Reversible carbonylation / decarbonylation of zeolite-entrapped tetrairidium clusters

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Iridium carbonyl clusters in NaY zeolite have been prepared from adsorbed [Ir(CO)$_2$(acad)]. The infrared spectra and the yellow color of the sample are consistent with the formation of Ir$_4$(CO)$_{12}$] in the zeolite cages, presumably the product of reductive carbonylation of the mononuclear precursor. The iridium carbonyl cluster in the zeolite could be decarbonylated by treatment with flowing H_2 at 300 ° C and 1 atm and recarbonylated by treatment with CO at 40 ° C and 1 atm. The carbonylation/decarbonylation process is reversible, provided that the temperature of the decarbonylation is low, which suggests that the decarbonylated clusters may be Ir$_4$. Treatment of the sample in H_2 at 425 ° C and 1 atm led to the formation of particles or iridium metal outside the zeolite pores.

Keywords: Zeolite Y; iridium clusters; tetrairidium clusters in zeolite; infrared spectroscopy

1. Introduction

Carbonyl clusters of Fe [1], Rh [2–8], Pd [9–11], Os [12–14], and Ir [3,15] have been formed in the cages of zeolites, often by “ship-in-a-bottle” syntheses starting with mononuclear metal complexes. Some of these clusters are stabilized by CO and catalyze CO hydrogenation [8,12,13], but activation of the clusters for other catalytic reactions usually requires their decarbonylation, which typically is accompanied by fragmentation of the clusters and migration and sintering of the metals outside the zeolite pores. Our goal was to decarbonylate metal clusters in zeolites without changing the nuclearity and thereby to prepare supported metal catalysts with unique structures.

Tetrairidium carbonyls are robust metal clusters, and EXAFS spectra indicate that [HIr$_4$(CO)$_{11}$]$^-$ supported on MgO could be decarbonylated without a

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substantial change in the metal nuclearity [16]. Here we report a similar result with iridium carbonyls in Y zeolite, including a new method for synthesis of iridium carbonyl clusters from [Ir(CO)$_2$(acac)] in zeolite cages and infrared spectra characterizing their reversible decarbonylation and carbonylation.

2. Experimental methods

SAMPLE PREPARATION

Crystalline NaY zeolite powder (LZY-52) was supplied by Union Carbide. It has a unit cell size of 24.7 Å and a SiO_2/Al_2O_3 molar ratio of 4.74. Prior to preparation of the zeolite-supported iridium sample, the zeolite was evacuated at 10^{-3} Torr at room temperature for two hours, but it was not rigorously dried. Reagent grade mixed hexanes were purged with N_2 for several hours before use as a solvent. [Ir(CO)$_2$(acad)] (Strem) was used without purification. He and H_2 (Matheson, 99.999%) were purified by passage through traps containing Cu_2O and activated zeolites to remove traces of O_2 and moisture, respectively. CO (Matheson, UHP grade) was purified by passage through a bed of activated alumina heated to a temperature exceeding 250 ° C to remove traces of metal carbonyls and through a bed of activated zeolite to remove moisture.

The samples were prepared under N_2 on a Schlenk line and in a Vacuum Atmospheres glove box. Sample handling and transfer to infrared cells were done in the glove box.

The zeolite was loaded as [Ir(CO)$_2$(acac)] (60 mg/g of NaY) was dissolved in hexanes and brought in contact with the pre-evacuated NaY powder. The white NaY powder became dark gray, and the initially black solution became clearer after stirring for several hours. After one day, the slurry was black. The mixture was filtered and the zeolite washed thoroughly with hexanes and dried under vacuum at room temperature for 12 h. The samples were stored in the glovebox.

