

## EXAFS and Fourier Transform IR Characterization of Platinum Carbonyl Clusters $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ( $n = 3, 4$ ) encapsulated in NaY Zeolites and Their Effective Catalysis in the CO + NO Reaction

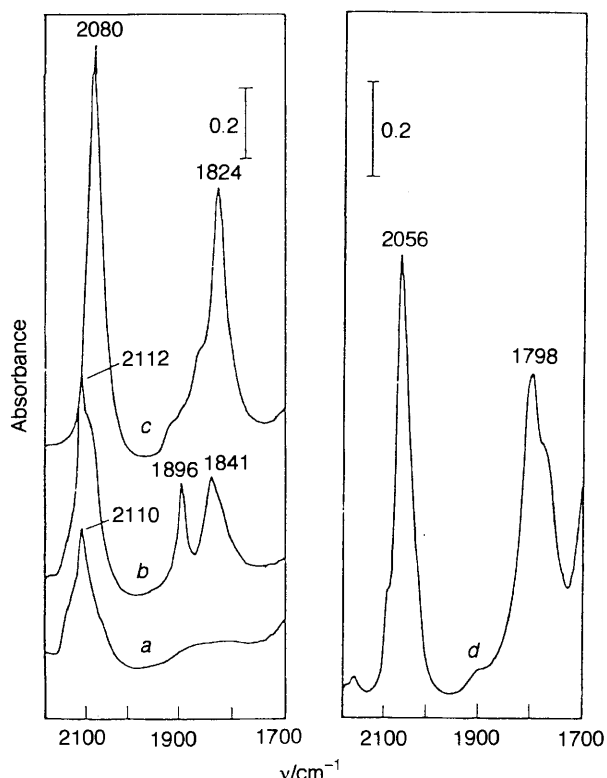
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The NaY zeolite-entrapped clusters  $[\text{Pt}_3(\text{CO})_6]_n^{2-}$  ( $n = 3, 4$ ), synthesized by a ship-in-bottle technique, were characterized by Pt-L edge EXAFS (extended X-ray absorption fine structure), Fourier transform IR and UV-VIS spectroscopy, and exhibited high catalytic activity in NO reduction by CO to give  $\text{N}_2$  and  $\text{N}_2\text{O}$  at 300–473 K.

Metal carbonyl clusters grafted on supports such as amorphous oxides, *e.g.*  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and zeolites, offer a great advantage in the rational preparation of tailored metal catalysts.<sup>1</sup> 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.<sup>2</sup> Some homometal and bimetal carbonyl clusters,

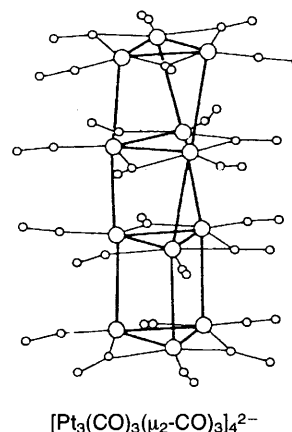
$\text{Rh}_6(\text{CO})_{16}$ ,<sup>3</sup>  $\text{Ir}_6(\text{CO})_{16}$ ,<sup>4</sup>  $\text{Pd}_{13}(\text{CO})_x$ <sup>5</sup> and  $[\text{HFe}_3(\text{CO})_{11}]^-$ ,<sup>6</sup> have been synthesized in NaY zeolites by the so-called 'ship-in-bottle' technique. Recently we synthesized intra-zeolite bimetallic clusters  $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}/\text{NaY}$ <sup>7</sup> and  $\text{Rh}_{6-x}\text{Ir}_x(\text{CO})_{16}/\text{NaY}$  ( $x = 2, 3, 4$ ).<sup>8</sup> We report here that the new series of trigonal prismatic platinum carbonyl cluster dianions of general formula  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$  ( $n = 3, 4, 5$ ) may be synthesized uniformly in NaY zeolites, and they have been



**Fig. 1** IR spectra of carbonyl species formed in the reaction of  $\text{Pt}^{2+}/\text{NaY}$  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  $[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY}$  with CO (500 Torr) after 20–30 h at 373 K

characterized by EXAFS, UV-VIS and Fourier transform IR (FT IR) spectroscopy. They exhibit high catalytic activity in NO reduction by CO to give  $\text{N}_2$  and  $\text{N}_2\text{O}$  at 300–473 K.

