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Preparation of Highly Dispersive Platinum Catalysts Impregnated on Titania-Incorporated Silica Support

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Abstract Highly dispersive silica-impregnated platinum catalysts were prepared by incorporating titania to the surface of silica support and by treating the impregnated platinum precursor with hydrogen peroxide. High dispersion of platinum on the titania-incorporated silica support was confirmed by XRD, TEM, EXAFS, and X-ray photoelectron spectroscopy (XPS) techniques. The platinum particles dispersed on silica ranged from 1 to 2 nm in size, although the loading amount of platinum was as high as 4 wt.%. The strong interaction between platinum and titania suppressed the migration and aggregation of the platinum particles on the surface, retaining a high dispersion of platinum. The platinum catalysts impregnated on the titania-incorporated silica showed higher catalytic activities in the combustion of methane than the platinum catalysts impregnated on the silica, while their catalytic activities were poor in the hydrogenation of nitrobenzene. Platinum dispersions and catalytic activities of the platinum catalysts on the silica support were discussed in relation to the strong interaction between platinum and titania.

Keywords Platinum · Dispersion · Silica · Titania incorporation · Hydrogen peroxide treatment

1 Introduction

Noble metals such as platinum, palladium and rhodium have been used for active phases in various hydrogenation and dehydrogenation processes in the petrochemical industry [1]. Noble metals have been the main components of catalytic converters used for removing nitrogen oxides, carbon monoxide, and unburned hydrocarbons contained in the exhaust gas from automobiles [2]. They work not only as active species in the combustion of volatile organic compounds to harmless water and carbon dioxide [3], but also as an essential material in fuel cells to produce energy through electrochemical processes [4].

Most noble metal catalysts have been prepared by impregnating the noble metals on highly stable inorganic supports with appropriate interaction with them such as alumina, silica, and activated carbon [5, 6]. The high dispersion of the noble metals on the supports is not only crucial in preparing highly active catalysts with a large number of exposed metal atoms, but it also reduces the loading levels of noble metals, thereby reducing the production cost. The high dispersion of noble metals on catalyst supports, therefore, makes it possible to prepare low-priced noble metal catalysts having a high-catalytic activity with sufficient thermal and mechanical stabilities.

γ-Alumina has been commonly used as a catalyst for noble metals because its moderate interaction with them results in their high dispersion and stability [7]. Its large surface area and high thermal stability also contribute to its high performance as a catalyst support. The weak acidity of γ-alumina, however, causes the formation of side products in organic reactions that take place on its acid sites, thereby lowering the yields of the desired products. The deposition of carbon on the acid sites also reduces the service life of the noble metal catalysts supported on γ-alumina. Moreover,

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the poor processibility of γ-alumina, due to the lack of hydroxyl groups on its surface, limits the shapes of the catalysts that can be prepared.

Another promising catalyst support for noble metals is silica. Its large surface area and high-thermal stability are very suitable for the preparation of noble metal catalysts. The large number of hydroxyl groups on its surface makes it possible to prepare catalysts with a wide variety of shapes. Furthermore, the inertness of silica supports suppresses the formation of side products and coke deposits. As a result, platinum catalysts impregnated on silica have been utilized in various liquid-phase hydrogenation reactions of organic materials [5]. Silica, however, is not generally used as a catalyst support for noble metals at elevated temperatures and under reducing atmospheres, because of their poor dispersion and stability. Even though there have been many attempts to enhance the dispersion of noble metals on silica, the negligible interaction between the surface of silica and the noble metal atoms have resulted in rapid sintering even at low temperatures. The drastic increase in their particle sizes results in severe catalytic deactivation.

Since titania interacts strongly with noble metals [8], the titania layer incorporated on silica improves the dispersion and stability of noble metals. The oxo radicals formed on the titania surface when it is treated with hydrogen peroxide oxidize the precursors of noble metals and combine titanium and platinum atoms through oxygen atoms. The strong interaction between the noble metal atoms and the surface of titania prevents the rapid sintering of noble metals, thus allowing them to maintain a high-dispersion even under a reduction atmosphere at high temperatures. The strong interaction, however, influences the chemical state of noble metals and may cause considerable changes in their activities in catalytic reactions.

Platinum has sometimes been impregnated on titania to enhance its photocatalytic activity [9]. Since the electronic interaction between platinum and titania accelerates the enhancement of photocatalytic activity, the dispersion of platinum supported on titania has not been considered an important factor. Titania catalysts that are dispersed on silica (TiO_2/SiO_2) have been found effective in the photocatalytic degradation of dyes [10]. The large surface area of silica increases the surface area of titania exposed to the reactants, thus resulting in a better catalytic activity.

