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Effect of reduction treatment on CO oxidation over Pt/SnO_2 catalyst

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ABSTRACT

Carbon monoxide oxidation over the supported platinum catalysts was investigated. The catalyst of Pt/SnO_2 exhibited superior catalytic activity despite the low surface area compared to Pt/γ-Al_2O_3. It was confirmed by the temperature-programmed reduction analysis that the reduction of platinum species over Pt/SnO_2 was initiated below room temperature. The platinum species reducible at lower temperature should be responsible for the high activity for the complete oxidation of carbon monoxide. Moreover, the influence of the reduction treatments on these supported platinum catalysts was studied. In the case of Pt/γ-Al_2O_3, the catalytic activity was improved as the reduction temperature was elevated. This is because the adsorption sites of CO on platinum particles increased by the reduction at higher temperature, leading to the high catalytic activity. In contrast, the activity of Pt/SnO_2 was enhanced even by the reduction at 25 °C and the catalyst reduced at 90 °C attained the highest activity. Correlations between the amount of adsorbed CO and the catalytic activity were observed in the Pt/γ-Al_2O_3 system, which were not found in the reduced Pt/SnO_2. These results suggest that the oxygen species of the SnO_2 support activated by the reduction treatments contribute to carbon monoxide oxidation. The activity of the sample was significantly degraded by the reduction at 400 °C. This behavior was attributed to a decrease in reaction sites due to the formation of intermetallic compounds.

1. Introduction

Carbon monoxide is a potent chemical asphyxiant [1] that may play a pivotal role in the creation of a continuous state of acidosis [2] and is produced under the incomplete combustion of carbon inclusions. When carbon monoxide is sucked in human lungs, the 40% of the carbon monoxide is absorbed into the human body, leading to hypoxemia. Besides, hydrogen fuel obtained from the reforming of hydrocarbon contains carbon monoxide. In polymer electrolyte fuel cells, even a few ppm of carbon monoxide triggers the serious deterioration in performance by CO poisoning of anode [3]. From these backgrounds, carbon monoxide is desired to be removed efficiently and completely in various situations. The metal oxide-supported precious metal catalysts are well-known as effective catalysts for carbon monoxide oxidation. For example, various metal oxide-supported gold catalysts have been investigated and confirmed to attain very high catalytic performance for carbon monoxide oxidation. Haruta et al. reported the oxidation of carbon monoxide was initiated under −70 °C with the use of Au/α-Fe_2O_3, Au/Co_3O_4 and Au/NiO catalysts [4] and proposed the mechanism of carbon monoxide oxidation over Au/TiO_2 catalyst [5]. Another group examined the active site for carbon monoxide oxidation on Au/γ-Al_2O_3 catalyst [6]. The platinum catalysts supported on metal oxides such as Fe_2O_3, NiO, ZnO and Al_2O_3 were also tested for the reaction [7,8]. Pd and CuO were used as alternative active species supported on metal oxides [9,10].

These metal oxide-supported precious metal catalysts are used not only for the oxidation of carbon monoxide, but also for various chemical reactions such as purification of automotive exhaust gases [11] and low-temperature combustion of volatile organic compounds (VOCs) [12,13]. Intriguingly, the chemical interaction between supported metal and metal oxide support is varied depending on the combination of metals and supports, preparation methods, and pretreatments. As the consequence, various characteristics of catalysts, e.g. electronic state of supported metal, adsorption property of reaction gas, redox property and catalytic activity, are drastically changed [7,10,13–17]. It was emphasized that chemical interaction between gold and metal oxide support affected the catalytic activity for carbon monoxide oxidation [18]. Recently, we have focused on the strong chemical interaction in Pt/SnO_2 catalyst system and investigated several properties of the catalyst. It was found that the drastic change in catalytic properties by the reduction treatments was ascribable to the strong metal–support interaction [19–21]. We reported that Pt/SnO_2 catalyst exhibited superior catalytic performance for acetaldehyde combustion regardless of the low surface area compared to Pt/ZrO_2 and Pt/CeO_2 catalysts [22]. Therefore, Pt/SnO_2 catalyst is expected to have a great potential for oxidation reactions. In this report,

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then, we investigated the effects of SnO_2 support on the carbon monoxide oxidation by comparing Pt/SnO_2 and $Pt/\gamma\text{-}Al_2O_3$. Moreover, as mentioned above, the catalytic activity would depend on the variation in the chemical interaction between metal and support materials by reduction treatments. Thus, the influence of the reduction treatment on the catalytic properties was also investigated.

2. Experimental

2.1. Catalyst preparation

Metal oxide-supported platinum catalysts were prepared by the impregnation method. The following oxides were selected as support materials: SnO_2 (purity ≥98%, Wako Pure Chemical Industries Ltd.) and $\gamma\text{-}Al_2O_3$ (purity ≥99.995%, JRC-ALO-8, The Catalysis Society of Japan). Tin oxide powder was calcined at 800 °C for 5 h prior to soaking, whereas $\gamma\text{-}Al_2O_3$ was used without any pretreatments. A nitric acid solution of $Pt(NO_2)_2(NH_3)_2$ (platinum content: 4.553 wt.%, Tanaka Kikinzoku Kogyo) was used as a platinum source. Support materials were impregnated with the solution. The mixture was kept on a steam bath at 80 °C until the solvent was evaporated. Subsequently, the resulting powder was calcined at 400 °C for 30 min in air. Metal loading in the samples was 1.0 or 10 wt.% in every case. The catalysts with heavier loading were prepared to clarify the changes in crystalline phase and electronic state. Obtained samples were reduced under various conditions (Table 1).

