TEMPERATURE DEPENDENCE OF THE Pt L₃-EDGE EXAFS OF PLATINUM CLUSTERS SUPPORTED ON NaY-ZEOLITE

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The temperature dependence of the Pt L₃-edge EXAFS spectra of the platinum clusters encaged in the cavities of the NaY-zeolite were observed by use of synchrotron radiation. A contraction of Pt-Pt bond by 0.07 Å from the distance in the bulk Pt metal is observed, which is likely to be associated with a strong electron deficiency of the platinum clusters. The temperature dependence of the mean square relative displacement (MSRD) shows that the static disorder in this system is large, while the thermal disorder is significantly smaller than that of the bulk metal. The estimated Debye temperature is 310 K, which is much higher than that of the bulk metal (240 K). This unusual phenomenon seems to be associated with the increase of the binding energy between platinum atoms and with the strong interaction between a cluster and zeolite-framework (the cage effect).

INTRODUCTION

EXAFS spectroscopy is a suitable technique to investigate the structural difference between a fine metal particle and a bulk metal. So far, much attention has been paid for the metal-metal bond distance and it has been often concluded that the bond distance becomes the shorter as the particle size is smaller. Another interesting structural aspect of a fine metal particle is the particle-size effect of thermal and/or static disorder. Recently Marques et al [1] measured the temperature dependence of EXAFS of supported clusters, and suggested that such an experiment is useful to investigate thermal vibrations and structural disorders as well as to determine the interatomic distance more correctly. In the present study we investigated the temperature dependence of EXAFS on platinum clusters encaged in the supercages of NaY-zeolite. The bond distance and disorder in this system are determined and discussed by comparing with those of the bulk metal and of the metal particles supported on Al₂O₃.

EXPERIMENTAL

Platinum clusters encaged in the supercages of the NaY zeolite were obtained according to the literature [2]. Decomposition of the [Pt(NH₃)₄]²⁺ complex in the

supercage was done by raising temperature slowly (0.3°C/min.) up to 300 °C in the flowing oxygen. Reduction was carried out under 300 Torr (1 Torr=133 Pa) of hydrogen at 300 °C. The resultant material (H/Pt = 0.95 ± 0.05) was transferred to an air-tight, pyrex-glass cell with kapton windows for EXAFS measurements which had been connected with the reactor glass line. The Pt L₃-edge EXAFS spectra (40~300 K) were taken by use of the EXAFS spectrometer at the Beam Line 10B of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) [3]. For comparison, the spectra for Pt/Al₂O₃ catalyst (H/Pt = 0.40 ± 0.05) and Pt foil (4μm thick) were also measured.

RESULTS

We took the following procedures of EXAFS data of analysis. After examining the Fourier transform, the inverse-Fourier transformation were carried out over the limited range (only first shell coordination) of the Fourier transform (Fourier filtering), and the amplitudes and the phases of the inverse-Fourier transforms were separately analyzed (ratio method). We used Eq (1) for the phase function of the sample, $\phi(k)$,

$$\frac{\phi(k) - \phi_0(k)}{2k} = \Delta R - \sum_{i=0}^{\infty} C_i k^{2i} \quad (1)$$

where $\phi_0(k)$ is the phase function of the reference material, $\Delta R (=R-R_0)$ is the difference of Pt-Pt distance between the sample and the reference, and $C_i k^{2i}$ are the correction terms for the radial distribution function with large disorder. The difference of the threshold energy (E_0) should be, in general, introduced in the equation (1). However, since E_0 is quite small in the present case (less than ± 1 eV in all the case) we neglected this correction for simplicity. If the distribution function is expressed as a gaussian with a small σ value, higher-order terms ($i \geq 1$) can be neglected and the zeroth-order term is approximately written by

$$C_0 = \frac{2\sigma^2}{R} - \frac{2\sigma_0^2}{R_0} \quad (2)$$

where the subscript o denotes the reference material. In the present study, $\phi_0(k)$ was derived from the EXAFS data of Pt foil measured at 38 K and R_0 was taken from the crystallographic data (2.775 Å). Fig. 1 which shows the plot corresponding to Eq (1) clearly exhibits that $[\phi(k) - \phi_0(k)]/2k$ is independent of k except for the range of very low k -value, indicating that the correction terms for higher order ($i \geq 1$) is negligible and the distribution function can be expressed by a simple gaussian function with rather small σ value. The mean Pt-Pt bond distance obtained (shown in table 1) is shorter than that of the bulk; this agrees well with the result given by B. Moraweck et al [4].

