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## Pt L<sub>3</sub>-edge XANES studies about the hydrogen adsorption on small Pt particles

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Pt L<sub>3</sub>-edge XANES spectra were measured on the inorganic oxide-supported Pt small particles with and without adsorbed hydrogen. A peak about 8 eV above the edge appeared in the difference spectra between the Pt samples with and without hydrogen adsorption. The peak position in difference spectra was invariant with the particle sizes, the amount of adsorbed hydrogen and coadsorbates, and kind of supports. The peak intensity was only proportional to the amount of adsorbed hydrogen. Multiple scattering calculation could reproduce the peak induced by the hydrogen adsorption and showed the peak energy was independent of the number and the adsorption site of hydrogen on Pt surface. The Pt L<sub>3</sub>-edge XANES will be a good tool for the quantitative analysis of the adsorbed hydrogen on small metal Pt particles.

**Keywords:** Pt L<sub>3</sub>-edge XANES, Hydrogen Adsorption, Supported Pt Particles

### 1. Introduction

Pt L<sub>2,3</sub>-edge XANES has been investigated to monitor the electronic state of supported Pt catalysts. Relation between the white line peak areas of Pt L<sub>2,3</sub>-edge and the total number of unfilled states in the d-band has been proposed (Lytle, Wei, Gregor, Via, & Sinfelt, 1979; Mansour, Cook, & Sayers, 1984). When hydrogen adsorbs on the surface of Pt particles, the Pt L<sub>2,3</sub>-edges are shifted to higher energy side and the edge peaks are broadened. Origin of the broadening has been discussed by several authors (Otten, Clayton, & Lamb, 1994; Vaarkamp, Modica, Miller, & Koningsberger, 1993; Vaarkamp, Mojet, Kappers, Miller, & Koningsberger, 1995; Samant & Boudart, (1991); Ichikuni & Iwasawa, 1993). In this paper we will discuss origin of the

broadening in Pt L<sub>2,3</sub>-edge XANES induced by the adsorption of hydrogen empirically and theoretically and the possibility for the application of the Pt L<sub>2,3</sub>-edge XANES to a new quantitative estimation of the amount of adsorbed hydrogen.

### 2. Experimental

Samples were prepared by ion exchange or impregnation methods as reported previously (Asakura, Kubota, Ichikuni, & Iwasawa, 1996; Kubota, Asakura, Ichikuni, & Iwasawa, 1996; Kubota, Asakura, & Iwasawa, 1997). [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> were used as precursors for ion-exchange methods and impregnation methods, respectively. The samples were then calcined under air and reduced with H<sub>2</sub> at appropriate temperatures to control the Pt particle sizes (0.8–10 nm). The samples were then transferred into *in-situ* cells. Pt L-edge XANES spectra were measured at BL-10B of Photon Factory in Institute for Materials Structure Science, (IMSS-PF). The synchrotron radiation was monochromatized by a Si(311) channel cut monochromator. The energy was calibrated using the inflection point of Pt foil, which was fixed to be 11563 eV. The obtained XANES spectra were processed by subtracting the pre-edge background absorption from the raw data and normalising them by edge height. The H/Pt was estimated volumetrically from the amount of irreversible adsorption of hydrogen. XANES calculation was carried out by full multiple scattering method described elsewhere (Fujikawa, T, 1993; Ohtani, Fujikawa, Kubota, Asakura, & Iwasawa, 1997).

### 3. Results and Discussion

Fig.1 shows L<sub>3</sub>-edge XANES spectra before and after H<sub>2</sub> adsorption on Pt particle with a particle size of 0.8 nm together with difference spectrum between the two. As reported in the literature, the edge was shifted to higher energy and the broadening of the edge peak occurred. In the previous papers, the change in L<sub>2,3</sub>-edge XANES spectra were analysed on the assumption that the d-band structure were not changed and thus the amount of unoccupied d-electron state were proportional to the intensity of L<sub>2,3</sub>-edge XANES. The shift of the edge was attributed to the shift of initial state caused by the electron transfer from Pt particle to hydrogen. Thus in the previous analysis, the absorption edges before and after H<sub>2</sub> adsorption were aligned and the difference spectra were calculated in order to derive the change of edge peak intensity. (Mansour, Cook, & Sayers, 1984; Otten, Clayton, & Lamb, 1994; Vaarkamp, Modica, Miller, & Koningsberger, 1993; Vaarkamp, Mojet, Kappers, Miller, & Koningsberger, 1995; Samant, M. G. & Boudart, M., 1991) However, If the edge shift took place due to the chemical shift of the initial state, the L<sub>1</sub>-edge should be shifted similarly. However, we did not observe any shift in the L<sub>1</sub>-edge of Pt after H<sub>2</sub> adsorption (Asakura, Kubota,