2.2. Catalytic combustion of carbon monoxide

The prepared catalyst (150 mg) was set in a fixed-bed flow reactor made of quartz in 6-mm inner diameter. Each catalyst was made into a tablet and pulverized into 10–26 mesh before catalytic reaction tests. A gaseous mixture composed of 5.0% CO, 15% O_2 and N_2 balance was fed with a flow rate of 80 ml min^{-1} (space velocity: 32,000 l kg^{-1} h^{-1}). The outlet gas composition was analyzed by the non-dispersive infrared gas analyzer (Shimadzu, CGT-7000). Reaction temperature was raised up to 160 °C at a heating rate of 1.5 °C min^{-1}. The measurements were started after the concentration of CO in the outlet gas became stable.

2.3. Catalyst characterization

The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), BET surface area, temperature-programmed reduction (TPR), and transmission electron microscopy (TEM) observation. XRD patterns were recorded by Cu Kα radiation on the RIGAKU Ultima IV diffractometer for the phase identification in the samples. XPS measurements were conducted on the Shimadzu ESCA-3400 using a Mg Kα source. In the case of reduced catalysts, the samples were transferred directly into the XPS chamber without exposure to air after reduction treatment. The binding energy was referenced to the Sn 3d peak (487.1 eV). The fraction of Pt/Sn on the surface of catalyst was calculated from the peak areas of the Pt 4f and Sn 3d peaks. BET surface area was determined by N_2 adsorption at the liquid nitrogen temperature using the BEL Japan Belsorp-mini II analyzer. TPR measurements were conducted using the Quantachrome CHEMBET 3000 system, and the amount of consumed hydrogen was measured by the thermal conductivity detector (TCD). A weighed amount (50 mg) of as-calcined catalysts was placed in a quartz tube reactor, and then a gaseous mixture of 5% H_2–95% Ar was fed to the reactor at 30 ml min^{-1}. The reaction temperature was raised up to 800 °C at a heating rate of 10 °C min^{-1}. The amount of H_2 detected by TCD was calibrated by the consumption of H_2 for the reduction of CuO. The morphology and lattice image of $Pt/\gamma\text{-}Al_2O_3$ samples reduced under various conditions shown in Table 1 were observed by TEM using the Philips CM200 FEG equipped with a field emission electron gun.

Table 1
Reduction treatment of 1.0 or 10 wt.% samples.

Sample name	Reduction treatment
As-calcined	As-calcined
Red. 25 °C	Reduction[a] at 25 °C for 2 h
Red. 90 °C	Reduction[a] at 90 °C for 2 h
Red. 200 °C	Reduction[a] at 200 °C for 1 h
Red. 400 °C	Reduction[a] at 400 °C for 0.5 h

[a] Reduction atmosphere: 10% H_2/N_2.

The amount of CO adsorbed onto the surface of catalysts was measured by using the Quantachrome CHEMBET 3000 system in order to investigate the correlation between CO adsorption and the activity of catalytic combustion. Prior to the measurement, 50 mg of sample was heat-treated as shown in Table 1. Carbon monoxide (0.244 ml) was pulsed repeatedly to the sample at room temperature until the amount of CO in the outlet reached a constant value, and then the amount of adsorbed CO was calculated. Subsequently, temperature-programmed desorption (TPD) was conducted in the temperature range of 25–800 °C for the resulting samples adsorbed with CO. The temperature was raised at a heating rate of 10 °C min^{-1} with a supply of He gas at 16 ml min^{-1}. The partial pressures of CO and CO_2 detected in the outlet gas were measured by using the mass spectrometer (Anelva M-QA 2000TS) and the fraction of CO_2 to total desorbed species was calculated.

3. Results and discussion

3.1. Carbon monoxide combustion over as-calcined catalysts

The results of catalytic activity tests over as-calcined 1.0 wt.% Pt/SnO_2 and 1.0 wt.% $Pt/\gamma\text{-}Al_2O_3$ are shown in Fig. 1. Over $Pt/\gamma\text{-}Al_2O_3$, the 20% of carbon monoxide conversion was attained at 147 °C and carbon monoxide was completely oxidized at *ca.* 160 °C. On the other hand, the conversion over Pt/SnO_2 achieved 20% at 103 °C and the complete oxidation of carbon monoxide was accom-

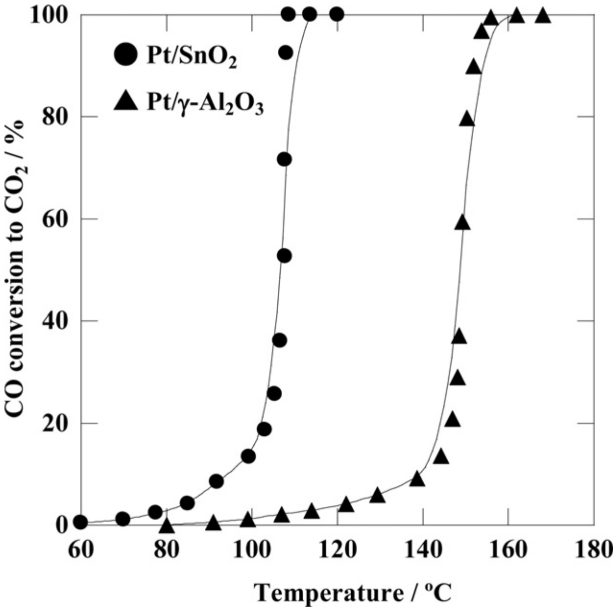

Fig. 1. Carbon monoxide conversion as a function of temperature over 1.0 wt.% Pt/SnO_2 and 1.0 wt.% $Pt/\gamma\text{-}Al_2O_3$. Reaction conditions: CO, 5.0%; O_2, 15.0%; N_2 balance; S.V. = 32,000 l kg^{-1} h^{-1}.

