

XAFS study of the additive cation effect on the oxidation-resistance of platinum catalyst

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The additive cation effect on the oxidation-resistance of platinum supported on alumina was investigated by Pt L_{III} and L_{II}-edge XAFS. The white line intensity at Pt L_{III}-edge of oxidized catalysts decreased with an increase in the electronegativity of the additive cation in the same way as the support effect previously reported: The addition of electrophilic cations make the supported platinum less oxidized state compared with the original Pt/Al₂O₃ and *vice versa*. Thus, it was revealed that the addition of more electrophilic cations provides the higher oxidation-resistance to platinum catalyst, even when platinum is supported on basic oxides.

Keyword: additive cation effect; oxidation-resistance; Pt L-edge XAFS; platinum catalyst.

1. Introduction

Supported noble metal catalysts are used in a number of important reactions; industrial process and emission control. The activity and the selectivity of supported noble metals are obviously varied with the support material and the additive cation in many catalytic reactions. There are many research papers concerned with the support and additive cation effect on the catalytic property of noble metal catalyst, but so far, many of them reported on the support and additive cation effect in the reducing atmosphere such as hydrogenation. It seems to be a general consensus that the changes in the catalytic performance are generally attributed to the change in the electronic property of noble metals, arisen from the interaction between metal particle and the support material and/or additive cation, and that the electrophilic supports and additive cations make noble metals cationic. On the other hand, in the oxidizing atmosphere such as hydrocarbon combustion, it is not systematically understood how the support materials and the additive cations affect the activity of noble metal catalysts although the catalytic activity of supported noble metals is known to be varied with the support materials and the additive cations. In this atmosphere, noble metal is oxidized to some extent under the reaction condition, and the oxidation state of noble metal is one of key factors to control its performance. Recently, in propane combustion over noble metal catalysts, the authors showed that the catalytic activity can be improved by the selection of support materials through the controlling the oxidation state of noble metal (Yazawa et al., 1999; Yoshida et al., 1999; Yazawa et al., 2000). In the case of platinum catalysts, the stronger acidic support gives the higher oxidation-resistance to platinum catalyst, leading to the higher catalytic activity for propane combustion, since combustion activity of platinum

decreases as platinum is oxidized (Voelter et al., 1987; Nunan et al., 1992). However, in the case of practical use of supported noble metal catalysts, the support material is usually selected by taking into account various factors such as the surface area, the thermal stability, the resistance to poisoning, and so on, and thus, the selected support is not always effective for the improvement of the catalytic activity. In the present study, the effect of additive cation, which may be selected under less limited conditions, on the oxidation-resistance of supported platinum catalyst is investigated by Pt L_{III} and L_{II}-edge XAFS.

2. Experimental

5 wt% Pt/Al₂O₃ was prepared by impregnating Al₂O₃ with an aqueous solution of Pt(NO₂)₂(NH₃)₂. Excess water was removed with suction at room temperature by rotary evaporator followed by drying at 383 K for 12 h, calcination at 673 K for 3 h, and reduction at 623 K for 3 h in flowing hydrogen to obtain Pt/Al₂O₃. Al₂O₃ employed was the reference catalyst of the Catalysis Society of Japan (JRC-ALO-4, Uchijima, 1990) with BET surface area of 177 m²/g. M/Pt/Al₂O₃ (M: additive cation, M/Pt=4 by mole) was prepared by impregnating Pt/Al₂O₃ with an aqueous solution of the Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, H₃PO₄, KNO₃, NH₄VO₃, Y(NO₃)₃·4H₂O, ZrO(NO₃)₂·2H₂O and H₂MoO₄, followed by drying and calcination procedures mentioned above.

Pt L_{III}, L_{II}-edge XAFS spectra were recorded at the BL-10B station (Nomura & Koyama, 1989) at KEK-PF with a Si(311) channel cut monochromator in transmission mode at room temperature. The catalysts were oxidized at 823 K (except for PtO₂·nH₂O, oxidized at 673 K) for 1 h, cooled down immediately to room temperature, and then sealed in polyethylene packs under nitrogen atmosphere.