Ichikuni, & Iwasawa, 1996). Thus the edge shift occurred not due to the change in the initial state but due to the change in electronic structure of the final state. This means the assumption that the band structure of the final state should be invariant is invalid and the previous analysis procedure can not be applied to change of XANES for the hydrogen-adsorbed Pt / SiO<sub>2</sub> system. Fig.2 shows the series of Pt L<sub>3</sub>-edge XANES spectra of Pt/SiO<sub>2</sub> with different amount of adsorbed hydrogen. First, hydrogen was adsorbed upto saturation coverage, i.e., H/Pt=1.2 (the ratio of adsorbed hydrogen atoms to total number of Pt atoms). The Pt/SiO<sub>2</sub> was then heated under vacuum at a ramping rate of 4 K/min to a given temperature and cooled down to room temperature rapidly. By this treatment adsorbed hydrogen was gradually desorbed. The XANES spectra at different treatment temperatures showed an isosbestic point. This fact indicates the change in XANES spectra induced by hydrogen adsorption arises from a localised Pt-H bond.

We take difference spectra without alignment of the edge position. In difference spectrum the positive peak denoted as "B" appears at 8 eV above the edge as shown in Fig.1(c). The photon energy for the peak B is independent of the support oxides (Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, and TiO<sub>2</sub>), amount of adsorbed hydrogen, particle size and coadsorbates (Kubota, Asakura, Ichikuni, & Iwasawa, 1996; Kubota, Asakura, & Iwasawa, 1997). Fig.3 shows the difference spectrum of Pt L<sub>3</sub>-edge XANES of Pt/SiO<sub>2</sub> between before and after H<sub>2</sub> coadsorption. The figure also includes the fitting results using the difference spectra of Pt/SiO<sub>2</sub> between before and after solo CO adsorption and solo H<sub>2</sub> adsorption. Since the negative part denoted as peak "A" in the difference spectra is located near the edge region and its shape and position are very sensitive to the chemical environment, we only consider the positive region as shown in Fig.3. The difference spectrum in positive region for Pt/SiO<sub>2</sub> with coadsorbed H<sub>2</sub> and CO can be expressed by a linear combination of difference spectra for hydrogen-adsorbed Pt/SiO<sub>2</sub> and CO-adsorbed Pt/SiO<sub>2</sub> without adjusting peak energy, indicating that the position of hydrogen induced peak B is not affected by coadsorbed species (Kubota, Asakura, & Iwasawa, 1997).

We carried out a multiple scattering calculation on Pt clusters with and without hydrogen using a partitioning method (Fujikawa, 1993; Fujikawa, Yanagisawa, Yiwata, & Ohtani, 1997). The calculation reproduces the change appearing in XANES spectra when the electron transfer from Pt 6s (or 6p) to H occurs and hydrogen eventually possesses the negative charge (0.54e) as shown in Fig.4. The calculated XANES is not sensitive to adsorption site of hydrogen on Pt. Hydrogen adsorption induces the change of final electronic state of Pt and alters the multiple scattering effect for the photoelectron (Ohtani, Fujikawa, Kubota, Asakura, & Iwasawa, 1997).

The area of the peak B is plotted against the number of adsorbed hydrogen per total number of Pt atoms (H/Pt) as shown in Fig.5. Hydrogen is adsorbed on Pt particles with

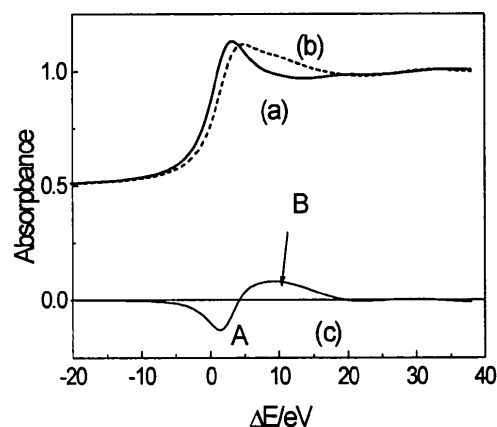


Figure 1. Pt L<sub>3</sub> edge-XANES of Pt/SiO<sub>2</sub> measured in vacuo(a) and after H<sub>2</sub> adsorption(b) together with the difference spectrum(c).