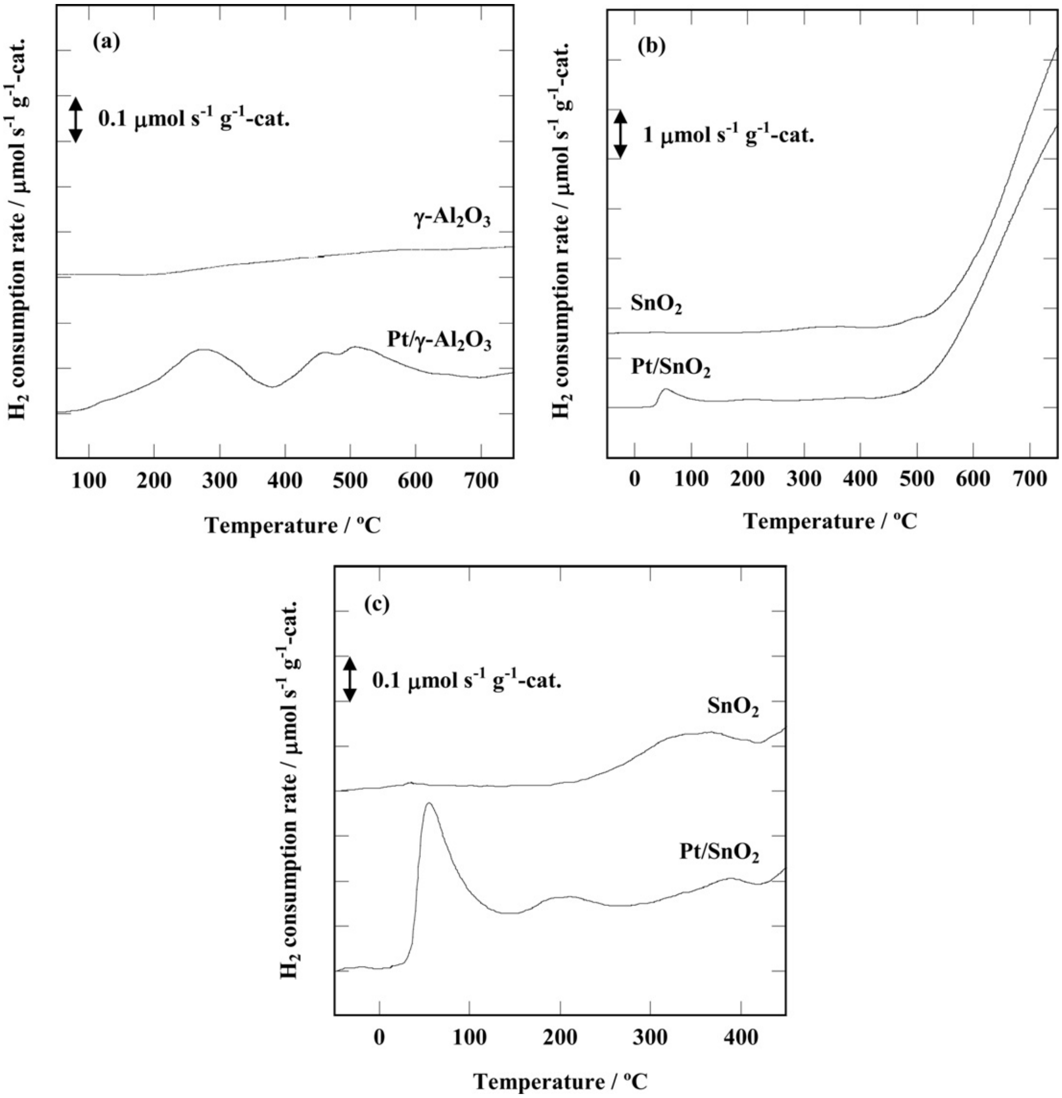

Fig. 2. Temperature-programmed reduction of metal oxide-support materials and metal oxide-supported platinum catalysts: (a) γ-Al_2O_3 and 1.0 wt.% Pt/γ-Al_2O_3, (b) SnO_2 and 1.0 wt.% Pt/SnO_2, and (c) magnified figure of (b) in the range of −50 °C to 450 °C.

plished at *ca.* 110 °C. The BET surface areas of Pt/γ-Al_2O_3 and Pt/SnO_2 were 159 $m^2\,g^{-1}$ and 8.7 $m^2\,g^{-1}$, respectively. Regardless of the low surface area, the activity of Pt/SnO_2 was much higher and carbon monoxide was oxidized at lower temperature by *ca.* 40 °C compared with the case of Pt/γ-Al_2O_3.

3.2. Characterization of as-calcined catalysts

TPR analysis was conducted so as to reveal the difference in catalytic activities of as-calcined samples, and the results are shown in Fig. 2. Fig. 2(a) shows the TPR profiles of γ-Al_2O_3 and 1.0 wt.% Pt/γ-Al_2O_3. While the γ-Al_2O_3 support itself was not reduced, the reduction peaks ascribable to the reduction of Pt species in the oxidation state were observed for Pt/γ-Al_2O_3. The H_2 consumption was determined from the area of two main peaks observed in TPR profiles, and also calculated theoretically by assuming the reduction of PtO_2 to Pt. It was found that the experimental value was roughly comparable to the theoretical one.

