A Robust Platinum Carbonyl Cluster Anion [Pt₃(CO)₆]₅²⁻ Encapsulated in an Ordered Mesoporous Channel of FSM-16: FTIR/EXAFS/TEM Characterization and Catalytic Performance in the Hydrogenation of Ethene and 1,3-Butadiene

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A robust trigonal prismatic cluster anion $[Pt_3(CO)_6]_5^{2-}$ ($\nu_{CO} = 2078$, 1878 cm⁻¹; $\lambda_{max} = 405$ and 702 nm; $R_1(\text{Pt}-\text{Pt}) = 2.68 \text{ Å} (\text{CN} = 2.0); R_2(\text{Pt}-\text{Pt}) = 3.08 \text{ Å} (\text{CN} = 1.5))$ is selectively synthesized in the ordered hexagonal channel of FSM-16 by the reductive carbonylation of $H_2PtCl_6/NR_4^+/FSM-16$ under a CO + H_2O atmosphere at 323 K. The Pt cluster anion extracted in THF solution by cation metathesis was identified as $[Pt_3(CO)_6]_5^{2-}$ by FTIR and UV-vis spectroscopic data. TEM observation showed that $[Pt_3(CO)_6]_5^{2-}$ was uniformly dispersed and aligned in the mesoporous channels of FSM-16. The Pt_{15} cluster anions formed in FSM-16 were relatively stabilized by the coimpregnated quaternary alkylammonium cations as NR_4^+ in the following order for the alkyl groups: butyl > ethyl > methyl, methyl viologen (MV) > hexyl \gg no countercations. The EXAFS and FTIR studies demonstrated that $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 was transformed by the controlled removal of CO at 300-343 K into the partially decarbonylated Pt₁₅ cluster (R₁(Pt-Pt) = 2.69 Å, CN = 2.2; $R_2(Pt-Pt) = 3.10$ Å, CN = 1.4). This sample showed IR spectra indicating a linear CO $(\nu_{\rm CO} = 2062 \text{ cm}^{-1})$ without a bridged one. The Pt carbonyl cluster was eventually converted by thermal evacuation exceeding 463 K to naked Pt particles (15 Å diameter; R(Pt-Pt) = 2.76 Å, CN = 7.8). The controlled removal of CO from $[Pt_3(CO)_{6-x}]_5^{2-}$ in FSM-16 by thermal evacuation at 300-423 K yields samples with marked catalaytic activities for hydrogenation of ethene and 1,3-butadiene at 300 K. 1,3-Butadiene is selectively hydrogenated to 1-butene on the partially decarbonylated Pt carbonyl clusters in FSM-16, whereas it is preferentially converted to *n*-butane on the naked Pt particles in FSM-16.

1. Introduction

Zeolites are aluminosilicate crystallites consisting of microporous cavities and channels of molecular dimensions (6-13)Å) with smaller windows. Such micropores can supply "a templating circumstance" for the selective synthesis of some bulky metal carbonyl clusters which fit into the interior cages as ultimate "nanometer-size reaction vessels". According to the analogy of a ship model in a bottle, an intrazeolitic preparation of metal complexes and clusters is referred to as a "ship-inbottle" synthesis.^{1,14} The metal ions and subcarbonyls in the microcavities of NaY and NaX zeolites were subsequently converted by the reductive carbonylation reactions with CO + H_2O or $CO + H_2$ to form metal carbonyl clusters such as $Rh_6(CO)_{16}^2$ [Pt₃(CO)₆]_n²⁻ (n = 3, 4),³⁻⁶ Pd₁₃(CO)_x,⁷ Ir₆(CO)₁₆,⁸ Ir₆(CO)₁₅^{2-,9} Rh_{6-x}Ir_x(CO)₁₆ (x = 0-6),¹⁰ Ru₆(CO)₁₈^{2-,11} and HRuCo₃(CO)₁₂;¹² these carbonyl cluster complexes are encapsulated in supercages of 13 Å diameter. The "ship-in-bottle" synthesis of homometallic and bimetallic clusters may open new opportunities for the rational design of tailoring metal catalysts having a uniform distribution of particle sizes and metal compositions.^{1,6} The resulting metal clusters in the micropores of NaY and NaX zeolites exhibit higher activities and catalytic stabilities for the water-gas-shift reaction, 4 NO + CO reaction, 5 alkane hydrogenolysis,¹⁴ olefin hydroformylation reaction,^{15,16} and CO hydrogenation to C_1-C_5 alcohols in comparison with conventional metal catalysts.^{13,18}

Recently, mesoporous molecular sieves such as MCM-41^{19,20} and FSM-16^{21,22} have been synthesized using different micelle surfactant templates. These materials consist of the ordered mesoporous channels of 20–100 Å diameter, which are much larger than those of the conventional zeolites such as ZSM-5, AlPO-5, and NaY. They are potential hosts for synthesizing bulky organometallic complexes²³ and metal particles which are accessible to larger substrates in the catalytic reactions. Additionally, they have been used for the templating fabrication of the quantum dots and wires of metals²⁴ and chalcogenides.²⁵

Chini type Pt carbonyl clusters such as $[Pt_3(CO)_6]_n^{2-}(n = 2-10)$ are synthsized by the reductive carbonylation of Pt salts such as H₂PtCl₆ and Pt(CO)Cl₃ in solution.³⁴ Gates et al.³⁹ have previously reported that a mixture of the Chini complexes was formed in the reaction of H₂PtCl₆ impregnated on MgO with CO and water. Furthermore, we have recently demonstrated that three-stacked ($[Pt_3(CO)_6]_3^{2-}$) and four-stacked ($[Pt_3(CO)_6]_4^{2-}$) clusters are selectively synthesized in the micropores of NaY by the reductive carbonylation of $[Pt(NH_3)_4]^{2+}/NaY^4$ and Pt^{2+}/NaY_5 respectively. However, owing to the size limitation of the zeolite micropores, so far greater than five-stacked clusters ($[Pt_3(CO)_6]_n^{2-}$) have not been synthesized by the ship-in-bottle technique. In this study, we extended the works for the intrazeolitic synthesis of larger Pt carbonyl clusters such as $[Pt_3(CO)_6]_n^{2-}$ ($n \ge 5$)) using the mesoporous channels of FSM-

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16 as a host material. The resulting Pt carbonyl cluster anions formed in FSM-16 were characterized by FTIR, UV-vis, and EXAFS spectroscopy. The structural transformation of Pt carbonyl clusters toward Pt particles has been also studied by EXAFS, TPD, and FTIR measurements and TEM observation during the controlled thermal evacuation of the Pt carbonyl clusters in FSM-16. The catalytic behaviors of the partially decarbonylated Pt cluster anions and Pt particles in FSM-16 are discussed for the hydrogenation of ethene and 1,3-butadiene in conjunction with their hydrogenation kinetics, activities, and selectivies, which are different from those of conventional metal catalysts.