On the other hand, since the distribution function is essentially gaussian, the amplitude function of the sample, $A(k)$ is given by

$$\ln \frac{A(k)}{A_0(k)} = \ln \frac{NR_0^2}{N_0 R^2} - 2(\sigma^2 - \sigma_0^2)k^2 \quad (3)$$

where N is the coordination number. σ_0^2 denotes the MSRD for the bulk Pt metal at 38 K, and can be estimated according to the theory proposed by Beni and Platzman [5]. Figure 2 shows the temperature dependence of MSRD determined for the Pt/NaY,

Pt/Al₂O₃ and the bulk Pt metal. The solid line for Pt foil in fig. 2 is also determined according to their theory. The experimentally-determined value for Pt bulk metal agrees well with the theoretical one. The values for Pt/NaY are much larger than that of the bulk metal as mentioned above, and increases linearly with temperature. However, the slope of the straight line for Pt/NaY is significantly smaller and the estimated Debye temperature, $310 \pm 30\text{K}$, is significantly higher than that of the bulk metal (240 K). This fact strongly indicates that in Pt/NaY-zeolite system, the thermal disorder is rather smaller while the static disorder is large.

Although the structural properties of the Pt clusters encaged in the cavities of the zeolite are concluded to be quite different from those of the bulk metal, Pt metal particles supported on Al₂O₃ exhibit properties rather similar to the bulk metal except for the existence of the static disorder. The Pt-Pt bond distance and the Debye temperature are essentially the same as compared with the bulk metal.

Fig. 1. Phase Plot (eq.(1))

Table Results of EXAFS analysis

sample		R (Å)	σ^2 (Å ²)
Pt foil (N=12.0)	38 K	(2.775)*	(1.41x10 ⁻³)*
	83 K	2.775	2.01x10 ⁻³
	130 K	2.775	2.70x10 ⁻³
	165 K	2.776	2.96x10 ⁻³
	209 K	2.776	3.74x10 ⁻³
	250 K	2.776	3.90x10 ⁻³
Pt/Al ₂ O ₃ (N=10.0)	290 K	2.776	4.28x10 ⁻³
	134 K	2.756	5.86x10 ⁻³
	233 K	2.757	7.16x10 ⁻³
Pt/NaY (N=7.5)	332 K	2.767	9.14x10 ⁻³
	50 K	2.695	7.09x10 ⁻³
	106 K	2.694	7.40x10 ⁻³
	175 K	2.692	7.99x10 ⁻³
	234 K	2.691	8.19x10 ⁻³
	280 K	2.687	8.69x10 ⁻³

* Model

Fig. 2. Temperature Dependence of MSRD

DISCUSSION

As we have mentioned, the Pt-Pt bond distance of the platinum clusters encaged in the supercages of the zeolite was found to be shorter than that of the bulk metal. However, such a bond contraction was not observed on Pt particles supported on silica [1], although the particle size is not so different from the present one. Therefore, we cannot conclude that the contraction of Pt-Pt bond distance in Pt/NaY is simply due to the particle-size effect. The electronic structures of Pt/NaY and Pt/SiO₂ were investigated by J. C. Vadrine et al [6]. According to their results obtained by ESR measurements of TCNE radical anions formed on the Pt/NaY-zeolite

and Pt/SiO₂, the charge-transfer from platinum clusters to the substrates is significantly stronger in the Pt/NaY system than in the Pt/SiO₂; that is, platinum clusters in the NaY-zeolite are more cationic than those on the SiO₂-support. Since the electrons which are transferred from Pt clusters to zeolite have been occupying the high-lying states of anti-bonding character, constructed by the Pt 5d and 6s bond, such electron deficiency should induce the increase of the Pt-Pt bonding energy. This may be the reason for the contraction of Pt-Pt bond in the zeolite-supported platinum. A similar effect is expected to appear also in other supported metal catalysts. In fact, we have found in the case of highly dispersed, electron-deficient rhodium clusters supported on TiO₂ prepared from Rh(π -allyl)₂, Rh-Rh bond distance is shorter than those of the bulk rhodium metal as well as those of the Rh/SiO₂ system[7].

The static disorder is very large in the present case possibly because of the metal-support interaction as suggested by Marques et al[1]. However, it should be noted that the thermal disorder is smaller in the Pt cluster of the Pt/NaY-zeolite system than in the bulk Pt metal. It is generally supposed that the thermal disorder becomes the larger as the particle is the smaller. The present results entirely contradict with this usual understanding. Seemingly, the small thermal disorder in the present system is associated with the increase of the Pt-Pt bonding energy. Another reason could be the cage effect. In this system, platinum clusters are located in the fixed framework of the NaY-zeolite. Therefore the metal-support interaction might cause the suppression of the thermal vibration of the surface platinum atoms.

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