[Ru₆(CO)₁₈]²⁻ in NaX Zeolite Cages: Characterization by EXAFS and FTIR Spectroscopy

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Ru^{III}(NH$_3$)$_6$ in the cages of NaX zeolite is converted in the presence of CO + H$_2$ into [Ru$_6$(CO)$_{18}$]$^{2-}$, which is reversibly fragmented and reconstructed under oxidative and reductive conditions, respectively.

Zeolite (mainly X- or Y-faujasite) cages are unique microcavities with the propensity to stabilize or entrap small metal clusters. Using FTIR and EXAFS spectroscopy, we recently demonstrated that some clusters, such as Rh$_6$(CO)$_{16}$,[1] Rh$_{6-x}$Ir$_x$(CO)$_{16}$ (x = 1–3),[2] [Pt$_3$(CO)$_6$]$_n^{2-}$ (n = 3,4),[3] and H$_4$Ru$_4$(CO)$_{12}$[4] were synthesized within the supercages of NaY zeolite by the 'ship-in-a-bottle' technique. Here we report the synthesis of ruthenium carbonyl cluster dianion [Ru$_6$(CO)$_{18}$]$^{2-}$ from Ru^{III}(NH$_3$)$_6$ in the supercages of NaX zeolite and the cluster has been characterized by UV–VIS, FTIR and EXAFS techniques.

A sample containing 3.2 mass% Ru was prepared by cation-exchange of NaX with Ru(NH$_3$)$_6$Cl$_3$ aqueous solution at room temp. for 2 days. NaX (Union shown K.K. 13X, Lot No. 980113, Si/Al = 2.3, surface area 870 m^2 g^{-1}) was chosen as the zeolite because it is moderately basic since the ruthenium carbonyl cluster dianion occurs in basic solution.[5] The infrared spectrum of the freshly prepared Ru^{III}(NH$_3$)$_6$/NaX (which is very unstable and readily changes into a mixture of Ru-red and Ru-brown)[6] shows a band at 1356 cm^{-1}, indicating the presence of ammonia ligands, [Fig. 1(a)]. This sample was exposed to CO + H$_2$ (200 + 200 Torr) in a closed circulating system at 353 K and IR bands arose at 2072, 2000 and 1939 cm^{-1} [Fig. 1(b)], with the latter predominant band assigned to [Ru^{II}(NH$_3$)$_5$(CO)]. At the same time, the original band at 1356 cm^{-1} shifts to 1331 cm^{-1} with decrease in intensity and a new band appears at 1468 cm^{-1}, attributed to v_4, δ(N–H) of NH$_4^+$. This change in the IR spectrum of the N–H vibrations is typical upon reduction of Ru^{III} in zeolites.[7] When the temperature was increased to 393 K, the IR spectrum showed peaks at 2088, 2048, 2014 and 1952 cm^{-1} [Fig. 1(c)]. The bands at 2088, 2014 and 2048, 1952 cm^{-1}

can be ascribed to Ru^I(CO)$_2$ and Ru^I(CO)$_3$ moieties, respectively.[8] In addition to carbonyl bands, an unidentified peak emerges at low wavenumber (862 cm^{-1}). Probably associated with the interaction of mononuclear ruthenium carbonyl species with oxygen of the zeolite framework.[9–11] After 22 h at 393 K, a steady-state spectrum [Fig. 1(d)] was observed, exhibiting carbonyl bands at 2000, 1970, 1743 and 1702 cm^{-1} (UV–VIS reflectance λ_{max}: 235 and 285 nm), while the peak at 862 cm^{-1} disappeared. These spectra closely resemble that of [N(PPh$_3$)$_2$]$_2$[Ru$_6$(CO)$_{18}$] in dichloromethane (v_{CO}: 2006s, 1986vs, 1930(sh) and 1754w; 235 and 287 nm, UV–VIS reflectance), but with shifting of the carbonyl bands to lower wavenumber. These shifts are consistent with the formation of contact ion pairs with alkali-metal ions or Lewis acid sites in the 'solvating' zeolite cages. In contrast to previous results,[1–3] the terminal carbonyl bands unexpectedly also shifted to lower frequency. A tentative explanation is that under the synthesis conditions, almost all the water is removed, as evidenced by the IR spectrum [Fig. 1(d)], and thus presumably most of the cations in the zeolite cages are unhydrated and interact more strongly as Lewis acids with not only the rather more strongly basic bridging CO ligands, but also the less basic terminal CO ligands of the ruthenium cluster dianion.

The final wafer sample was orange, as is [N(PPh$_3$)$_2$]$_2$[Ru$_6$(CO)$_{18}$] in THF solution. Attempts to extract the ruthenium carbonyl species from the zeolite with THF or with [N(PPh$_3$)$_2$]Cl in THF were unsuccessful, consistent with stable entrapment of the cluster in the supercages of the zeolite.

