Catalysis Letters 20 (1993) 87–95

In situ d electron density of Pt particles on supports by XANES

Nobuyuki Ichikuni and Yasuhiro Iwasawa[1]

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113, Japan

The dependency of d electron density of Pt in Pt/SiO_2 catalysts on the particle size was investigated by means of in situ X-ray absorption near-edge structure (in situ XANES) spectroscopy. The d electron density of Pt particles was measured under vacuum, H_2 and ethene, to gain information about ethene hydrogenation on Pt/SiO_2. The intensities of the white lines at L_{III} and L_{II} edges in XANES spectra, which are regarded to reflect the unoccupied density of state, varied with the change of particle size under both vacuum and reaction gas atmospheres. The interaction between Pt particle and adsorbates was weak with small particles below 1.5 nm. A new peak induced by Pt–H bonding in the XANES spectra under H_2 was observed for the samples with Pt particle size $\leqslant 1.5$ nm. This is related to the change of the turnover frequency and activation energy for ethene hydrogenation by Pt particle size.

Keywords: In situ XANES; d electron density of Pt particles; Pt/SiO_2 catalyst; ethene hydrogenation; particle size effect

1. Introduction

The electronic properties of metal particles belong to the most important ingredients to understand the genesis and mechanism of noble-metal catalysis. The change in the d electron density of metal particles should be essential for metal catalysis since the adsorption or activation of reactants and hence the resultant surface reaction processes are affected largely by the interaction of d electrons with frontier orbitals of reactants. It is often said that static characterization of catalysts produces different results from in situ characterization [1–3]. Then, it is important to characterize the d electron density of state under in situ conditions. X-ray absorption near-edge structure (XANES) spectroscopy can provide this information. The white lines of Pt L_{III} and L_{II} edges, stemming from photo-excitation from the $2P_{3/2}$ or $2P_{1/2}$ state to the 5d state, respectively, have been demonstrated to reflect the unoccupied electron density of the 5d orbital of Pt [4].

We have already investigated the correlation between the activity of Na_2O-

---

[1] To whom correspondence should be addressed.

doped Pt/SiO_2 catalysts for ethene hydrogenation and the d electron density of the Pt particles under vacuum and ethene [1,2]. The d electron density of Pt under vacuum increased by the addition of Na_2O, indicating electron donation from Na_2O to Pt, whereas it was found that under the reaction conditions (the Pt surface is nearly saturated with ethene at low temperature) most of the d electrons donated from Na_2O moved to adsorbed ethene and as a result, hydrogen (its dissociative adsorption is rate determining for ethene hydrogenation) feels no change of d electron density of Pt irrespective of the donation of electrons from Na_2O. This may lead to a structure insensitive reaction for ethene hydrogenation on Pt/SiO_2 in an electronic sense.

The d electron density of Pt particles may also be controlled by the Pt particle size. This is related with the classification of the structure sensitive/insensitive reaction on Pt catalysts. The hydrogenation reaction has been classified to be structure insensitive, but recently opposite results were presented [5].

In this article, the d electron density of Pt particles in Pt/SiO_2 catalysts under vacuum and under in situ conditions, its change by the particle size, and observation of a Pt–H induced peak, are reported by means of in situ XANES.

2. Experimental

SiO_2 (Aerosil 200; surface area: 200 $m^2\ g^{-1}$ and Aerosil 300: 300 $m^2\ g^{-1}$) were used as support. Platinum loading was regulated to 1.5 wt%. Two methods of preparation were applied to change the particle size; one is the ion-exchange method using an aqueous solution of $Pt(NH_3)_4Cl_2$, and the other is an impregnation method using an aqueous solution of H_2PtCl_6. Each catalyst was placed in a U-shaped pyrex glass tube combined with a closed circulating system and treated with oxygen at 573 K for ion exchanged catalysts and at 673 K for impregnated catalysts, followed by reduction with hydrogen at the same temperature as oxidation. The temperature and duration of the pretreatments were varied to change the size of Pt particles. The particle size was estimated by irreversible hydrogen chemisorption assuming a stoichiometric ratio of $H/Pt = 1$.

