Reversible Deformation of SiO₂-Supported PtAu₆ Cluster Induced by the CO Adsorption by *In Situ* EXAFS

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Structure and behavior of [(PPh₃)Pt(Au(PPh₃))₅](1) supported on SiO₂ surface have been studied by *in-situ* EXAFS. The structure of the cluster 1 is maintained after deposition on SiO₂ at room temperature. Upon adsorption of CO little change in coordination number for Pt-Au is found in Pt L₃-edge EXAFS though the coordination number of Au-Au slightly increases in Au L₃-edge EXAFS and the peak corresponding to Pt(-Au)-P remarkably increases in the Fourier transformation of Pt L₃-edge EXAFS. We have interpreted the increase in the intensity of the peak corresponding to Pt(-Au)-P by the multiple scattering effect owing to the change of Pt-Au-P angle. The original EXAFS oscillations are regenerated for both Pt and Au L₃-edges after the evacuation for 2 h at 353 K accompanied by the desorption of CO. From these EXAFS results and the analogy to the PtAu₆ chemistry in solution, the PtAu₆ framework transforms its structure to a more compact one by CO adsorption with the change in the angle of Pt-Au-P. Unlike the PtAu₆ cluster in solution, CO reversibly desorbs from the cluster without collapse of the PtAu₆ framework.

1. Introduction

Metal clusters used as homogeneous catalysts have some difficulty for their use as catalysts and for the *in-situ* structural studies because their frameworks easily collapse or they aggregate to large metal particles in solutions during the reactions. Deposition of the metal clusters onto inorganic oxides often stabilizes the cluster framework against heat treatment as well as reaction process. Hence supported clusters are feasible in the investigation of the relation between structure and catalytic behavior *in situ* under operating conditions[1]. We have prepared a SiO₂-supported PtAu₆ catalyst derived from [(PPh₃)Pt(Au(PPh₃))₅](NO₃)₂ cluster (1(NO₃)₂) which shows high activity for H₂-D₂ exchange reaction[2]. This reaction is poisoned by the adsorption of CO. During the structural study of 1 on SiO₂ by means of *in-situ* EXAFS spectroscopy, we have found reversible change of the cluster structure induced by the adsorption and desorption of CO. In this paper we will report this reversible behavior of 1 on SiO₂ during CO adsorption and desorption processes obtained from *in-situ* EXAFS analysis.

2. Experimental

The preparation of 1/SiO₂ was described elsewhere[2]. The EXAFS measurements were carried out at BL-10B of Photon Factory operated at 2.5 GeV with a ring current 250-300 mA. X-rays were monochromatized by a Si(311) channel cut crystal and detected by ionization chambers filled with N₂ and Ar(25%)/N₂(75%) for I₀ and I chambers, respectively. EXAFS data were accumulated at room temperature. Analyses of EXAFS were carried out by removal of background using cubic smoothing and normalized by edge height whose energy dependency was taken into account using McMaster equation[3]. Curve fitting analyses were carried out using phase shift and amplitude functions were calculated by the FEFF program[4]. A total reduction factor and Debye-Waller factors were adjusted by fitting EXAFS data 1(NO₃)₂ as a reference compound.

3. Results

3.1 Structure of [(PPh₃)Pt(Au(PPh₃))₅](NO₃)₂/SiO₂

Figs. 1a and 2a show the Fourier transforms of Pt L₃- and Au L₃-edges $k^3\chi(k)$ EXAFS oscillations of the 1/SiO₂, respectively. Because Au L₃-edge appears at 14.353 keV, about 500 eV higher than the Pt L₃-edge, we can obtain the data in only $k=30-90$ nm⁻¹ range. However, the Pt-P and Pt-Au peaks are well separated from each other and can be analyzed by means of curve fitting. A small peak is present at about 0.45 nm which might be corresponding to a Pt(-Au)-P interaction. Curve fitting analyses are given in Table 1 together with the crystallographic data of 1(NO₃)₂, indicating the retention of the PtAu₆ framework structure shown in Fig. 3.

