Quantitative analysis of hydrogen adsorbed on Pt particles on SiO_2 in the presence of coadsorbed CO by means of L_3-edge X-ray absorption near-edge structure spectroscopy

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X-ray absorption near-edge structure (XANES) spectra at the Pt L_3-edge for Pt particles supported on SiO_2 under CO adsorption and CO + H_2 coadsorption were recorded to analyze the amount of adsorbed hydrogen in the coadsorbed state on the Pt particles. Adsorbed CO on the Pt particles revealed a new peak at 6 eV above the Pt L_3-edge in the difference spectra before and after CO adsorption in the coverage range 0.10–0.51. Subsequent adsorption of hydrogen at various coverages on the CO-preadsorbed Pt particles broadened and shifted the peak to the higher energy side. The peak was deconvoluted to two components due to adsorbed hydrogen and CO by a linear least-squares fitting technique. It was found that the fitting coefficient with respect to adsorbed hydrogen was proportional to the amount of adsorbed hydrogen. The XANES difference spectra provide a quantitative analysis method for adsorbed hydrogen on supported Pt particles in the presence of coadsorbates like CO.

Keywords: X-ray absorption near-edge structure (XANES), adsorbed hydrogen, adsorbed CO, Pt/SiO_2

1. Introduction

Hydrogen plays an important role in metal catalysis for many industrial processes such as hydrogenation, hydrogenolysis, dehydrogenation and isomerization, and hence quantitative analysis of adsorbed hydrogen is a key issue for understanding reaction mechanisms and developing new catalytic systems [1]. Surface hydrogen not only behaves as a reactant itself but also alters reaction paths through the induction of surface reconstruction or the production of different reaction intermediates [1–4]. However, it is rather difficult to characterize the adsorbed hydrogen especially in situ under reaction conditions because hydrogen has a low electron density and high mobility on the surface. In situ NMR and FT-IR have been the only tools to be used for the characterization of adsorbed hydrogen [5–7]. However, the data analysis of solid-state NMR is not easy and the sensitivity of FT-IR is not high enough for surface hydrogen so that they cannot be routinely used. In our previous papers, we found a new peak in the difference spectra between Pt $L_{2,3}$-edge XANES before and after H_2 adsorption on Pt particles on oxides [8,9]. This new peak appeared at a definite photon energy independent of the amount of adsorbed hydrogen, the size of Pt particles or clusters, and the kind of supports.

Moreover, the peak intensity was proportional to the amount of adsorbed hydrogen. These results demonstrate that the L_3-edge peak can be used as a quantitative scale for the amount of adsorbed hydrogen on the supported Pt particles, especially under in situ conditions relevant to catalytic reactions. To develop this method as a practical tool for the quantitative analysis of adsorbed hydrogen under reaction conditions, it is necessary to investigate the behavior of Pt $L_{2,3}$ XANES spectra in coadsorbed systems of H_2 and other reactants such as CO. In this paper we report Pt L_3-edge XANES spectra of Pt particles coadsorbed with H_2 and CO. It was found that there is a direct correlation between the amount of adsorbed hydrogen and the fitting coefficient which appears in the difference spectra before and after CO + H_2 coadsorption.

2. Experimental

2.1. Sample preparation

A Pt/SiO_2 catalyst was prepared by an ion-exchange method using an aqueous solution of $[Pt(NH_3)_4]Cl_2$ (Soekawa Chemical Co.) [8,9]. Aerosil 300 (Nippon Aerosil Co., surface area: 300 $m^2\ g^{-1}$) was used as support. The obtained sample was dried at 373 K and calcined at 573 K in a flow of O_2. The Pt loading in the sample was determined to be 1.3 wt%. The sample was placed in a U-shaped Pyrex-glass tube combined in a closed circulating system, and was oxidized with oxygen of 13.3 kPa for 30 min at 573 K, followed by reduction

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with hydrogen of 13.3 kPa for 1 h at the same temperature. The sample was then evacuated for 30 min at 573 K. The amount of hydrogen adsorbed on the Pt particle was volumetrically determined at 293 K. The dispersion of the Pt particles (H/Pt) was 0.97 which is defined as the amount of adsorbed hydrogen divided by the amount of Pt atoms involved in the catalyst. The amounts of adsorbed hydrogen and CO are shown in table 1.