In this study, we modified the surface of a silica support with titania of different amounts. The platinum precursor of cationic type was impregnated on the titania-incorporated silica supports and treated with hydrogen peroxide. Platinum catalysts impregnated on silica and titania-incorporated silica supports were obtained by subsequent calcination followed by reduction. Various techniques such as XRD, X-ray photoelectron spectroscopy (XPS), EXAFS, and carbon monoxide adsorption were employed to investigate the effect of titania incorporation on the dispersion and chemical property of platinum impregnated. In addition, the catalytic activity of platinum catalysts prepared were studied in the hydrogenation of nitrobenzene and in the combustion of methane to verify the effect of the interaction between platinum and titania on the catalytic performance of platinum.

2 Experimental

2.1 Preparation of Catalysts

Amorphous silica (Rhodia 175C) with a BET surface area of 142 m^2/g was used as the support for platinum. The dehydrated silica was added to an ethanol solution of titanium butoxide (Johnson Matthey Co., Stoke-on-Trent, UK, >99%). The titanium species were incorporated into silica through their reaction with the surface hydroxyl groups, thereby releasing butanol [11]. The non-reacted titanium butoxide was removed by washing it with anhydrous ethanol. The titania-incorporated silica was obtained by calcining at 400 °C for 2 h. The amount of titania incorporated on the silica was controlled by changing the amount of titanium butoxide in ethanol solution. For the preparation of TiO_2(I)-SiO_2, the amount of titanium butoxide was fixed at about 1/5 of hydroxyl groups present on the silica as mole. However, the amount of titanium butoxide was increased to twice the hydroxyl groups for the preparation of TiO_2(II)-SiO_2 catalyst with a high coverage of titania. Tetraamineplatinum (II) nitrate (Aldrich, Tanfkirchen, Germany 97%) was impregnated on the titania-incorporated silica supports by an incipient wetness method. After drying, the platinum precursor-loaded silica was wetted with hydrogen peroxide (Daejung, 30%). The treatment it with hydrogen peroxide might enhance the strong contact between platinum precursor and the strong contact between platinum precursor and the titania-incorporated silica. Finally, the platinum catalysts supported on the titania-incorporated silicas were obtained by reduction at 400 °C in a reducing gas flow (H_2/N_2 = 1/1 as mole). A high-platinum loading of 4 wt.% was set for all the platinum catalysts to examine its dispersion at a high-loading level.

As a reference catalyst, the platinum catalyst impregnated on the unmodified silica was also prepared. The catalytic activities of the platinum catalysts prepared by us and that of a commercial platinum catalyst impregnated on alumina (Aldrich, 643165) were compared in the hydrogenation and combustion reaction. The platinum catalysts are referred to herein as Pt/SiO_2, Pt/Al_2O_3, Pt/TiO_2(I)-SiO_2, and Pt/TiO_2(II)-SiO_2, in accordance with their supports, and the amount of titania incorporated.

2.2 Characterization of Prepared Catalysts

The X-ray diffraction patterns of the platinum catalysts were recorded on a high-resolution X-ray diffractometer (Rigaku, Tokyo, Japan, UltimaIII) operated at 40 kV and 40 mA using CuKα radiation ($\lambda = 0.154178$ nm). The amounts of titania incorporated on the silica were calculated from the EDX results obtained using an SEM/EDX (Hitachi, Tokyo, Japan, S-4700/Horiba, EX-200). The transmission electron micrographs of the platinum catalysts were obtained on a Jeol JEM-2000FXII electron microscope operating at 200 kV.

A *Lab*-EXAFS spectrometer (Rigaku, R-XAS) equipped with a 3 kW X-ray generator, Mo target, W filament, and Ge (220) bent crystal, was employed to confirm the microstructure of platinum on the prepared catalysts. Two ionization chambers were used as detectors. All the spectra were recorded in transmission mode above the L_{III}-edge of Pt (11,549 eV) in air at ambient temperature.

The chemical and dispersive states of platinum on the prepared catalysts were deduced from their XPS spectra recorded on a VG MultiLab 2000 with non-monochromatic MgKα radiation (1,253.6 eV) at a pressure of $<10^{-9}$ Torr. All the spectra were obtained at room temperature, and the binding energies (BE) of elements were referenced to the C1s peak at 285.0 eV.

The IR spectra of the carbon monoxide adsorbed on the platinum catalysts were recorded on an FT-IR spectrophotometer (Bio-Rad, Hercules, CA, USA, FTS 175C). A self-supported catalyst wafer with a weight of 10 mg was evacuated at 500 °C for 1 h. After cooling to 50 °C, the catalyst wafer was exposed to carbon monoxide (Matheson) at a pressure of 50 Torr. The IR spectra were obtained after removing the gaseous carbon monoxide by evacuation.