2. Experimental and Procedures

2.1. Sample Preparation. The host FSM-16 was synthesized using a commercial-grade Kanemite as a layered aluminosilicate (SiO₂/Al₂O₃ = 320; Fe, below 0.02%, supplied by Hokkaido Soda Co. Ltd.) and C₁₆H₃₃NMe₃Cl as a surfactant template according to the published procedures.^{21,22} Kanemite was mixed with a water solution of $C_{16}H_{33}Me_3N^+Cl$ (0.143 mol L⁻¹, 280 mL; EP-Grade Tokyo Kasei Co. Ltd.) and was subsequently heated at 343 K for 3 h with vigorously stirring. The precipitated material was filtered out and dispersed into 500 mL of water; this was heated at 343 K for 3 h, keeping a pH value of 8.5. After washing with water to remove residual Na⁺, the resulting materal of FSM-16 thus prepared was calcined to remove the organic template under an O₂ flow (25 mL/min) at 823 K for 14 h. The N₂-adsorption isotherm showed that the calcined FSM-16 powder has a surface area of 950 m^2/g and a pore size of 27 Å. It consists of the well-defined hexagonal mesoporous channels (27.5 Å diameter) which are characterized by X-ray powder patterns in the low-angle region $(2\theta = 2.26, 3.44, 4.50 \text{ and } 5.90)$ and by TEM observation.

The powdered FSM-16 was impregnated with a quaternary alkylammonium salt NR₄X (R = Me, Et, Bu, Hex; X = Br, Cl, OH; 99% purity, purchased from Nakarai Co. Ltd.) from an aqueous solution, and the impregnated material was dried by vacuum evaporation; this is referred to as NR₄X/FSM-16. The loading amount of NR₄X in FSM-16 was 1.37×10^{-4} mol/g_{cat}. The 5.0 mass wt % Pt samples of H₂PtCl₆/NR₄X/FSM-16 were prepared by the conventional impregnation of NR₄X/FSM-16 with an aqueous solution of H₂PtCl₆ (99%, Wako Co. Ltd.). The sample of H₂PtCl₆/FSM-16 without alkylammonium cation was similarly prepared by the impregnation of FSM-16 with H₂PtCl₆. Each powdered sample was exposed to 26.7 kPa of CO (99.9999%, Takachiho Co. Ltd.) and/or a mixture of CO (26.7 kPa) and H₂O (2.7 kPa) in a closed circulating reactor for 5-15 h by ramping the temperature from 300 to 323 K. The Chini-type Pt carbonyl cluster anions were independently synthesized from H₂PtCl₆ in an alkaline solution of methanol and isolated as $[NEt_4]_2[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4, and 5) according to the literature method.³² The reference samples of $[Pt_3(CO)_6]_3^{2-1}$ and $[Pt_3(CO)_6]_4^{2-}$ encapsulated in NaY zeolite were prepared by the similar reductive carbonylation of $[Pt(NH_3)_4]^{2+}/NaY$ and Pt²⁺/NaY according to the "ship-in-bottle technique".^{4,5}

2.2. IR and UV–Vis Spectroscopy and TEM Observation. The impregnated samples such as $H_2PtCl_6/FSM-16$ or $H_2PtCl_6/NR_4X/FSM-16$ were pressed into a self-supporting wafer (1.5 mm i.d., 12–20 mg/cm²) with pressure of 300 kg f/cm². The wafer was mounted in an in situ IR cell equipped with CaF₂ windows. IR spectra were recorded using a Fourier transform infrared spectrometer (Shimadzu FTIR 8100 M) with the resolution of 2 cm⁻¹ and co-accumulation of 100 interferograms to improve the signal/noise ratios of the IR spectra.

 TABLE 1: Crystallographic Data Characterizing the

 Reference Compounds and Fourier Transform Range Used

 in the EXAFS Analysis^a

	crystallographic data			Fourier transform		
samples	shell	CN	<i>R</i> /Å	$\Delta k/\text{\AA}^{-1}$	$\Delta R/\text{\AA}$	n
Pt foil ^b	$Pt-Pt^d$	12	2.7742	3.5-18.0	1.9-3.0	3
$W(CO)_6^c$	$W-C^e$	6	2.063	3.5 - 18.0	1.2 - 2.1	3
	W-O ^f	6	3.206	3.5 - 18.0	1.2 - 2.1	3

^{*a*} Notation: CN, coordination number for absorber–backscatterer pair; *R*, absorber–backscatterer distance; Δk , limits used for forward Fourier transformation; ΔR , limits used for shell isolation (*R* is distance); *n*, power of *k* used for Fourier transformation. ^{*b*} From ref 28. ^{*c*} From ref 29. ^{*d*} Reference for Pt–Pt. ^{*e*} Reference for Pt–C. ^{*f*} Reference for Pt–O.

The diffuse reflectance UV-vis spectra for the powdered sample of Pt carbonyl complexes formed in FSM-16 charged in a quartz-plated cell (1 mm thickness) and the absorption spectra of the extracted species in solution were recorded using a Shimadzu UV-vis spectrometer under nitrogen and CO atmosphere at 300 K.

Transmission electron micrographs were taken using a JEOL JEM-2000EX at an accelerating voltage of 200 kV. The power samples were dispersed on a carbon foil with a microgrid from the suspended solution of ethanol and/or acetone. The TEM images were observed with minimum damage to the structures and morphology of the samples by the electron beams.

2.3. EXAFS Measurement and Analysis. The powdered and disk samples were charged under N2 in an in-situ EXAFS cell with a Kapton film window (500 μ m) to prevent exposure of the sample to air. Pt-L_{III} edge (11 562 eV) EXAFS (extended X-ray absorption fine structure) spectra were measured on BL-10B at the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF; Tsukuba, Japan). The energy and the current of the electron (or positron) were 2.5 GeV and 250 mA, respectively. The Si(311) channel cut monochromator was used. The transmission X-ray absorption spectrum was detected using the ion chambers filled with a mixture gas of Ar and N₂. The spectra were analyzed by a computer program supplied by Technos Co. Ltd.²⁷ The background absorption was subtracted using a McMaster function, and the baseline was estimated by the cubic sprain method. The k^3 -weighted EXAFS function was Fourier transformed into *R*-space using the *k*-range from 3.5 to 18 Å⁻¹. The Hanning function used was $\delta = 0.5$ Å⁻¹. The phase shift was not corrected for the preliminary Fourier transformation. The inverse Fourier transform was calculated to obtain a filtered EXAFS function. The R range of an inverse Fourier transformation was taken from 1.09 to 3.31 Å. The Hanning function of $\Delta = 0.05$ Å was used as a window function. The filtered EXAFS function of the sample is analyzed by the curve-fitting method using the following equation:²⁸

$$\chi_{\rm T}(k) = \sum_{i} (N_i [f_i(k)] [S_i(k)]) / (kr_i^2) \sin(2kr_i + \phi_i(k))$$
$$\exp(-2\sigma^2 k^2)$$
(1)

where $\chi_T(k)$, N_i , r, σ , $f_i(k)$, $S_i(k)$, and $\phi_i(k)$ are the calculated EXAFS function, the coordination number, the interatomic distance, the Debye–Waller factor, the backscattering amplitude, the reduction factor, and the phase shift function, respectively. The fitting EXAFS parameters of the sample were determined for N_i and r_i to minimize σ_i and for the correction of threshold energy (ΔE_0). The backscattering amplitudes and phase shift functions of the Pt–Pt, Pt–C, and Pt–O (of Pt–CO) bonds were calculated using those of Pt foil (Pt–Pt)²⁸ and W(CO)₆

