Hexairidium carbonyl clusters in the micropores of faujasite zeolites: evidence from transmission electron microscopy

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$[Ir_6(CO)_{16}]$ was formed in the pores of zeolite NaY by adsorption of $[Ir(CO)_2(acac)]$ followed by treatment in $CO + H_2$. $[Ir_6(CO)_{15}]^{2-}$ in zeolite NaX was prepared similarly. Each sample was characterized by high-resolution transmission electron microscopy. The images indicate the presence of the iridium clusters in the zeolite micropores, with almost no scattering centers indicating iridium outside these pores. The supported $[Ir_6(CO)_{16}]$ and $[Ir_6(CO)_{15}]^{2-}$, which have previously been characterized by infrared and extended X-ray absorption fine structure spectroscopies, are among the most uniform and structurally best defined supported metal clusters.

Keywords: iridium carbonyl clusters, zeolite NaY, zeolite NaX, transmission electron microscopy, metal clusters

1. Introduction

Some supported catalysts incorporate metal clusters that are extremely small and nearly molecular in character. For example, platinum clusters, some containing as few as about five atoms each, on average, have been identified in zeolite LTL [1]; supported catalysts of this type are used commercially for naphtha reforming to give aromatics. The structural evidence of the platinum clusters is based on extended X-ray absorption fine structure (EXAFS) spectroscopy [1–4], hydrogen chemisorption [1–3], infrared spectroscopy [5], and transmission electron microscopy (TEM) [1,4,6]. None of these methods alone is sufficient to characterize supported clusters satisfactorily; TEM is the best for distinguishing clusters in zeolite pores from clusters or particles outside the pores [4,6–9], but there are only a few results [8,9] demonstrating the presence of metal clusters in zeolite pores but not outside the pores; these indicate platinum clusters prepared from salt precursors preferentially located in the relatively large cages of $\{111\}$ twin planes in faujasite.

Zeolite-supported metal clusters prepared from organometallic precursors offer the prospect of being nearly uniform molecular or ionic species. For example, $[Ir_6(CO)_{16}]$ has been prepared by a “ship-in-a-bottle” synthesis from $[Ir(CO)_2(acac)]$ in zeolite NaY and characterized by infrared and EXAFS spectroscopies; the spectra and the observation that the clusters could not be extracted from the zeolite are consistent with the hypothesis that the clusters were trapped in the zeolite supercages [10]. Similarly, infrared results suggest the formation of $[Ir_6(CO)_{15}]^{2-}$ from $[Ir(CO)_2(acac)]$ in zeolite NaX [11–13].

These samples, consisting of molecular or ionic species in uniform intracrystalline pores, may be the most nearly uniform supported metal clusters, but the reported characterization data are not sufficient to demonstrate whether the samples incorporated larger clusters than those identified spectroscopically or whether the metal was present almost entirely inside the zeolite pores. Our goal was to investigate these samples with high-resolution TEM to provide images of the clusters to locate them and assess sample uniformity.

2. Experimental

Iridium carbonyl clusters in zeolites were prepared by adsorption of $[Ir(CO)_2(acac)]$ followed by carbonylation [10–13]. The zeolite NaY-supported sample, containing 1 wt% Ir, was treated in $CO + H_2$ at 250 °C and 20 bar for 3 days in a once-through flow reactor under conditions of catalytic CO hydrogenation [10]. The zeolite NaX-supported sample, also containing about 1 wt% Ir, was treated in $CO + H_2$ at 175 °C and 1 bar for 1 day in the flow reactor under conditions of catalytic CO hydrogenation [12].

Each sample was removed from the synthesis reactor under dry N_2 and stored in a sealed container, but it came in contact with air as it was handled for TEM. The TEM experiments were carried out with a Hitachi HF 2000 transmission electron microscope equipped with a cold field emitter system (typical magnification 120 000×; accelerating voltage 200 kV; objective aperture 70 μm; limit of structural resolution better than 0.2 nm). Particles of sample were suspended in ethanol and supported on a carbon film with a thickness of 6 nm, which was mounted on a copper grid (400 meshes/inch). Other details of the procedure are as reported elsewhere [14].

3. Results and discussion

TEM images of the samples (figures 1(a), 2(a), and 3) clearly show individual zeolite crystals, and the "views from above" show in part the hexagonal structure (encircled in figure 1(a)) along the channel direction of the micropore openings characteristic of faujasites. Figure 1(b) shows an optical diffraction pattern from figure 1(a) (with the Fourier transform showing the lattice plane spacing to be 1.4 nm for the first order). Figure 1(c) is a reconstructed image of the hexagonal structures of the faujasite with the iridium clusters. The dark spots in figure 1(a) are inferred to be scattering centers indicative of iridium clusters, and these are clearly located within the micropores.