The amount of carbon monoxide adsorbed on the platinum catalysts was measured using a chemisorption measuring apparatus (BEL, BEL-CAT). The catalysts were activated in a helium flow at 400 °C for 2 h to remove the adsorbed water. After adjusting the temperature of the catalyst bed to 50 °C, pulses of carbon monoxide [CO/He = 5/95 (as vol.%), Deokyang] were added to the catalysts till they were saturated with carbon monoixde. The amounts of carbon monoxide adsorbed on the platinum catalysts were calculated from the decrease in the peak area of carbon monoxide due to its adsorption on the catalysts.

2.3 Catalytic Reactions

Hydrogenation of nitrobenzene on the platinum catalysts was carried out in a three-neck flask. The catalyst of 0.1 g was charged in the flask and activated in a hydrogen flow of 100 ml/min at 300 °C for 3 h. The reactant was composed of nitrobenzene (Duksan, Seoul, South Korea, 95%) of 0.25 ml and ethanol (Daejung, 99.5%) of 250 ml. The hydrogenation of nitrobenzene was started by adding the reactant to the flask containing the activated catalyst at 300 °C. Samples of 2 ml were taken from the flask and analyzed on a gas chromatograph (Donam, Kimhae City, South Korea, DS6200) equipped with a FID detector and HP-5 column. Conversions of nitrobenzene were defined as the percentage of nitrobenzene converted to hydrogenated products.

The catalytic activities of the platinum catalysts in the combustion of methane were examined using a conventional atmospheric flow reactor [12]. A 0.1 g sample of the platinum catalysts was charged at the center of a quartz tube reactor (O.D. = 1/2″) and activated at 250 °C for 1 h. The reactor was then cooled to ambient temperature in the nitrogen flow. The reactant gas (Shinil gas) was composed of methane (2,000 ppm), oxygen (10 vol.%), and nitrogen (balanced). The flow rate of the reactant gas was adjusted to 110 ml/min using a mass flow controller. The reactor temperature was increased with a ramping rate of 5 °C/min from ambient temperature to 600 °C. The product gas was sampled using a six-port sampling valve with given intervals, and the samples were sent to a directly coupled gas chromatograph (Shimadzu, Kyoto, Japan, 14B). A FID detector and HP-5 column were employed for the analysis of product pulses. The conversion of methane was defined as its percentage consumed in the combustion reaction.

3 Results

The compositions of the platinum catalysts prepared are listed in Table 1. The amounts of platinum impregnated on the silica were similar, while the amounts of titania incorporated on the silica showed considerably different values of 0.1 and 3.4 wt.% on the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2, respectively.

The dispersive states of platinum and titania on the platinum catalysts induced different XRD patterns as shown in Fig. 1. The broad peaks at $2\theta = 23°$ attributed to amorphous silica were the same on all the catalysts, while the sharp peaks at 39.7, 46.2, and 67.4° attributed to platinum metal showed a considerable difference depending on the preparation methods employed. The sharp and high peaks on the Pt/SiO_2 catalysts indicate the poor dispersion of platinum. These peaks are small on the Pt/TiO_2(I)-SiO_2 catalysts, representing the considerable improvement of the platinum dispersion by the incorporation of titania. Since these peaks are not clearly observed on the Pt/TiO_2(II)-SiO_2 catalyst, the dispersion of platinum on the catalyst must be high on the silica support incorporated with a large amount of titania.

Table 1 Composition and platinum dispersion of catalysts prepared

Catalyst	Composition (wt%)		CO adsorption (cm^3/g)[a]	Pt dispersion (%)	
	Pt	Ti		D^{b}_{Chem}	D^{c}_{TEM}
Pt/SiO$_2$	4.3	-	0.25	6	16
Pt/TiO$_2$(I)-SiO$_2$	3.4	0.1	0.67	15	60
Pt/TiO$_2$(II)-SiO$_2$	3.9	3.4	0.46	10	63

[a] measured by cheimsorption at 50 °C

[b] calculated from the amount of CO chemisorption

[c] calculated from TEM photos

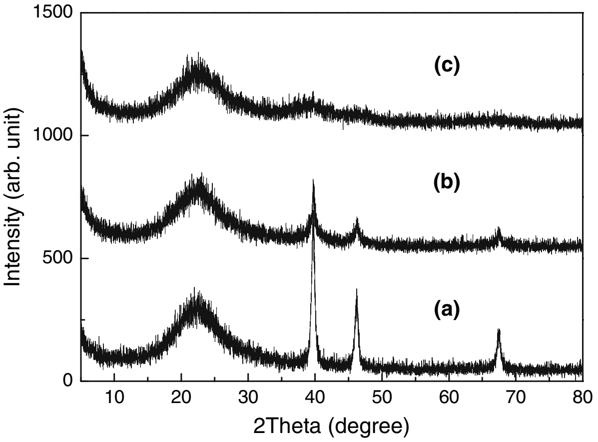

Fig. 1 X-ray diffraction patterns of **a** Pt/SiO$_2$, **b** Pt/TiO$_2$(I)-SiO$_2$, and **c** Pt/TiO$_2$(II)-SiO$_2$ catalysts

