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Ship-in-Bottle Synthesis of $[Pt_{15}(CO)_{30}]^{2-}$ Encapsulated in Ordered Hexagonal Mesoporous Channels of FSM-16 and Their Effective Catalysis in Water-Gas Shift Reaction

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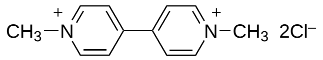
There are current interests in mesoporous materials such as MCM-41[1] and FSM(folded-sheet mesoporous material)-16[2] having honeycomb structures with ordered enormous channels of 20−100 Å diameters, which are larger than microporous cavities (6−13 Å) of conventional zeolites such as NaY, ALPO-5, and ZSM-5. They are potential hosts for the inclusion of bulky organic and inorganic species, thus opening up new applications for the design of tailored metal catalysts[3] accessible to larger substrates and the quantum dots/wires of chalcognites.[4] We have recently developed the concept of “ship-in-bottle” technique for the challenges in rational synthesis of uni- and bimetal carbonyl clusters such as $Rh_{6-x}Ir_x(CO)_{16}(x = 0-6)$,[5] $Ru_6(CO)_{18}^{2-}$,[6] and $[Pt_3(CO)_6]_n^{2-}$ (n = 3,4)[7] encapsulated in NaY and NaX zeolite micropores as the ultimate nanometer-size vesssels. They are useful for preparing discrete metal/alloy clusters (less than 10 Å size) which catalyze the alkane hydrogenolysis,[5] CO hydrogenation toward C_1-C_5 alcohols[8] and the olefin hydroformylation reaction.[9] This communication describes a novel “ship-in-bottle” synthesis of robust carbonyl clusters such as $[Pt_{15}(CO)_{30}]^{2-}$ uniformly encapsulated in the ordered mesoporous channels of FSM-16 which are thermally stabilized with organic cations such as R_4N^+(R = Me, Et, Bu, and Hex) and MV^{2+} (methyl viologen cation). They exhibited markedly higher catalytic activities for ^{13}CO exchange and water-gas shift reactions at ambient temperatures compared with Pt_9-Pt_{12} carbonyl clusters restricted by a NaY microporous constraint.

According to the published procedures,[2] the host FSM-16 was synthesized using a layered polysilicate (Kanemite; $NaHSi_2O_5$-$3H_2O$) and $C_{16}H_{33}NMe_3Cl$ as a micelle surfactant template, similar to MCM-41.[1] After calcination at 823 K, the resulting material (surface area, 950 m^2/g) presents well-defined hexagonal mesoporous channels (27.5 Å) with silanol groups (3745 cm^{-1}) which were identified by X-ray powder patterns in the low angle region (2θ = 2.26, 3.44, 4.50, and 5.90) and TEM techniques. A sample containing 5.0 mass% Pt was prepared by impregnation of FSM-16 with an aqueous solution of H_2PtCl_6. This sample was exposed to CO (200 Torr) in a closed circulating system by ramping the temperature from 300 to 323 K, resulting in the IR bands at 2188, 2149, and 2119 cm^{-1}, as presented in Figure 1 (a). From the analogy of the previously reported Pt carbonyl species,[10] the IR bands at 2188, 2149, and 2119 cm^{-1} can be ascribed to *cis*-$Pt(CO)_2Cl_2$ (2188 and 2148 cm^{-1}) and $Pt(CO)Cl_3$ (2121 cm^{-1}). The Pt carbonyls were converted by subsequent admission of H_2O vapor (15 Torr) onto the CO atmosphere to make an olive-green product (sample A) exhibiting a steady-state spectrum (Figure 1(b)) of carbonyl bands (ν_{CO} = 2086s and 1882m cm^{-1}) and UV−vis reflectance (λ_{max}; 452 and 805 nm). The final spectrum closely resembles that of $[Et_4N]_2[Pt_{15}(CO)_{30}]$ in MeOH (ν_{CO} = 2056s (terminal) and 1872m (bridged) cm^{-1}, λ_{max}; 408 and 697 nm) and crystal,[11] Attempts to extract the platinum carbonyl species from sample A with THF (tetrahydrofuran) and MeOH were unsuccessful but did occur with $[(Ph_3P)_2N]Cl$ in THF, which selectively gave an appreciable amount of $[(Ph_3P)_2N]_2[Pt_{15}(CO)_{30}]$ (ν_{CO} = 2056s and 1872m cm^{-1}; λ_{max}; 405 and 702 nm in THF). Accordingly, a tentative explanation suggests that $[Pt_{15}(CO)_{30}]^{2-}$ was uniformly formed in mesoporous channels of FSM-16 by the reductive carbonylation of H_2PtCl_6/FSM-16, which may react by the homogeneous synthesis in solution.[11]