(Pt–C and Pt–O).²⁹ Table 1 presents crystallographic data and the Fourier transform range of the some reference compounds used in the EXAFS analysis. Although the atomic weight of W atoms is four times smaller than that of platinum, $W(CO)_6$ is taken as a good reference compound because of the narrow distribution of W–O(CO) distances. The effect of multiple scattering can be included by using the backscattering amplitude and phase shift function of W(CO)₆. To evaluate the justification of a curve-fitting, the residual factor *R* is defined and used in the following equation:

$$R = \sqrt{\frac{\sum_{j=j_{s}}^{j_{e}} |k_{j}^{n} \chi_{obs}(k_{j}) - k_{j}^{n} \chi_{F}(k_{j})|^{2}}{\sum_{j=j_{s}}^{j_{e}} |k_{j}^{n} \chi_{obs}(k_{j})|^{2}}}$$
(2)

where χ_{obs} is a Fourier filtered EXAFS function, χ_F is a calculated EXAFS function using equation 1, *j* is an index of data points, k_j is the *k* value of the *j*th data, and j_s and j_e are initial and final data points of the curve-fitting. The EXAFS parameters for discussion were fixed around the optimum value, and the residual factor *R* was calculated to offer the optimum values for the other parameters. The real value was estimated using a residual factor *R* which is smaller than twice the optimum value.

2.4. Catalytic Reactions and TPD Measurements. The catalytic reactions were carried out using a closed-circulating system equipped with a Pyrex-glass tubing reactor, which mounted each sample of 50 mg. The hydrogenation of ethene and 1,3-butadiene proceeded at the temperatures of 278-303 K. The pressures of reactant gases were $p(H_2) = p(olefin) = 13.3$ kPa, where olefins are ethene and 1,3-butadiene. The dead volume of the reactor was 250 cm³. Products were analyzed by a Shimadzu 8A gas chromatograph (gc) with a TCD (thermal conductive detector) using the columns VZ-10 (4 m, 313 K) and VZ-7 (6m, 300 K) for ethene, ethane, 1- and *cis/trans*-2-butenes, and 1,3-butadiene, respectively. Helium was used as a carrier gas (30 mL/min) for the gc analysis.

TPD (temperature programmed decomposition) measurements using a mass spectrometer (ANELVA-100) were conducted to study the reactivities of the Pt carbonyl clusters in FSM-16.

3. Results and Discussion

3.1. Synthesis and Characterization of Pt Carbonyl Complexes in FSM-16 by the Reductive Carbonylation of H₂PtCl₆/NEt₄Cl/FSM-16. A sample of H₂PtCl₆/NEt₄Cl/FSM-16 contaning 5.0 mass % Pt was prepared by a coimpregnation of NEt₄Cl/FSM-16 and H₂PtCl₆. This sample was exposed to CO and/or a saturated water vapor in a closed circulating system by ramping the temperature from 300 to 323 K. After the exposure of H2PtCl6 in NEt4Cl/FSM-16 to CO the reaction was measured by in-situ IR spectroscopy. The CO bands at 2188, 2149, and 2119 cm⁻¹ were gradually developed as shown in Figure 1a,b. From the analogy of the reference Pt carbonyl species,³¹ the IR bands at 2188, 2149, and 2119 cm⁻¹ can be assignable to cis-Pt(CO)₂Cl₂ (2188 and 2148 cm⁻¹) and Pt(CO)- Cl_3 (2121 cm⁻¹), respectively. The mono-Pt carbonyls were subsequently converted by the admission of a mixture of CO (26.7 kPa) and H₂O (2.7 kPa), leading to the homogeneous formation of an olive-green product. The final IR spectrum of



Figure 1. IR spectra of carbonyl species formed by the reductive carbonylation of $H_2PtCl_6/NEt_4Cl/FSM-16$. The $H_2PtCl_6/NEt_4Cl/FSM-16$ sample was exposed to CO (p(CO) = 26.6 kPa) at 323 K for (a) 1 h and (b) 3 h. Then the sample was exposed to CO + H_2O (p(CO) = 26.6 kPa, $p(H_2O) = 2.0 \text{ kPa}$) at 323 K for (c) 1 h, (d) 3 h, (e) 12 h, and (f) 24 h. The background IR absorption spectrum of $H_2PtCl_6/NEt_4Cl/FSM-16$ was subtracted from each spectrum recorded after the reductive carbonylation of the sample.

TABLE 2: Wavenumber of v(CO) of Pt Carbonyl Clusters

Pt carbonyl clusters	NR ₄ X/FSM-16 or NaY	$ \frac{\nu(\text{CO})_{\text{terminal}}}{\text{cm}^{-1}} $	$\nu({ m CO})_{ m bridge}/$ ${ m cm}^{-1}$
[Pt ₃ (CO) ₆] ₅ ^{2- a}	FSM-16	2086	1882
	Me ₄ NCl/FSM-16	2075	1877
	Et ₄ NCl/FSM-16	2075	1875
	Et ₄ NOH/FSM-16	2076	1879
	Bu ₄ NCl/FSM-16	2070	1878
	Bu ₄ NOH/FSM-16	2076	1881
	He ₄ NBr/FSM-16	2079	1884
	MVCl ₂ /FSM-16	2074	1882
$[Pt_3(CO)_6]_4^{2-b}$	NaY	2080	1824
$[Pt_3(CO)_6]_3^{2-b}$	NaY	2056	1798
$[Pt_3(CO)_6]_5^{2-c}$	in solution (THF)	2055	1870
$[Pt_3(CO)_6]_4^{2-c}$	in solution (THF)	2045	1860

^{*a*} This work. ^{*b*} From refs 4 and 5. ^{*c*} From ref 32.

the sample consists of two intense bands of the linear CO at 2079 and bridging CO at 1880 cm⁻¹ as shown in Figure 1c-f. As it was previously reported,²⁶ an olive-green sample was similarly formed by the reductive carbonylation of H₂PtCl₆// FSM-16 with CO + H₂O at 300-323K. The resulting sample of Pt carbonyl cluster anions showed two intense IR carbonyl bands at 2086s and 1882 m cm⁻¹. The CO bands observed in the sample of H₂PtCl₆/NEt₄Cl/FSM-16 after the prolonged reaction closely resemble those of the Chini-type Pt carbonyl clusters such as $[Et_4N]_2[Pt_3(CO)_6]_n$, where n = 3-5 in crystal and solution,³² and $[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4) in NaY,^{4,5} although the band positions of linear and bridging CO are relatively shifted to lower frequencies, as presented in Table 2.