$[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY}$  (4 wt% Pt loading) was prepared from NaY zeolite powder (Linde LZY-52, Lot No. 030785, Si/Al = 5.6, surface area  $910 \text{ m}^2 \text{ g}^{-1}$ ) by cation-exchange with an aqueous solution of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  (pH = 8.90;  $2.6 \text{ mmol dm}^{-3}$ ).  $[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY}$  was calcined under flowing oxygen ( $120 \text{ ml min}^{-1}$ ) at 573 K for 2 h to give the grey  $\text{Pt}^{2+}/\text{NaY}$ . The sample  $\text{Pt}^{2+}/\text{NaY}$  was heated from 298 to 373 K under CO (550–760 Torr) with a trace of  $\text{H}_2\text{O}$ , 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.  $\text{Pt}(\text{CO})\text{Cl}_3$ <sup>9</sup> and  $\text{Pt}_3(\mu_2\text{-CO})_3(\text{PPh}_3)_4$ ,<sup>10</sup> that  $\text{Pt}^{2+}/\text{NaY}$  reacts with CO forming  $\text{Pt}(\text{CO})/\text{NaY}$  [ $2100 \text{ cm}^{-1}$ ; Fig. 1(a)] and a proposed intermediate trigonal species  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]/\text{NaY}$  [2112s, 1896m and 1841s  $\text{cm}^{-1}$ ; 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  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$  in tetrahydrofuran (THF) solution.<sup>11</sup> On the other hand, the  $[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY}$  provided stoichiometrically the orange-brown cluster species (II) [2056vs and 1798s  $\text{cm}^{-1}$ , as shown in Fig. 1(d); 300, 435 and 710 nm, UV-VIS] in the reductive carbonylation with CO (550–760 Torr) and  $\text{H}_2\text{O}$  at 298–373 K, which correspond to data for the purple  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  in solution.<sup>11</sup> De Mallmann *et al.*<sup>12</sup> have previously reported that a red-purple complex was prepared from  $[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY} + \text{CO}$  which gave different IR carbonyl bands (2026 and  $1800 \text{ cm}^{-1}$ ). It is of interest that the terminal CO bands of the intrazeolite  $\text{Pt}_9$  and  $\text{Pt}_{12}$  cluster anions shift to higher frequencies (26–40  $\text{cm}^{-1}$ ),



**Fig. 2** Structure of trigonal prismatic  $\text{Pt}_{12}$  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  $\text{Pt}/\text{Al}_2\text{O}_3$ <sup>a</sup>

Catalyst	NO conversion $\text{N}_2$ formation		Selectivity $\text{N}_2/(\text{N}_2 + \text{N}_2\text{O})$
	$10^{-3} \text{ molecules Pt}^{-1} \text{ s}^{-1}$		
$[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$	2.00	0.56	0.56
$[\text{Pt}_9(\text{CO})_{18}]^{2-}/\text{NaY}$	2.83	0.68	0.48
$\text{Pt}/\text{Al}_2\text{O}_3$	0.58	0.05	0.15

<sup>a</sup> Initial pressure:  $P_{\text{NO}} = P_{\text{CO}} = 50 \text{ Torr}$ .