Fig. 2(b) shows the TPR profiles of SnO_2 and 1.0 wt.% Pt/SnO_2. A large peak over 550 °C is ascribable to the reduction of the bulk of tin oxide. The reduction of Pt species over SnO_2 was initiated at *ca.* 35 °C as shown in the magnified figure (Fig. 2(c)). The amount of H_2 consumption at 35–130 °C approximately corresponded to the theoretical value of the complete reduction of PtO_2 into Pt metal as in the case of Pt/γ-Al_2O_3. Accordingly, the Pt species on Pt/SnO_2 was readily reduced at low temperatures, leading to the high activity for the carbon monoxide oxidation. In addition, it was noted that the peak attributable to the reduction of tin oxide surface appeared at *ca.* 230 °C. Other researchers also support the reduction of tin oxide surface at low temperature [23,24]. This indicates that SnO_2 support in the vicinity of Pt particles was also reducible at low temperature.

3.3. Carbon monoxide combustion over reduced catalysts

As shown in Fig. 2, the reduction behavior of supported Pt species was different between Pt/γ-Al_2O_3 and Pt/SnO_2. Then, the effect of reduction treatment on carbon monoxide oxidation for the supported Pt catalysts was studied to clarify the correlation between the reduction behavior and the catalytic activity. After the as-calcined catalyst was reduced in the test reactor under various conditions, the catalytic activity test was performed. The results over 1.0 wt.% Pt catalysts are shown in Fig. 3. As shown in Fig. 3(a), the catalytic activities over Pt/γ-Al_2O_3 were enhanced by the reduction treatments at 200 °C and 400 °C. The reduction of supported Pt proceeded during the pretreatment at 200 °C or 400 °C in 10%

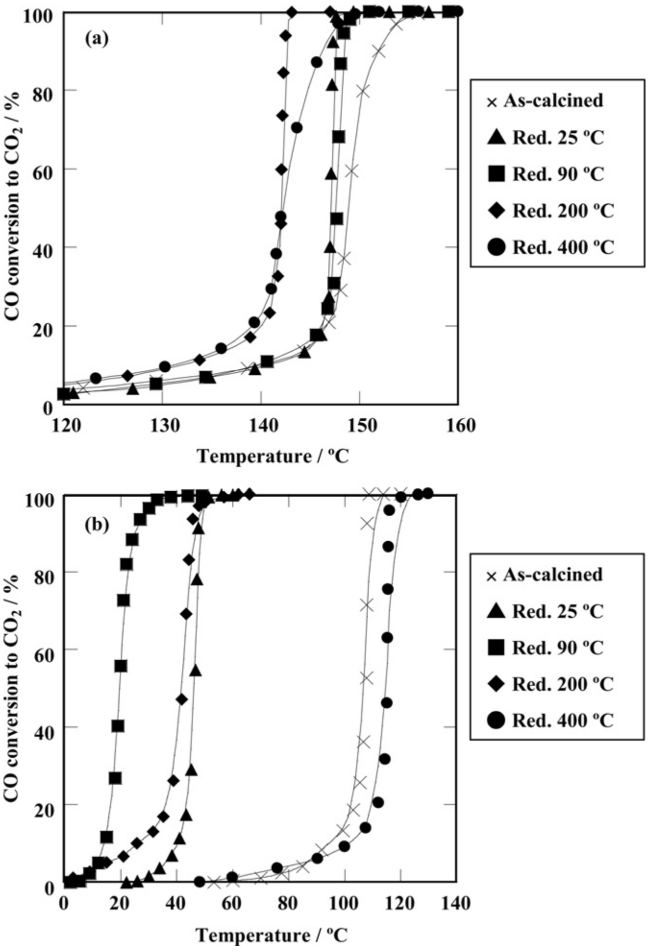

Fig. 3. Carbon monoxide conversion as a function of temperature over 1.0 wt.% Pt catalysts reduced in various conditions: (a) Pt/γ-Al_2O_3 and (b) Pt/SnO_2. Reaction conditions: CO, 5.0%; O_2, 15.0%; N_2 balance; S.V. = 32,000 l kg^{-1} h^{-1}.

H_2/N_2 as evidenced by the TPR profile of 1.0 wt.% Pt/γ-Al_2O_3. As a consequence, the active sites on the surface of metallic Pt particles increased by the sufficient reduction treatment.

On the other hand, the reduction treatment significantly affected the activities of Pt/SnO_2 catalysts as shown in Fig. 3(b). The catalytic activity was enhanced considerably by the reduction treatment at 25 °C and the 20% of conversion was attained at 44 °C. Moreover, the catalyst reduced at 90 °C exhibited the highest activity; the 20% of conversion was achieved at 17 °C and carbon monoxide was oxidized completely at room temperature. It is noted that the temperature of the 20% conversion was reduced by *ca.* 75 °C for this sample as compared with the as-calcined sample. However, the catalytic activity was degraded when the reduction temperature was elevated to 200 °C. The sample reduced at 400 °C exhibited the lowest catalytic activity.