It was found that $[Pt_{15}(CO)_{30}]^{2-}$ in FSM-16 (sample A) is relatively unstable, and evacuation of sample A at 10^{-4} Torr and 300−323 K led to an irreversible transformation due to partial removal of CO to give the brownish product (ν_{CO} = 2063s and 1820w cm^{-1}), which resembles those of the higher nuclearity Pt carbonyl clusters such as $[Pt_{24}(CO)_{48}H_x]^{2-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ (ν_{CO} = 2060−2043s and 1832−1820w cm^{-1}) in THF solution.[12] As presented in Figure 2, the electron micrograph of the evacuated sample A showed that platinum aggregates having a ca. 15 Å diameter, probably composed of 35−55 Pt atoms were uniformly distributed along the ordered mesoporous channels of FSM-16 crystals with a negligible formation of external particles.

On the other hand, the thermostable $[Pt_{15}(CO)_{30}]^{2-}$ in FSM-16 was successfully prepared using the FSM-16 which was coimpregnated with H_2PtCl_6 and quaternary alkyl ammonium salts (R_4NX;R = methyl, ethyl, butyl, and hexyl; X = Cl, Br, and OH) and methyl viologen chloride, $[MV^{2+}]Cl_2$; from each aqueous solution. The reductive carbonylation of each coimpregnated sample resulted in an olive-green product (UV−vis reflectance at 450 and 805 nm), showing the intense CO bands which appeared at 2075−2079s and 1875−1884m cm^{-1} relatively shifted to higher frequencies by varying the larger quaternary alkyl ammonium cations. It is worthy to note that those organic cations play a role in stabilizing the robust Pt_{15} carbonyl cluster dianion and their thermostabilities in the FSM-16 channels at 323−393 K decreased by varying the used quaternary ammonium cations (R_4N^+ and MV^{2+}) in the following order: ethyl > butyl > methyl > MV > hexyl ≫ non.



EXAFS measurements at the Pt L_{III} edge (11 562 eV) were carried out in the transmission mode at the BL-10B, Photon Factory at National Laboratory for High Energy Physics (KEK-PF) with a stored energy of 2.5 Gev and ring currents between 100 and 250 mA. The backscattering amplitude and phase-

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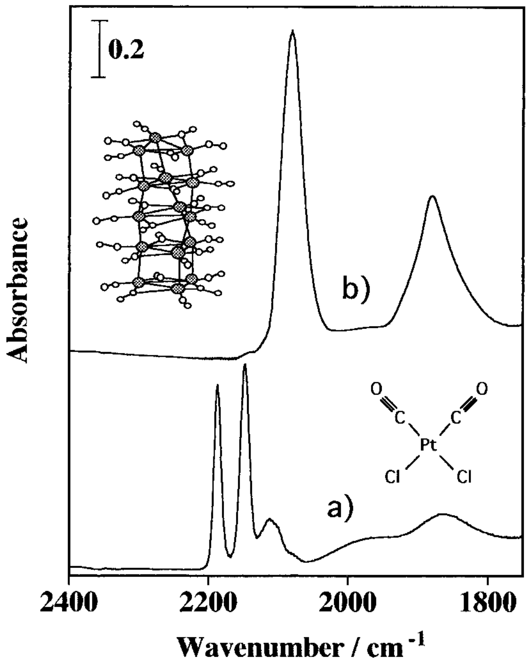

Figure 1. In-situ FTIR spectra in the reaction of H_2PtCl_6/FSM-16 with CO(200 Torr) at 323 K for 12 h (a) and with CO (200 Torr) + H_2O (15 Torr) at 323 K for 6 h (b).