The attempts to extract the Pt carbonyl species from the resulting sample of $H_2PtCl_6/NEt_4Cl/FSM-16$ after reductive carbonylation was conducted using THF (tetrahydrofuran) and MeOH as a polar solvent were unsuccessful. By contrast, the greenish-blue complex was extracted from the sample under

N₂ atmosphere by cation metathesis with a quaternary alkylammonium salt in THF and MeOH. Figure 2 shows the IR spectrum of Pt carbonyl cluster complexes (Figure 2a) which were extracted using [(Ph₃P)₂N]Cl in THF solution from the sample of H₂PtCl₆/NEt₄Cl/FSM-16 after reductive carbonylation, comparing with that of [NEt₄]₂[Pt₃(CO)₆]₅ in MeOH (Figure 2b) (2056 vs, 1896 w, 1873 s, and 1848 w cm⁻¹). It was found that the IR spectrum of the extracted sample (2054 vs for linear CO and 1896 w, 1872 s, and 1845 w cm^{-1} for bridging CO) is in good agreement with that of a five-stacked [Pt₃(CO)₆]₅ anion only excepting for the minor shoulder bands at 2046 and 1860 cm^{-1} . The weak shoulder bands at 2046 and 1860 cm^{-1} are reasonably assigned to a smaller Chini Pt cluster anion such as $[Pt_3(CO)_6]_4^{2-}$, which was a minor byproduct in the reductive carbonylation of H₂PtCl₆ in FSM-16. The UV-vis absorption spectrum of the extracted sample in THF (Figure 3a) was observed at 405 and 702 nm, which resembles that of $[Pt_3(CO)_6]_5^{2-}$ in MeOH (Figure 3b; $\lambda_{max} = 408$ and 697 nm).³⁴ The IR carbonyl bands and UV-vis spectra of the family of Chini-type complexes $[Pt_3(CO)_6]_n^{2-}$ (n = 2-10) in solution depend basically on the size of Pt cluster dianions. In comparison with the characteristic UV-vis bands at 367, 422, 506, and 562 nm for $[Pt_3(CO)_6]_3^{2-}$ and those at 394, 513, and 620 nm for $[Pt_3(CO)_6]_4^{2-}$, respectively, the extracted species is assigned to $[Pt_3(CO)_6]_5^{2-}$ in THF solution. Accordingly, the IR and UV-vis data as shown in Figures 1-3 and Table 2 reasonably suggest that [Pt₃(CO)₆]₅²⁻ was homogeneously formed in the mesoporous channel of FSM-16 by the reductive carbonylation of H2PtCl6/NEt4Cl/FSM-16, similarly in solution, as follows:

$$H_2PtCl_6 + 3CO + H_2O → cis-Pt(CO)_2Cl_2 + CO_2 + 4HCl$$

(3n)cis-Pt(CO)_2Cl_2 + (3n + 1)H_2O + (6n)HCl +
(3n + 1)CO_2 → H_2[Pt_3(CO)_6]_5 + (6n)HCl + (3n + 1)CO_2

In the first stage of the cluster formation, the preadsorbed water in H₂PtCl₆/FSM-16 was consumed for the reduction of H₂PtCl₆ with CO to form *cis*-Pt(CO)₂Cl₂ with a small amount of Pt(CO)Cl₃. As shown in Figure 1, it is suggested that an excess amount of water with CO is enough to promote the watergas shift reaction and the successive conversion of cis- $Pt(CO)_2Cl_2$ to $[Pt_3(CO)_6]_5^{2-}$ in the channels of FSM-16. The differences in the positions of the CO bands (shifting to higher frequency $\Delta \nu = 18-8 \text{ cm}^{-1}$ for the sample of $[Pt_3(CO)_6]_5^{2-1}$ encapsulated in FSM-16, compared with those in THF solution, may be explained due to the interaction of Pt cluster anions^{4,5} with the acidic sites such as protons and Al³⁺ on the internal wall of FSM-16 (Si/Al = 320), similarly for $[Pt_3(CO)_6]_n^{2-}$ (n = 3 and 4) in NaY.^{4,5} There is a similar band shift and difference for the relative peak intensity in the reflectance UVvis spectrum for the dark-brownish powdered sample of [Pt₃(CO)₆]₅²⁻ encapsulated in FSM-16, compared with the absorption spectrum of the green solution of the extracted species in THF (Figure 3a). Nevertheless, it is interesting to find that the dark-brownish sample ($\lambda_{max} = 261$ (w), 444 (s) and 760 (w) nm) changed reversibly to a dark-green one (λ_{max} = 405 (s) and 705 (m) nm) by the exposure of THF, which resembles that of $[Pt_3(CO)_6]_5^{2-}$ in MeOH solution (Figure 3b). The difference in the reflectance UV-vis spectrum of the dried sample may be caused by an assembling of Pt cluster anions in the ordered mesoporous channels of FSM-16 like the darkbrownish solid/crystal of the corresponding Pt₁₅ cluster anion salt. According to the FTIR and UV-vis data obtained in this



Figure 2. IR spectra of (a) Pt carbonyl species extracted with TPP-(Ph₃P)₂NCl in THF from the sample C of H₂PtCl₆/NEt₄Cl/FSM-16 after the reductive carbonylation at 323 K and (b) the reference [NEt₄]₂[Pt₃(CO)₆]₅²⁻ in MeOH.



Figure 3. UV-vis spectra of (a) Pt carbonyl species extracted with $(Ph_3P)_2NCl$ in THF from the sample C of $H_2PtCl_6/NEt_4Cl/FSM-16$ after the reductive carbonylation at 323 K and (b) the reference $[NEt_4]_2[Pt_3(CO)_6]_5^{2-}$ in MeOH solution.

study, it is suggested that a robust $[Pt_3(CO)_6]_5^{2-}$ is formed by the reductive carbonylation of H_2PtCl_6 in the mesoporous channels of FSM-16. The Pt_{15} cluster anion is accommodated with the alkylammonium cations in FSM-16.

3.2. EXAFS Characterization. EXAFS measurements were conducted to obtain direct information about the structures of the Pt carbonyl clusters synthesized in FSM-16. Figure 4 shows the Fourier transforms of k^3 -weighted EXAFS of [NEt₄]₂-[Pt₃(CO)₆]₅/BN (sample A), [Pt₃(CO)₆]₄²⁻/NaY (sample B), and [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 (sample C). Figure 5 shows the EXAFS spectra of each sample as presented in Figure 4. The backscattering amplitude and phase shift of Pt-Pt and Pt-CO were extracted from the EXAFS spectra of Pt foil and W(CO)₆, respectively. It was interesting to find that the observed Pt L-edge FT patterns of samples B and C were similar to that of the reference sample of [NEt₄]₂[Pt₃(CO)₆]₅ diluted in boron nitride (sample A). The *R*-range of 1.09–3.31 Å in the spectra of Figure 5 was inverse Fourier transformed, which was reasonably fitted by five shells, consisting of two Pt-Pt



Figure 4. Fourier transforms of k^3 -weighted EXAFS of (a) [NEt₄]₂-[Pt₃(CO)₆]₅/BN (sample A), (b) [Pt₃(CO)₆]₄²⁻/NaY (sample B), and (c) [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 (sample C).