XANES measurements of the catalysts at Pt L_{III} and L_{II} edges were performed at BL-10B in the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) (Proposal No. 91-171). The storage ring was operated at 2.5 GeV with the ring current 200–300 mA. Samples were prepared in the closed circulating system and transferred to glass cells with Kapton windows without contacting air. The XANES spectra were measured at room temperature under vacuum, hydrogen of 8.0 kPa, and ethene of 8.0 kPa, in a transmission mode. The synchrotron radiation was monochromatized by a Si(311) channel cut monochrometer. The energy calibration was carried out using Pt foil based on Pt inflection points of the L_{III} and L_{II} edges. The data collection was carried out by using the ionization chambers filled with nitrogen for I_0 (before sample) and I (after sample), with the length 17 and 34 cm, respectively. Edge jumps of the samples were regulated to about 0.5 for the L_{III} edge.

XANES data were analyzed as follows. Background subtraction from XANES data was performed with the Victoreen's equation,

$$\mu t = a_0 + a_3\lambda^3 + a_4\lambda^4$$

where μt is the absorption coefficient and λ is the wave length. The total amount of unoccupied electron density of d orbital of Pt samples, h_T, was calculated in the following equation [4]:

$$h_T = (1 + f_d)h_r\,, \tag{2}$$

where h_r is unoccupied d electron density of standard Pt (Pt foil) reported to be 0.30–0.40 [6,7]. Thus, f_d can be used as indicator of the unoccupied d electron density of the Pt sample. The f_d was expressed as

$$f_d = (\Delta A_{III} + 1.11\Delta A_{II})/(A_{IIIr} + 1.11A_{IIr})\,, \tag{3}$$

$$\Delta A_{III} = A_{III} - A_{IIIr}, \quad \Delta A_{II} = A_{II} - A_{IIr}\,. \tag{4}$$

Here, A_{III} and A_{II} are the intensities of the white lines at L_{III} and L_{II} edges. A_{IIIr} and A_{IIr} are the corresponding white line intensities for the reference sample. The intensity of a white line was determined from the result of the fitting with arctangent and Lorentzian functions for the normalized spectrum [8]. The area of the Lorentzian is attributed to the intensity of the white line.

3. Results and discussion

The particle size of supported platinum was varied in the range of 1.0–5.0 nm, which was determined by hydrogen chemisorption at 273 K. The range of particle sizes was wide enough to examine the particle size effect on chemical and physical properties.

The f_d of the supported Pt particles under vacuum is shown in fig. 1. Under vacuum, the d electron density of the Pt particles was almost constant in particle sizes larger than 1.5 nm, where the f_d was 0.07. However, the smaller the particle size in the region below 1.5 nm, the more the Pt particle became electron deficient. The f_d value changed from 0.07 for 1.5 nm to 0.12 for 1.0 nm. Although the shape and intensity of the Pt white line may be influenced by d–s rehybridization, the f_d should reflect the change in d electron density of state arising from particle size, adsorption and metal–support interaction [1–3,9–13]. To reduce the composite effect, we used the same support for five catalysts. Although a sample possessing the smallest particle (1.0 nm) was prepared by using a different support (Aerosil 300) from others (Aerosil 200), the differences of the nature of support were not so serious. The XPS binding energy (BE) of Pt particles also increases below 2 nm [14–17].