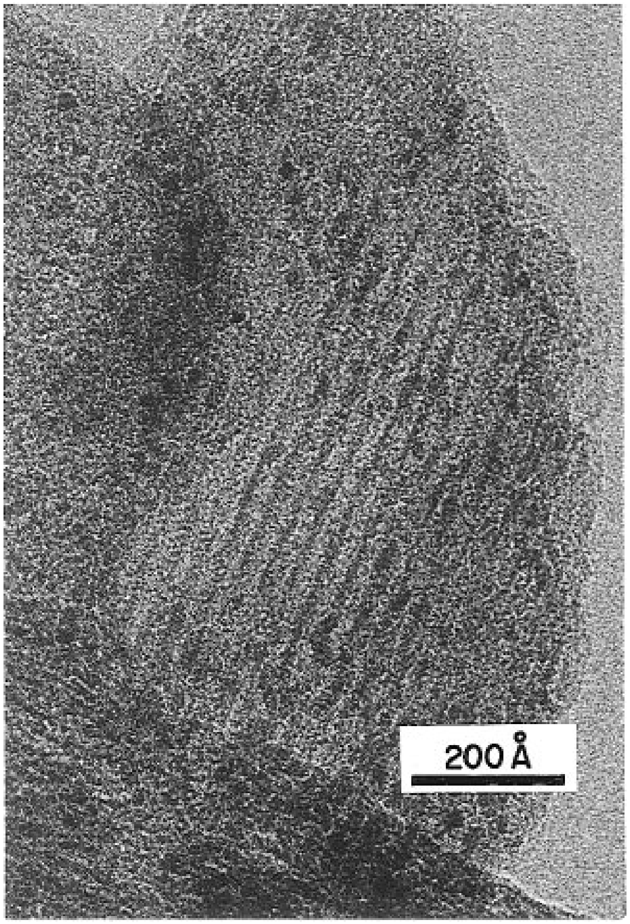

Figure 2. Transmission electron microgram of (a) $[Pt_{15}(CO)_{30}]^{2-}$/FSM-16 (sample A) after evacuation at 300−323 K for 2 h, where the speckles having sizes of 10−20 Å are uniformaly distributed in the mesoporous hexagonal channels (27.5 Å diameter) of FSM-16.

Table 1. Catalytic Performances in ^{13}CO Exchange and Water-Gas Shift Reaction (WGSR) on $[Pt_{15}(CO)_{30}]^{2-}$ Bound with Organic Cations in FSM-16, $[Pt_3(CO)_6]_n^{2-}$ ($n = 3,4$)/NaY and Pt/γ-Al_2O_3

Pt carbonyl clusters/ FSM-16 or NaY	^{13}CO exchange reaction k/min (300 K)[a]	WGSR k'/min(300 K)[b]
$[Pt_{15}(CO)_{30}]^{2-}[NEt_4]^+$/FSM-16	123	12
$[Pt_{15}(CO)_{30}]^{2-}[NBu_4]^+$/FSM-16		4.8
$[Pt_{15}(CO)_{30}]^{2-}[MV]^{2+}$/FSM-16		22
$[Pt_{12}(CO)_{24}]^{2-}$/NaY	7	0.42
$[Pt_9(CO)_{18}]^{2-}$/NaY	9	0.75
Pt/γ-Al_2O_3[c]		0.02

[a] ^{13}CO(100 Torr); TOF (mmol/Pt atom/min). [b] CO (200 Torr) + H_2O (15 Torr); TOF (CO_2) (mmol/Pt atom/min) X 10^{-2}. [c] The catalyst was prepared conventionally by H_2-reduction at 673 K for 2 h after H_2PtCl_6 impregnated on γ-Al_2O_3 (4 mass% Pt).