These scattering centers are nearly uniform in size in each sample, with the exception of a small fraction which are larger. The typical cluster diameter determined from the image is about 0.8 nm; the Ir_6 cluster frame is expected to be about 0.6–0.8 nm in diameter. A small part of the sample was amorphous, a consequence of the zeolite synthesis and not of impingement of the electron beam. The randomly distributed clusters in the amorphous part of the support (figure 2(a)) are nearly the same size as the clusters in the zeolite micropores, as would be expected for the iridium clusters on γ-Al_2O_3 [15].

The image of the border of the zeolite particle in figure 2(a) demonstrates the presence of metal clusters in some but not all of the pores, as expected from the low metal loadings. This "view from the side" in figure 2(a) shows clusters arranged almost randomly in the zeolite micropores. Figure 2(b) shows the optical power spectrum from figure 2(a), and figure 2(c) shows this after a 2D-FFT-filtering.

Similar images (not shown) were obtained for a zeolite NaY-supported sample prepared as described, except that it was treated for 8 days in flowing $CO + H_2$. These results indicate the stability of the zeolite-entrapped clusters in $CO + H_2$.

We conclude on the basis of the literature data [10] and the present results that almost all the iridium in zeolite NaY was present as $[Ir_6(CO)_{16}]$ and that almost all of the iridium was present in the pores of the zeolite.

Similar spectroscopic results show that almost all the iridium in the zeolite NaX sample was also present as clusters, suggested on the basis of the infrared spectra to be $[Ir_6(CO)_{15}]^{2-}$ [11–14], and the TEM results (figure 3) show that almost all the iridium in this zeolite was present in the micropores as well.

The results point to these clusters in the faujasites as some of the most nearly uniform and structurally best-defined supported metal clusters. TEM results could also help to determine whether the clusters formed by decarbonylation of these clusters [16,17] are similarly uniform.

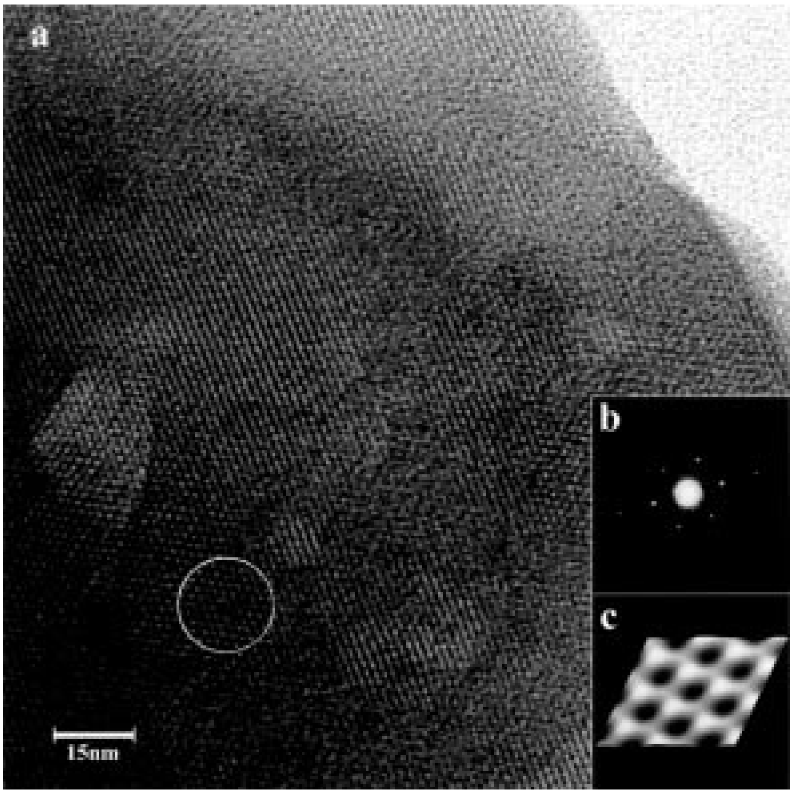

Figure 1. (a) Transmission electron micrograph of $[Ir_6(CO)_{16}]$ in zeolite NaY; referred to as view from above; (b) optical diffractogram (Fourier transform) from different regions of the sample showing a lattice plane spacing of 1.4 nm for the first order, corresponding to the faujasite structure; and (c) reconstructed image, view along the pore direction; black areas represent the metal clusters.