The titania incorporated on the silica did not induce any diffraction peaks which may be attributed to anatase or rutile. Titania was chemically attached to the surface of silica in the form of a thin layer through the reaction between titanium alkoxide and hydroxyl group of silica [11]. Although the amount of titania incorporated was not small on the Pt/TiO$_2$(II)-SiO$_2$ catalyst, the high dispersion of titania caused no diffraction peaks.

The TEM photos clearly showed the size of platinum particles dispersed on the silicas. As shown in Fig. 2, the sizes of the platinum particles were significantly varied according to the method of preparation. Large particles were observed on the Pt/SiO$_2$ catalyst. The size distribution of the platinum particles was wide in the range of 5–20 nm. On the other hand, the platinum particles dispersed on the Pt/TiO$_2$(I)-SiO$_2$ and Pt/TiO$_2$(II)-SiO$_2$ catalysts were very small and uniform. The histogram showed that their diameters were in the range of 1–3 nm. The most probable particle size of the Pt/TiO$_2$(II)-SiO$_2$ catalyst was 2 nm, indicating an exceptionally high dispersion of platinum. Thus, the incorporation of titania on the silica proved to be very effective in improving the dispersion of platinum impregnated on the silica.

Although the TEM photos of the platinum catalysts give direct information on the size of platinum particles, they do not provide an overall view of the platinum particles dispersed on the silica. The EXAFS spectra of platinum, on the other hand, provide the averaged information on the microstructure of the platinum particles dispersed on the supports. Figure 3 shows the Fourier transformed radial distributions of platinum obtained from the platinum catalysts. The height of the peaks at 2.7 Å, which corresponds to the Pt–Pt atomic pairs of platinum particles, varied depending on the method of preparation [13]. The peak at 2.7 Å was high in the spectrum of the Pt/SiO$_2$ catalyst, but very low in the spectrum of the Pt/TiO$_2$(II)-SiO$_2$ catalyst. The low intensity of this peak in the spectra of the platinum catalyst on the titania-incorporated silica indicated that the particles of platinum dispersed were extremely small.

The simulation results for the EXAFS spectra using XFIT software are listed in Table 2. The coordination number of the platinum dispersed on the Pt/SiO$_2$ catalyst was 9.33, indicating the presence of large platinum particles [14], while that of the platinum dispersed on the Pt/TiO$_2$(II)-SiO$_2$ was 4.75. This smaller coordination number of platinum indicates its high dispersion, thus confirming the improvement of the platinum dispersion by incorporating titania on the silica. Since the coordination number of platinum on the Pt/TiO$_2$(II)-SiO$_2$ catalyst was about 5, the estimated size of platinum particles is about 2 nm [15].

Only Pt–Pt atomic pair was required to simulate the radial distribution of platinum on the Pt/SiO$_2$ catalyst. However, two more Pt–O atomic pairs were required for the fitted radial distribution to be similar to the experimentally obtained distribution of the Pt/TiO$_2$(II)-SiO$_2$ catalyst.

This means that some of the platinum atoms on this Pt/TiO$_2$(II)-SiO$_2$ catalyst have oxygen atoms as their closest neighbors. The sum of the coordination numbers of Pt–O atomic pairs is about 2. The small coordination number of the Pt–O atomic pairs excludes the possibility of PtO or PtO$_2$ being formed. Accordingly, the fact that the Pt–O atomic pair is required for reasonable fitting indicates that some of the platinum atoms are combined with silicon or