3.4. Characterization of reduced catalysts

3.4.1. XRD measurements of Pt supported catalysts

After the reduction treatments, the catalytic activities of Pt/γ-Al_2O_3 were improved and those of Pt/SnO_2 significantly depended on the temperature of pretreatment. Then, the characterizations of the catalysts were performed before and after the reduction treatments to elucidate the factors affecting the catalytic activities. First, XRD measurements of 1.0 wt.% Pt/γ-Al_2O_3 and 1.0 wt.% Pt/SnO_2 were carried out, but platinum particles on metal-oxide supports were too small to be detected [21]. Then, the catalysts of 10 wt.% Pt/γ-Al_2O_3 and 10 wt.% Pt/SnO_2 were used alternatively, as shown in Fig. 4. In every diffraction pattern of Pt/γ-Al_2O_3, the diffraction peaks ascribable to Pt species were undetectable because of the overlapping with the broad diffraction pattern of γ-Al_2O_3. The diffraction patterns of Pt/SnO_2 catalyst were changed by the reduction treatments, as shown Fig. 4(b). The pattern of as-calcined sample was identical to that of SnO_2, and no peaks attributable to Pt species were observed. The diffraction lines of sample reduced at 25 °C consisted of those of Pt and SnO_2, indicating that the Pt species was reduced at room temperature. As the sample was reduced at higher temperatures, the reduction of Pt species further proceeded and the intensity of the metallic Pt lines increased. The pattern of sample reduced at 400 °C contained the new phases assigned to Sn and PtSn. Accordingly, it was revealed that SnO_2 support was partially reduced by the pretreatment at 400 °C.

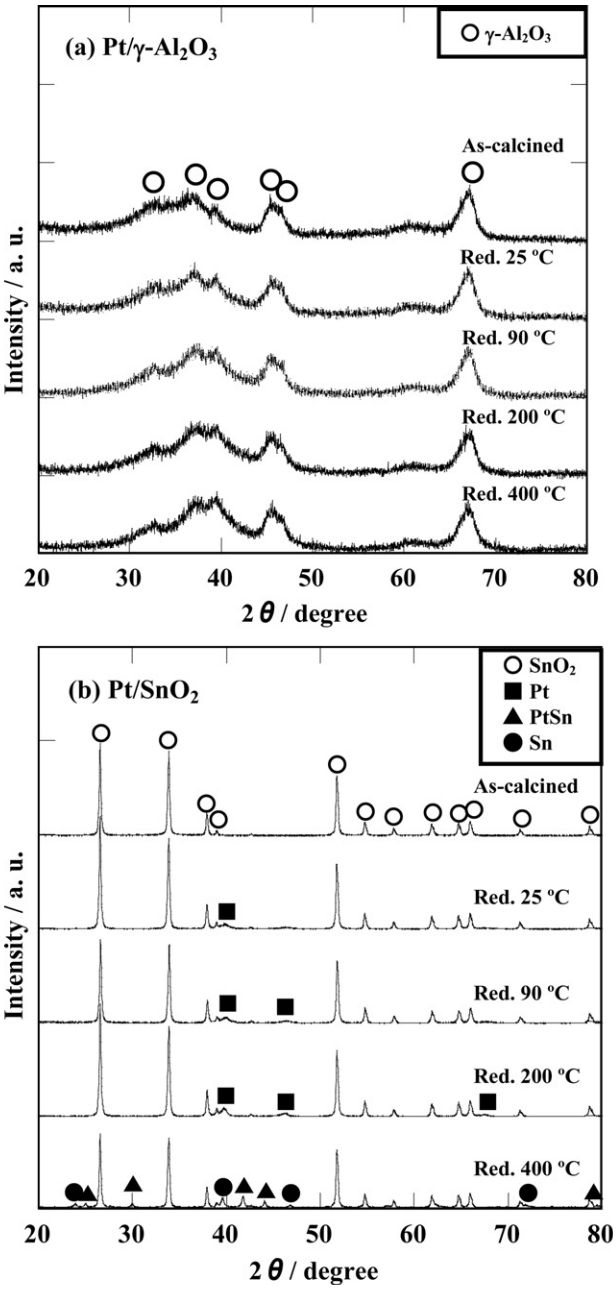

Fig. 4. XRD patterns of 10 wt.% Pt catalysts: (a) Pt/γ-Al_2O_3 and (b) Pt/SnO_2.

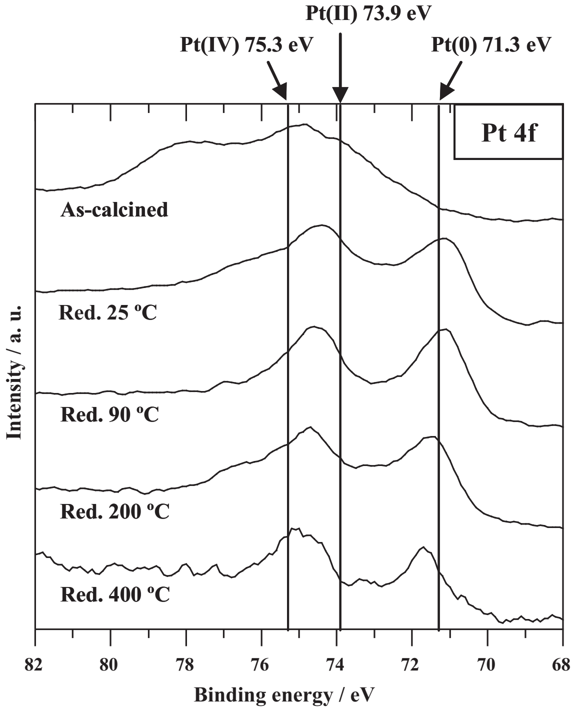

Fig. 5. XPS spectra of 10 wt.% Pt/SnO_2 catalysts treated under various conditions.

