EXAFS and Fourier Transform IR Characterization of Platinum Carbonyl Clusters $[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4) encapsulated in NaY Zeolites and Their Effective Catalysis in the CO + NO Reaction

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The NaY zeolite-entrapped clusters $[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4), synthesized by a ship-in-bottle technique, were characterized by Pt-L edge EXAFS (extended X-ray absorption fine structure), Fourier transform IR and UV–VIS spectroscopy, and exhibited high catalytic activity in NO reduction by CO to give N_2 and N_2O at 300–473 K.

Metal carbonyl clusters grafted on supports such as amorphous oxides, *e.g.* SiO_2, Al_2O_3 and zeolites, offer a great advantage in the rational preparation of tailored metal catalysts.[1] Among inorganic supports zeolites are the most promising for accommodating metal clusters in cages without cluster aggregation, which exhibited unique catalytic performance in CO hydrogenation based on molecular shape selectivity.[2] Some homometal and bimetal carbonyl clusters, $Rh_6(CO)_{16}$,[3] $Ir_6(CO)_{16}$,[4] $Pd_{13}(CO)_x$[5] and $[HFe_3(CO)_{11}]^-$,[6] have been synthesized in NaY zeolites by the so-called 'ship-in-bottle' technique. Recently we synthesized intrazeolite bimetallic clusters $[Fe_2Rh_4(CO)_{16}]^{2-}$/NaY[7] and $Rh_{6-x}Ir_x(CO)_{16}$/NaY (x = 2, 3, 4).[8] We report here that the new series of trigonal prismatic platinum carbonyl cluster dianions of general formula $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ (n = 3, 4, 5) may be synthesized uniformly in NaY zeolites, and they have been

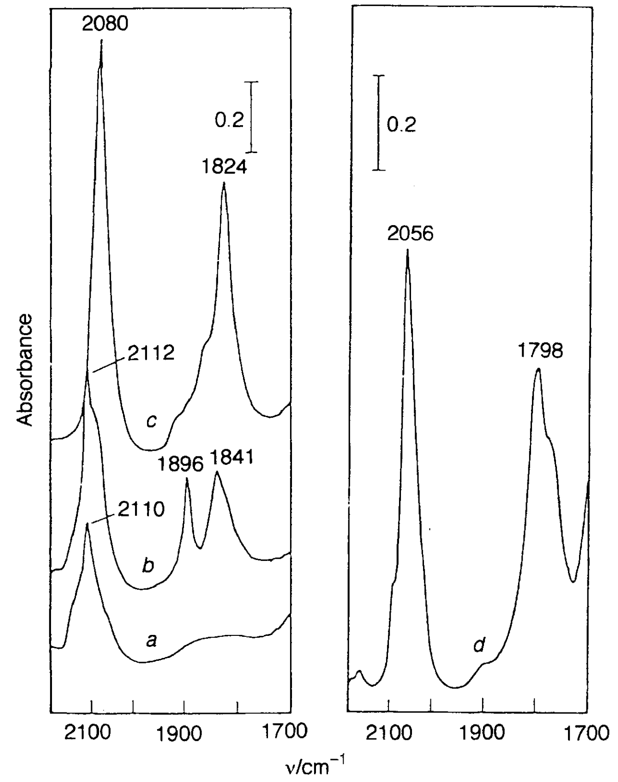
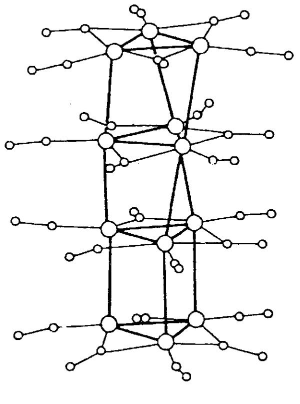


Fig. 1 IR spectra of carbonyl species formed in the reaction of Pt^{2+}/NaY with CO (500 Torr): (*a*) after 3 min at 298 K; (*b*) after 5 min at 353 K; (*c*) after 6–10 h at 353 K; (*d*) in the reaction of $[Pt(NH_3)_4]^{2+}$/NaY with CO (500 Torr) after 20–30 h at 373 K



$[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_4{}^{2-}$

Fig. 2 Structure of trigonal prismatic Pt_{12} carbonyl clusters by X-ray crystal structure analysis, from ref. 13

