[Ir$_6$(CO)$_{15}$]$^{2-}$ in NaX Zeolite: Catalyst for Carbon Monoxide Hydrogenation

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[Ir(CO)$_2$(acac)] (Hacac = pentane-2,4-dione) in the pores of NaX zeolite was converted in the presence of CO into [HIr$_4$(CO)$_{11}$]$^-$ or [Ir$_6$(CO)$_{15}$]$^{2-}$; the sample containing the latter is catalytically active for CO hydrogenation, giving high yields of alkenes

Metal clusters in the molecular-scale cages of zeolites are selective catalysts for CO hydrogenation.[1-3] Anionic osmium[4a] and rhodium[4b] carbonyl clusters in strongly basic zeolites have been implicated as selective and stable CO hydrogenation catalysts. The structures of the metal or metal carbonyl clusters in these catalysts are not known. The goal of this research was to prepare well characterized metal carbonyl clusters in a zeolite and determine the catalytic properties for CO hydrogenation.

NaX zeolite (Union Carbide, Linde type 13X, Si/Al molar ratio about 2.5) was chosen as the zeolite because it is moderately basic and has been used as a support for rhodium carbonyl clusters (with unidentified structures) that appear to catalyse alkene hydroformylation.[5] [Ir(CO)$_2$(acac)] 1 was chosen as the catalyst precursor because it is small and diffuses readily into the zeolite supercages.

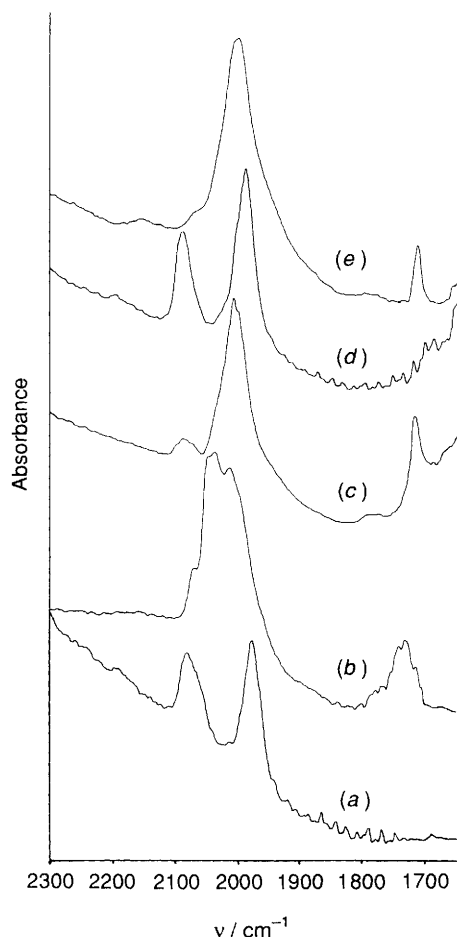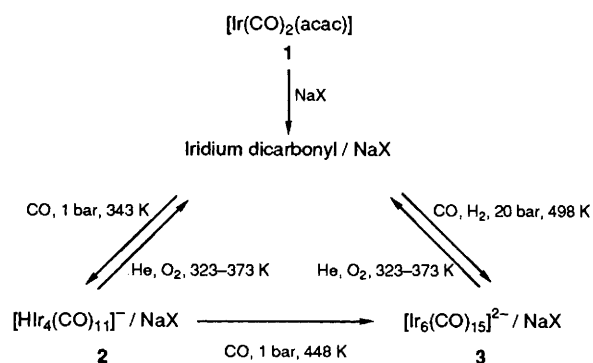The catalyst was prepared from 1 in hexane, which was brought in contact with zeolite that had been evacuated for

Fig. 1 IR spectra taken during treatment of the samples made from [Ir(CO)₂(acac)] and NaX zeolite: (a) initially prepared sample after evacuation for 12 h at room temperature; (b) sample from (a) after treatment in CO at 343 K and 1 bar for 8 h; (c) sample from (b) after treatment in CO at 448 K and 1 bar for 2 h; (d) sample from either (b) or (c) after contact with a stream of 2% O₂ in He at 323–373 K; (e) sample from (a) after treatment in CO + H₂ (equimolar) at 498 K and 20 bar for 3 d

Scheme 1 Chemistry of iridium carbonyl clusters in NaX zeolite (Hacac = pentane-2,4-dione)

several hours at 298 K. The slurry was dark brownish-green in colour. After two days of stirring, the metal-containing zeolite was separated by filtration, washed thoroughly with hexane, and dried *in vacuo* at 298 K for 12 h; the solid was brownish-yellow in colour. The uptake of Ir by the zeolite was nearly complete; the zeolite contained approximately 0.7 wt% Ir. The IR spectrum (v_{CO}: 2082s and 1984s cm⁻¹) [Fig. 1(a)] suggests the presence of an iridium dicarbonyl.