3. Results and discussion

Fourier transforms of Pt L_{III}-edge EXAFS spectrum (Δk is 4–16 Å⁻¹) of representative samples oxidized at 823 K are depicted in Figure 1. Pt-Pt shell is observed at 2.6 Å on the spectrum of Pt-foil (Fig. 1a), whereas Pt-O shell and Pt-Pt shell is observed at 1.7 Å and 3.0 Å, respectively, on the spectrum of PtO₂ (Fig. 1e). On Pt/Al₂O₃ (Fig. 1b), with no additive cation, an intense peak due to Pt-O shell was seen at 1.7 Å and very weak one at 2.6 Å due to metallic platinum, indicating that platinum on Al₂O₃ is not fully oxidized. By the introduction of the additive cation, the Pt-O shell intensity scarcely changed but the intensity of Pt-Pt shell at 2.6 Å varied in some cases. The intense peak due to Pt-Pt shell, much larger than that on Pt/Al₂O₃, was observed by the addition of molybdenum (Fig. 1d), phosphorous and vanadium (not shown), indicating that the oxidation-resistance is raised by these additive cations. On the other hand, the other additive cations weaken the intensity of Pt-Pt shell, for example, the Pt-Pt shell almost disappeared by potassium addition (Fig. 1c). Thus, the intensity of Pt-Pt shell seems to change with electronic property of the additive cation, but the quantitative relation can not be obtained by Fourier transforms of EXAFS spectrum.

XANES should be more sensitive for the electronic charge of absorbing atom than EXAFS. Pt L_{III} and L_{II}-edge XANES

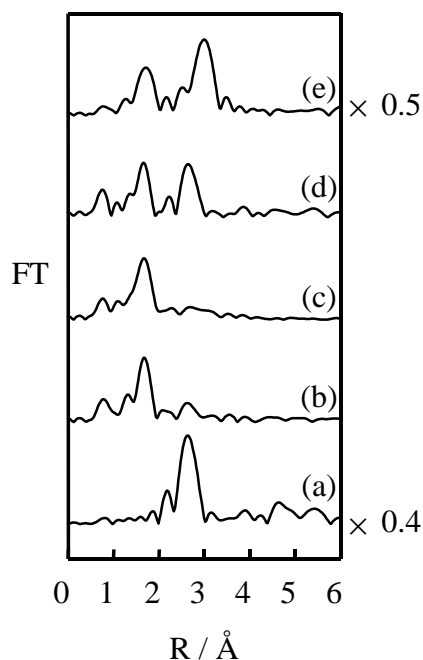


Figure 1

Fourier transforms of Pt L_{III} -edge EXAFS spectrum of Pt-foil (a), Pt/ Al_2O_3 (b), K/Pt/ Al_2O_3 (c), Mo/Pt/ Al_2O_3 (d) and PtO₂·nH₂O (e). The supported samples were oxidized at 823 K.

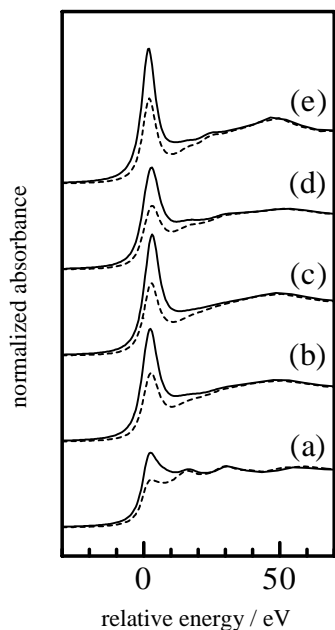


Figure 2

L_{III} (solid line) and L_{II} (broken line) -edge XANES spectra of Pt-foil (a), Pt/ Al_2O_3 (b), K/Pt/ Al_2O_3 (c), Mo/Pt/ Al_2O_3 (d) and PtO₂·nH₂O (e). The supported samples were oxidized at 823 K.