INFRARED SPECTROSCOPY

Transmission infrared spectra of the zeolite samples were collected with a Nicolet 7199 spectrometer with a resolution of 4 cm^{-1}. Samples were pressed into semitransparent wafers in the glove box and mounted in the infrared cell. The infrared experiments were performed with the samples in controlled atmospheres; purified He, N_2, CO, or H_2 (or any of these gases containing some water) could be delivered to the cell, which was part of a flow system. A typical gas flow rate was 20–30 mL/min (NTP). Samples were scanned 32 or more times and the data averaged.

Samples of the zeolite were examined by transmission electron microscopy with a Philips EM400T instrument. Particles of the zeolite in hexane were sonicated, and a drop of the slurry was placed on a holey carbon film on a Cu grid. The hexane was removed by evacuation. Samples came in contact with air for about 20 min in these experiments.

3. Results

The uptake of the [$Ir(CO)_2(acac)$] by the zeolite required some hours and was not complete after a day of contacting. The infrared spectrum of the solution showed that some [$Ir(CO)_2(acac)$] was still present, and there was no evidence of other metal carbonyls. With this partial uptake of the Ir, the Ir content of the zeolite was slightly less than 2 wt%.

Upon evacuation of the solvent from the black [$Ir(CO)_2(acac)$]-containing zeolite, the solid became tan. Reintroduction of the solvent gave a brown material, which became tan again upon evacuation.

The sample was exposed to flowing CO at 40 ° C, and the spectrum developed as shown in fig. 1. The shoulder on the 2070-cm^{-1} peak of spectrum D disappeared after a longer time, and the resulting spectrum [2117(w), 2070(s), 2032(m, sh) cm^{-1}] closely resembled that of [$Ir_4(CO)_{12}$] in tetrahydrofuran solution [2110(vw), 2068(vs), 2028(m, sh) cm^{-1}]. The solid sample was light yellow, the color of [$Ir_4(CO)_{12}$]. When the CO in this treatment was replaced by a stream of CO containing a small amount of water or with an equimolar $CO + H_2$ mixture, the same results were observed. Heating the initially prepared sample to 50 ° C and holding for four hours in flowing CO at 1 atm in a copper-lined tubular flow reactor also gave the same results.

Attempts to extract the iridium carbonyl from the zeolite with tetrahydrofuran or with [PPN] [Cl] in tetrahydrofuran were not successful (although [$Ir_4(CO)_{12}$] is slightly soluble in tetrahydrofuran). The supernatant solutions remained colorless and had no infrared absorptions in the carbonyl stretching region, and the solid remained yellow.

The iridium-containing zeolite in the infrared cell was treated in H_2 at 1 atm (fig. 2). Exposure for one hour at 50 ° C led to no change in the spectrum, but as the temperature increased beyond 75 ° C, the peaks in the carbonyl region decreased in intensity, broadened, and shifted to lower frequencies. After treatment of the sample in H_2 at 300 ° C for two hours, the carbonyl bands had disappeared. The sample was then evacuated for 15 min at 300 ° C and cooled under vacuum to room temperature. It was then beige.

This decarbonylated sample was exposed to CO in the infrared cell as the temperature was raised (fig. 3). When the temperature reached 40 ° C, infrared bands grew in at 2035 and 2070 cm^{-1}. The growth in intensity continued for about four hours (fig. 2), with the spectrum finally becoming virtually the same as that prior to decarbonylation. Again, the sample was light yellow.

