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XAFS Characterization of Platinum Clusters Synthesized in the Channel of a Mesoporous Zeolite

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Abstract: $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ was synthesized by reductive carbonylation of H_2PtCl_6 in the channels of FSM-16 modified with NEt_4Cl . The platinum clusters in the channels whose diameter was 28 Å were characterized by Pt L_{III} edge EXAFS as well as FT-IR, UV-vis spectroscopy, and TEM measurements. After exposure of $\text{H}_2\text{PtCl}_6/\text{NEt}_4\text{Cl}/\text{FSM-16}$ to $\text{CO} + \text{H}_2\text{O}$ at 323 K, Pt carbonyl clusters were selectively produced. The Pt L_{III} edge EXAFS spectrum of this sample was exactly the same as that of $[\text{NEt}_4]_2[\text{Pt}_{15}(\text{CO})_{30}]$, and gave Pt-Pt distances typical of these types of platinum clusters at 2.68 and 3.08 Å. Uniform platinum "particles" (15 Å diameter) were observed in the channels of FSM-16 by a TEM measurement; this suggests that $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ was synthesized in the channel of FSM-16. The platinum clusters in the channel were converted to platinum metal particles by evacuation above 363 K. Pt L_{III} EXAFS spectra of these samples revealed that the bridge CO of the clusters were desorbed by the evacuation at 343 K while retaining their cluster framework; the clusters were converted to Pt_{50-60} particles by evacuation above 363 K.

1. Introduction

Synthesis of metal clusters clearly characterized at the molecular level in the channel or cage of zeolite, so called "ship-in-bottle synthesis" has great advantages for rational preparation of the catalytic active site. Using this method, the structure of, the surroundings of the active site as well as the active site structure can be defined because zeolite is well-defined porous crystal [1].

Meso porous materials such as MCM-41[2,3] and FSM-16 [4,5] have been recently synthesized. These mesoporous materials have ordered channels with a uniform diameter. The size of the channels can be changed from 20 to 100 Å by using different alkyl-trimethyl-ammonium as template. Since the size of the channels of MCM-16 and FSM-16 was much larger than that of conventional zeolites such as ZSM-5, AIPO-5, and NaY, they are potential hosts for inclusion of bulky organic and inorganic species. This allowed us to use new applications for the design of tailored metal catalysts accessible to larger substrates.

Chini type Pt clusters are composed of "Pt₃(CO)₆" units; the units were stacked to form $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ clusters[6]. The cross section of the Pt₃(CO)₆ unit is about 8 Å in diameter, and the inter trigonal distance in the cluster is about 3 Å. In the super cage of NaY, $[\text{Pt}_3(\text{CO})_6]_3^{2-}$ and $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ were available to be produced [7-10], while because of the size limitation of the supercage (13 Å), $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n > 4$) was not produced in the NaY supercage.

The goal of this paper is to characterize the Pt clusters synthesized in the channel of FSM-16 using EXAFS spectroscopy as well as IR and UV spectroscopy and TEM measurement. Further, structure transformation of the cluster was investigated.

2. Experimental

FSM-16 was synthesized as described in the literature [4]. FSM-16 was impregnated with NEt_4Cl in aqueous solution to provide counter cations of Pt clusters. The NEt_4Cl modified FSM-16 was impregnated with H_2PtCl_6 in aqueous solution. The loading of NEt_4Cl and Pt atoms were 1.37×10^{-4} mol/gcat and 5wt% respectively. The sample was exposed to a mixture of CO (26.7 kPa) and H_2O (2.7 kPa) at 323 K to produce Pt carbonyl clusters.

Pt- L_{III} edge EXAFS (extended X-ray absorption fine structure) spectra were measured at BL-10B at the Photon Factory of the National Institute for High Energy Physics (Tsukuba, Japan). The energy and current of electrons in the storage ring were 2.5 GeV and 250-365 mA respectively. A Si(311) channel cut monochromator was used. X-ray was detected in ion chambers filled with a mixture of Ar and N₂ gases. The spectra were measured at room temperature in the transmission mode.