2.2. Xanes measurements and analysis

Pt L_3-edge XANES spectra were measured at BL-10B in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF) in a transmission mode (Proposal No. 96G161). Detailed conditions about XANES measurements were described in the previous papers [8,9]. The sample treated in a closed circulating system was exposed to given pressures of CO (0.6–3.1 kPa) for 1 h to obtain various CO coverages. The sample was transferred to a XANES cell with two Kapton windows without contacting air. The XANES spectra of the supported Pt particles with preadsorbed CO were first measured in vacuum, then the CO-preadsorbed sample was exposed to 8.0 kPa of hydrogen for 30 min. The gas phase analysis showed no desorption of CO by the admission of H_2. After evacuating the sample for 30 min at room temperature the XANES measurement was carried out. The normalized XANES spectra were obtained by subtracting the pre-edge background from the raw data with a modified Victoreen's equation and normalizing them by the edge height estimated by a cubic spline method.

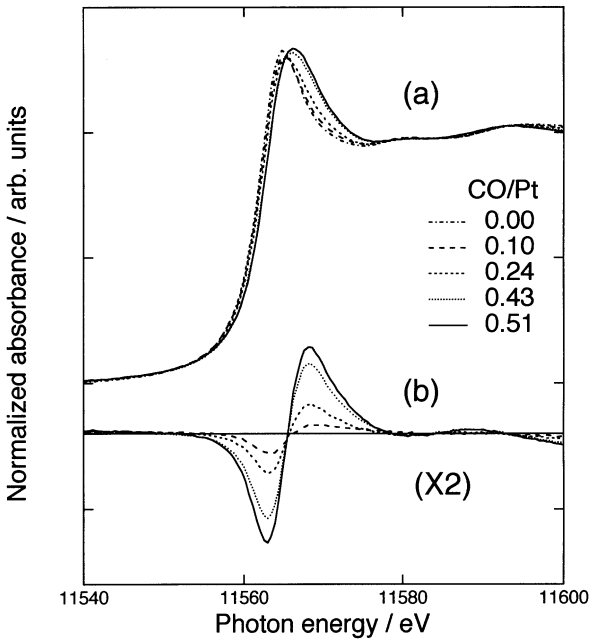

Figure 1. (a) Normalized Pt L_3-edge XANES spectra for CO-preadsorbed and CO-free Pt/SiO_2; (b) difference spectra between them.

3. Results and discussion

Figure 1a shows Pt L_3-edge XANES spectra for Pt/SiO_2 after CO adsorption, where CO coverages (CO/Pt) were varied in the range 0.10–0.51. The XANES spectrum for Pt/SiO_2 before CO adsorption is also shown in figure 1a. The Pt L_3-edge spectrum of the CO-free Pt/SiO_2 was broadened and shifted to the higher energy side by CO adsorption, as reported previously [10,11]. As shown in figure 1a, the broadening was enhanced by increasing CO coverage on the Pt particles. Interestingly, there is an isosbestic point in the spectra. Figure 1b shows the difference spectra derived from figure 1a before and after CO adsorption. A peak appeared at 6 eV above the Pt L_3-edge. The peak position was independent of the CO coverage as shown in figure 1b. This value is 2 eV lower than the peak energy induced by adsorbed hydrogen previously reported [8,9]. Figure 2a shows the Pt L_3-edge XANES spectra after subsequent exposure of the CO-preadsorbed Pt/SiO_2 to 8.0 kPa of H_2. The CO/Pt values in figure 2a denote the amount of preadsorbed CO per Pt. Comparing figure 2a with figure 1a, the edge position shifted to the higher energy side and the white line peak was broadened on the higher energy side upon H_2 adsorption. To clarify this matter we took the difference spectra between the spectra for the $CO + H_2$ coadsorbed Pt/SiO_2 and the spectrum for the fresh Pt/SiO_2 in figure 2b. One can find the more broadening of the peak in the difference spectra compared to that in the CO-adsorbed system. The broadening of the difference peak is reasonable because