Figure 5. k^3 -weighted EXAFS spectra of (a) [NEt₄]₂[Pt₃(CO)₆]₅/BN (sample A), (b) [Pt₃(CO)₆]₄²⁻/NaY(sample B), and (c) [Pt₃(CO)₆]₅^{2-/} NEt₄/FSM-16 (sample C) in the Fourier transformed *k* range of 3.5–18 Å⁻¹.

contributions (Pt–Pt contribution in the Pt₃ triangle and between the triangles), two Pt–C contributions (terminal and bridge CO), and one Pt–O contribution. Figure 6 shows the results of the curve-fitting analysis. The Fourier transform of the filtered k^3 weighted EXAFS for the sample of [Pt₃(CO)₆]₅^{2–}/NEt₄Cl/FSM-16 is in a good agreement with that of the curve-fitting.



Figure 6. Fourier filtered k^3 -weighted EXAFS spectrum (solid line) and their curve fittings (dotted line) for the Pt–Pt, Pt–C, and Pt–O shells of $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ (sample C) in the Fourier transformed *k* range of 4–14 Å⁻¹.

TABLE 3: Structural Parameters of Platinum Clusters Derived by Pt L_{III}-Edge EXAFS

	•	0			
shell	CN	<i>R</i> /Å	$\Delta E_0/\mathrm{eV}$	$\Delta\sigma^2/10^{-3}{ m \AA}^2$	residual (%)
$[NEt_4]_2[Pt_3(CO)_6]_5$					
Pt-Pt	2.1	2.68	6.5	-1.1	7.5
Pt-Pt	1.5	3.07	-8.5	5.8	
Pt-C(b)	1.5	2.10	0.4	2.0	
Pt-C(t)	1.0	1.89	-5.9	1.3	
Pt-O	1.0	2.99	4.6	4.5	
		П	$Pt_3(CO)_6]_4^{2-1}$	/NaY	
Pt-Pt	2.2	2.67	6.5	-1.6	12.2
Pt-Pt	1.4	2.99	-8.5	7.4	
Pt-C(b)	1.6	2.14	0.4	2.0	
Pt-C(t)	0.9	1.99	-5.8	0.9	
Pt-O	1.0	2.99	-4.6	1.3	
[Pt ₃ (CO) ₆] ₅ ²⁻ /NEt ₄ Cl/FSM-16					
Pt-Pt	2.3	2.68	3.7	-0.7	9.6
Pt-Pt	1.7	3.08	-6.4	7.0	
Pt-C(b)	2.2	2.08	-7.6	5.8	
Pt-C(t)	1.3	1.90	-10.0	2.6	
Pt-O	1.0	3.01	-2.3	3.0	

The number of independent parameters is determined by the following equation (Nyquist law):³⁰

$$N_{\rm max} = 2(\Delta k)(\Delta R)/(\pi + 1) \tag{3}$$

In this study, with Δk and ΔR being 14.5 Å⁻¹ and 2.22 Å, respectively, N_{max} is calculated to be 12. Table 2 shows the coordination number (CN), interatomic distance (R), correction of threshold energy (ΔE_0), and difference of Debye–Waller factor ($\Delta\sigma^2$) from the synthesized samples and reference compounds which are determined by the curve-fitting analysis of EXAFS spectra. The experimental errors in the Pt-Pt distance and CN were estimated as 0.02 Å and 0.08 for Pt-Pt, and those for Pt-C and Pt-O were estimated as 0.05 Å and 0.2, respectively. The Chini-type complexes $Pt_3(CO)_6]_n^{2-}$ are composed of Pt₃(CO)₆ triangular units which are stacked together to form trigonal prismatic Pt cluster frameworks, as depicted in Table 3. According to the X-ray crystal analysis, the cross section of Pt₃(CO)₆ units is about 8 Å in diameter and the interfacial distances of "Pt₃(CO)₆" units are varied from 3.08 to 3.10 Å for [Pt₃(CO)₆]_{n^{2-}} (n = 3-5).³⁴ As summerized in Table 3, the observed intra-Pt-Pt atomic distrance ($R_1 =$ 2.68 Å) and interfacial distances between adjacent triplatinum plane ($R_2 = 3.08$ Å) for the synthesized sample of [Pt₃(CO)₆]₅^{2-/} NEt₄Cl/FSM-16 (sample C) are in a good agreement with those of the reference $[NEt_4]_2[Pt_3(CO)_6]_5$ in BN (sample A) ($R_1 =$ 2.68 Å; $R_2 = 3.07$ Å in the X-ray analysis) within experimental



Figure 7. Transmission electron micrograph of $[Pt_3(CO)_6]_5^{2-}/NEt_4-Cl/FSM-16$ (sample C).

error (0.02 Å). In fact, the EXAFS parameters of the Pt-Pt interatomic distances and CN were determined in good accuracy based on the Debye factor ($\Delta \sigma^2$) and *R* factor of less than 10%. By contrast, as shown in Table 3, it is worthy to note that, for [Pt₃(CO)₆]₄²⁻/NaY (sample B), the Pt-Pt distance of an inter-Pt₃ triangle was substantially shorter (R(Pt-Pt) = 2.99 Å) than that of the reference compound $[NEt_4]_2[Pt_3(CO)_6]_5$ in BN (R_2 = 3.07 Å) and $[Pt_3(CO)_6]_5^{2-}$ synthesized in the mesoprous FSM-16 ($R_1 = 2.68$ Å; $R_2 = 3.08$ Å). This may be caused by the confining effect due to the intrazeolitic constraint in the microcavity of NaY (13 Å in diameter). On the contrary, the mesoporous channels of FSM-16 are large enough (28 Å in diameter) to accommodate Pt15 carbonyl clusters in the channel with negligible structural distortion. Heaton et al.³⁶ studied by the ¹⁹⁵Pt NMR technique the structure of $[Pt_3(CO)_6]_5^{2-}$ in solution and demonstrated that the Pt₃ triangle was fluxionally rotated in the Pt₃ plane of the trigonal prismatic framework, which causes the wide distribution of the Pt-Pt interatomic distances of the cluster frameworks. Accordingly, it is suggested that the slight elongation of the Pt-Pt interatomic distance in the [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 may be associated with the fluxional rotation of the $[Pt_3(CO)_6]_5^{2-}$ anions (8 × 12 Å van der Waals diameter) in the mesoporous channels of FSM-16 (27.5 Å).

To elucidate the location of the $[Pt_3(CO)_6]_5^{2-}$ cluster anions in the mesoporous channel of FSM-16, a transmission electron micrograph has been determined for the sample of $[Pt_3(CO)_6]_5^{2-1}$ NEt₄Cl/FSM-16. Figure 7 shows a TEM picture of [Pt₃(CO)₆]₅²⁻ clusters in NEt₄Cl/FSM-16. It was found by close observation of the TEM picture that the Pt clusters as small speckles of 10-15 Å size were uniformly scattered and aligned in the ordered channel of FSM-16. The relatively large particles of 20 Å may be induced by the exposure of the electron beams under the TEM observation. Nevertheless, no Pt particles were observed at the external surface of the FSM-16 channel. Moreover, it was demonstrated by TEM observation that the Pt carbonyl cluster anions such as [NEt₄]₂[Pt₃(CO)₆]₅ were difficultly introduced inside the mesoporous channels of FSM-16 from the THF solution. Most of the Pt carbonyl cluster anions preferentially agglomerated as large particles and rods of more than 100 Å diameter, which were deposited on the external surface of FSM-16. According to the EXAFS and TEM studies, it was found that $[Pt_3(CO)_6]_5^{2-}$ cluster anions are formed uniformly by the reductive carbonylation of H₂PtCl₆ in FSM-16, which were encapsulated in the ordered channel of FSM-16.