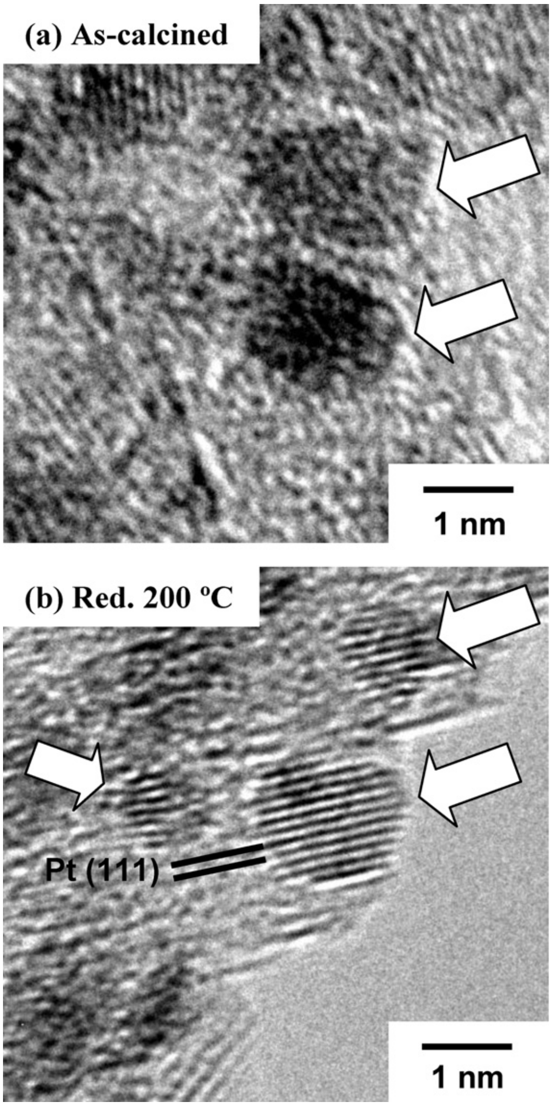

Fig. 6. TEM images of 10 wt.% Pt/γ-Al_2O_3 catalysts: (a) As-calcined and (b) Red. 200 °C.

3.4.2. XPS measurements of Pt/SnO_2 catalyst

The electronic state of Pt species on γ-Al_2O_3 and SnO_2 supports was investigated by XPS measurements. In the case of reduced catalysts, the measurements were carried out in situ without exposing the samples in the ambient atmosphere after reduction treatments. The XPS study of Pt/γ-Al_2O_3 catalysts has a known problem reported elsewhere [14]; the XPS analysis of Pt species is difficult because the binding energy of the Al 2p of the support overlaps with that of the Pt 4f which is generally used for the evaluation of the electronic state of platinum. Therefore, we evaluated the state of platinum on γ-Al_2O_3 by TEM observation and CO adsorption method as mentioned later.

The results of XPS measurements for Pt/SnO_2 catalysts are shown in Fig. 5 and the atomic ratio of the catalytic surface calculated from the spectra is summarized in Table 2. In Fig. 5, the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks were confirmed in the range of 68–82 eV for all samples. The spectrum of as-calcined sample indicated the existence of Pt species in the oxidized state (PtO (Pt $4f_{7/2}$ = 73.9 eV), PtO_2 (Pt $4f_{7/2}$ = 75.3 eV) [25]). On the other hand, the binding energy of Pt species in the reduced catalysts was almost identical to that of Pt^0 (Pt $4f_{7/2}$ = 71.3 eV) [25] and the Pt species in the electronic states of Pt^0 would lead to the high catalytic activities. The sample reduced at 400 °C showed slightly higher binding energy than the Pt metal. This result suggests the electron transfer from the Pt species to Sn species ascribable to the formation of Pt–Sn bond by strong metal–support interaction (SMSI) [21]. In addition, the fraction of Pt atom on catalytic surface decreased with an increase in the reduction temperature. This implies that the reduction treatment should promote the formation of intermetallic compounds, which could not be detected by XRD analysis for the samples reduced at and below 200 °C.

Table 2
Binding energy of Pt 4f analyzed by XPS and surface composition calculated from the peak area of Pt 4f and Sn 3d over 10 wt.% Pt/SnO_2.

Sample	Binding energy (eV)	Surface composition (%)	
	Pt $4f_{7/2}$	Pt 4f	Sn 3d
As-calcined	74.8	18.5	81.5
Red. 25 °C	71.2	21.8	78.2
Red. 90 °C	71.1	21.6	78.4
Red. 200 °C	71.5	18.6	81.4
Red. 400 °C	71.7	3.56	96.4

Binding energy: Pt(0) = 71.3 eV, Pt(II) = 73.9 eV, Pt(IV) = 75.3 eV.

3.4.3. TEM observation of Pt/γ-Al_2O_3 catalyst

For the Pt/γ-Al_2O_3 catalysts, the state of Pt species was investigated by TEM observation before and after the reduction treatment. Most of the Pt particles in the as-calcined sample were in the amorphous state as shown in Fig. 6(a). On the other hand, the lattice image of crystalline Pt particles in the sample reduced at 200 °C was clearly observed and the lattice spacing was 2.34 Å, which approximately agreed with Pt(1 1 1) lattice spacing of 2.27 Å (Fig. 6(b)). The TEM images of the samples reduced at other temperatures also revealed that the Pt species existed as metal.