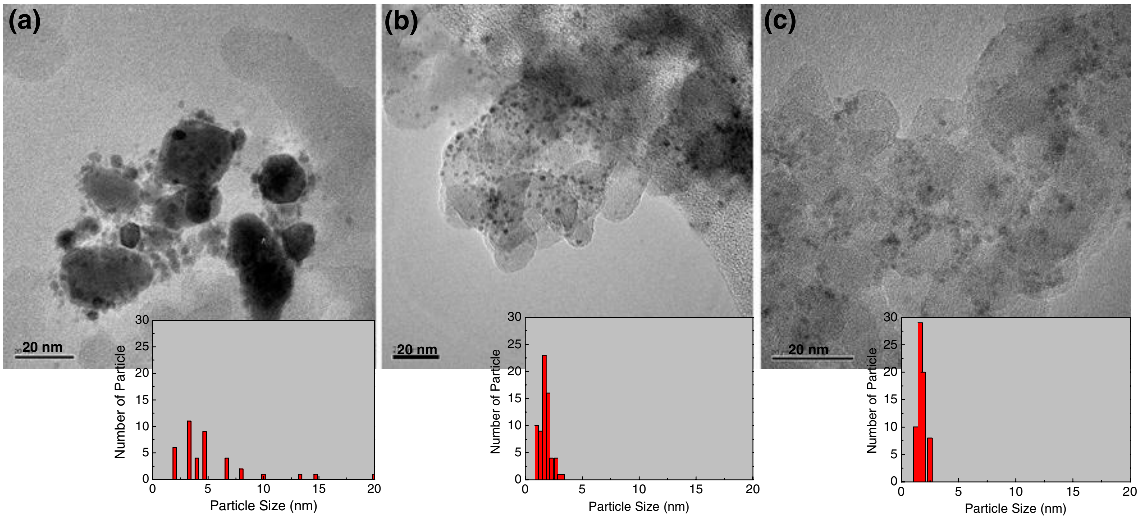

Fig. 2 TEM photos of **a** Pt/SiO_2, **b** $Pt/TiO_2(I)-SiO_2$, and **c** $Pt/TiO_2(II)-SiO_2$ catalysts

Fig. 3 Fourier transformed radial distributions of platinum obtained from EXAFS spectra of **a** Pt/SiO_2 and **b** $Pt/TiO_2(II)-SiO_2$ catalysts

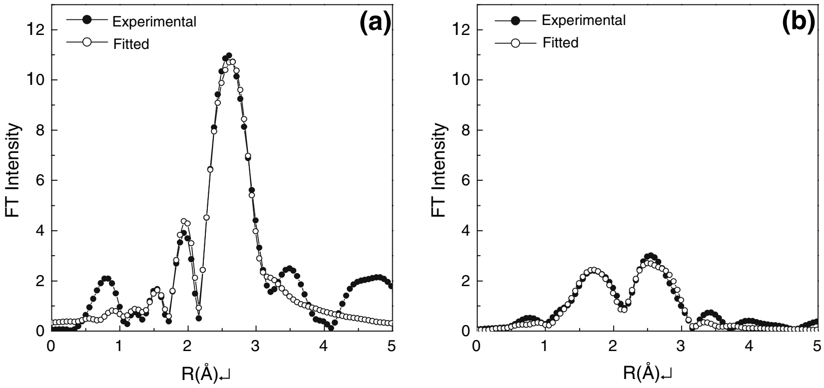

Table 2 Structural parameters of platinum impregnated on silica[a]

Catalyst	Atomic Pair	R (A)	CN	σ^2
Pt/SiO_2	Pt-Pt	2.77	9.33	0.001
$Pt/TiO_2(II)-SiO_2$	Pt-O	1.95	0.65	0.001
	Pt-O	2.01	1.53	0.001
	Pt-Pt	2.77	4.75	0.007

[a] determined from the fitted EXAFS spectra for the Pt L_{III}-edge of catalysts

titanium atoms through oxygen linkages [16]. Therefore, the platinum atoms that are present at the outer circle of the platinum particles are in contact with the titania layer as in the forming of Pt–O–Ti bonds. The chemical bonds formed between platinum and titania atoms through oxygen atoms may be the cause of the high dispersion of platinum on the titania-incorporated silica.

X-ray photoelectron spectroscopy was helpful in examining the dispersion and chemical states of platinum dispersed on silica. Figure 4 shows the XPS spectra of the Pt/SiO_2, $Pt/TiO_2(I)-SiO_2$, and $Pt/TiO_2(II)-SiO_2$ catalysts. The peaks observed at 71.6 and 74.9 eV were assigned to 4f peaks of metallic platinum, and those observed at 73.1 and 76.4 eV to 4f peaks of oxidized platinum [17]. The deconvoluted peaks of 4f peaks indicate the presence of oxidized platinum as well as metallic platinum, although the fraction of oxidized platinum is not high. The intensity and binding energy of platinum peaks are different depending on the method of preparation. The intensities of Pt4f peaks on the Pt/SiO_2 catalyst were small, but the peaks of the platinum catalysts impregnated on the titania-incorporated silica were considerably high. The large peaks on the $Pt/TiO_2(II)-SiO_2$ catalyst indicate the high population of platinum on the surface because of its high dispersion. As the intensity of Pt4f peaks increased, their BE shifted to lower values with an increasing amount of titania incorporated on the silica. The BE of Pt^0 on the Pt/SiO_2 catalyst was 71.6 eV, while those on the $Pt/TiO_2(I)-SiO_2$ and $Pt/TiO_2(II)-SiO_2$ catalyst were 71.1 and 70.6 eV, respectively, indicating a gradual increase in the electron density of platinum metal with an increasing amount of