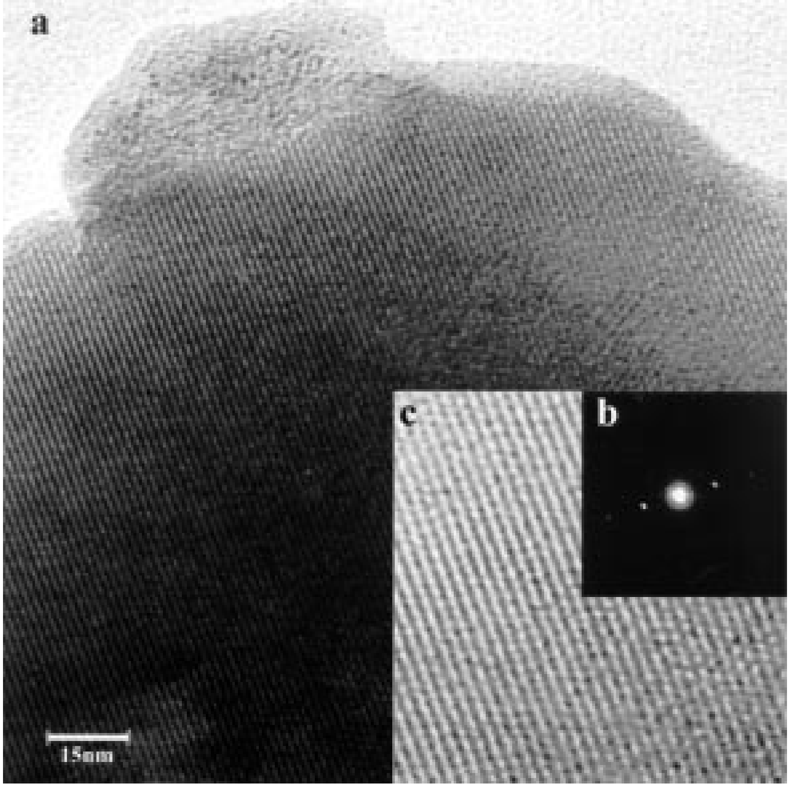

Figure 2. (a) Transmission electron micrograph of $[Ir_6(CO)_{16}]$ in zeolite NaY, view from the side; (b) optical diffractogram showing lattice plane spacing of 1.4 nm for the first order, corresponding to the faujasite structure; and (c) 2D-FFT-filtered micrograph.

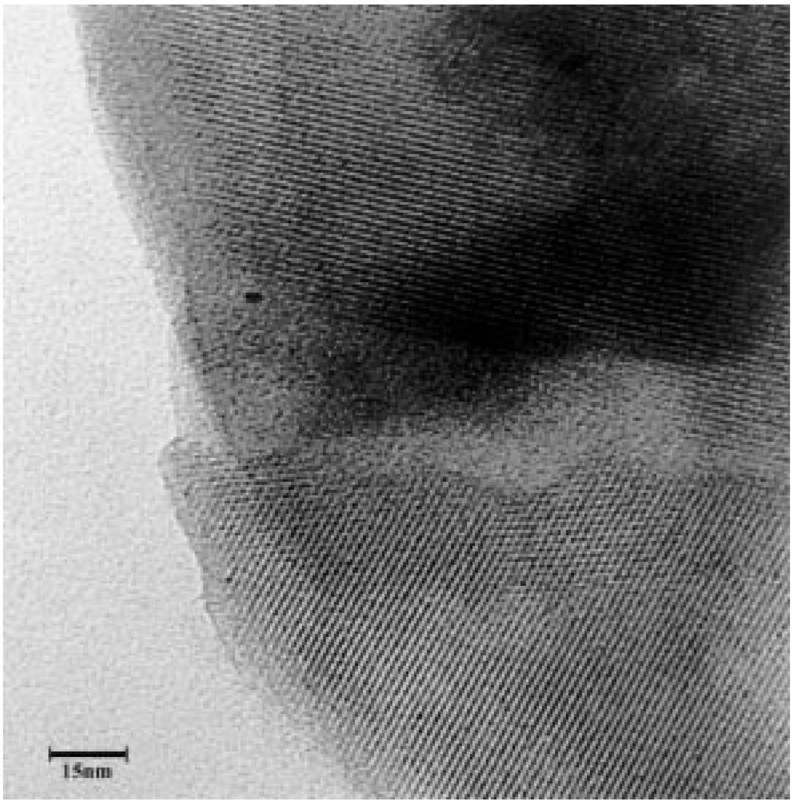

Figure 3. Transmission electron micrograph of $[Ir_6(CO)_{15}]^{2-}$ in zeolite NaX.

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