3.4.4. CO adsorption over Pt supported catalysts

The amount of adsorbed CO onto the surface of catalysts was measured for the evaluation of the chemical state of platinum. Prior to the measurement, a catalyst was heat-treated in various condi-

Table 3
Amount of adsorbed CO and catalytic activity for CO oxidation over 1.0 wt.% Pt/γ-Al_2O_3.

Sample	Amount of adsorbed CO ($\mu mol\ g^{-1}$)	Metal surface area ($m^2\ g^{-1}$)	T_{20}[a] (°C)	BET surface area ($m^2\ g^{-1}$)
As-calcined	10.0	0.48	147	159
Red. 25 °C	19.1	0.92	146	146
Red. 90 °C	21.6	1.04	146	150
Red. 200 °C	50.2	2.42	140	158
Red. 400 °C	44.6	2.15	139	156

[a] Temperature at which 20% conversion is achieved.

tions as shown in Table 1. In the case of 1.0 wt.% Pt/γ-Al_2O_3 except the sample reduced at 400 °C, it was revealed that the reduction at higher temperature increased the amount of adsorbed CO as shown in Table 3. Considering that this behavior of CO adsorption was associated well with the catalytic activity, the platinum species over γ-Al_2O_3 reduced upon the pretreatment should directly contribute to the carbon monoxide oxidation. However, for the sample reduced at 400 °C, the amount of adsorbed CO decreased compared to the one reduced at 200 °C because a part of Pt particles was aggregated accompanied with the decrease in surface area.

It is generally considered that the catalytic activity is influenced by the electronic state of Pt species. Carbon monoxide is a π-acceptor ligand and carbon atom is directly bonded to a metal atom. The 5σ orbital with lone electron pair of carbon atom overlaps with the unoccupied *d* orbital of the metal atom, resulting in the formation of weak σ-bond. As a result of electron transfer from 5σ orbital of carbon to the unoccupied *d* orbital of metal atom, an increase in the electron density on the metal atom gives rise to a further electron transfer from the *d* orbital of metal atom to the unoccupied $2\pi^*$ orbital of carbon atom. As a consequence, carbon monoxide is adsorbed on the metal [26]. Therefore, the amount of adsorbed CO was small for as-calcined Pt/γ-Al_2O_3 sample because the *d* orbital of Pt species in the oxidation state should be occupied. In reduced catalysts, the electron transfer to the unoccupied *d* orbital readily occurred for the metallic Pt. Then, the increasing amount of adsorbed CO led to high catalytic activity as compared with the as-calcined catalyst. Moreover, the pretreatment at higher temperatures promoted the reduction of Pt species, resulting in an increase in the adsorbed sites on Pt metal particles and the enhancement of catalytic activities. Consequently, it is clear that the Pt metal plays a critical role in carbon monoxide combustion.

As shown in Table 4, the Pt/SnO_2 catalysts showed the difference in CO adsorption behavior from the Pt/γ-Al_2O_3 catalyst. The CO adsorption on Pt/SnO_2 was promoted by the reduction at 25 °C, because the adsorption sites on platinum increased by the reduction of the Pt species to the metallic state. For the samples reduced at higher temperatures, the amount of adsorbed CO decreased with increasing reduction temperature. This was attributed to the formation of intermetallic compounds between Pt and Sn, which was clarified by the change in surface composition (Table 2) and the appearance of PtSn phase (Fig. 4). It can be concluded that inhibited CO adsorption gives rise to low catalytic activity for the sample reduced at 400 °C. On the other hand, the samples treated at 90 °C and 200 °C exhibited high catalytic performance, though the adsorbed amount decreased upon these pretreatments. Therefore, for Pt/SnO_2 catalysts, it is reasonable to consider that other factors such as support effect contributed to carbon monoxide oxidation effectively.

Table 4
Amount of adsorbed CO and catalytic activity for CO oxidation over 1.0 wt.% Pt/SnO_2.

Sample	Amount of adsorbed CO ($\mu mol\ g^{-1}$)	Metal surface area ($m^2\ g^{-1}$)	T_{20}[a] (°C)	BET surface area ($m^2\ g^{-1}$)
As-calcined	16.2	0.78	103	8.7
Red. 25 °C	21.8	1.05	44	7.7
Red. 90 °C	11.1	0.53	17	6.4
Red. 200 °C	3.75	0.36	37	7.7
Red. 400 °C	0.00	–	112	5.0

[a] Temperature at which 20% conversion is achieved.

Table 5
Fraction of CO_2 desorbed from Pt/γ-Al_2O_3 and Pt/SnO_2 catalysts.

Pt/γ-Al_2O_3	$CO_2/(CO + CO_2)$	Pt/SnO_2	$CO_2/(CO + CO_2)$
As-calcined	0.469	As-calcined	0.346
Red. 90 °C	0.430	Red. 25 °C	0.349
Red. 400 °C	0.131	Red. 90 °C	0.342

3.4.5. *TPD measurements of Pt supported catalysts*

TPD measurements were conducted for the catalysts after CO adsorption experiments mentioned above. Fractions of desorbed CO_2 to total desorption species were calculated for Pt/γ-Al_2O_3 and Pt/SnO_2 as summarized in Table 5, respectively. In the case of Pt/γ-Al_2O_3 catalysts, the sample reduced at higher temperature exhibited lower fraction of CO_2 because of the small number of oxygen species adsorbed on Pt metal surface. In contrast, the fraction of CO_2 desorbed from the as-calcined sample was relatively high due to the sufficient oxidation of carbon monoxide by the abundant oxygen species in PtO_2.