3.2 Structure of [(PPh₃)Pt(Au(PPh₃))₅](NO₃)₂/SiO₂ after CO adsorption

When the cluster is exposed to 300 Torr CO at room temperature, one CO is adsorbed on one cluster. FT-IR spectrum shows a single peak at 1975 cm⁻¹ corresponding to the linear CO adsorbed on Pt. Figs. 1b and 2b show the Fourier transforms of Pt L₃- and Au L₃-edges $k^3\chi(k)$ EXAFS oscillations, respectively. Peaks appear in 0.1-0.35 nm in Pt L₃-edge Fourier transform mainly due to Pt-P and Pt-Au bondings. Because we had to carry out 4-term curve fitting analysis (Pt-C, Pt-P, Pt-Au, and Pt-(C)-O) for Pt L₃-edge EXAFS which requires 16 fitting parameters more than the maximum number of freedom (

Figure 1: Fourier transforms of Pt L_3 -edge EXAFS (a) $1/\text{SiO}_2$, (b) $1+\text{CO}/\text{SiO}_2$, (c) subsequent evacuation at 353 K. Fourier transformation of $k^3\chi(k)$ was carried out over 30-90 nm^{-1} .

Figure 2: Fourier transforms of Au L_3 -edge EXAFS (a) $1/\text{SiO}_2$, (b) $1+\text{CO}/\text{SiO}_2$, (c) subsequent evacuation at 353 K. Fourier transformation of $k^3\chi(k)$ was carried out over 30-130 nm^{-1} .

Figure 3: Proposed surface transformation accompanied by the CO adsorption and desorption.

Figure 4: Fourier transforms of FEFF simulation based on the model $1(\text{NO}_3)_2$ (a) and $2(\text{PF}_6)_2$ (b). Fourier transformation was carried out over $k=30-90 \text{ nm}^{-1}$.

Table 1: Curve fitting results of $1/\text{SiO}_2$ and its derivatives.

Sample	Pt-P		Pt-Au		Au-P		Au-Pt		Au-Au	
	N	r / nm	N	r / nm	N	r / nm	N	r / nm	N	r / nm
$1(\text{NO}_3)_2$	1*	0.228*	6*	0.268*	1*	0.229*	1*	0.268*	2.67*	0.285*
$2(\text{PF}_6)_2$	1*	0.234*	6*	0.269*	1*	0.229*	1*	0.269*	3*	0.289*
$1/\text{SiO}_2$	1.1(1)	0.228(1)	6.0(5)	0.268(1)	1.0(1)	0.228(1)	1.1(1)	0.268(1)	2.6(3)	0.285(1)
$1/\text{SiO}_2$ after adsorption of CO**	1.2(4)	0.231(4)	5.8(9)	0.269(3)	1.0(1)	0.228(1)	1.1(1)	0.269(1)	3.0(3)	0.290(1)
$1/\text{SiO}_2$ after desorption of CO	1.1(1)	0.229(1)	5.9(5)	0.269(1)	1.0(1)	0.228(1)	1.1(1)	0.268(1)	2.7(3)	0.285(1)

The range for inverse Fourier transformation was 0.12 -0.35 nm for both Pt and Au EXAFS. Curve fitting ranges were 30-90 nm^{-1} for Pt EXAFS and 30-130 nm^{-1} for Au EXAFS, respectively.

Parentheses indicated the estimated errors

* indicates the average values derived from crystallographic data[5].

** Bond distances of Pt-C and Pt-(C)-O are 0.194 nm 0.309 nm, respectively.

$2\Delta r\Delta k/\pi \approx 10$), we fixed ΔE and σ values. The curve fitting results in Table 1 indicate that the retention of the Pt-P and Pt-Au bondings after CO adsorption. The peak at about 0.45 nm becomes almost twice as large as that of $1/\text{SiO}_2$, indicating a certain change occurs in the Au-P bonding. On the other hand, for Au L_3 -edge, no increase is found in the intensity of the first peak attributable to Pas shown in Fig.2b. The curve fitting analysis of Au L_3 -edge shows the slight increase in the Au-Au coordination number but the Au-P and Au-Pt coordination numbers remain almost 1. The PtAu_6 framework structure is maintained with a small deformation after CO adsorption.