The carbonyls of [Ru$_6$(CO)$_{18}$]$^{2-}$ in NaX zeolite underwent isotopic exchange with ^{13}CO in the presence of hydrogen. On exposure of [Ru$_6$(CO)$_{18}$]$^{2-}$/NaX to ^{13}CO + H$_2$ (20 + 20 Torr) at 353 K for 2 h, the bands of linear CO at 2000, 1970 cm^{-1} and bridging CO at 1754 cm^{-1} were completely replaced by new bands at 1954, 1922 and 1708 cm^{-1}, respectively. The values of the band shift after isotopic exchange was 44–48 cm^{-1}, roughly in the range as that calculated according to the two-atom model (Δv=39–44 cm^{-1}). Furthermore, this process was reversible when normal CO + H$_2$ was introduced under the same conditions. These results suggest there is no change in the metal skeleton of the ruthenium carbonyl cluster during isotopic exchange. However, in the absence of hydrogen isotopic exchange does not proceed and the ruthenium carbonyl cluster dianion is unstable upon exposure to carbon monoxide alone even at 323 K.

The structure of [Ru$_6$(CO)$_{18}$]$^{2-}$/NaX is very sensitive to oxygen. When the sample wafer was brought in contact with 100 Torr O$_2$ at room temp., the bridging carbonyl band of [Ru$_6$(CO)$_{18}$]$^{2-}$ quickly disappeared. After 2 h at 403 K, a new spectrum was obtained, showing carbonyl bands at 2088 and 2016 cm^{-1}, indicative of Ru^I(CO)$_2$ (see above). At the same time, a low wavenumber peak at 880 cm^{-1} is also present, suggesting an adduct of a mononuclear ruthenium carbonyl
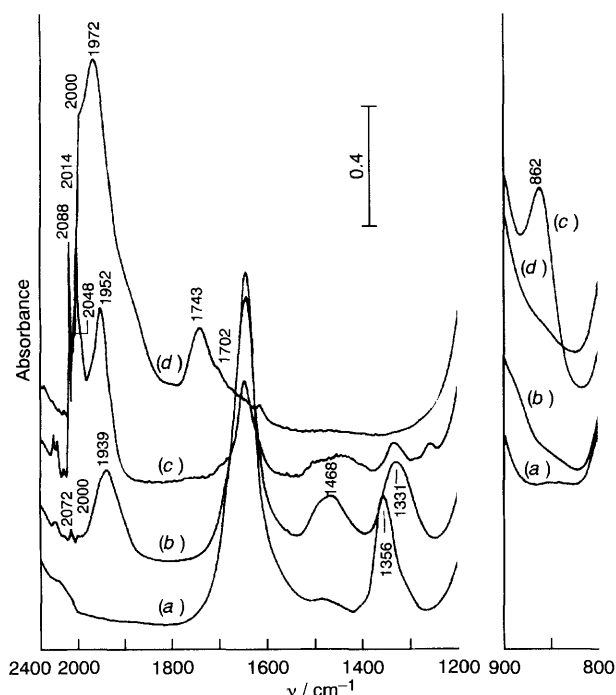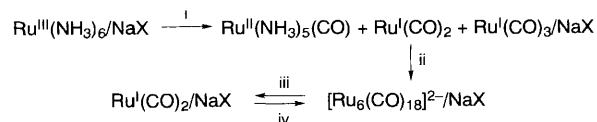

Fig. 1 *In-situ* FTIR spectra in the reaction of Ru^{III}(NH$_3$)$_6$/NaX with CO + H$_2$ (200 + 200 Torr) at 298–393 K; (a) initial spectrum *in vacuo*, 298 K, (b) 353 K, (c) 393 K, 30 min, (d) 393 K, 22 h

Scheme 1 Chemistry of ruthenium carbonyl species in NaX zeolite. Reagents and conditions: i, CO–H$_2$, room temp. to 393 K; ii, CO–H$_2$, 393 K, 22 h; iii, O$_2$, 403 K; iv, CO–H$_2$, 393 K

species with oxygen of zeolite probably of type $(CO)_2Ru^L-O-Al(Si)$. It is of interest that after exposure to CO + H$_2$ at 393 K for 12 h, the IR spectrum changed back to that observed prior to oxidation. This process could be repeated several times, infering that the oxidation fragmentation—reductive reformation was reversible in the zeolite cages (Scheme 1).