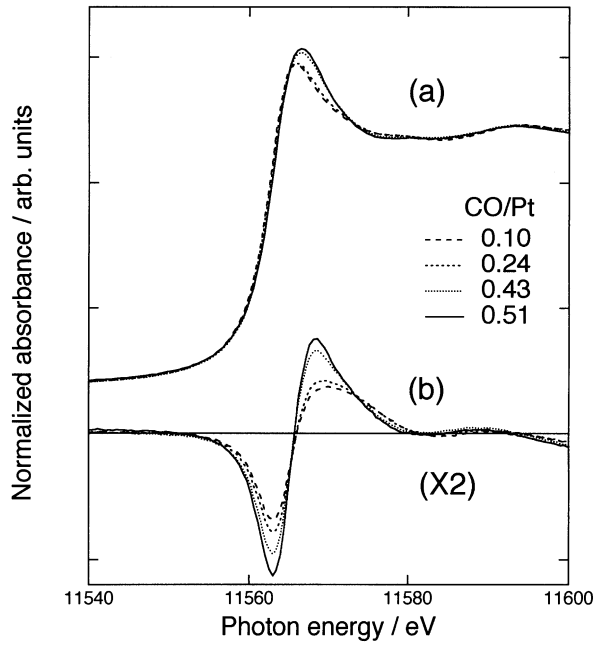

Figure 2. (a) Normalized Pt L_3-edge XANES spectra for $CO + H_2$ coadsorbed Pt/SiO_2; (b) difference spectra obtained by subtracting the CO-free spectra measured in vacuum from spectra (a).

the peak induced by H_2 adsorption appeared at 8 eV above the Pt L_3-edge [8,9]. We first analyzed the difference spectra μd(CO + H) between the spectrum for the CO + H_2 coadsorbed Pt particles and that for the bare Pt particles by a linear combination of μd(H) and μd(CO) (eq. (1)) although there should be broadening of the peak due to interaction of the adsorbed CO and H:

$$\mu\mathrm{d(CO + H)} = x \cdot \mu\mathrm{d(CO)} + y \cdot \mu\mathrm{d(H)}\,, \qquad (1)$$

where μd(CO) and μd(H) denote the difference spectra before and after the mono-adsorptions of H_2 at the coverage of 0.97 and of CO at the coverage of 0.51, respectively (figure 3a). The x and y are the coefficients in the linear combination of two components. Fitting range was chosen in 11566–11595 eV because the difference spectra in the energy region less than 11566 eV are strongly affected by the abrupt change of edge jump. The energy scale of the spectra is not adjusted in the fitting process. The observed difference spectra and the calculated difference spectra according to eq. (1) for the Pt/SiO_2 with different CO coverages are shown in figure 3b. Each component in the calculated spectra ($x \cdot \mu$d(CO) and $y \cdot \mu$d(H) is also shown in figure 3b. The calculated spectra show good agreement with the observed spectra. Thus the peak in the XANES difference spectra at Pt L_3-edge can be deconvoluted to the linear combination of the difference spectra for the CO and H mono-adsorbed systems. It seems that the interaction between adsorbed H and CO affects little the Pt L_3-edge XANES. Recently, we found the linear relation between the amount of adsorbed hydrogen and the peak height in the difference spectra before and after H_2 adsorption on Pt/oxides (oxides: SiO_2, Al_2O_3, and MgO). Here, to examine whether or not the correlation between the coefficient (y) for μd(H) in the linear combination (eq. (1)) and the amount of adsorbed hydrogen exists, the fitting coefficient (y) was plotted as a function of the amount of hydrogen estimated from gas adsorption in table 1. Figure 4 shows the plots of y vs. H/Pt, where the linear relationship between them is evident. This line has the same slope as that observed in the hydrogen mono-adsorbed system previously reported [8]. These results demonstrate that the fitting coefficient for adsorbed hydrogen (y) in the coadsorbed system is directly related to the number of hydrogen atoms adsorbed on the Pt particles. The fitting coefficient for adsorbed CO(x) also varied nearly linearly with the