3.3 Structure of $[(\text{PPh}_3)_2\text{Pt}(\text{Au}(\text{PPh}_3))_2](\text{NO}_3)_2/\text{SiO}_2$ after CO desorption

When the CO adduct of the complex $1/\text{SiO}_2$ is subsequently evacuated at 353 K, the CO is desorbed. Figs.1c and 2c show the Fourier transforms of Pt L_3 - and Au L_3 -edges $k^3\chi(k)$ EXAFS, respectively. No decomposition of the framework structure of PtAu_6 is observed. The peak at 0.45 nm decreases in the Fourier transform of Pt L_3 -edge EXAFS, as shown in Fig.1c. Curve fitting analysis shows that the coordination number of Au-Au decreases to the same value as that of $1/\text{SiO}_2$. We have concluded that the original structure of $1/\text{SiO}_2$ is recovered after the desorption of CO.

4. Discussion

We have observed a reversible structure transformation of $1/\text{SiO}_2$ by the adsorption and desorption of CO without any destruction of PtAu_6 framework. There are two features in this transformation found in EXAFS.

- (1) The Au-Au coordination number increases with the adsorption of CO.
- (2) The peak of Pt-(Au)-P increases in the Fourier transform of Pt L_3 -edge though no increase in the coordination number of P around Au is observed.

Thus the changes only occur in the Au atoms surrounding Pt.

A CO adduct compound $[(\text{PPh}_3)(\text{CO})\text{Pt}(\text{Au}(\text{PPh}_3))_2](\text{PF}_6)_2$ ($2(\text{PF}_6)_2$) can be easily derived from $1(\text{NO}_3)_2$ under the presence of 1 atom CO in CH_2Cl_2 solution[5]. This compound $2(\text{PF}_6)_2$ has a more compact structure in PtAu_6 framework and larger coordination number of Au-Au than that of $1(\text{NO}_3)_2$ as shown in Table 1 which is the same change found in the cluster 1 on SiO_2 after the CO adsorption.

The increase of Pt-(Au)-P Fourier peak can be explained by the change of the angle Pt-Au-P to be closer to 180° , creating a strong focusing effect. The average angle of Pt-Au-P in clusters $1(\text{NO}_3)_2$ and $2(\text{PF}_6)_2$ are 162.5° and 164.8° , respectively, based on the crystallographic data. We have calculated the Pt-(Au)-P EXAFS oscillations using FEFF programs on the assumption that cluster structures on SiO_2 before and after CO adsorption are the same as the ones in the compounds $1(\text{NO}_3)_2$ and $2(\text{PF}_6)_2$ given in the literature[5], respectively. The results are depicted in Fig.4. Because of the ambiguity in Debye-Waller factors, the relative height of the simulated Fourier transforms have some meaning. The height around 0.45 nm in $1(\text{NO}_3)_2$ is 1.1 and it increases to 2.0 in $2(\text{PF}_6)_2$. Therefore the increases in the peak of Pt L_3 -edge EXAFS at 0.45 nm can be explained by the transformation of the surface structure from 1 to 2 by the adsorption of CO. Note that the difference in average Pt-(Au)-P angles between $1(\text{NO}_3)_2$ and $2(\text{PF}_6)_2$ is 2.3° though the peak height is almost twice as large in $1(\text{NO}_3)_2$ as $2(\text{PF}_6)_2$. According to the FEFF calculation of the peak height of Pt-(Au)-P in Fourier transform for several angles, the peak height sensitively changes with the angle at more than 160° .

From these EXAFS results, we have concluded that structure transformations similar to the ones found in solutions may occur during CO adsorption and desorption as shown in Fig.3. However, the desorption of CO from Pt atom has never been observed in the compound $2(\text{PF}_6)_2$ in a solution system unless the framework structure is destroyed. The immobilization of the cluster 1 on the oxide surface has made it possible to undergo the reversible structure change without collapse of the framework likely to $\text{Ru}_6\text{C}(\text{CO})_{12}/\text{MgO}$ [6]. Such a reversible structure change of the framework structure of clusters just in the presence or absence of adsorbed CO may lead to be a molecular actuator for molecular machines and molecular devices.

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