shift of Pt−Pt, Pt−CO were extracted from EXAFS spectra of Pt foil and $W(CO)_6$, respectively. EXAFS data for $[Pt_{15}(CO)_{30}]^{2-}$/NEt_4/FSM-16 (sample B), $[Pt_{12}(CO)_{24}]^{2-}$/NaY (sample C) prepared according to the published procedure[7] and $[NEt_4]_2[Pt_{15}(CO)_{30}]$ diluted in BN (boron nitride) as a reference (sample D) were obtained under a N_2 atmosphere at 300 K. The observed Pt L-edge shapes for samples B and C were similar to that of $[NEt_4]_2[Pt_{15}(CO)_{30}]$/BN (sample D) and EXAFS analysis of the neighboring Pt−Pt frameworks in terms of coordination number (N_c) and interatomic distances (R) provided direct evidence for the stoichiometric formation of trigonal prismatic $[Pt_3(CO)_6]_n^{2-}$ ($n = 4, 5$) cluster complexes within the FSM-16 channels and NaY cavities. It is of interest to find that for $[Pt_{15}(CO)_{30}]^{2-}$ encapsulated in FSM-16 (sample B) the average interatomic distances of Pt−Pt between adjacent triplatinum planes($R_2 = 3.08$ Å; $N_c^2 = 1.6$) are slightly enlongated, compared with that of $[NEt_4]_2[Pt_{15}(CO)_{30}]$/BN (sample D) ($R_2 = 3.07$ Å; $N_c^2 = 1.5$) and the X-ray analysis of $[PPN]_2[Pt_{15}(CO)_{30}]$ in crystal ($R_2 = 3.05$ Å; $N_c^2 = 1.5$).[11] In contrast, the inter-triplatinum distances of the Pt_{12} cluster frameworks in NaY micropores (sample C; $N_c^2 = 1.5$, $R_2 = 2.99$ Å) are fairly shorter ($\Delta R = 0.08$ Å) for that of $[PPN]_2[Pt_{12}(CO)_{30}]$/BN ($R_2 = 3.07$ Å; $N_c^2 = 1.5$) within the experimental error ($\Delta R = 0.02$ Å). The NMR study by Heaton et al.[13] on the structure of $[Pt_{15}(CO)_{30}]^{2-}$ in solution showed that the Pt_3 triangle was fluxionally rotated in the Pt_3 plane, which causes the wide distribution of the Pt−Pt distances of the inter-Pt_3 triangle planes. Hence, the slight elongation of the Pt−Pt distance of the inter-Pt_3 planes for sample B may be caused by the fluxional rotation of the Pt_3 triangle of the Pt_{15} carbonyl clusters (8 × 12.3 Å van der Waals diameter) in the enormous channels of FSM-16 (27.5 Å). In contrast, the Pt_{12} carbonyl clusters (8 × 10 Å rod) encapsulated in the NaY micropores may be frozen due to the intrazeolitic constraint (12 Å effective diameter).

The WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$) was performed at reduced pressure ($P_{CO} = 50$ Torr, $P_{H_2O} = 20$ Torr) using a closed circulating Pyrex glass reactor charged with the powdered samples of $[Pt_{15}(CO)_{30}][R_4N^+]$/FSM-16(R = Et and Bu), $[Pt_{15}(CO)_{30}][MV^{2+}]$/FSM-16, $[Pt_{12}(CO)_{24}]^{2-}$/NaY, and $[Pt_9(CO)_{18}]^{2-}$/NaY at 300−373 K. The products were analyzed by GC using Porapack Q (2m; 363 K) and MS-5A (1 m; 363 K) columns with a thermal conductivity detector. As shown in Table 1, $[Pt_{15}(CO)_{30}]^{2-}$ clusters with organic cations in FSM-16 exhibited remarkably higher activities (20−100 times) in the WGS reaction to form an equimolar mixture of CO_2 and H_2 than those on $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ in NaY and the conventional Pt/Al_2O_3 catalyst (4 mass% Pt). Moreover, it was demonstrated that the carbonyls of $[Pt_{15}(CO)_{30}]^{2-}$ in FSM-16 underwent facile isotopic exchange of ^{13}CO at 300 K. As shown in Table 1, the exchange rates in TOF varied upon the sorts of organic cations in FSM-16, whereas the carbonyl exchange of Pt_9 and Pt_{12} clusters in the NaY micropores proceeded very slowly. From this evidence, it is suggested that $[Pt_{15}(CO)_{30}]^{2-}$ entrapped in the ordered mesoporous channels of FSM-16 exhibits higher activities in the WGSR and ^{13}CO exchange reactions probably due to their flexible cluster frameworks and sufficient diffusibility of reactant gases compared with the Pt_9 and Pt_{12} carbonyl clusters which are restricted by a NaY micropore constraint.

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