The EXAFS spectra were analyzed by a computer program supplied by Technos Co. LTD [11]. The background was subtracted using the McMaster function, and the baseline was estimated using the cubic spline method. The k^3 weighted EXAFS function was Fourier transformed into R-space and inverse Fourier transformed into k-space. The k and R ranges were 3.5-18 Å⁻¹ and 1.09-3.31 Å respectively. The Fourier filtered EXAFS functions were fitted according to calculated EXAFS functions. Backscattering amplitude and phase shift functions of Pt-Pt, Pt-C and Pt-O (of Pt-CO) used in this analysis were obtained

experimentally from Pt foil (Pt-Pt) and $W(CO)_6$ (Pt-C and Pt-O) respectively.

3. Results and discussion

3.1. Formation of Pt clusters in FSM-16

Figure 1 shows Fourier transformed Pt L_{III} EXAFS functions of Pt clusters synthesized in $NEt_4Cl/FSM-16$, $Pt_{12}(CO)_{24}/NaY$, and $[NEt_4]_2[Pt_{15}(CO)_{30}]$. The EXAFS function of the Pt clusters in $NEt_4Cl/FSM-16$ is similar to that of $[Pt_3(CO)_6]_5^{2-}$. These spectra were inverse Fourier transformed and fitted to five shells, two Pt-Pt, two Pt-C, and one Pt-O contribution. Table 1 shows coordination number (CN), inter-atomic distance (R), correction of threshold energy (ΔE_0), and the difference of the Debye-Waller factor from reference compounds ($\Delta\sigma^2$). The structural parameters of the Pt cluster in $NEt_4Cl/FSM-16$ agree with those of $[Pt_3(CO)_6]_5^{2-}$ in the error bar. The results of the EXAFS confirmed that the $[Pt_3(CO)_6]_5^{2-}$ cluster was produced in the channel of FSM-16. In the case of $Pt_{12}(CO)_{24}/NaY$, the Pt-Pt distance of inter Pt_3 triangles was shorter than that of the reference compound and $Pt_{15}/FSM-16$. This may be caused by the effect of the zeolite wall on NaY. Since the size of the supercages of NaY is 13 Å in diameter, the Pt clusters in NaY may be distorted. In contrast, since the channel of FSM-16 is large enough (30 Å in diameter), the Pt clusters in the channel were not distorted. No contribution of Pt-Cl was observed, which means that most H_2PtCl_6 was converted to $[Pt_3(CO)_6]_5^{2-}$ clusters. IR and UV-vis spectra of the Pt clusters synthesized in $NEt_4Cl/FSM-16$ suggested that $[Pt_3(CO)_6]_5^{2-}$ was synthesized by reductive carbonylation of $H_2PtCl_6/NEt_4Cl/FSM-16$. In the TEM photo-graph, small Pt clusters 15 Å in diameter were observed; large crystals were not observed, which clearly showed that the Pt clusters were dispersed in the channel of FSM-16.

3.2. Formation of small Pt particles from the Pt clusters in $NEt_4Cl/FSM-16$

Figure 2 shows Fourier transformed EXAFS functions of Pt clusters ($[Pt_3(CO)_6]_5^{2-}$) in $NEt_4Cl/FSM-16$ evacuated at 300, 343, 363, 393, and 473 K respectively. No phase shift correction was carried out in Fig.2. By the evacuation at 343 K, the peak at 2.75 Å decreased, and the peak at 2.4 Å shifted to 2.6 Å when the sample was evacuated at 363 K.

Table 2 shows structural parameters derived by EXAFS analysis. When the sample was evacuated at 343 K, CN of Pt-C (bridge) decreased from 2.1 to 1.1. In contrast, other parameters such as distance and co-ordination number of two Pt-Pt contributions, Pt-C (terminal) and Pt-O bridge remain unchanged. These results suggest that bridge CO was desorbed by evacuation at 343 K and the cluster framework remain unchanged. The CN of Pt-O remains unchanged while CN of Pt-C(b) decreased. This suggests that the contribution of Pt-O mainly comes from Pt-O of the terminal CO.