3.3. Thermal Stability of $[Pt_3(CO)_6]_5^{2-}$ with Quaternary Alkylammonium in FSM-16. As it was previously reported,²⁶ an olive-green Pt15 carbonyl cluster anion was formed similarly by the reductive carbonylation of H₂PtCl₆/FSM-16 without any quaternary alkylammonium cation under $CO + H_2O$ atmosphere, whereas the Pt cluster anion is readily decomposed by evacuation even at 300-323 K. This is caused by the irreversible transformation due to the successive removal of CO, resulting in a brownish product (2063 s and 1820 w cm^{-1}). Its IR spectrum resembled those of higher nuclear Pt carbonyl clusters such as $[Pt_{55}(CO)_x]^{n-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ (2060–2043 s and 1832–1820 w cm⁻¹) in THF solution.³⁵ By contrast, it was demonstrated that a thermostable $[Pt_{15}(CO)_{30}]^{2-}$ was successfully prepared using the modified FSM-16 as a host which was coimpregnated with the quaternary ethylammonium salts used in the present work. As shown in Figure 1, each coimpregnated sample of H₂PtCl₆/NR₄Cl/FSM-16 ($R = CH_3$, C_2H_5 , C_4H_9 , methyl viologen (MV), and C_6H_{13}) was converted by reductive carbonylation to form an olive-green product, showing the intense IR carbonyl bands characteristic of linear and bridging carbonyls which appear around 2075-2079 (s) and 1870-1884 (m) cm⁻¹, respectively. Table 2 summerizes the IR data for CO bands for Pt₁₅ carbonyl clusters in FSM-16, without and in the presence of various countercations NR₄Cl. The linear and bridging CO bands of $[Pt_{15}(CO)_{30}]^{2-}$ in FSM-16 relatively shifted to higher frequencies by varying the larger quaternary alkylammonium cations. The red-shift of CO bands is possibly due to the electronic interaction of Pt carbonyl anions with the countercations. In particular, both CO bands of the Pt15 carbonyl cluster anions formed in FSM-16 without a quaternary alkylammonium cation shift to much higher frequencies($\Delta \nu$ (CO) = 28–10 cm⁻¹). These frequency shifts are observed for the formation of contact ion pairs between the Pt carbonyl anions and acidic protons located on the silicate wall of FSM-16. The thermostability of $[Pt_3(CO)_6]_n^{2-}$ formed in FSM-16 was studied with the change of IR spectra before and after the thermal evacuation for 1 h by ramping the temperature 323-363 K. It was found that the Pt carbonyl clusters in FSM-16 without the countercations are readily transformed to higher nuclear carbonyl clusters by removal of CO at 300 K. On the other hand, the samples of $[Pt_3(CO)_6]_n^{2-1}$ with the bulky countercations such as NBu₄ and NEt₄ are thermostable up to the higher temperatures above 343 K. The order of thermal stability for [Pt₃(CO)₆]₅²⁻/NR₄/FSM-16 was measured by TPD (temperature-programmed decomposition) studies, in terms of the temperatures to start the cluster decomposition owing to the removal of CO, as follows:

butyl > ethyl > methyl, methyl viologen (MV) \gg hexyl > no countercation

This order of the cluster stability depends on the size of NR₄ cations used, which is consistent with that of the carbonyl frequency shift of $[Pt_3(CO)_6]_5^{2-}$ as shown in Table 2. This implies that a Pt carbonyl cluster anion is protected with NR₄ cations from the strong acidic protons on the hydrophobic channels of FSM-16. The tetrahexylammonium cation as an exception is possibly not accessible to the Pt carbonyl cluster anions formed in the mesoporous channels of FSM-16 (28 Å) owing to its size limitation.

3.4. Cluster Transformation of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/



Figure 8. IR spectra of $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ (sample C) after the thermal evacuation for 1 h at various temperatures (a) 300 K, (b) 323 K, (c) 343 K, (d) 373 K, (e) 423 K, (f) 473 K, and (g) 523 K, respectively.

FSM-16. It was demonstrated by the in-situ FTIR and EXAFS observation that the thermostable [Pt15(CO)30]²⁻/Et4NCl/FSM-16 (2075 s and 1875 m cm⁻¹) was gradually transformed by evacuation at 10^{-4} Torr by ramping the temperature from 300 to 343 K, resulting in a partially decarbonylated species which showed the characteristic CO IR bands (2060 s and 1870 vw cm⁻¹). Figure 8 represents the change of IR spectra of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 by the thermal evacuation at various temperatures. When the sample was evacuated at 323 K, a band intensity of bridging CO preferrentially decreased and eventually disappeared, compared with those of terminal CO. The linear CO band was relatively enhanced and broadened. In addition, the peak position of linear CO shifted to lower frequencies around 2062 cm⁻¹ by the prolonged thermal evacuation. By the ramping of temperatures above 523 K, the terminal CO gradually decreased and eventually disappeared. The results suggest that the bridging CO of $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 was partially switched to the linear one by controlled thermal evacuation, which was followed with a subsequent removal of the linear CO. Both CO bands characteristic of $[Pt_3(CO)_6]_5^{2-}$ were not regenerated by the admission of CO upon the decarbonylated sample, implying that an irreversible transformation of the Pt carbonyl cluster proceeds by thermal evacuation. Figure 9 shows the Fourier transforms of k^3 weighted EXAFS of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 before and after the sample was evacuated at 300, 343, 363, 393, and 473 K, respectively. The peaks at 2.4, 2.7, and 3.0 Å in the Pt L-edge Fourier transforms are mainly attributed to Pt-Pt of the intra-Pt₃ triangle, Pt-C (for the bridging CO), and Pt-Pt of inter-Pt3 units, respectively. Table 4 shows the structural parameters obtained by the EXAFS analysis of the samples before and after the thermal treatments in a vacuum. When the sample of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 was evacuated at 343 K, the CN of Pt-C(bridging CO) decreased from 2.1 to 1.1 owing to the linear-bridging transformation and removal of CO, while the interatomic distances and coordination numbers



Figure 9. Fourier transforms of k^3 -weighted EXAFS of $[Pt_3(CO)_6]_5^{2-7}$ / NEt₄Cl/FSM-16 (sample C) evacuated at (a) 300 K, (b) 343 K, (c) 363 K, (d) 393 K, (e) 473 K, and (f) Pt foil in the *k* range of 3.5–18 Å⁻¹.