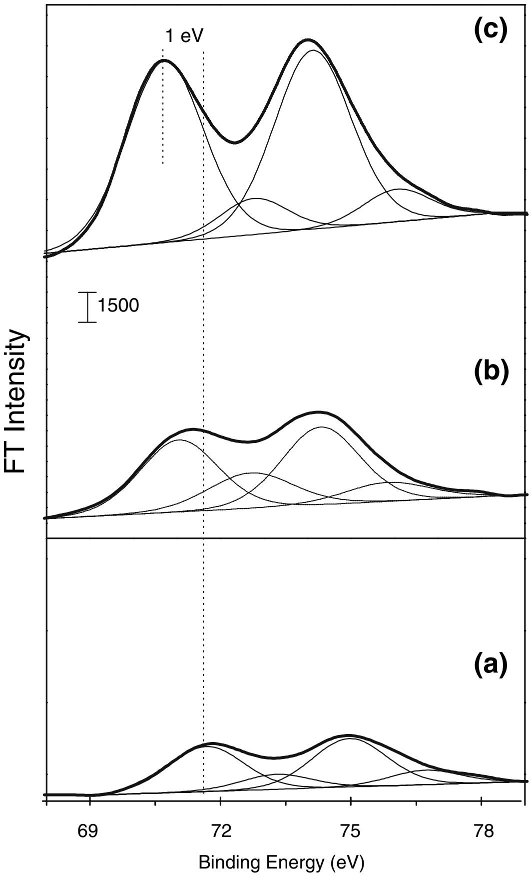

Fig. 4 XPS spectra of Pt4f peaks of **a** Pt/SiO_2, **b** Pt/TiO_2(I)-SiO_2, and **c** Pt/TiO_2(II)-SiO_2 catalysts

titania incorporated on the silica. The strong metal support interaction (SMSI) between platinum and titania lowered the BE of Pt4f peaks.

Figure 5 shows the IR spectra of the carbon monoxide adsorbed on the platinum catalysts at 50 °C. Large absorption bands of carbon monoxide were observed at 2,070 cm on the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2 catalysts, while no appreciable bands were found on the Pt/SiO_2 catalyst. The appearance of the bands indicates the presence of platinum atoms on the surface of the platinum catalysts that are impregnated on the titania-incorporated silica. Since the absorption band of carbon monoxide at 2,077 cm is attributed to the carbon monoxide adsorbed on platinum metal [18], The IR spectra confirmed the metallic character of platinum dispersed on the silica. However, the band corresponding to the carbon monoxide adsorbed on the Pt/SiO_2 catalyst was extremely small, indicating a poor dispersion of platinum on this catalyst.

The amounts of carbon monoxide adsorbed on the platinum catalysts were measured using the chemisorption measuring apparatus. As shown in Table 1, the amounts of carbon monoxide adsorbed on the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2 catalysts were considerably large, but that on the Pt/SiO_2 catalyst was small. However, the difference was not so significant. These results suggest that the amounts of carbon monoxide adsorbed on the catalysts do not correspond to the dispersion of platinum on them. The dispersion of platinum on the platinum catalysts varied in the experimental methods employed as listed in Table 1. The dispersions calculated from the amounts of carbon monoxide adsorbed were very low for all catalysts. On the other hand, the dispersions calculated from the size distributions of platinum particles dispersed on the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2 catalysts obtained from TEM photos showed considerably high dispersions of 60%. EXAFS results also supported the high dispersion of platinum on the platinum catalysts that are impregnated on the titania-incorporated silica. Since TEM photos and EXAFS data are clearly showing the sizes of platinum particles, the high dispersion of platinum on the titania-incorporated silica must be real. However, the SMSI between platinum and titania suppresses the adsorption of carbon monoxide [17], resulting in the poor dispersions of platinum when they are calculated from the adsorption amounts of carbon monoxide.