while the bridging CO bands shift to lower frequencies (40–50  $\text{cm}^{-1}$ ), compared with those in THF solution {2030, 1840  $\text{cm}^{-1}$  for  $[\text{Pt}_9(\text{CO})_{18}]^{2-}[\text{NET}_4]_2$  and 2040, 1870  $\text{cm}^{-1}$  for  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}[\text{NET}_4]_2$ .<sup>11</sup> 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  $\text{H}^+$  and  $\text{Al}^{3+}$ , as for  $\text{Rh}_6(\text{CO})_{16}/\text{NaY}$ .<sup>1</sup> 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  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$  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  $[\text{Pt}_3(\text{CO})_6]_n^{2-}$  ( $n = 3\text{--}5$ ) clusters within the zeolite cavity. For sample (I) the individual intratriangular Pt–Pt distances ( $R_1$ ),  $R_1 = 2.64 \text{ \AA}$ ,  $N_c^1 = 1.5$ , and intertriangular Pt–Pt distances ( $R_2$ ) between adjacent triplatinum planes,  $R_2 = 2.97 \text{ \AA}$ ,  $N_c^2 = 1.4$ , and, for sample 2,  $R_1 = 2.63 \text{ \AA}$ ,  $N_c^1 = 1.8$ ,  $R_2 = 2.96 \text{ \AA}$ ,  $N_c^2 = 1.2$ , 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  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}[\text{NET}_4]_2$  mixed with boron nitride ( $R_1 = 2.64 \text{ \AA}$ ,  $N_c^1 = 2.0$ ;  $R_2 = 2.97 \text{ \AA}$ ,  $N_c^2 = 1.5$ ). The X-ray structural analysis for  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$  and  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  crystals gave  $R_1 = 2.66\text{--}2.67 \text{ \AA}$  and  $R_2 = 3.01\text{--}3.03 \text{ \AA}$ <sup>13</sup> as shown in Fig. 2. It is suggested from the EXAFS data that the intertriangular Pt planes of the  $\text{Pt}_9$  and  $\text{Pt}_{12}$  carbonyl cluster anions are slightly distorted inside the intrazeolite constraint.

The more basic  $[\text{Pt}(\text{NH}_3)_4]^{2+}/\text{NaY}$  ( $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$ ) gave smaller Pt clusters such as  $[\text{Pt}_9(\text{CO})_{18}]^{2-}/\text{NaY}$ , whereas  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$  was formed from the calcined

Pt<sup>2+</sup>/NaY. This trend in cluster aggregation is in accordance with increasing basicity, e.g. OH<sup>-</sup> and NH<sub>3</sub> inside NaY, as in the synthesis of a series of Pt carbonyl clusters in solution.<sup>10</sup>

The NO + CO reaction was performed at reduced pressure ( $P_{\text{CO}} = 50$  Torr,  $P_{\text{NO}} = 50$  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<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub>, compared with those on conventional Pt/Al<sub>2</sub>O<sub>3</sub> (4 wt% Pt) catalysts. N<sub>2</sub>O was an intermediate in the CO + NO reaction and was subsequently converted to N<sub>2</sub> in the reaction on the samples (I) and (II). The conversion of CO + NO and selectivity for formation of N<sub>2</sub> were maintained for prolonged on-stream reactions of NO + CO (40 h) on these catalyst samples.

Upon exposure of [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup>/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<sub>12</sub> carbonyl cluster even at 298 K to give a trigonal intermediate 'Pt<sub>3</sub>(CO)<sub>6</sub>' (2112, 1896 and 1841 cm<sup>-1</sup>) and Pt(CO) (2110 cm<sup>-1</sup>) in forming N<sub>2</sub>O (2236 cm<sup>-1</sup>) and CO<sub>2</sub> (2353 cm<sup>-1</sup>) in the gas phase. Furthermore, it was found that [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup>/NaY was reversibly regenerated from the Pt carbonyl fragments such as Pt(CO) and Pt<sub>3</sub>(CO)<sub>6</sub> 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<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup>/NaY, N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> were catalytically formed at 323–473 K, with the original Pt<sub>12</sub> cluster framework being retained inside the zeolites.

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