Table 1 Specific activity for NO + CO reaction at 473 K on NaY-entrapped Pt carbonyl clusters and Pt/Al_2O_3[a]

Catalyst	NO conversion	N_2 formation	Selectivity $N_2/(N_2 + N_2O)$
	10^{-3} molecules Pt^{-1} s^{-1}		
$[Pt_{12}(CO)_{24}]^{2-}$/NaY	2.00	0.56	0.56
$[Pt_9(CO)_{18}]^{2-}$/NaY	2.83	0.68	0.48
Pt/Al_2O_3	0.58	0.05	0.15

[a] Initial pressure: $P_{NO} = P_{CO} = 50$ Torr.

characterized by EXAFS, UV–VIS and Fourier transform IR (FT IR) spectroscopy. They exhibit high catalytic activity in NO reduction by CO to give N_2 and N_2O at 300–473 K.

$[Pt(NH_3)_4]^{2+}$/NaY (4 wt% Pt loading) was prepared from NaY zeolite powder (Linde LZY-52, Lot No. 030785, Si/Al = 5.6, surface area 910 m^2 g^{-1}) by cation-exchange with an aqueous solution of $[Pt(NH_3)_4]Cl_2$ (pH = 8.90; 2.6 mmol dm^{-3}). $[Pt(NH_3)_4]^{2+}$/NaY was calcined under flowing oxygen (120 ml min^{-1}) at 573 K for 2 h to give the grey Pt^{2+}/NaY. The sample Pt^{2+}/NaY was heated from 298 to 373 K under CO (550–760 Torr) with a trace of H_2O, resulting in the successive formation of different carbonyl species which show their characteristic carbonyl IR bands as shown in Fig. 1(*a*)–1(*c*). It is suggested from the analogy with IR bands of previously reported platinum carbonyl complexes, *e.g.* $Pt(CO)Cl_3$[9] and $Pt_3(\mu_2\text{-}CO)_3(PPh_3)_4$,[10] that Pt^{2+}/NaY reacts with CO forming Pt(CO)/NaY [2100 cm^{-1}; Fig. 1(*a*)] and a proposed intermediate trigonal species $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]$/NaY [2112s, 1896m and 1841s cm^{-1}; Fig. 1(*b*)]. They are eventually converted into the dark-green Pt carbonyl cluster species (**I**) [2080vs and 1824s; Fig. 1(*c*); 290, 445 and 640 nm, UV–VIS reflectance], data which resemble those of the blue-green $[Pt_{12}(CO)_{24}]^{2-}$ in tetrahydrofuran (THF) solution.[11] On the other hand, the $[Pt(NH_3)_4]^{2+}$/NaY provided stoichiometrically the orange-brown cluster species (**II**) [2056vs and 1798s cm^{-1}, as shown in Fig. 1(*d*); 300, 435 and 710 nm, UV–VIS] in the reductive carbonylation with CO (550–760 Torr) and H_2O at 298–373 K, which correspond to data for the purple $[Pt_9(CO)_{18}]^{2-}$ in solution.[11] De Mallmann *et al.*[12] have previously reported that a red-purple complex was prepared from $[Pt(NH_3)_4]^{2+}$/NaY + CO which gave different IR carbonyl bands (2026 and 1800 cm^{-1}). It is of interest that the terminal CO bands of the intrazeolite Pt_9 and Pt_{12} cluster anions shift to higher frequencies (26–40 cm^{-1}), while the bridging CO bands shift to lower frequencies (40–50 cm^{-1}), compared with those in THF solution {2030, 1840 cm^{-1} for $[Pt_9(CO)_{18}]^{2-}$-$[NEt_4]_2$ and 2040, 1870 cm^{-1} for $[Pt_{12}(CO)_{24}]^{2-}$-$[NEt_4]_2$}.[11] These CO frequency shifts are interpreted in terms of the interaction between the O end of the cluster bridging carbonyls and the intrazeolite acid sites such as H^+ and Al^{3+}, as for $Rh_6(CO)_{16}$/NaY.[1] The sample (**I**) was washed with methanolic tetraethylammonium chloride, but no coloured eluate was observed and no CO IR bands appeared in the spectra of the solution. This suggested that the $[Pt_{12}(CO)_{24}]^{2-}$ complex is formed inside NaY with a negligible amount of external complex.