In order to obtain more structural information about the ruthenium species formed in NaX zeolite, EXAFS measurements were carried out in the transmission mode at BL −10B of the photon factory in the National Laboratory for High Energy Physics. Fig. 2 presents the raw EXAFS function and the Fourier transform for the $[Ru_6(CO)_{18}]^{2-}$/NaX sample. The raw EXAFS function [Fig. 2(a)] shows oscillations up to K ca. 15
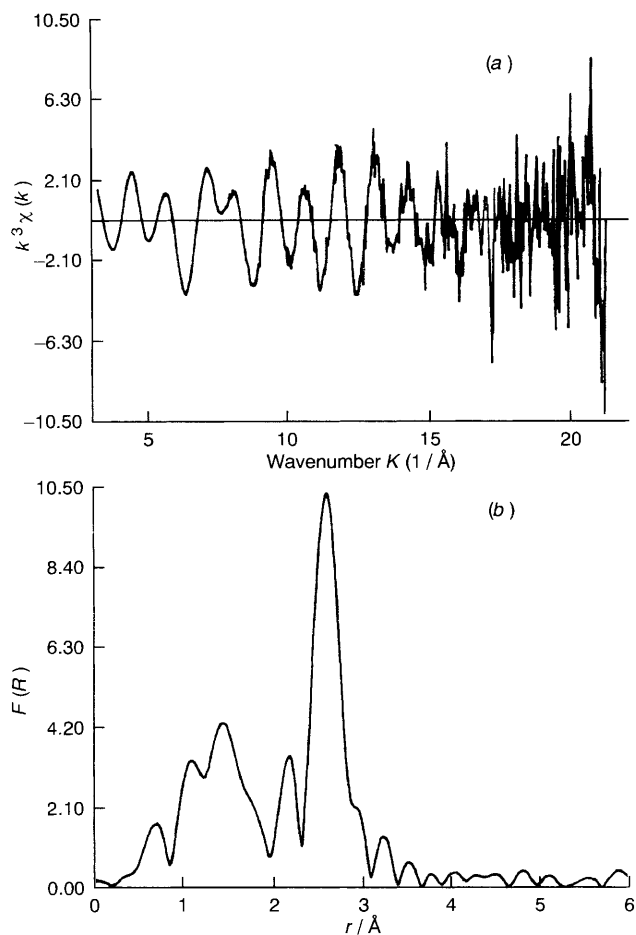

Fig. 2 Ru K-edge EXAFS data for $[Ru_6(CO)_{18}]^{2-}$/NaX; (a) K^3-weighted EXAFS function, (b) Fourier transform

Table 1 EXAFS results for $[Ru_6(CO)_{18}]^{2-}$ in NaX zeolite[a]

Shell	CN	R/Å	ΔE_0/eV	σ/Å
Ru–Ru	3.5	2.82	12.85	0.067
Ru–C	3.1	1.86	−6.67	0.060
Ru–O (support)	1.4	2.26	3.66	0.085

[a] CN, r, ΔE_0 and σ represent coordination number, interatomic distance, change in energy threshold and Debye–Waller factor, respectively.

Å^{-1}, clearly indicating the presence of near-neighbour high atomic weight backscatters, which are inferred to be Ru. The Fourier transform [Fig. 2(b)] was obtained from the raw EXAFS data with a K^3-weighting over the range $3.1 < K < 15$ Å^{-1}. Because the Ru–Ru and Ru–O (carbonyl) peaks in r-space are superimposed, separation of these two contributions is not straightforward. The best way to isolate the Ru–Ru contribution was found to be an estimation in K-space. Since C and O cause negligible backscattering at values of $K > ca. \sim 10–11$ Å^{-1},[12] the EXAFS spectrum for $K > 10$ Å^{-1} is almost entirely due to the Ru–Ru shell. Table 1 lists the results of the data analysis for the $[Ru_6(CO)_{18}]^{2-}$/NaX sample. The Ru–Ru coordination number of 3.5 suggests a cluster containing only 4–6 Ru atoms, while the Ru–Ru distance of 2.82 Å is nearly the same as the value found in $[N(PPh_3)]_2[Ru_6(CO)_{18}]$ in the crystalline state (2.80–2.89 Å).[13] Since the coordination number for $[Ru_6(CO)_{18}]^{2-}$ is 4, it can be induced that about 87% of Ru atoms are present in the $[Ru_6(CO)_{18}]^{2-}$ cluster state, based on the ratio of 3.5:4. The contribution of Ru–O(zeolite) indicates that, in addition to $[Ru_6(CO)_{18}]^{2-}$, there are other ruthenium species formed, which are bonded to the zeolite support via oxygen. A resonable explanation is that the minor species present along with the cluster dianion are mononuclear carbonyl species, which results in a Ru–Ru coordination number of < 4.

In summary, the EXAFS data, which agree well with the UV–VIS and FTIR results, are consistent with the formation of $[Ru_6(CO)_{18}]^{2-}$ encaged within NaX zeolite cages. These results indicate that ca. 80–90% of Ru atoms were present as $[Ru_6(CO)_{18}]^{2-}$ cluster dianions.

Footnote

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