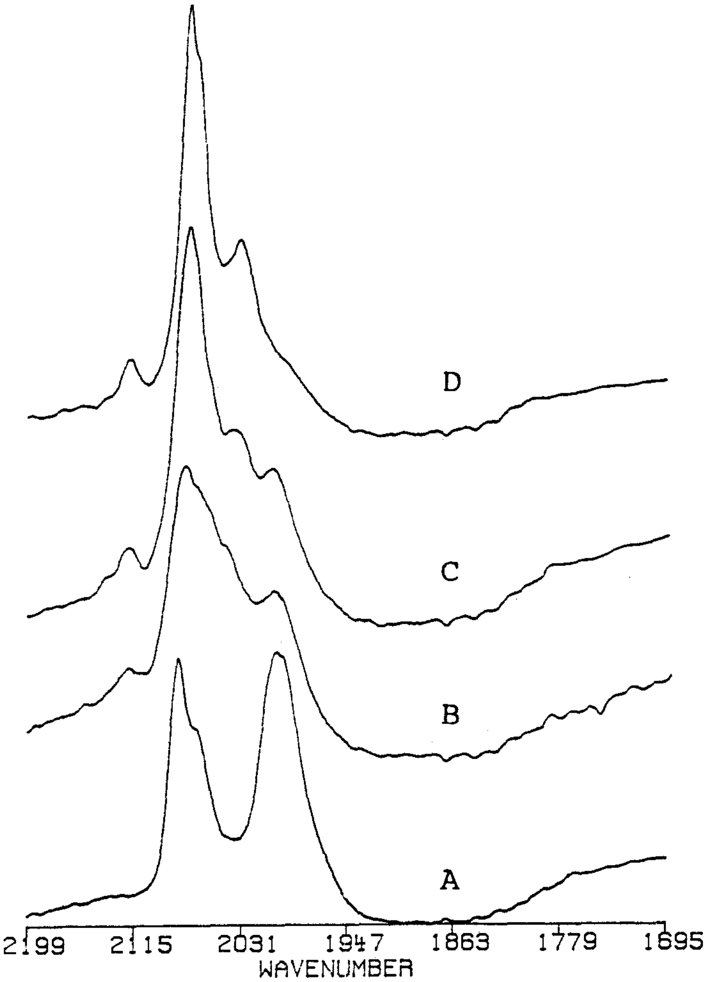

Fig. 1. Infrared spectra taken during treatment of the initially prepared sample made from $[Ir(CO)_2(acac)]$ and NaY zeolite. A, sample after evacuation for 12 h at room temperature; the other spectra indicate the change resulting from contact with flowing CO at 1 atm and 40 °C: B, after 1/2 h; C, after 1 h; D, after 2 h.

The carbonylation-decarbonylation process was reversible under these conditions; the process was carried out three times without any significant change in the spectrum of the carbonylated form. However, when much more severe conditions were used for the decarbonylation (e.g., H_2 at 1 atm and 425 °C for 2 h), the sample turned dark gray and could not be recarbonylated as before to give the infrared spectrum matching that of $[Ir_4(CO)_{12}]$. Instead, the spectrum [2056(s, br) cm^{-1}] became similar to those of CO adsorbed on particles of Ir metal supported on alumina [17]. Scattering centers associated with particles of metal (typically about 80–100 Å in diameter) were evident in electron micrographs of the sample.

4. Discussion

The close agreement between the spectrum of the zeolite-supported iridium carbonyl after treatment in CO and that of $[Ir_4(CO)_{12}]$ in tetrahydrofuran solution suggests that this cluster formed in the zeolite cages. The color of the sample is consistent with this inference. Others [3] have also reported the synthesis of $[Ir_4(CO)_{12}]$ in NaY zeolite from a mononuclear iridium carbonyl in the presence of CO.

