Time-Resolved DXAFS Study of Adsorption and Release of Hydrogen on Pt /MCM-41

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Abstract. We have clarified the adsorption and release mechanism of hydrogen to/from Pt clusters on an MCM-41 surface by using the XAFS technique. After reduction, the icosahedral Pt₁₃ cluster of $r(\text{Pt-Pt}) = 0.273$ nm is formed. In contrast, a very small oxidized metal particle of $r(\text{Pt-Pt}) = 0.254$ nm is formed after the oxidation. We have measured time-resolved energy dispersive XAFS in order to clarify the adsorption and release mechanism of hydrogen to/from Pt clusters on an MCM-41 surface. Although the reduction process can be explained as the sum of the initial and the final species, a third species should be considered in the oxidation process.

Keywords: adsorption and release of hydrogen, Time-resolved XAFS

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INTRODUCTION

Adsorbed hydrogen on many metal surfaces plays important roles in catalytic processes such as hydrogenation, hydrogenolysis, hydroformylation and so on. Hydrogen chemisorption property changes according to the preparation method and conditions for supporting Pt clusters [1-4]. We have clarified the cluster structures of Pt/MCM-41 at reduced and oxidized states by using XAFS. Then we have carried out time-resolved energy dispersive XAFS experiment (DXAFS) [5] in order to clarify the structure change, the Pt cluster reduction/oxidation process and to propose a reaction mechanism.

EXPERIMENTAL

3.5 wt % Pt/MCM-41 catalyst was prepared by an ion-exchange method using an aqueous solution (pH 9) of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ (Soekawa Chemical Co.). The obtained sample was dried in an oven at 353 K overnight and calcined at 573 K in a flow of O_2 (200 ml/min).

Static XAFS measurements were carried out in transmission mode at BL-7C (PF, KEK) with a Si(111) double crystal monochromator, whereas the DXAFS measurements were carried out at NW2A(PF-AR, KEK). Fig. 1 shows the schematic diagram of the optics layout for the DXAFS system.

FIGURE 1. Schematic diagram of the DXAFS setup. The glancing angle of the X-ray beam varies continuously across the crystal surface and results in different X-ray energies being reflected from different points on the crystal surface.

Polychromatic X-rays were obtained with a Si(111) bent crystal (Bragg-type) attached to a concave copper block whose radius is 3 m. The copper block was water-cooled by circulating thermostatically controlled water at 298 K. A self-scanning photodiode array (Hamamatsu Photonics, S3904-1024N) was used as a position sensitive detector.

We measured DXAFS spectra at the Pt L_{III} edge in the energy range of 11.4 ~ 12.2 keV. The position of each sensing element was converted into the corresponding X-ray energy by comparing the

measured spectrum of a Pt foil with that obtained at BL-7C.

The sample was pelletized, followed by the evacuation in a sample cell for 30 min. at 573 K. In-situ DXAFS spectra were recorded every 60 ms at 298 K. Hydrogen adsorption experiments were carried out twice and the sample was evacuated for 10 min. between them. The difference of these measurements represents the chemisorption part. These experiments were carried out simultaneously with the DXAFS measurements. The hydrogen uptake per Pt atom was calculated using the method described by Wilson and Hall [6]. XAFS data analysis was performed by using the UWXAFS package and the backscattering amplitudes, phase shift and mean free paths were calculated with the FEFF8 code.

RESULTS AND DISCUSSION

The chemisorption experiments show $H_{\text{strong}}/\text{Pt} = 0.9$ and $H_{\text{weak}}/\text{Pt} = 0.4$, irrespective of the Pt loadings in the range of 0.5 and 5 wt%, which suggests the Pt13 structure was invariant against the loadings at reduced condition. The reduction and the oxidation reactions reproduced well at 298 K.

Fig. 2 shows EXAFS oscillations (a) and their Fourier transforms (FT) (b) at Pt L_{III} edge of Pt/MCM-41 under reduced (1) and oxidized (2) conditions at 298 K.