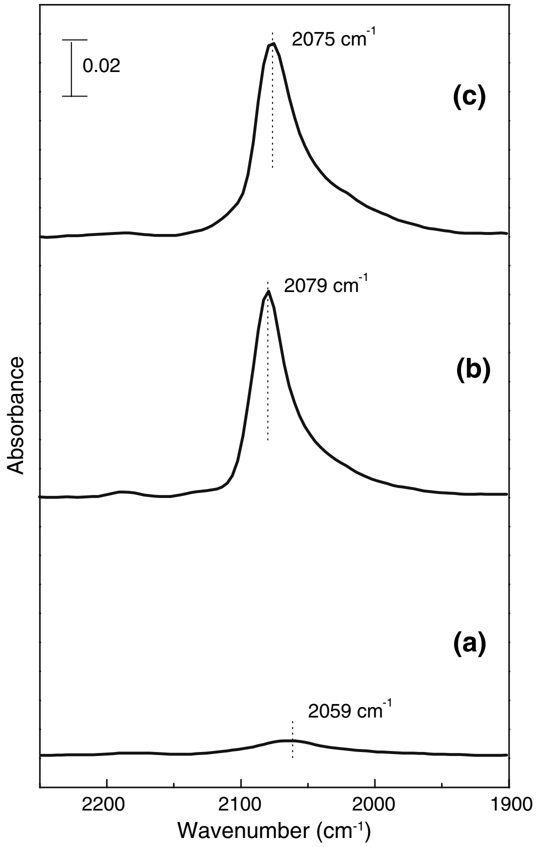

Fig. 5 FT-IR spectra of CO adsorbed on **a** Pt/SiO_2, **b** Pt/TiO_2(I)-SiO_2, and **c** Pt/TiO_2(II)-SiO_2 catalysts. The catalysts were evacuated at 500 °C for 1 h before exposing to carbon monoxide of 50 Torr at 50 °C

The activities of platinum catalysts in hydrogenation and oxidation reactions are generally dependent on the dispersion of platinum because the platinum atoms dispersed on the surface work as active sites. The purchased catalyst and those prepared by us showed a difference in performance in the hydrogenation of nitrobenzene and the combustion of methane as shown in Fig. 6. The activities of the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2 catalysts were very much lower than that of the Pt/Al_2O_3 catalyst in the hydrogenation of nitrobenzene, regardless of the titania incorporation. Although the dispersions of platinum were very high on the Pt/TiO_2(I)-SiO_2 and Pt/TiO_2(II)-SiO_2 catalysts, their catalytic activities were unexpectedly low. This means that the chemical property of platinum particles that are impregnated on a titania layer is different from that of platinum particles impregnated on alumina. The low activity of the Pt/SiO_2 catalyst is attributed to the poor dispersion of platinum, but the low activities of the platinum catalysts that are impregnated on the titania-incorporated silica are due to the strong interaction between platinum and titania.

The catalytic performance of the platinum catalysts in the combustion of methane was considerably different from that in the hydrogenation of nitrobenzene. The high activity on the Pt/Al_2O_3 catalyst and low activity on the Pt/SiO_2 catalyst in the combustion of methane remained the same as those in the hydrogenation reaction, while the Pt/TiO_2(II)-SiO_2 catalyst with a high dispersion of platinum showed an activity comparable to the Pt/Al_2O_3 catalyst. Since the activation of oxygen on platinum is essential for the combustion of methane, the high conversion of the Pt/TiO_2(II)-SiO_2 catalyst even at low temperature indicates high dispersion of platinum. The SMSI between platinum and titania does not inhibit the adsorption and activation of oxygen on platinum [19]. Consequently, the platinum catalysts that are impregnated on the titania-incorporated silica show high activities in the combustion reaction.

4 Discussion

The incorporation of titania on the surface of silica support followed by the treatment of the impregnated platinum precursor with hydrogen peroxide was highly effective in enhancing the dispersion of platinum. The TEM photos show a clear difference in the sizes of platinum particles in accordance with the methods of preparation employed. The diameters of the platinum particles on the Pt/TiO_2-SiO_2 catalysts were in the range of 1–3 nm, while those on the Pt/SiO_2 catalyst were in the range of 5–20 nm. This improvement in the dispersion of platinum afforded by the incorporation of titania was comprehensively confirmed by the XRD, EXAFS, and XPS techniques. The activities of the Pt/TiO_2-SiO_2 catalysts in the combustion of methane are higher than the activities of the Pt/SiO_2 catalyst, which is also attributed to the improvement in the dispersion of platinum. However, the platinum catalysts that were impregnated on the titania-incorporated silica were not active in the hydrogenation of nitrobenzene, although the dispersions of platinum were very high. Moreover, the amounts of carbon monoxide adsorbed on platinum catalysts were far less than what the TEM pictures led us to expect.

The formation of a titania layer on the pore walls of mesoporous materials has been reported in our previous paper [11]. Titanium alkoxide molecules have been found to react with the hydroxyl groups of mesoporous materials, and covalent bonds were formed between the titanium and silicon atoms. Sufficient calcination treatment has resulted in the formation of a titania layer attached to the surface of the mesopores. XPS studies of titania incorporated on glass fiber have revealed that a high proportion of the titanium atoms have low-oxidation states [10]. These titanium atoms are reactive toward hydrogen peroxide, producing yellow oxo radicals on the surface. These radicals are active in the partial oxidation of various organic molecules, such as 2,6-di-*tert*-butylphenol [20], and acetone [21].