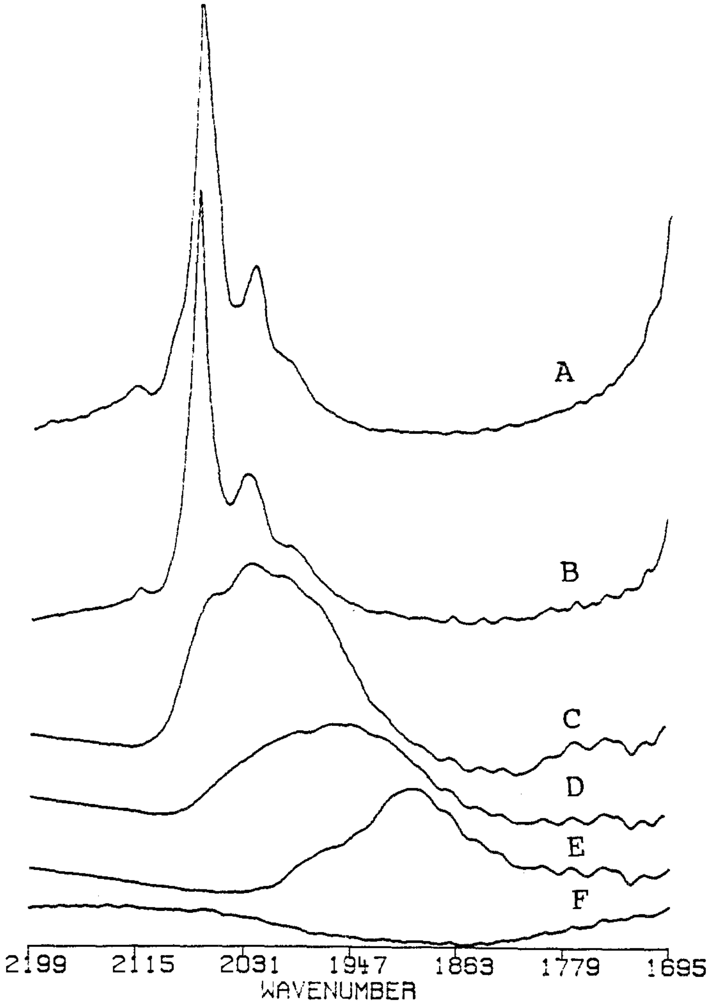

Fig. 2. Decarbonylation of the iridium cluster that had been formed in NaY zeolite by treatment of the adsorbed precursor in CO: effects of treatment in flowing H_2 at 1 atm as the temperature was raised at a rate of about 3°C/min. A, sample following treatment in CO (the spectrum is virtually the same as that of $[Ir_4(CO)_{12}]$ in tetrahydrofuran solution). The other spectra show the effects of treatment of this sample in H_2 for various times at various temperatures: B, 50°C for 1 h; C, 125°C for 10 min; D, 200°C for 10 min; E, 275°C for 10 min; F, 300°C for 2 h.

