significant part of the EXAFS spectrum originates from the metal-support interface. To separate the Ir–Ir contribution from the overall EXAFS signal, a k^3-weighted fit was carried out to emphasize the high-k (metal) part of the spectrum. Moreover, the fit was started at $k = 6$ Å^{-1} to deemphasize the contribution of the metal-support interface. The agreement between the best fit and the isolated data in k space and in r space is demonstrated in fig. 3 A and B. The resulting coordination parameters are presented in table 1. The difference between the Fourier transform of the data and the calculated Ir–Ir contribution (using the Ir–Ir coordination parameters given in table 1) (fig. 3D) is a measure of the contribution of the metal-support interface, which will be reported elsewhere.

The Ir–Ir coordination number is still 3 within experimental error (±20%), consistent with the inference that most of the clusters retained the Ir_4 framework throughout the treatment sequence.

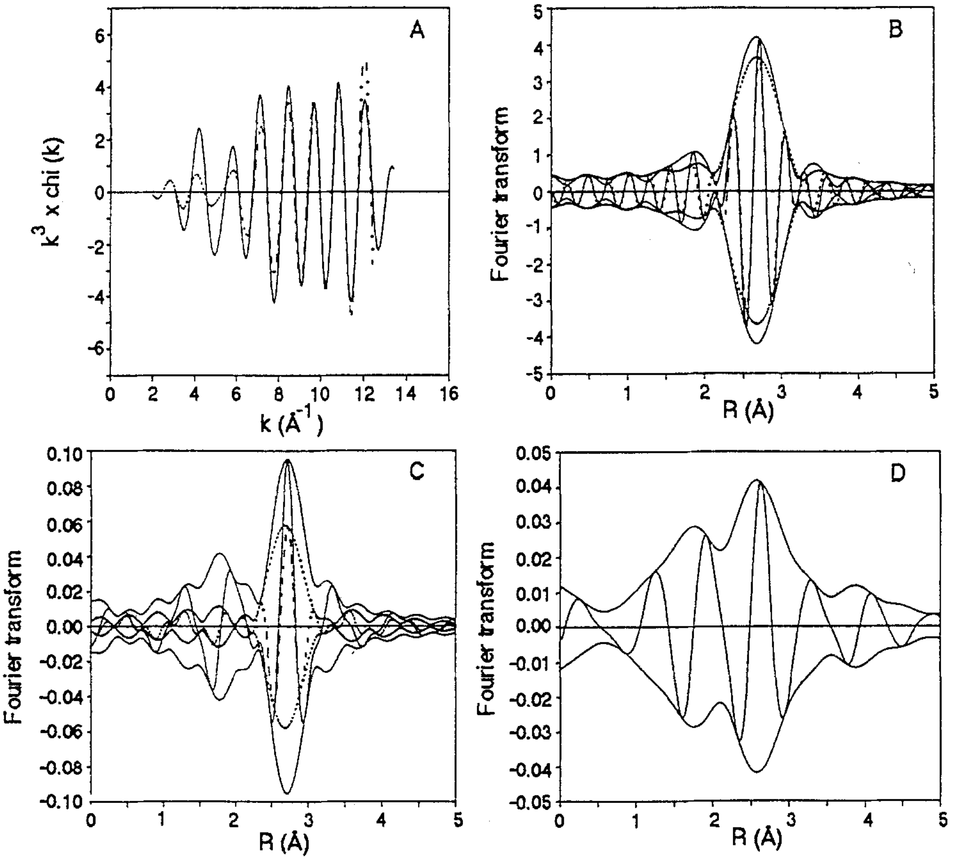

Fig. 3. EXAFS analysis results for the decarbonylated sample prepared by bringing $[Ir_4(CO)_{12}]$ in contact with MgO. Experimental results (solid line) and best-fit Ir–Ir contributions (dashed line), (A) k^3-weighted EXAFS, (B) k^3-weighted Fourier transform fit, Ir–Ir phase corrected ($\Delta k = 5.4$–11.7 Å^{-1}), (C) k^1-weighted Fourier transform, Ir–Ir phase corrected ($\Delta k = 3.8$–11.7 Å^{-1}), (D) Fourier transform of the experimental results minus the Ir–Ir contribution, k^1-weighted, Ir–O phase corrected ($\Delta k = 3.8$–9.7 Å^{-1}).

Table 1
Structural parameters determined by EXAFS spectroscopy for the samples prepared from $[Ir_4(CO)_{12}]$ supported on MgO

Sample	Contribution [a]	Coordination number, N	Distance (Å)	Debye-Waller factor (Å^2)	E_0 (eV)
Fresh sample	Ir–C_t	2.8	1.86	0.0058	−0.22
	Ir–C_b	1.5	2.10	−0.003	−2.76
	Ir–Ir	3.2	2.71	0.002	3.81
	Ir–O*	1.9	3.04	−0.0004	−8.26
After treatment in He followed by H_2	Ir–Ir	3.1	2.69	0.0011	1.22

[a] C_t refers to C of terminal carbonyl. C_b refers to C of bridging carbonyl. O* refers to oxygen of carbonyl.

In summary, the results show that $[Ir_4(CO)_{12}]$ forms a structure on MgO that can be decarbonylated to give dispersed Ir_4 entities without substantial fragmentation or sintering. The resulting sample, Ir_4/MgO, is one of the simplest and structurally best-defined supported metals.

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