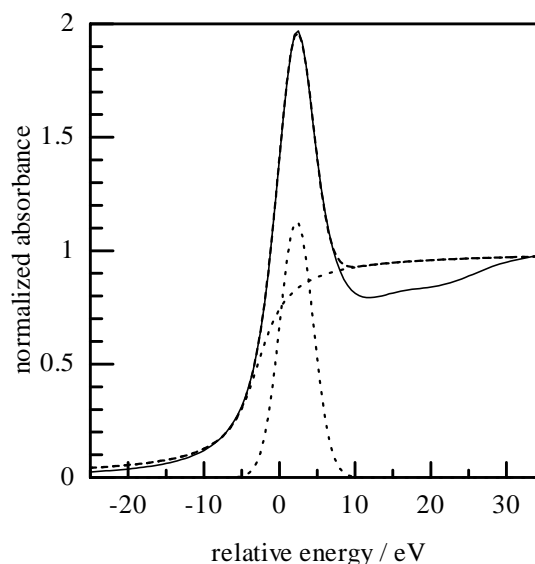


Figure 3

Pt L_{III} -edge XANES spectrum of Pt/ Al_2O_3 (solid line). The dotted line and broken line show components for curve fitting (an arctangent and a gaussian functions) and the sum of them, respectively.

spectra of representative M/Pt/ Al_2O_3 oxidized at 823 K and reference (Pt-foil and PtO₂) are shown in Figure 2. Since the white line (the large peak at the absorption edge) at Pt L_{III} and L_{II} -edge is assigned to the electron transition mainly from 2p to 5d, the larger intensity of white line indicates the larger vacancy in 5d orbital. Thus, the white line intensity is regarded as an indication of the oxidation state of platinum. It is obvious from the comparison with the spectra of Pt-foil and PtO₂ that the spectra of the catalysts are similar to that of PtO₂ rather than that of Pt foil, but the white line intensity varied with the kind of the additive cation. The white line at both L_{III} and L_{II} -edge decreased in the sequence of K/Pt/ Al_2O_3 > Pt/ Al_2O_3 > Mo/Pt/ Al_2O_3 . This result clearly shows that potassium addition accelerates the oxidation of platinum and, contrary, molybdenum addition depresses the oxidation of platinum.

It is considered that the white line intensity at Pt L_{III} -edge XANES spectrum is more informative than that at L_{II} -edge for elucidating the oxidation state of platinum, since white line at L_{III} -edge is assigned to the electron transition to 5d_{3/2} and 5d_{5/2}, and that at L_{II} -edge is transition to 5d_{3/2}. The area intensity of white line at Pt L_{III} -edge XANES spectrum was evaluated by the curve fitting analysis by using an arctangent and a Gaussian functions (Yoshida & Tanaka, 1996). The example of curve fitting analysis is shown in Figure 3. The relationship between electronegativity of the additive cation and white line intensity at Pt L_{III} -edge XANES spectra is shown in Figure 4. The electronegativity of the additive cation was calculated by the equation (Tanaka & Ozaki, 1967)

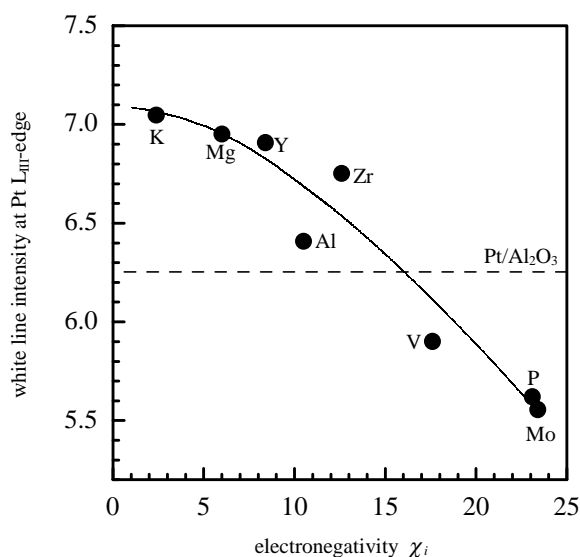


Figure 4

The relationship between electronegativity of additive cation and the white line intensity at Pt L_{III}-edge XANES spectra of M/Pt/Al₂O₃.