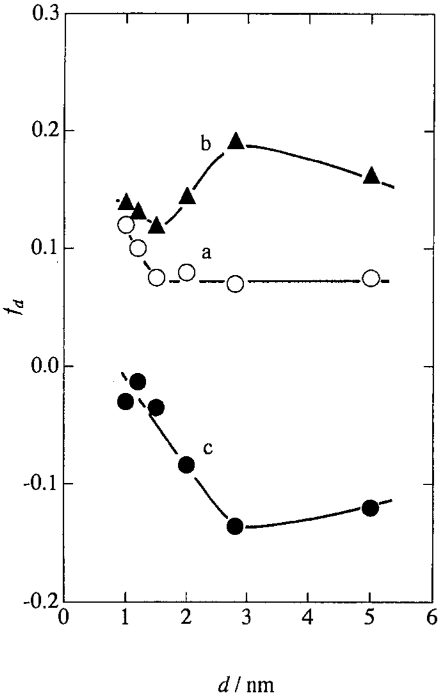

Fig. 1. f_d for Pt/SiO$_2$ as a function of diameter of Pt particles (d); (a) under vacuum, (b) under 8.0 kPa of ethene, (c) under 8.0 kPa of hydrogen.

These results suggest that the smaller Pt particles (1–2 nm in diameter) are electronically deficient as compared with bulk Pt.

Fig. 1 also shows the f_d of the supported Pt particles under reaction-gas atmosphere (ethene or hydrogen). It was observed that the f_d was changed by electron transfer of Pt particle from/to adsorbates. Exposure of the Pt samples to ethene at 293 K caused an upshift of f_d, indicating the withdrawal of d electrons by ethene. On the other hand, the adsorption of hydrogen shifted the d electron states to more rich electron density, suggesting that hydrogen behaved as an electron donor. Comparing these f_d values with those under vacuum, we can obtain the difference of f_d under vacuum and reaction conditions, Δf_d, for each particle size as shown in fig. 2. Since the difference was caused by adsorbates, Δf_d was divided by the amount of chemisorbed ethene or hydrogen on Pt. The normalized Δf_d ($\Delta f_d'$) is also shown in fig. 2. The tendency of the particle size effect is similar to both adsorptions, though the direction of electron transfer is opposite. The larger the particle size in the range $\leqslant 3.0$ nm, the more the electron transfer between Pt particles and adsorbates increased. These phenomena can be explained partly by the increase of BE under vacuum for smaller particles of Pt below 2.0 nm [14–17]. This may weaken the electronic interaction between smaller particles and ethene on the smaller Pt particles than 2.0 nm.

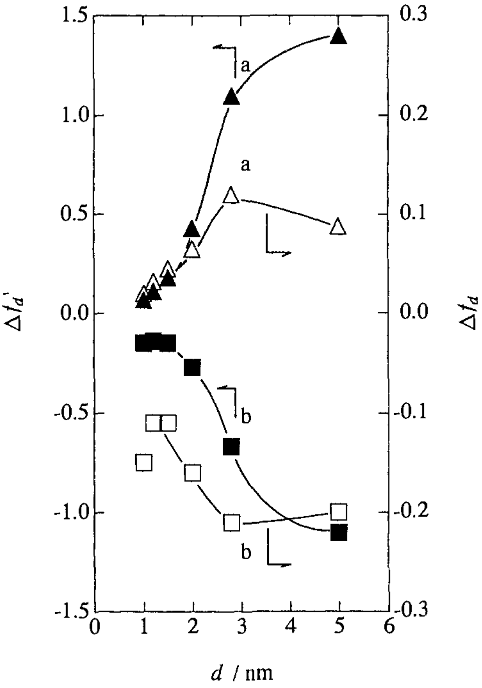

Fig. 2. Δf_d (f_d (C_2H_4) $-f_d$(vacuum) (△) or $f_d(H_2)-f_d$(vacuum) (□)) as a fuction of diameter of Pt particles (*d*); (a) under 8.0 kPa of ethene, (b) under 8.0 kPa of hydrogen; (▲) and (■) $\Delta f_d'$ (Δf_d divided by the number of adsorbates per Pt).