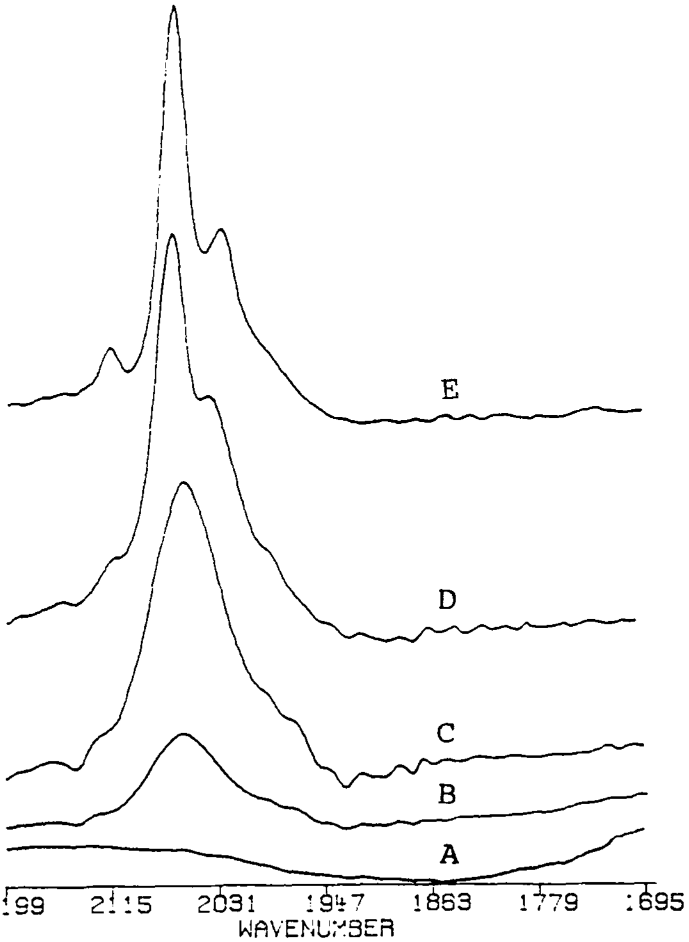

Fig. 3. Recarbonylation of the decarbonylated iridium cluster in NaY zeolite. The sample was treated in flowing CO at 1 atm and 40 °C, with spectra measured at various times: A, sample in the decarbonylated form. The remaining spectra were measured with the sample in CO for the indicated times: B, 1/2 h; C, 1 h; D, 2 h; and E, 4 h.

The inference that $[Ir_4(CO)_{12}]$ formed in the zeolite cages is consistent with the solution chemistry of the formation of the cluster from iridium salts. $[Ir_4(CO)_{12}]$ is made from Na_3IrCl_6 in the presence of CO at 100–150 °C and 250 atm; alternatively, it is made from hydrated $IrCl_3$ in CO under milder conditions, 150 °C and 1 atm [18]. The chemistry in the zeolite also takes place under mild conditions, and the comparison with the solution chemistry suggests that water may play a role. Traces of water are expected to have been present in the samples; addition of small amounts of water to the CO did not change the chemistry. The results are therefore inferred to be consistent with the suggestion that water played a role in the synthesis of $[Ir_4(CO)_{12}]$ in the zeolite.

The growth of $[Rh_6(CO)_{16}]$ on the surface of alumina has been suggested to be initiated by attack of adsorbed H_2O on rhodium subcarbonyls to give mobile, nucleophilic $[Rh(CO)_4]^-$, which was envisaged to react with the rhodium subcarbonyl in a reductive condensation giving the cluster [19,20]. We suggest that similar chemistry occurred in the formation of the iridium carbonyl cluster in the NaY zeolite and also in the formation of $[Rh_6(CO)_{16}]$ in NaY zeolite [7]. The hypothesis about formation of the rhodium carbonyl cluster is supported by the fact that Rao et al. [7] used CO containing a small amount of water in their synthesis of the cluster from a mononuclear rhodium precursor.

The results are consistent with a ship-in-a-bottle synthesis. The precursor $[Ir(CO)_2(acac)]$ is inferred to be small enough to fit into the interior of the zeolite, as similar, but larger, metal carbonyls have been shown to fit: $[CpM(CO)_2]$, $[Cp^*M(CO)_2]$, and $[CpM(C_2H_4)_2]$ [$M = Rh, Ir$; $Cp = C_5H_5$; $Cp^* = (CH_3)_5C_5$] [21]. Furthermore, $[Ir_4(CO)_{12}]$ (with a diameter of about 9 Å) is easily small enough to fit in the supercages of zeolite Y (which have diameters of about 12 Å) but too large to diffuse rapidly through the apertures (which have diameters of about 7.4 Å). Therefore it is plausible that the clusters, once formed, would be trapped in the supercages and not removed when the sample came in contact with tetrahydrofuran.

The infrared spectra clearly demonstrate the reversibility of the decarbonylation of the entrapped clusters as long as the conditions are sufficiently mild. At the highest temperature in H_2, however, the metal sinters outside the zeolite cages and the reversibility of the carbonylation is lost. These observations suggest that the decarbonylated form of the sample prepared under mild conditions incorporates tetrairidium clusters similar to those that have been inferred to form by decarbonylation of $[HIr_4(CO)_{11}]^-$ supported on MgO [16]; it is possible that the clusters are stabilized by the rigid environment of the zeolite cages and migrate and sinter less rapidly than they would on a support with larger pores. However, the form of the iridium in the decarbonylated state is unknown; we plan to characterize it with EXAFS spectroscopy.

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