TABLE 4: Structural Parameters of $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ Evacuated at Various Temperatures Derived by Pt L_{III} -Edge EXAFS

CN	<i>R</i> /Å	$\Delta E_0/\mathrm{eV}$	$\Delta\sigma^2/10^{-3}{ m \AA}^2$	residual (%)			
Evacuation at 300 K							
2.3	2.68	3.0	-0.8	11.8			
1.7	3.10	-2.1	5.6				
2.1	2.10	3.8	6.2				
1.3	1.90	-9.9	2.6				
1.0	3.03	-0.8	2.8				
Evacuation at 343 K							
2.2	2.69	-2.5	0.4	9.5			
1.4	3.10	-7.5	6.0				
1.1	2.13	-1.6	6.4				
1.5	1.91	-8.9	5.8				
1.0	3.02	-1.3	4.5				
Evacuation at 363 K							
7.3	2.73	-2.9	3.5	8.8			
0.4	1.87	-7.8	-2.8				
0.3	3.07	4.5	2.2				
Evacuation at 393 K							
8.3	2.73	-2.9	3.5	0.2			
0.3	1.88	-7.8	-2.8				
0.3	3.07	4.5	2.2				
Evacuation at 473 K							
7.8	2.72	-3.2	2.7	9.0			
	CN 2.3 1.7 2.1 1.3 1.0 2.2 1.4 1.1 1.5 1.0 7.3 0.4 0.3 8.3 0.3 0.3 7.8	CN R/Å Ev 2.3 2.68 1.7 3.10 2.1 2.10 1.3 1.90 1.0 3.03 Ev 2.2 2.9 1.4 1.1 2.13 1.5 1.91 1.0 3.02 Fv 7.3 0.4 1.87 0.3 3.07 Ev 8.3 0.3 1.88 0.3 3.07 Fv 7.8	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $			

of two Pt–Pt contributions (R_1 and R_2), Pt–C(t) (terminal CO), and Pt–O(CO) were basically unchanged. This suggests that the trigonal prismatic Pt cluster framework may be retained after the controlled removal of CO at 343 K. This may be explained because the lens effect of carbon of terminal CO is much larger than that of bridged CO, and that of the oxygen of bridge CO was relatively small in the EXAFS spectra. Hence Pt–O contribution mainly comes from terminal CO. The EXAFS evaluation showed that the decrease of peak height of the Pt–O contribution in Figure 9b was not caused by the decrease of CN of Pt–O but by the increase of the Debye–Waller factor of the Pt–O bond. This may be because of enhancing the mobility of CO by the partial removal of CO of $[Pt_3(CO)_6]_5^{2-}$. These EXAFS data are consistent with those of IR observation about the switching of bridging CO to linear CO by the



Figure 10. Temperature-programmed desorption (TPD) profiles of CO and CO₂ formation monitored by a mass spectrometer on $[Pt_3(CO)_6]_5^{2-7}$, NEt₄Cl/FSM-16 (sample C) by heating from 300 to 523 K (ramping rates of 5 K/min).

controlled evacuation of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16. Furthermore, when the sample of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 was evacuated at 363 K, the Fourier transform pattern of the Chini cluster complexes drastically changed to that of a single Pt–Pt peak (R = 2.73 Å, CN = 7.3) which is characteristic of metal Pt particles. The averaged value of CN of the Pt-Pt bond was evaluated as 7.3. This suggests that a Pt particle formed in FSM-16 by the thermal evacuation at 363 K consist of 50-60 Pt atoms having a diameter of 15 Å. Besides, the Pt-C and Pt-O contribution was observed at 1.87 and 3.07 Å in the Fourier transformed k^3 function in Figure 9c-e. The CN of Pt-C and Pt-O being 0.3-0.4 implies that all the surface Pt atoms of the particle were coordinated with CO (CO/Pt = 0.4). The estimated dispersion (CO/Pt = 0.4-0.45) of Pt particles in FSM-16 was roughly consistent with the average size of Pt particle of 15 Å because of the Pt-Pt coordination number of 7.3. The adsorbed CO on the Pt particles is decreased by the further evacuation at temperatures exceeding 473 K, resulting in the naked Pt particles (Pt-Pt CN = 7.8; Pt-C(O), CN = 0) owing to the complete removal of CO (Figures 8g-h and 9f). The EXAFS, TEM, and IR data in Figures 9 and 8 suggest that the Pt₁₅ carbonyl clusters in the channels of FSM-16 were subsequently transformed and converted to a robust carbonyl cluster of Pt₅₅ at 363 K (Figure 9d) and eventually to a naked Pt particle of 15 Å diameter (CN = 7.8) at 473 K (Figure 9e).

3.5. TPD and TEM Studies on [Pt₃(CO)₆]₅²⁻/NEt₄Cl/ FSM-16 during the Thermal Transformation. To study the reactivities of Pt carbonyl clusters in FSM-16, a temperatureprogrammed desorption (TPD) measurement was conducted on [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16, as shown in Figure 10. Three desorption peaks of CO (m/e = 28) were observed at 359, 397, and 454 K, while the peak of CO_2 (m/e = 44) was negligible. Peaks at 397 and 454 K, correspond to the desorption peak of CO chemisorbed on Pt particle because the position of the CO peaks in TPD measurement was similar to that of the conventional Pt/SiO₂.³⁷ The peak at 359 K can be assigned to the partial desorption of CO due to the cluster transformation from $[Pt_3(CO)_6]_5^{2-}$ to a carbonylated cluster of Pt_{55} in FSM-16. The carbonylated Pt cluster was transformed by the complete removal of CO to a naked Pt particle at 454 K. Figure 11 shows a TEM photograph of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 after thermal evacuation at 473 K for 2 h. Small Pt particles of 15-20 Å diameter were observed uniformly scattered and aligned



Figure 11. Transmission electron micrograph of $[Pt_3(CO)_6]_5^{2-}/NEt_4-Cl/FSM-16$ (sample C) after the thermal evacuation at 473 K for 1 h.

SCHEME 1: Proposed Cluster Transformation of $[Pt_3(CO)_6]_5^2$ – Encapsulated in FSM-16 by the Controlled Removal of CO with Thermal Evacuation at Various Temperatures, Deduced by EXAFS, FTIR, and TEM Characterization Data



in the mesoporous channels of FSM-16. This TEM observation was consistent with the EXAFS results in terms of the CN = 7.8. According to the data of the EXAFS, FTIR, TPD, and TEM studies, $[Pt_3(CO)_6]_5^{2-}$ encapsulated in the channels of FSM-16 is proposed to be transformed as depicted in Scheme 1, owing to the controlled removal of CO by the thermal evacuation at 300-473 K. $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 is partially decarbonylated at 343 K in keeping the Pt cluster framework of a trigonal prism. When the sample was evacuated above 363 K, $[Pt_3(CO)_6]_5^{2-}$ was subsequently converted to a larger cluster such as Pt_{50-60} , which is bound with linear CO. The resulting Pt carbonyl cluster was completely desorbed by the evacuation at 473 K, resulting in the naked Pt particles having diameters of 15-20 Å. Domen et al.³⁸ previously reported by IR study that $[Pt_3(CO)_6]_5^{2-}$ impregnated on SiO₂ was trans-



Figure 12. Turnover frequency (TOF) of ethene and 1,3-butadiene hydrogenation at 300 K on $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ after thermal evacuation at various temperatures for 1 h. $p(C_2H_4) = p(H_2) = 13.3$ kPa or $p(C_4H_6) = p(H_2) = 13.3$ kPa.

formed by thermal evacuation at 573 K to Pt particles of 20 Å in a high dispersion via the mechanism of the removal of CO.