Fig. 3 shows the normalized XANES spectra at L_{III} and L_{II} edges under vacuum and 8.0 kPa of H_2. In fig. 3, the fitting analyses by arctangent and Lorentzian for the XANES spectra are also shown. White lines for the larger particles ($\geqslant$2.0 nm) under both vacuum and hydrogen are characterized by a Lorentzian peak as shown in fig. 3A. White lines of the particles below 1.5 nm were broadened by H_2 adsorption, so the second Lorentzian function was needed to fit the peak well as shown in figs. 3B and 3C. They were reproduced only by two Lorentzian peaks and never by one Lorentzian peak. The second peak was observed in both L_{III} and L_{II} edge spectra. And the new peak position was independent of particle size to be ca. 6 eV higher from the inflection point of the edge. The new peak disappeared by evacuation of adsorbed hydrogen and appeared again by H_2 adsorption (fig. 3). Although the thickness effect may distort the white line area as reported by Meitzner et al. [18], its effect is estimated to be below ca. 5% of the edge jump intensity, but our second peak was much larger than it (ca. 10 times) as shown in figs. 3B and 3C. The thickness effect may also lead to a little high values for f_d, which would, however, not change the present discussion based on the relative f_d values and their difference.

The relative areas of the second peak normalized by the second peak for the smal-

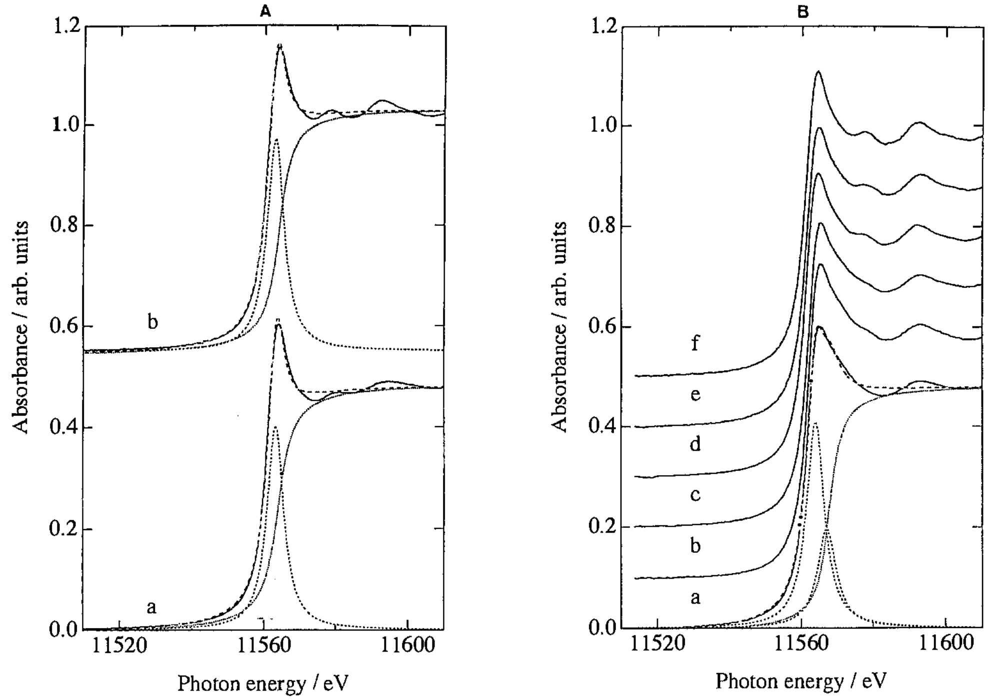

Fig. 3. (A) Normalized XANES spectra at L_{III} edge under vacuum (without adsorbed hydrogen); (a) $d = 1.0$ nm, (b) $d = 2.8$ nm. (B) Normalized XANES spectra at L_{III} edge under 8.0 kPa of hydrogen; (a) $d = 1.0$ nm, (b) $d = 1.2$ nm, (c) $d = 1.5$ nm, (d) $d = 2.0$ nm, (e) $d = 2.8$ nm, (f) $d = 5.0$ nm. (C) Normalized XANES spectra at L_{II} edge under 8.0 kPa of hydrogen; (a) $d = 1.0$ nm, (b) $d = 1.2$ nm, (c) $d = 1.5$ nm, (d) $d = 2.0$ nm, (e) $d = 2.8$ nm, (f) $d = 5.0$ nm.