On the other hand, TPD results of Pt/SnO_2 catalysts were different from those of Pt/γ-Al_2O_3 catalysts. The fraction of CO_2 was almost the same in three samples of As-calcined, Red. 25 °C, and Red. 90 °C. It is reasonable to assume that adsorbed CO on reduced catalysts is scarcely oxidized considering the results of Pt/γ-Al_2O_3 catalysts mentioned above. However, the fraction of CO_2 was relatively high for the sample reduced at 90 °C. This finding suggests that the oxygen species of SnO_2 support significantly contributed to carbon monoxide oxidation on the Pt surface or at the perimeter sites of the Pt–SnO_2 boundary. In conclusion, the oxygen species of SnO_2 support was activated by the reduction treatment at 90 °C, resulting in the noticeably high catalytic performance.

4. Conclusions

The effect of SnO_2 support in Pt/SnO_2 catalyst on carbon monoxide oxidation was investigated by comparing Pt/γ-Al_2O_3 catalyst. Despite the low surface area, carbon monoxide was oxidized over Pt/SnO_2 at lower temperature by *ca.* 40 °C than Pt/γ-Al_2O_3. The Pt species was readily reduced over SnO_2 support at low temperature, leading to the high activity. Moreover, the influence of reduction treatment on the reaction was studied to clarify the correlation between the reduction behavior and the catalytic activity. In the case of Pt/γ-Al_2O_3, the reduction of supported platinum species proceeded during the pretreatments at higher temperatures, giving rise the slight improvement in the catalytic activities. On the other hand, the catalytic activity of Pt/SnO_2 significantly depended on the reduction temperature. The highest activity was attained by the reduction at 90 °C, though the amount of CO adsorbed on the catalyst decreased. These results implied that the oxygen species of SnO_2 support was activated by the reduction treatment at 90 °C, and then contributed to the oxidation reaction over Pt. The sample reduced at 400 °C exhibited lower catalytic activity than the as-calcined sample. This was because the intermetallic compounds between Pt and Sn elements were formed and the amount of adsorbed CO decreased by the reduction treatment. Consequently, it is important to control the chemical interaction between metal and metal oxide support by reduction treatments for the catalytic activity enhancement of carbon monoxide oxidation.

References

[1] IEH Assessment on Indoor Air Quality in the Home (2): Carbon Monoxide, 1998.
[2] J.C. Nicholls, Med. Hypotheses 57 (5) (2001) 591.
[3] H. Igarashi, T. Fujino, M. Watanabe, J. Electroanal. Chem. 391 (1995) 119.
[4] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[5] M. Haruta, CATTECH 6 (2002) 3.
[6] C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, Appl. Catal. A: Gen. 232 (2002) 159.
[7] S. Li, G. Liu, H. Lian, M. Jia, G. Zhao, D. Jiang, W. Zhang, Catal. Commun. 9 (2008) 1045.
[8] C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 1.
[9] H. Zhu, Z. Qin, W. Shan, W. Shen, J. Wang, J. Catal. 225 (2004) 267.
[10] X. Tang, B. Zhang, Y. Li, Y. Xu, Q. Xin, W. Shen, Catal. Today 93 (2004) 191.
[11] S. Matsumoto, Catal. Today 90 (2004) 183.
[12] K. Eguchi, H. Arai, Appl. Catal. A: Gen. 222 (2001) 359.
[13] T. Mitsui, K. Tsutsui, T. Matsui, R. Kikuchi, K. Eguchi, Appl. Catal. B: Environ. 81 (2008) 56.
[14] A.S. Ivanova, E.M. Slavinskaya, R.V. Gulyaev, V.I. Zaikovskii, O.A. Stonkus, I.G. Danilova, L.M. Plyasova, I.A. Polukhina, A.I. Boronin, Appl. Catal. B: Environ. 97 (2010) 57.
[15] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256.
[16] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. López Cartes, J.A. Pérez Omil, J.M. Pintado, Catal. Today 77 (2003) 385.
[17] T. Mitsui, T. Matsui, R. Kikuchi, K. Eguchi, Top. Catal. 52 (2009) 464.
[18] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.
[19] T. Matsui, T. Okanishi, K. Fujiwara, K. Tsutsui, R. Kikuchi, T. Takeguchi, K. Eeguchi, Sci. Technol. Adv. Mater. 7 (2006) 524.
[20] T. Okanishi, T. Matsui, T. Takeguchi, R. Kikuchi, K. Eguchi, Appl. Catal. A: Gen. 298 (2006) 181.
[21] N. Kamiuchi, T. Matsui, R. Kikuchi, K. Eguchi, J. Phys. Chem. C 111 (2007) 16470.
[22] T. Mitsui, K. Tsutsui, T. Matsui, R. Kikuchi, K. Eguchi, Appl. Catal. B: Environ. 78 (2008) 158.
[23] M. D'Arino, F. Pinna, G. Strukul, Appl. Catal. B: Environ. 53 (2004) 161.
[24] R. Sasikala, S.K. Kulshreshtha, J. Therm. Anal. Calorim. 78 (2004) 723.
[25] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie, MN, 1992.
[26] M. Primet, J.M. Basset, M.V. Mathieu, M. Prettre, J. Catal. 29 (1973) 213.