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XANES study of the support effect on the state of platinum catalysts

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Pt L_{III} and L_{II}-edges XANES clarified the oxidation state of platinum catalysts supported on various metal oxides. The acid-base property seemed one of the most dominant factors to control the electron state of platinum. On the reduced samples, there was a tendency that acidic support reduced the 5d-electron density of platinum, while the oxidized samples on acidic support contained more metallic platinum. The latter tendency agreed well with high activity of platinum catalysts on acidic supports toward propane combustion in oxidizing condition, and it was explained by a hypothetical mechanism for prevention of oxidation of platinum by acidic supports.

Keyword: Pt catalyst; Pt L-edge XANES; d-electron density; support effect; oxidation state of platinum.

1. Introduction

Precious metal catalysts such as platinum and palladium are widely recognized to be the most active for catalytic combustion. The catalytic activity of platinum catalyst was often affected by the structural parameters such as metal dispersion and the properties of support materials. The support effect on the low temperature catalytic combustion has been left unclear (Cullis and Willatt, 1983), except for the report that supported platinum catalyst in the combustion of methane is active in the order of Pt/SiO_2-Al_2O_3 > Pt/Al_2O_3 > Pt/SiO_2 (Niwa *et al.*, 1983). Recently, the catalytic performance of supported platinum catalyst in propane combustion was found to be enhanced by the use of acidic metal oxide as support material (Ishikawa *et al.*, 1994, Sugaya *et al.*, 1994). Since metal platinum was assigned to be active sites in this system, it was suggested that acidic support material prevented platinum from the oxidation and then promoted the catalytic activity. However, it was not clearly shown that acidic support has such a function and nothing was given for the mechanism of such a support effect. In the present study, the electronic states of platinum catalysts supported on various oxides are investigated by XANES to discuss the effect of the acid-base property of support materials.

2. Experimental

Catalysts were prepared by impregnating various oxides listed in Table 1 with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$ followed by drying at 383 K for 12 h. They were calcined at 673 K for 3 h and reduced at 623 K for 3 h in flowing hydrogen. Pt content was 5 wt%.

Pt L_{III}, L_{II}-edges XAFS spectra of samples 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 or reduced at 823 K for 2 h and sealed in polyethylene packs under He atmosphere.

3. Results and discussion

Properties of catalysts such as acid strength and BET specific surface area of employed support materials and dispersion of Pt catalysts are listed in Table 1 with the conversion of propane in catalytic combustion. The support effect that the catalyst on acidic support exhibits higher activity was clearly observed also in the present case. There was no clear correlation between the dispersion of platinum and catalytic activity, showing that the catalytic activity is controlled mainly by acid-base property rather than by dispersion as reported in literatures (Ishikawa *et al.*, 1994, Sugaya *et al.*, 1994).

Figure 1 shows Pt L_{III} and L_{II}-edge XANES spectra of supported Pt catalysts reduced at 823 K and those of Pt foil and PtO_2 for reference. The spectra of catalysts are presented in the order of acid strength of the support. It is obvious from the comparison with the spectra of Pt foil and PtO_2 that the platinum on all the reduced catalysts was metallic rather than oxide. Since the white line (the large peak at the absorption edge) is assigned to the electron transition from 2p to 5d mainly, larger intensity of white line indicates larger vacancy in 5d orbital. Unoccupied d-electron density was calculated according to the manner described by Mansour *et al.* (1984a) from the comparison of the area intensities in the range from -10 to 25 eV in L_{III} and L_{II}-edge XANES of catalysts with those of Pt foil assuming that unoccupied d-electron density per Pt atom for metallic platinum is 0.30 (Mansour *et al.*, 1984b). A tendency could be observed that the platinum on the stronger acid support has the larger unoccupied *d* electron density, except for the silica-supported catalyst, or, in other words, acidic support, which is electrophilic,

Table 1

The property of a series of platinum catalysts.

Support	Surface area of support[a] (m^2g^{-1})	Acid strength of support[b] (pKa)	Pt dispersion[c] (%)	Conversion[d] (%)
MgO [e]	65	22.3	86	0.6
La_2O_3 [f]	7.3	18.4	1	0.0
ZrO_2 [g]	66	9.3	63	3.8
Al_2O_3 [h]	177	3.3	70	7.5
SiO_2 [i]	341	-5.6	30	19.3
SiO_2-Al_2O_3 [j]	532	-12.0	79	28.2
SO_4^{2-}-ZrO_2 [k]	111	-13.2	19	47.8

[a] BET surface area measured through N_2 adsorption at 77K, [b] acid strength determined by Hammett indicator method, [c] dispersion measured through the pulse-adsorption of CO in a flow of the He gas, [d] the conversion of catalytic combustion of C_3H_8 at 523 K measured in a flow reactor under the followed condition; C_3H_8 0.25%, O_2 3%, N_2 balance; 200 ml/min, [e] JRC-MGO-1 (JRC: Japan Reference Catalyst), [f] purchased by Kishida chemicals, [g] prepared by calcination of $Zr(OH)_2$, which was obtained by hydrolysis of $ZrOCl_28H_2O$, [h] JRC-ALO-4, [i] JRC-SIO-8, [j] JRC-SAL-2 (SiO_2-Al_2O_3 mixed oxide with 13 wt% Al_2O_3), [k] obtained in the same manner as in the literature (Ishikawa *et al.*, 1994).