Table 1
Amounts of adsorbed CO and hydrogen per Pt atom on Pt/SiO_2

CO/Pt	0	0.10	0.24	0.43	0.51
H/Pt	0.97	0.84	0.62	0.43	0.36

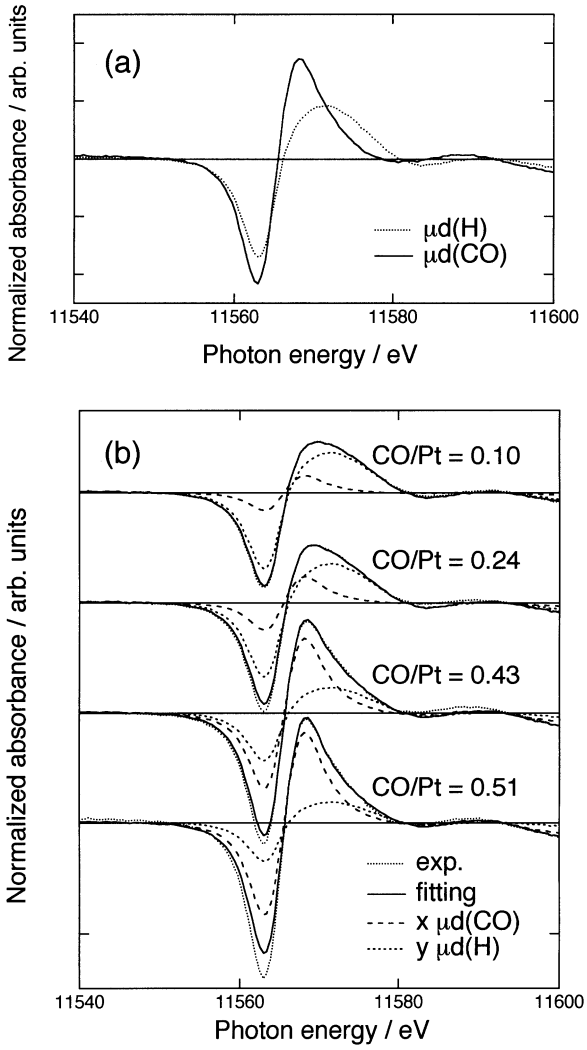

Figure 3. (a) Normalized Pt L_3-edge difference spectra before and after the mono-adsorptions of H coverage (0.97) and CO coverage (0.51); (b) normalized Pt L_3-edge difference spectra measured for CO + H coadsorption (solid line) and calculated spectra according to eq. (1) (dotted line), and component spectra for the calculation (two kinds of broken line).

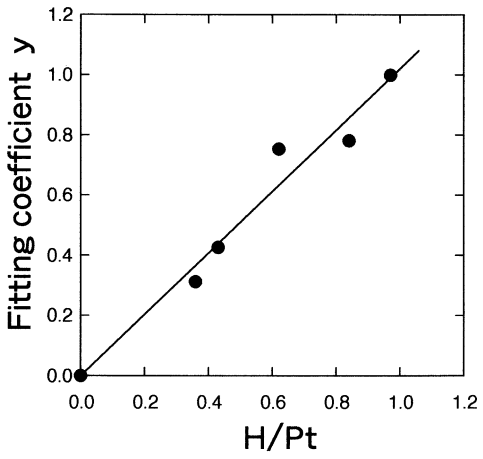

Figure 4. Plots of the fitting coefficients for adsorbed hydrogen as a function of H/Pt.

amount of adsorbed CO in the range of CO coverage 0.10–0.51. Although we need further investigation for the whole phenomenon, it is to be noted that the L_3-edge peak can be used as a quantitative measure for the amount of adsorbed hydrogen on the supported Pt particles in coadsorption systems and this technique can be applied to in situ conditions relevant to catalytic reactions involving adsorbed hydrogen. The present results also indicate that the difference spectra in the coadsorbed system reflect the local change of electronic states before and after H_2 adsorption on the Pt atoms with CO preadsorbates. Coadsorbed CO may change the H adsorption site and hence the local electronic state of Pt–H bonding, but the change in the XANES spectra due to this CO-induced effect would be too small to be detected by the present spectroscopy with an energy resolution of about 1.5 eV at BL-10B in the Photon Factory. The change in the XANES spectra by adsorption may be caused not only by the Pt–adsorbate electron transfer and the decrease in the electron density of the unoccupied d state but also by the change of electronic states due to the formation of Pt–adsorbate bonding.

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References

[1] Z. Paàl and P.G. Menon, *Hydrogen Effects in Catalysis* (Dekker, New York, 1988).
[2] K. Christmann, Surf. Sci. Rep. 9 (1988) 1.
[3] M.A. Barteau, E.I. Ko and R.J. Madix, Surf. Sci. 102 (1981) 99.
[4] G.S. Kellner and A.T. Bell, J. Catal. 75 (1982) 251.
[5] M.A. Chesters, K.J. Packer, D. Lennon and H.E. Viner, J. Chem. Soc. Faraday Trans. 91 (1995) 2191.
[6] M.A. Chesters, K.J. Packer, H.E. Viner, M.A.P. Wright and D. Lennon, J. Chem. Soc. Faraday Trans. 91 (1995) 2203.
[7] T. Szilagyi, J. Catal. 121 (1990) 223.
[8] T. Kubota, N. Ichikuni, K. Asakura and Y. Iwasawa, Chem. Phys. Lett. 256 (1996) 445.
[9] K. Asakura, T. Kubota, N. Ichikuni and Y. Iwasawa, *Proc. 11th Int. Congres on Catalysis*, Baltimore, Stud. Surf. Sci. Catal., Vol. 101 (Elsevier, Amsterdam, 1996) p. 911.
[10] B.L. Mojet and D.C. Koningsberger, Catal. Lett. 39 (1996) 191.
[11] I.T. Bae and A. Scherson, J. Phys. Chem. 100 (1996) 19215.