When the sample was evacuated at 363 K, Pt-Pt distance changed. Pt-Pt distances characteristic to $[Pt_3(CO)_6]_5^{2-}$ disappeared and a Pt-Pt distance of metal Pt particles was observed at 2.73 Å with CN of 7.3. The CN of 7.3 suggests that particle size was Pt_{50-60} with a diameter of 15 Å. Pt-C and Pt-O contributions were also observed at 1.87 and 3.07 Å. The CN of Pt-C was 0.4 and suggests that all surface Pt atoms were coordinated by adsorbed

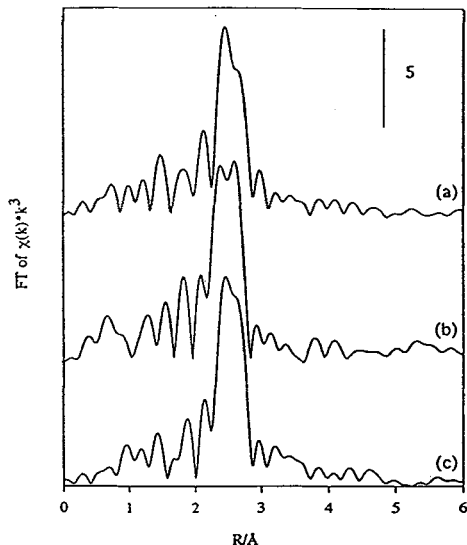


Figure 1. Fourier Transformed k^3 weighted EXAFS function of (a) $[NEt_4]_2[Pt_3(CO)_6]_5^{2-}/BN$ (BN=Boron nitride), (b) $[Pt_3(CO)_6]_4^{2-}/NaY$, and (c) Pt clusters in $NEt_4Cl/FSM-16$.

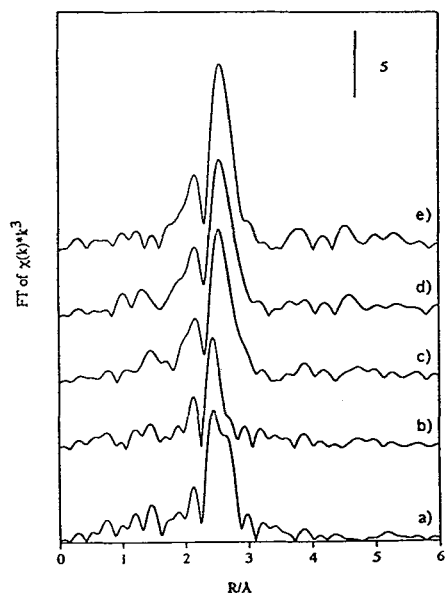


Figure 2. Fourier transformed k^3 weighted EXAFS function of Pt clusters in $NEt_4Cl/FSM-16$ evacuated at a) 300 K, b) 343 K, c) 363 K, d) 393 K and e) 473 K.

CO, because the proportion of surface Pt atoms was estimated to be 0.45 from the CN of Pt-Pt. The CN of adsorbed CO on the Pt particles decreased as the evacuation temperature increased; adsorbed CO was disappeared at 473 K.

IR spectra of the Pt clusters in FSM-16 evacuated at various temperatures agree with EXAFS data. When the sample was evacuated at 343 K, bridge CO at 1871 cm^{-1} disappeared. Terminal CO adsorbed on Pt₅₀₋₆₀ cluster began to desorb at 373 K and disappeared at 473 K. The TEM photograph showed that Pt₅₀₋₆₀ clusters were dispersed homogeneously in the channel of FSM-16. No large Pt particles were observed in the TEM photograph.

From EXAFS, IR, and TEM results, we propose a scheme of the formation and transformation of $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ in $\text{NEt}_4\text{Cl}/\text{FSM-16}$ as shown in scheme 1. $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ clusters were produced by the reductive carbonylation of H_2PtCl_6 . By the evacuation at 343 K, the bridge CO of the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ in the channel of FSM-16 was desorbed, while the cluster framework remained. By the evacuation at 363 K, the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ clusters were converted to Pt₅₀₋₆₀ particles whose surface Pt atoms were saturated by adsorbed CO. The adsorbed CO on the Pt particles were desorbed by the evacuation at 473 K. TEM results clearly show that the Pt particle exists in the channel of FSM-16 and that the size of the Pt particle was homogeneous.