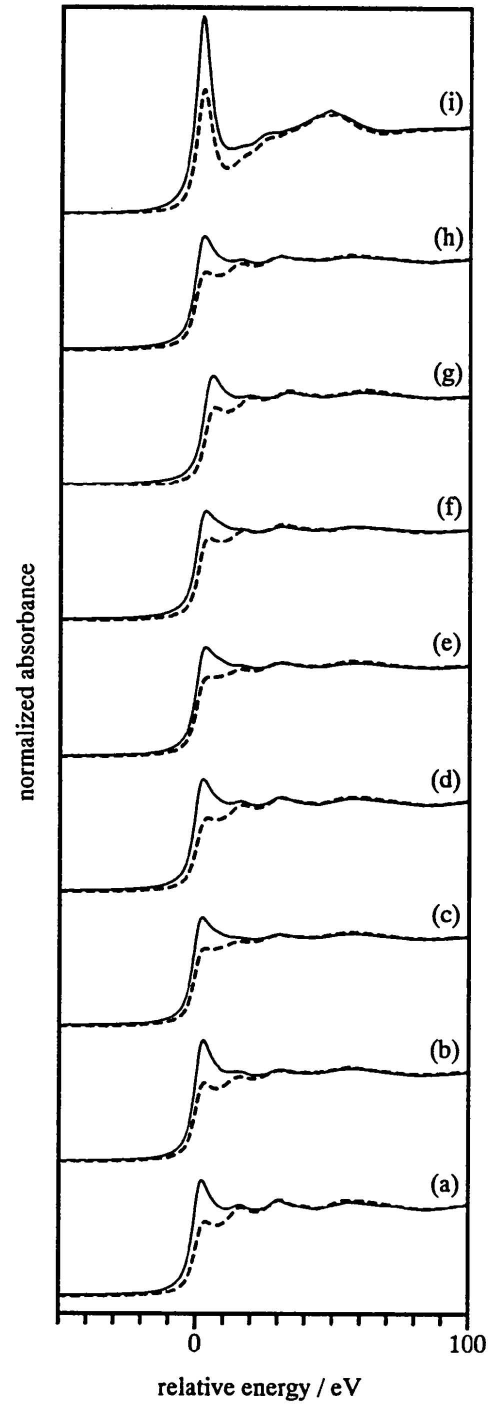

Figure 1

Pt L_{III} (solid line) and L_{II} (broken line)-edge XANES spectra of reduced platinum catalysts supported on SO_4^{2-}-ZrO_2 (b), SiO_2-Al_2O_3 (c), SiO_2 (d), Al_2O_3 (e), ZrO_2 (f), La_2O_3 (g) and MgO (h), and those of Pt foil (a) and PtO_2 (i) for reference. Energy offsets were 11559 eV for L_{III}-edge and 13267 eV for L_{II}-edge.

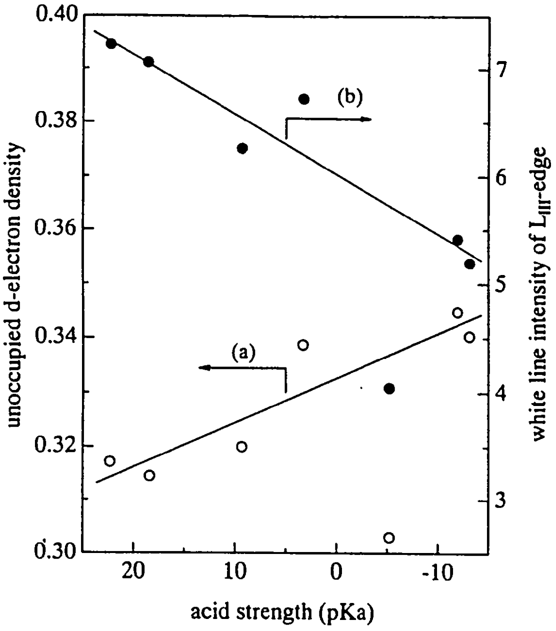

Figure 2

Unoccupied d-electron density of reduced platinum catalysts (a) and white line intensity of Pt L_{III}-edge of oxidized platinum catalysts (b) as a function of acid strength of support materials.

takes more electrons from the 5d-obital of platinum metal than the basic support does.