3.6. Catalytic Performances for Olefin Hydrogenation on $[Pt_3(CO)_6]_5^{2-}/FSM-16$ after the Controlled Removal of CO. To investigate the catalytic performances of $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 concerning their structural transformations caused by the controlled removal of CO, we have carried out the hydrogenation of ethene and 1,3-butadiene on $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ after thermal evacuation for 1 h at various temperatures. It was found preliminarily that $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ is catalytically inactive for the hydrogenation of ethene and 1,3-butadiene at 300–323 K.

Figure 12 shows the structural dependence of the rates of formation in terms of turnover frequencies (TOF) for the hydrogenation of ethene and 1,3-butadiene as a function of evacuation temperatures of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16. The TOFs were calculated by the rate of olefin consumption divided by the total number of Pt atoms used. The reaction rates of ethene hydrogenation increased by the evacuation of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 after thermal evacuation above 320 K, whereas the hydrogenation of 1,3-butadiene proceeded appreciably only after the controlled removal of CO by evacuation above 363 K. For both reactants, the hydrogenation rates substantially increased during the cluster transformation of $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ caused by thermal evacuation. Actually, the rates of ethene hydrogenation at 300 K were enhanced by a 30 times magnitude and that of 1,3-butadiene hydrogenation by 15 times by the thermal evacuation of [Pt₃(CO)₆]₅²⁻/NEt₄Cl/FSM-16 at 393 K, compared with those evacuated at 343 K. The hydrogenation of both olefins was almost completely suppressed by the exposure of CO (10 Torr) at 300 K to the resulting partially decarbonylated samples.

Figure 13 shows the product selectivity in the hydrogenation of 1,3-butadiene. The molar selectivity toward butenes as the half-hydrogenated products was above 97% for the sample $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ after evacuation at 323, 343, and 363 K. The butene products consist of 1-butene (76%), *cis*-2-butene (10%), and *trans*-2-butene (14%). *n*-Butane was formed in less than 5% selectivity, regardless the reaction temperatures and time on stream. Nevertheless, as shown in Figure 13, the selectivities of 1,3-butadiene hydrogenation markedly changed after the resulting sample was further decarbonylated above 393 K; the selectivity for 1-butene decreased from 76% to 22%,



Figure 13. Selectivity of C₄ hydrocarbon products in the hydrogenation of 1,3-butadiene at 300 K on $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ after thermal evacuation at various temperatures for 1 h. $p(C_4H_6) = p(H_2) = 13.3$ kPa.



Figure 14. Arrhenius plots for the hydrogenation of 1,3-butadiene on $[Pt_3(CO)_6]_5^{2-}/NEt_4Cl/FSM-16$ (sample C) after thermal evacuation at (a) 343 K (sample D) and (b) 363 K (sample E) for 1 h.

but those of *n*-butane and *trans*-2- and *cis*-2-butenes increased to 38%, 21%, and 19%, respectively. The results suggest that the isomerization of 1-butene proceeded simultaneously to *trans*and *cis*-2-butenes on the partially decarbonylated sample. On the naked Pt particles of 15–20 Å size in FSM-16 which was prepared by thermal evacuation above 523 K, the hydrogenation of 1,3-butadiene proceeded nonselectively at 300 K toward *n*-butane in 70–90% selectivity. Hence, it was suggested that $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 after the controlled removal of CO exhibited catalytic activities for the selective hydrogenation of 1,3-butadiene toward butenes mainly consisting of 1-butene, while the naked Pt particles (15–20 Å size) in FSM-16 lost selectivity for 1-butene, resulting in the complete hydrogenation of butadiene to *n*-butane even at 300 K.

As depicted in Scheme 1, it is suggested that $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 is transformed to form a partially decarbonylated Pt clusters by the thermal evacuation at 343 K (catalyst D) and to Pt_{50-60} particles bound with CO (catalyst E) above 363 K. They are active for the selective hydrogenation of 1,3-butadiene toward 1-butene at 300 K. On the other hand, the reaction proceeded nonselectively toward butane on the naked Pt particles, similar to the conventional metal catalysts.

Figure 14 shows Arrhenius plots for 1,3-butadiene hydrogenation on samples D and E. The activation energy of the hydrogenation on sample D was 95.2 kJ mol⁻¹, and that of sample E was 59.3 kJ mol⁻¹. For both catalysts, the selectivities of butenes (above 97%) such as 1-butene were independent of the reaction temperatures. The difference of the activation energy for the hydrogenation of 1,3-butadiene may be owing to the stronger adsorption of butadiene on the partially carbonylated Pt carbonyl clusters in FSM-16. It is of interest to find that ethene as a smaller molecule than 1,3-butadiene is readily hydrogenated on the sterically less crowded $[Pt_3(CO)_6]_5^{2-1}$ in FSM-16 (samples D and E) by controlling the removal of CO as a function of evacuation temperature, as shown in Figure 12. The active site area of sample E accessible for 1,3-butadiene as a larger reactant molecule is estimated to be larger than that for sample D. Sample E consists of the sterically less crowded Pt clusters, which are more opened to accommodate the larger olefin molecules compared to sample D. Regarding the hydrogenation of 1,3-butadiene, it was demonstrated that the higher selectivites toward butenes (above 90%) were obtained regardless the reaction temperature and evacuation temperatures of the sample up to 373 K. As discussed above, the ratedetermining step is the adsorption of 1,3-butadiene, and thus, the activation energy may represent the activation barrier for the removal of butadiene which prevents the adsorption of monoolefin products for further hydrogenation to *n*-butane.

4. Conclusion

(1) Bulky Pt carbonyl clusters such as $[Pt_3(CO)_6]_5^{2-}$ are synthesized in the mesoporous channels of FSM-16 by the reductive carbonylation of H₂PtCl₆ with CO + H₂O at 323 K. Guest $[Pt_3(CO)_6]_5^{2-}$ was extracted from the sample with TPP salt into the THF solution by cation metathesis. This was characterized by FTIR, EXAFS, and UV-vis spectroscopy.

(2) $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 is stabilized by coimpregnated countercations NR₄⁺. The thermal stability of the Pt cluster anion in FSM-16 was evaluated in the following order for the alkyl groups: R = butyl, ethyl > methyl, methyl viologen (MV) \gg hexyl > no countercations.

(3) EXAFS, TEM, and FTIR studies suggest that $[Pt_3(CO)_6]_5^{2-}$ anions in FSM-16 are transformed by the controlled removal of CO to the partially decarbonylated Pt clusters and eventually converted into naked Pt particles of 15 Å size by evacuation exceeding 473 K, as indicated in Scheme 1.

(4) $[Pt_3(CO)_6]_5^{2-}$ in FSM-16 exhibits catalytic activities for the hydrogenation of ethene and 1,3-butadiene selectively toward butenes (above 97% selectivety) after the controlled removal of CO by thermal evacuation that are different from those on conventional metal catalysts.

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