The sample was exposed to flowing CO at 343 K and 1 bar, and after 8 h gave a pale yellow solid; the IR spectrum (v_{CO}: 2072w, 2044sh, 2035s, 2011m, 2000sh and 1765mw cm⁻¹) [Fig. 1(b)] is almost the same as that of [NBu₄][HIr₄(CO)₁₁], [NBu₄][2], in tetrahydrofuran (THF) (v_{CO}: 2030sh, 2020s, 1990m, 1975m and 1820mw cm⁻¹) except for a shift of about 15 cm⁻¹ of the major terminal carbonyl band to higher wavenumber and a shift of about 55 cm⁻¹ of the bridging carbonyl band to lower wavenumber. These shifts are consistent with the formation of contact ion pairs, with Na⁺ being the counter cation in the 'solvating' zeolite cage. Similar shifts indicate the formation of contact ion pairs between Na⁺ and 2 in diethyl ether.[6] Attempts to extract 2 from the zeolite with [PPN][Cl] [PPN = (Ph₃P)₂N] in THF were unsuccessful, consistent with the entrapment of 2 in the zeolite cages.

When this sample was treated in CO at 448 K and 1 bar for 2 h, it became reddish-brown in colour with an IR spectrum (v_{CO}: 2001s, 1993s and 1710m cm⁻¹) [Fig. 1(c)] that is similar to the spectrum of [PPN]₂[Ir₆(CO)₁₅], [PPN]₂[3], in THF

(v_{CO}: 1987s, 1979s, 1771m and 1716w cm⁻¹)[7] or that of [NEt₄]₂[3] in THF (v_{CO}: 2020sh, 1980s, 1770m and 1745m cm⁻¹).[8] Again, the shifts in the spectra (about 12 cm⁻¹ of the terminal carbonyl bands to higher wavenumber and about 60 cm⁻¹ of the bridging carbonyl band to lower wavenumber) suggest ion pairing of 3 with the Na⁺ in the zeolite cage. The zeolite-supported 3 could not be extracted with [PPN][Cl] in THF, consistent with the entrapment of the cluster in the zeolite.

When either of the two samples was brought in contact with a stream of 2% O₂ in He, the IR spectrum changed back to that of the initial species formed from 1 [Fig. 1(d)]. This process was repeated three times; we infer that the reductive carbonylation–oxidative fragmentation was reversible in the zeolite cages (Scheme 1).

In a catalysis experiment, a sample of the material prepared from NaX zeolite and 1 was placed in a tubular flow reactor in the absence of air. Flow of equimolar CO + H₂ began at 20 bar and room temperature, and the temperature was increased at *ca.* 3 K min⁻¹ to 498 K. The product stream was analysed periodically by gas chromatography; conversions at 498 K were about 0.3%. The organic products were principally C₁–C₅ alkanes and alkenes. The catalytic reaction rate was roughly 10⁻⁵ mol of CO converted (mol of Ir)⁻¹ s⁻¹. The catalyst was stable, with the activity remaining almost unchanged during 3 d of steady-state operation. The product distribution changed; the alkene to alkane molar ratio increased from about 1.5 to about 2.8. Initially, the catalyst gave a non-Schulz–Flory distribution of products, with a maximum at C₄, but the distribution changed and approached the Schulz–Flory distribution after 30 h.

The catalyst that had been in the reactor for 3 d was removed in the absence of air. It was reddish-brown in colour. The IR spectrum (v_{CO}: 2000s, 1990s and 1710m cm⁻¹) [Fig. 1(e)] and the colour indicate the presence of 3. An attempt to extract the anions with [PPN][Cl] in THF was unsuccessful, suggesting the stable entrapment of the cluster in the zeolite.

These results indicate a simple chemistry of iridium carbonyl anions in the moderately basic zeolite NaX. This chemistry parallels the chemistry of these anions in basic solutions[8] and on the surface of basic MgO.[7] However, [Ir₈(CO)₂₂]²⁻ 4, which is formed from 2 in basic solution or on MgO, was not observed in the zeolite cages; it is perhaps too large to fit.

When a less basic zeolite, NaY, having an Si/Al molar ratio of 4.74, was used instead of NaX, 1 in CO at 1 bar and 313 K was converted to [Ir₄(CO)₁₂];[9] in CO at 1 bar and 398 K it was converted to the isomer of [Ir₆(CO)₁₆] 5 that has edge-bridging CO ligands;[10] and in CO + H₂ at 20 bar and 548 K it was converted to the isomer of 5 that has face-bridging CO ligands.[10] These results show that neutral iridium carbonyl clusters form in the less basic NaY cages, whereas anionic clusters form in the more basic NaX cages.

The CO + H₂ atmosphere in the catalytic reactor evidently stabilized 3 at 498 K; isolation of the clusters in the cages may

have contributed to the stabilization. Species **3** is the only organometallic species that was detected by IR spectroscopy in the catalyst, and it may be a catalyst precursor.

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