Figure 3 shows Pt L_{III}-edge XANES spectra of supported Pt catalysts after the oxidation at 823 K. The spectra of the catalysts were similar to that of PtO_2 except for silica-supported catalyst which exhibited the spectrum similar to that of Pt foil. Especially the catalyst on the basic support such as MgO and La_2O_3 exhibited the spectra essentially identical to that of PtO_2 even in fine structure in higher energy region, indicating that the platinum on the basic support was fully oxidized. On the other hand, the white line intensity of the platinum on the acidic support was low, indicating that they were not fully oxidized. Only silica-supported catalyst showed similar spectrum to those of Pt foil. The silica-supported catalyst has been also reported to be the exception in the relationship between the acid strength of support and the conversion in propane combustion (Ishikawa *et al.*, 1994).

The area intensity of white line of L_{III}-edge XANES in Figure 3 was evaluated by the decomvolution analysis by using an arctangent and a Gaussian curves (Yoshida, S. & Tanaka, T., 1996), and the results were depicted in Figure 2b as a function of acid strength of support materials. Good correlation was obtained between the acid strength of support and white line intensity, except for silica-supported one. Similar correlation was obtained for white line intensity of L_{II}-edge. These correlations indicate that the acidic property of support prevented platinum from the oxidation, which is in good agreement with the suggestion in the previous work (Ishikawa *et al.*, 1994). Further, high performance of catalyst supported on acidic oxide agrees well with that more metallic platinum species remain on the acidic support than on the basic support, since metallic species are more active for the catalytic combustion (Volter et al., 1987, Nunan et al., 1992).

The above results lead us to propose the following mechanism of the support effect on the oxidation state of platinum and on the catalytic activity in oxidative atmosphere. The electron density of the 5d orbital of platinum on the acidic support was slightly reduced because of the electrophilic property of the acidic support. Since electron transfer from metal to absorbed oxygen is necessary for dissociation of oxygen (Godoiets, 1983), oxygen adsorbed on platinum on the acidic support could be dissociated less easily compared with that on the basic support. Therefore, the oxidation of platinum on acidic support would be restricted than on basic support during catalytic combustion.

Although a general tendency that acidic support prevents platinum from oxidation was shown here, the exception has not been justified yet and the influences of other possible factors have not been clarified completely. Further investigation is in progress to confirm this hypothesis.

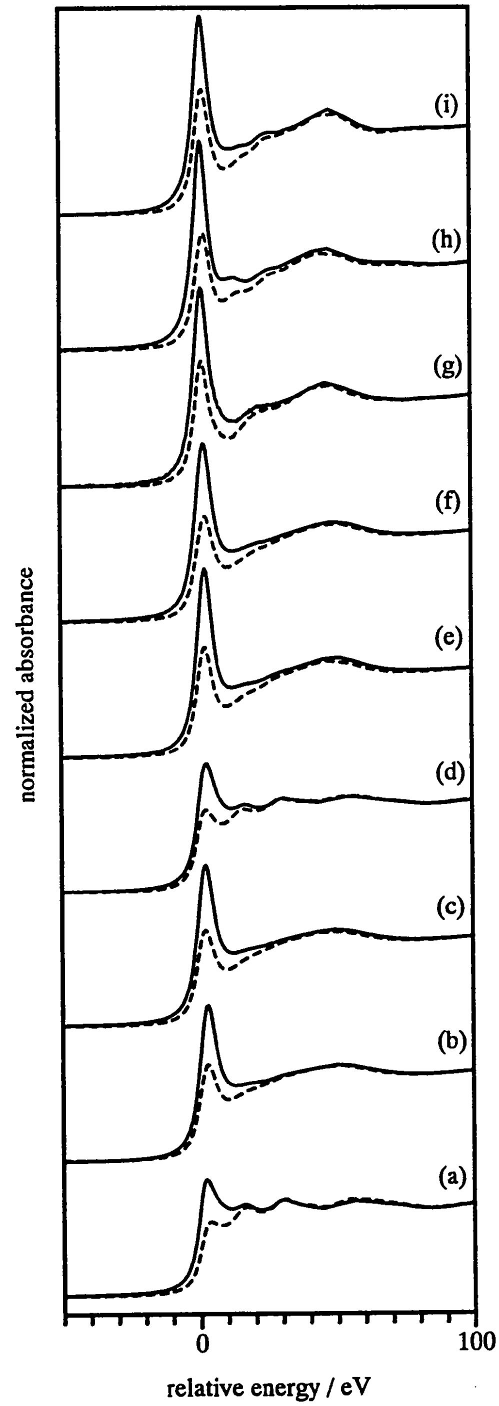

Figure 3

Pt L_{III}-edge XANES spectra of oxidized platinum catalysts supported on SO_4^{2-}-ZrO_2 (b), SiO_2-Al_2O_3 (c), SiO_2 (d), Al_2O_3 (e), ZrO_2 (f), La_2O_3 (g) and MgO (h), and those of Pt foil (a) and PtO_2 (i) for reference. Energy offset was 11559 eV.

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