lest particles with 1.0 nm size at L_{III} edge, are plotted against Pt particle size in fig. 4. The areas of the second peak divided by the amount of adsorbed hydrogen were calculated as shown by the solid lines in fig. 4. The peak areas for three samples with the particle size $\leqslant 1.5$ nm are on the lines. These results suggest that the new peak is due to the direct interaction between Pt surface and adsorbed hydrogen atoms. Samant and Boudart [19] observed a similar peak at about 9 eV above the edge in the difference XANES spectra between the spectra in H_2 and that in He for Pt/Y zeolite. They claimed that adsorbed hydrogen on the Pt particles created the occupied bonding state below the d band and unoccupied antibonding state above the d band. We tentatively assign this new peak at ca. 6 eV above the edge inflection point to be due to the Pt–H bond by the present arctangent–Lorentzian analysis, though a multiple exciting mode like shake up cannot be excluded. This is supported by the following fact; first, the peak appears only under hydrogen atmosphere and second, the peak areas were linearly correlated with the amount of adsorbed hydrogen.

The second peak due to Pt–H bonding was observable with the particles below

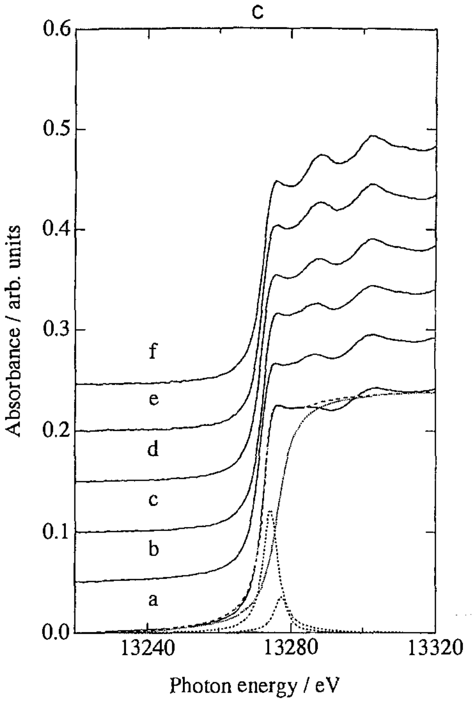

Fig. 3. (continued).

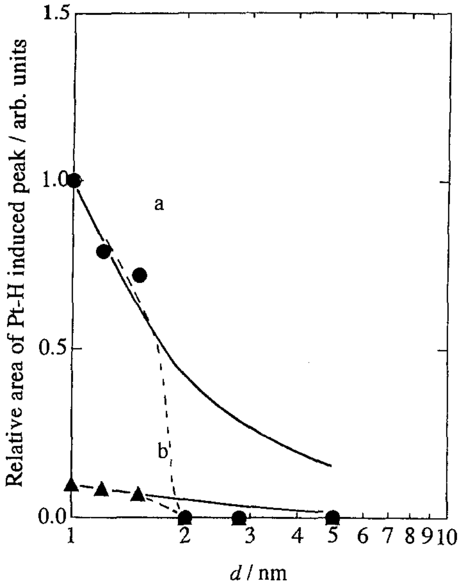

Fig. 4. Variation of relative area of the second Lorentzian peak under 8.0 kPa of hydrogen with diameter of Pt particles; (a) L_{III} edge, (b) L_{II} edge. The solid lines are simulated from the ratio of surface Pt atom to bulk Pt atoms as a function of the particle size.