4. Conclusions

- $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ is produced in the channel of FSM-16 by the reductive carbonylation of H_2PtCl_6 impregnated in FSM-16 which was modified with NEt_4Cl .
- The bridge CO of $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ in the FSM-16 channel was selectively removed by evacuation at 343 K, and the clusters were converted to Pt₅₀₋₆₀ particles by evacuation above 363 K. Resulting Pt particle of ca. 15 Å size was formed uniformly inside the ordered mesoporous channels of 28 Å diameter.

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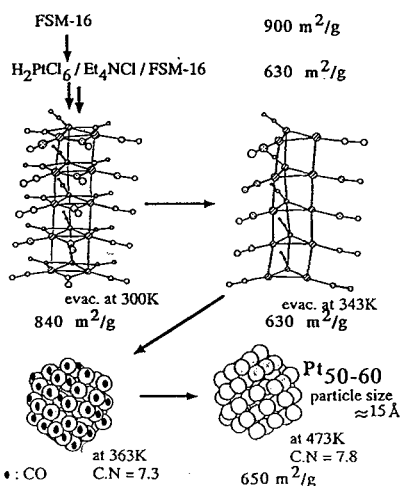
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Table 1. Structural parameters of Pt carbonyl clusters derived from Pt L_{III} EXAFS.

Compound/shell	CN	R/A	$\Delta E_p/\text{eV}$	$\Delta\sigma^2/10^{-3}\text{\AA}^2$	Residual(%)
$[\text{NEt}_4]_2[\text{Pt}_3(\text{CO})_6]_5$					
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	
$[\text{Pt}_{12}(\text{CO})_{24}]/\text{NaY}$					
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	-3.8	0.9	
Pt-O	1.0	2.99	-4.6	1.3	
$[\text{Pt}_{13}(\text{CO})_{26}]/\text{NEt}_4/\text{FSM-16}$					
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	

Table 2. Structural parameters of Pt clusters ($[\text{Pt}_3(\text{CO})_6]_5^{2-}$) in $\text{NEt}_4\text{Cl}/\text{FSM-16}$ evacuated at various temperatures.

evac. temp./shell	CN	R/A	$\Delta E_p/\text{eV}$	$\Delta\sigma^2/10^{-3}\text{\AA}^2$	Residual(%)
evac. at 300 K					
Pt-Pt	2.3	2.68	3.0	-0.8	11.8
Pt-Pt	1.7	3.10	-2.1	5.6	
Pt-C(b)	2.1	2.10	3.8	6.2	
Pt-C(t)	1.3	1.90	-9.9	2.6	
Pt-O	1.0	3.03	-0.8	2.8	
evac. at 343 K					
Pt-Pt	2.2	2.69	-2.5	0.4	9.5
Pt-Pt	1.4	3.10	-7.5	6.0	
Pt-C(b)	1.6	2.13	-1.6	6.4	
Pt-C(t)	0.9	1.91	-8.9	5.8	
Pt-O	1.0	3.02	-1.3	4.5	
evac. at 363 K					
Pt-Pt	7.3	2.73	-2.9	3.5	8.8 ^f
Pt-C	0.4	1.87	-7.8	-2.8	
Pt-O	0.3	3.07	4.5	2.2	
evac. at 393 K					
Pt-Pt	8.3	2.73	-2.9	3.5	0.2
Pt-C	0.3	1.88	-7.8	-2.8	
Pt-O	0.3	3.07	4.5	2.2	
evac. at 473 K					
Pt-Pt	7.8	2.72	-3.2	2.7	9.0



Scheme 1 Structure transformation of Pt clusters ($[\text{Pt}_3(\text{CO})_6]_5^{2-}$) in $\text{NEt}_4\text{Cl}/\text{FSM-16}$