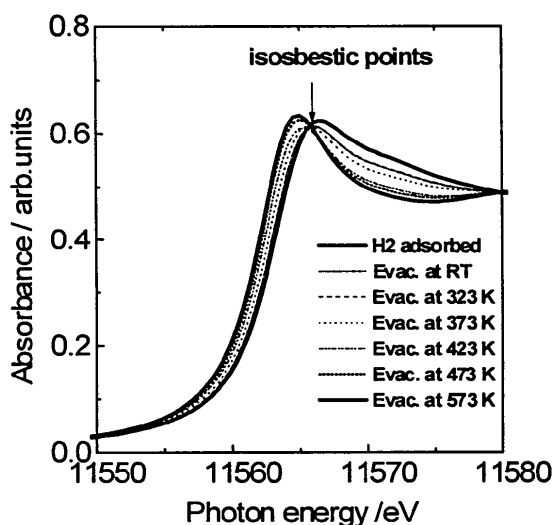
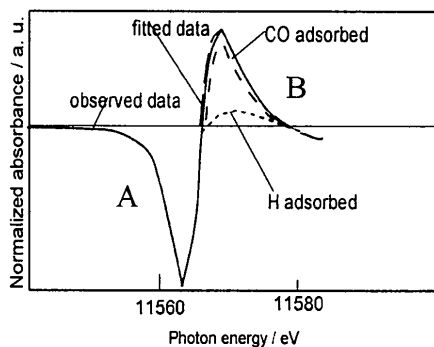
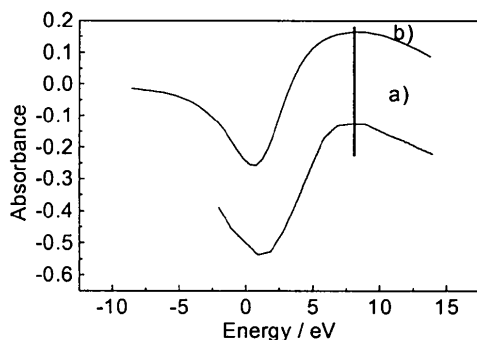


Figure 2. Pt L<sub>3</sub>-edge XANES spectra of Pt/SiO<sub>2</sub> (H/Pt=1.1) after the room temperature adsorption of H<sub>2</sub> and evacuation at given temperatures.

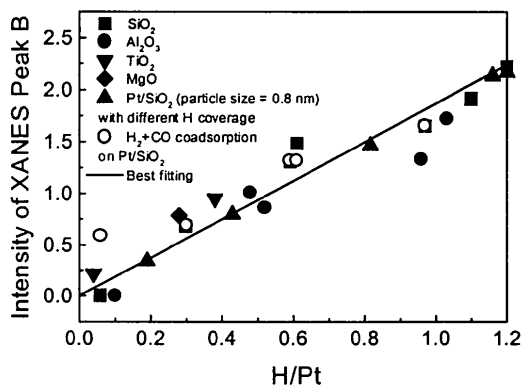
different particle sizes and with different supports upto a saturation level. We have found a linear correlation between the peak area and H/Pt. Moreover, when the same plots are carried out for the samples with the same particle size but different hydrogen coverages and the samples coadsorbed with different amount of CO and H<sub>2</sub>, these plots are distributed around the same line (filled triangles and open circles, respectively). This means the intensity of the peak B can be used to estimate the amount of adsorbed hydrogen. Since XANES experiment is possible in the presence of gas phase and at high temperature, amount of adsorbed hydrogen can be estimated from the XANES spectra under the reaction conditions.



**Figure 3.** XANES difference spectrum for CO + H<sub>2</sub> coadsorbed Pt/SiO<sub>2</sub> (solid line), CO-adsorbed (short broken line), H-adsorbed (dotted line) and fitted data produced by a linear combination of CO-adsorbed and H-adsorbed ones (long broken line). Each difference spectrum was taken between before and after adsorption of the gases.



**Figure 4** Different spectra of Pt L<sub>3</sub> edge between with and without hydrogen adsorption. (a) calculated one based on multiple scattering (Ohtani, Fujikawa, Kubota, Asakura & Iwasawa 1997). (b) corresponding observed spectra.



**Figure 5.** Relation between amount of saturatedly adsorbed hydrogen per total number of Pt atoms (H/Pt) and the area of peak B in Pt L<sub>3</sub>-edge XANES spectra for several different supports with different particle sizes.

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