$$\chi_i = (1+2i) \cdot \chi \quad (1)$$

where χ_i is the electronegativity of the additive cation, i the valence of the cation and χ the electronegativity of the additive element as metal. The white line intensity clearly changes with the electronegativity of the additive cation; the addition of more electrophilic cations makes the platinum less oxidized state compared with the original Pt/Al₂O₃ and *vice versa*. It is known that the oxidation of noble metals with less electrophilic cation, e.g., alkali and alkaline earths, leads to the formation of complex oxide (Bergner and Kohlhaas, 1973; McVicker et al., 1978), which may stabilize oxidized state of noble metals. This is in accordance with the result that the addition of less electrophilic cations, e.g., potassium, magnesium, and so on, makes the platinum highly oxidized state as shown in Figure 4. By the addition of highly electrophilic cations, e.g., phosphorus, molybdenum, and so on, the platinum is less oxidized compared with the original Pt/Al₂O₃. This result may be rationalized by supposing that the highly electrophilic cations suppress such effect of Al₂O₃ support which is relatively less electrophilic, resulting in higher oxidation-resistance which, in turn, leads to higher catalytic activity in propane combustion.

In the previous paper, the authors reported that the white line intensity at Pt L_{III}-edge XANES spectra of platinum catalysts supported on various oxides decreases with an increase in the acid strength of support materials (Yoshida et al., 1999; Yazawa et al., 2000). The present study revealed that the additives have the same effect. Further, the white line intensity changed to the same extent as observed in the support effect. These results indicate that the cation located near the noble metal may control the oxidation state of noble metal depending on its electronegativity irrespective of its state, i.e., the support material or the additive cation. This is very important from the practical viewpoint. Thus, the additive cations can be changed more widely and selected with less limitation

compared with the support materials, and the high oxidation-resistance can be provided by the addition of electrophilic cations to the noble metals supported even on basic oxides.

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References

- Bergner, V. D. & Kohlhaas, R. (1973). *Z. anorg. Allg. Chem.* **401** 15-20.
- McVicker, G. B., Garten, R. L. & Baker R. T. K. (1978). *J. Catal.* **54** 129-142.
- Nomura, M. & Koyama, A. (1989). *KEK Report* **89-16**, 1-21.
- Nunan, J. G., Robota, H. J., Cohn, M. J. & Bradley, S. A. (1992). *J. Catal.* **133** 309-324.
- Tanaka, K. & Ozaki, A. (1967). *J. Catal.* **8** 1-7.
- Uchijima, T. (1990). *Catalytic Science and Technology*, Vol. 1, edited by Yoshida, S., Takezawa, N. & Ono, T., pp.393.
- Voelter, J., Lietz, G., Spindler, H. & Lieske, H. (1987). *J. Catal.* **104** 375-380.
- Yazawa, Y., Yoshida, H., Takagi, N., Komai, S., Satsuma, A. & Hattori, T. (1999). *J. Catal.* **187**, 15-23.
- Yazawa, Y., Yoshida, H., Takagi, N., Kagi, N., Komai, S., Satsuma, A., Murakami, Y. & Hattori, T. (2000). *Stud. Surf. Sci. Catal.* **130**, 2189-2194.
- Yoshida, H., Yazawa, Y., Takagi, N., Satsuma, A., Tanaka, T., Yoshida, S. & Hattori, T. (1999). *J. Synchrotron Rad.* **6**, 471-473.
- Yoshida, S. & Tanaka, T. (1996). *X-ray Absorption Fine Structure for Catalysts and Surfaces* (World Scientific Series on Synchrotron Radiation Techniques and Applications, Vol. 2), edited by Iwasawa, Y., Chapter 8.2.2, pp.308.