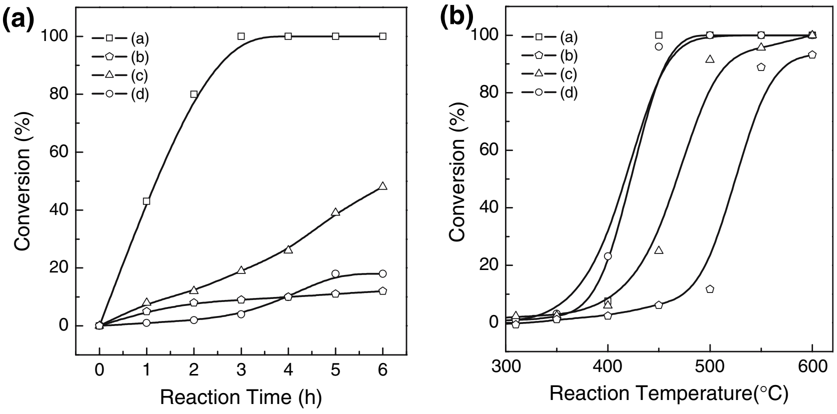

Fig. 6 Catalytic performance of **a** Pt/Al_2O_3, **b** Pt/SiO_2, **c** Pt/TiO_2(I)-SiO_2, and **d** Pt/TiO_2(II)-SiO_2 catalysts in the hydrogenation of nitrobenzene (A) at 30 °C and the combustion of methane (B)

Our method of preparing the highly dispersive platinum catalysts that are impregnated on silica is composed of two steps; incorporation of a titania layer on the silica support and treatment of the platinum precursor impregnated on the titania-incorporated silica with hydrogen peroxide. The titania layer that is incorporated on the silica interacts with the platinum atoms, and this interaction may contribute to the improvement in dispersing platinum atoms. The binding energy of Pt^0 on the $Pt/TiO_2(II)$-SiO_2 catalyst was 70.6 eV, which is very similar to that of platinum supported on bulk titania. Although the platinum particles are highly dispersed on the titania-incorporated silicas as shown in TEM photos, the chemisorption amounts of hydrogen and carbon monoxide are extremely small, resulting in their low-catalytic activities for the hydrogenation of nitrobenzene. However, they showed high catalytic activity for methane oxidation. These observations are highly coincident with those observed on the platinum catalysts which were supported on bulk titania [22]. A part of platinum atoms that have combined with titanium atoms through oxygen linkages are also effective in enhancing the dispersion of platinum atoms. However, the fraction of oxidized platinum atoms is not high. Consequently, the SMSI between platinum and titania plays a major role in preventing the sintering of platinum rather than the Pt–O–Ti bonds.

This so-called SMSI between platinum and titania reduces the adsorption of hydrogen and carbon monoxide on platinum, while the SMSI's effect on the adsorption of oxygen is not significant [19]. Actually, the adsorption amounts of carbon monoxide on the platinum catalysts that are impregnated on the titania-incorporated silica were considerably small. Therefore, the suppression of hydrogen adsorption on platinum due to the SMSI resulted in the poor activities of the platinum catalysts that are impregnated on the titania-incorporated silicas in the hydrogenation of nitrobenzene. On the other hand, these platinum catalysts showed high activities in the combustion of methane as expected from their dispersion of platinum. It is evident that the dispersion of platinum on the platinum catalysts that are impregnated on the silica is considerably improved by the incorporation of titania, but the catalytic activities of these platinum catalysts are strongly dependent on the types of reactions because of the SMSI generated at the interface between platinum and titania.

5 Conclusions

Based on the incorporation of titania and the subsequent treatment with hydrogen peroxide, this method of preparing highly dispersed silica-supported platinum catalysts may be valid for the preparation of platinum catalysts that are supported on silica. The size of the platinum particles dispersed on the platinum catalysts prepared by this method was uniform and in the range of 1–2 nm, even though the loading amount of platinum was as high as 4 wt.%. The titania incorporated on the silica interacted strongly with the platinum (SMSI) and enhanced the dispersion of platinum. However, the platinum catalysts show poor activities in the hydrogenation because of the SMSI. Nevertheless, application of noble metals as catalysts to various oxidation reactions requiring the activation of oxygen such as catalytic combustion, removal of VOCs, and purification of automobile exhausts, is very promising because of their high dispersion and stability. We are continuing to study the changes in the physical and chemical states of platinum during the preparation of the platinum catalysts that are impregnated on the titania-incorporated silica with in situ EXAFS.

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