In situ EXAFS data were conducted for samples (**I**) and (**II**), on the SOR beam line 10B of the National Laboratory for High Energy Physics (KEK-PF). Pt L-edge EXAFS analysis of the first neighbour Pt–Pt frameworks in terms of coordination number (N_c) and atomic distances (R) for sample (**I**) and (**II**) provided direct evidence for the stoichiometric formation of trigonal prismatic $[Pt_3(CO)_6]_n{}^{2-}$ (n = 3–5) clusters within the zeolite cavity. For sample (**I**) the individual intratriangular Pt–Pt distances (R_1), R_1 = 2.64 Å, $N_c{}^1$ = 1.5, and intertriangular Pt–Pt distances (R_2) between adjacent triplatinum planes, R_2 = 2.97 Å, $N_c{}^2$ = 1.4, and, for sample 2, R_1 = 2.63 Å, $N_c{}^1$ = 1.8, R_2 = 2.96 Å, $N_c{}^2$ = 1.2, were obtained by the FT curve-fitting of the EXAFS oscillation data. These structural values are in good agreement with those observed by EXAFS for crystalline samples of $[Pt_{12}(CO)_{24}]^{2-}$-$[NEt_4]_2$ mixed with boron nitride (R_1 = 2.64 Å, $N_c{}^1$ = 2.0; R_2 = 2.97 Å, $N_c{}^2$ = 1.5). The X-ray structural analysis for $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ crystals gave R_1 = 2.66–2.67 Å and R_2 = 3.01–3.03 Å[13] as shown in Fig. 2. It is suggested from the EXAFS data that the intertriangular Pt planes of the Pt_9 and Pt_{12} carbonyl cluster anions are slightly distorted inside the intrazeolite constraint.

The more basic $[Pt(NH_3)_4]^{2+}$/NaY ($NH_3 + H_2O \rightarrow NH_4{}^+ + OH^-$) gave smaller Pt clusters such as $[Pt_9(CO)_{18}]^{2-}$/NaY, whereas $[Pt_{12}(CO)_{24}]^{2-}$/NaY was formed from the calcined

Pt^{2+}/NaY. This trend in cluster aggregation is in accordance with increasing basicity, *e.g.* OH^- and NH_3 inside NaY, as in the synthesis of a series of Pt carbonyl clusters in solution.[10]

The NO + CO reaction was performed at reduced pressure (P_{CO} = 50 Torr, P_{NO} = 50 Torr) by using a closed circulating Pyrex glass reactor charged with the sample (**I**) and (**II**) at 423–523 K. As shown in Table 1, they showed high activities (10–15 times higher) for formation of N_2O, N_2 and CO_2, compared with those on conventional Pt/Al_2O_3 (4 wt% Pt) catalysts. N_2O was an intermediate in the CO + NO reaction and was subsequently converted to N_2 in the reaction on the samples (**I**) and (**II**). The conversion of CO + NO and selectivity for formation of N_2 were maintained for prolonged on-stream reactions of NO + CO (40 h) on these catalyst samples.

Upon exposure of $[Pt_{12}(CO)_{24}]^{2-}$/NaY to NO (150 Torr), *in situ* FT IR studies demonstrated that NO breaks the intra- and inter-trigonal Pt–Pt bonds of the Pt_{12} carbonyl cluster even at 298 K to give a trigonal intermediate '$Pt_3(CO)_6$' (2112, 1896 and 1841 cm^{-1}) and Pt(CO) (2110 cm^{-1}) in forming N_2O (2236 cm^{-1}) and CO_2 (2353 cm^{-1}) in the gas phase. Furthermore, it was found that $[Pt_{12}(CO)_{24}]^{2-}$/NaY was reversibly regenerated from the Pt carbonyl fragments such as Pt(CO) and $Pt_3(CO)_6$ inside NaY by the reaction with CO and water at 300–353 K. In contrast, *in situ* FT IR and GC–MS studies suggested that when a mixture of CO and NO was admitted onto $[Pt_{12}(CO)_{24}]^{2-}$/NaY, N_2, N_2O and CO_2 were catalytically formed at 323–473 K, with the original Pt_{12} cluster framework being retained inside the zeolites.

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