FIGURE 2. k^3 -weighted EXAFS oscillations(a) and their Fourier transforms (b) of 3.5 wt% Pt/MCM-41 under the reduced (1) and oxidized (2) conditions at the Pt L_{III} edge by conventional XAFS.

After reduction, the main peak of the FT represents Pt-Pt interactions. The results of the EXAFS data analyses of Pt/MCM-41 are given in Table 1. The interatomic distance (R) and coordination number (CN) are 0.273 nm and 5.2 for Pt-Pt; namely, the cuboctahedral Pt13 cluster is formed. This result

agrees well with that estimated from hydrogen adsorption experiments. On the contrary, the amplitude at high k -region decreased and the oscillation period increased by the oxidation. R and CN of Pt-Pt changed from 0.273 to 0.254 nm and from 5.2 to 1.3. Additionally, a new peak corresponding to Pt-O interaction appeared in FT; $R=0.204$ nm and $CN=1.6$. These structural parameters indicate that the oxidized metal particle is very small (2-4 atoms per particle). The Debye-Waller factor was not so large, thus the distorted Pt13 cluster model can be excluded. Such structural transformation of Pt clusters on MCM-41 occurs reversibly.

Fig. 3(a) shows the time-resolved XANES spectra at the Pt L_{III} edge during the reduction process of Pt/MCM-41 under 3 kPa H_2 at 298 K. The energy resolution is reasonably good even if it is compared with conventional XAFS methods. The oxidized sample is placed under vacuum and the intense white line indicates that the platinum on MCM-41 is oxidized. When hydrogen gas is introduced at 0 s, the XANES spectrum changes drastically between 11564 and 11584 eV. The intensity of the white line decreases and a shoulder appeared in the region of 11574-11584 eV. This shoulder increases its intensity with the increase of adsorbed hydrogen and is ascribed to the multiple scattering from Pt-H [7]. This result indicates that the oxidized surface species of Pt is reduced and becomes metallic Pt. When oxygen is introduced again, the DXANES spectrum of oxidized species is reproduced.

FIGURE 3. (a) A series of DXAFS spectra under the reduction process and (b) the ratio of the initial (C_0 , -), final (C_1 , -) species and the residual factor (R_f , x) derived from XANES during the oxidation [O] and the reduction [H] process.

TABLE 1. Structural parameters for Pt/MCM-41 under the reduced (1) and oxidized (2) states.

abs.-scat	CN	R / 10 ⁻¹ nm	$\sigma^2/10^{-5}$ nm ²
Reduced (1)			
Pt-Pt	5.2 ± 0.5	2.73 ± 0.02	4.1 ± 2
Pt-Pt	0.2 ± 0.5	2.57 ± 0.02	6.0 ± 3
Oxidized (2)			
Pt-Pt	1.3 ± 0.5	2.54 ± 0.02	6.1 ± 2
Pt-Pt	0.3 ± 0.5	2.69 ± 0.02	6.3 ± 2
Pt-O	1.6 ± 0.5	2.04 ± 0.02	4.0 ± 2

In order to estimate the populations of the initial (reduced Pt cluster) and the final species (oxidized Pt cluster), we try to reproduce the observed XANES spectra (11.2~11.6 keV) by linear combinations of the reference spectra, as shown in eq. (1).

$$X(t)_{\text{obs}} = C_0 X_0 + C_1 X_1$$

$$R_f = \Sigma |(\chi_{\text{obs}} - \chi_{\text{calc}})| / \Sigma |\chi_{\text{obs}}| \quad (1)$$

where $X(t)_{\text{obs}}$ represents an observed X-ray-absorption near-edge structure (XANES) spectrum at t , X_0 and X_1 represent XANES of the initial and the final species and C_0 and C_1 represent their time-dependent proportions. Fig. 3(b) shows C_0 , C_1 and the residual factor R_f (%) during the oxidation process. The XANES spectra change drastically between 1 and 10 s and can not be reproduced by a linear combination of X_0 and X_1 , which means that a third species should be considered.

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