1.5 nm. According to the f_d under vacuum in fig. 1, the nature of the Pt particles changed at 1.5–2.0 nm. The amount of d electrons transferred was less with particle sizes $\leqslant$1.5 nm than for the larger particles. This trend seems reverse to the one expected from the change of f_d and BE. The reason is not clear at present, but the Pt–H bond character may be different for different particle sizes; the hydrogen on Pt particles $\leqslant$1.5 nm may covalently bond with the surface Pt atoms, where electrons do not move to the Pt atom so much in net, while hydrogen atoms on Pt particles $\geqslant$2.0 nm can move at the surface, where each H atom may interact multiply with Pt atoms like at three-fold hollow sites for the (111) surface and at four-fold hollow sites for the (100) surface.

The different behavior of the Pt particles below and above 1.5 nm in the XANES spectra under H_2 and C_2H_4 was reflected in the kinetic data for ethene hydrogenation. The equilibrium constant for ethene adsorption was smaller with the particles $\leqslant$1.5 nm than for the particles $\geqslant$2.0 nm, which coincides with the results in fig. 2. The activation energy for ethene hydrogenation on the smaller Pt particles $\leqslant$1.5 nm was found to be 16 kJ mol^{-1}, while the activation energy for the larger particles of 2.8 and 5.0 nm was 34 kJ mol^{-1}.

Ethene hydrogenation is a reaction investigated for a long time, but the precise mechanism involving electronic and geometric behaviors of adsorbates by metal–adsorbate and adsorbate–adsorbate interaction is still the subject of controversy. However, it is to be noted that the d electron density of Pt particles on SiO_2 changed drastically by the coexistence of reactant gas and also by the particle size, which are characterized by in situ XANES. Further investigation is needed for comprehensive understanding of the present XANES data.

References

[1] H. Yoshitake and Y. Iwasawa, J. Phys. Chem. 95 (1991) 7368.
[2] H. Yoshitake and Y. Iwasawa, J. Catal. 131 (1991) 276.
[3] H. Yoshitake and Y. Iwasawa, J. Phys. Chem. 96 (1992) 1329.
[4] A.N. Mansour, J.W. Cook Jr. and D.E. Sayers, J. Phys. Chem. 88 (1984) 2330.
[5] C. Michel and C.O. Bennett, Adv. Catal. 36 (1989) 55.
[6] M. Brown, R.E. Peierls and E.A. Stern, Phys. Rev. B 15 (1977) 738.
[7] L.S. Mattheiss and R. Deitz, Phys. Rev. B 22 (1980) 1663.
[8] J.A. Horsley, J. Chem. Phys. 76 (1982) 1451.
[9] D.R. Short, A.N. Mansour, J.W. Cook Jr., D.E. Sayers and J.R. Katzer, J. Catal. 82 (1983) 299.
[10] P. Gallezot, R. Weber, R.A. Dalla Betta and M. Boudart, Z. Naturforsch. 34a (1979) 40.
[11] T. Fukushima, J.r. Katzer, D.E. Sayers and J.W. Cook Jr., *Proc. 7th Int. Congr. on Catalysis* (1980) p. 79.
[12] F.W. Lytle, P.S.P. Wei, R.B. Greegor, G.H. Via and J.H. Sinfelt, J. Chem. Phys. 70 (1979) 4849.
[13] F.W. Lytle, R.B. Greegor, E.C. Marques, D.R. Sandstrom, G.H. Via and J.H. Sinfelt, J. Catal. 95 (1985) 546.
[14] M.G. Mason, L.J. Gerenser and S.T. Lee, Phys. Rev. Lett. 39 (1977) 288.

[15] T. Huizinga, H.F.J. van 't Blick, J.C. Vis and R. Prins, Surf. Sci. 135 (1983) 580.
[16] A. Masson, B. Bellamy, G. Colomer, M. M'bedi, P. Rabette and M. Che, *Proc. 8th Int. Congr. Catalysis*, Vol. 4 (1984) p. 333.
[17] A. Masson, B. Bellamy, Y. Hadj Romdhane, M. Che, H. Roulet and G. Dufour, Surf. Sci. 173 (1986) 479.
[18] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Phys. Chem. 96 (1992) 4960.
[19] M.G. Samant and M. Boudart, J. Phys. Chem. 95 (1991) 4070.