Effect of reduction–oxidation treatment on the catalytic activity over tin oxide supported platinum catalysts

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Abstract

In precious metal-oxide catalyst system, the support materials strongly affect the catalytic activity. Especially the term of strong metal–support interaction is well known: Tauster et al. reported that partially reducible oxide such as titanium oxide could modify the chemisorption of H2 and CO [S.J. Tauster, S.C. Fung, R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170; S.J. Tauster, S.C. Fung, J. Catal. 55 (1978) 29; S.J. Tauster, S.C. Fung, R.T.K. Baker, J.A. Horsley, Science 211 (1978) 1121]. It was also demonstrated that this interaction could modify the catalytic activity of precious metals in different reactions. Accordingly, elucidating these phenomena will be the useful guide for the development of new class of active catalysts. Thus, we had focused on the chemical interaction between platinum and oxide and reported several results. Tin oxide supported platinum catalysts were heat-treated under oxidizing or reducing atmospheres at various temperatures, and their catalytic activity for methane combustion and electrochemical oxidation of CO was investigated. The resulting catalysts exhibited the peculiar microstructure and catalytic activity because of the metal–support interaction.

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Keywords: Chemical interaction; Platinum; Tin oxide; Carbon monoxide; Methane; Polymer electrolyte fuel cells

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1. Introduction

Various kinds of precious metal catalysts have been studied so far and used in a wide variety of applications. The catalytic combustion of hydrocarbons at low temperatures employing these catalysts is attractive because of high efficiency and low thermal NOx emission compared to the conventional flame combustion systems [1–3]. These catalysts are also expected to be used as ignition catalysts of gas-turbine engines. In the fuel cell technology, highly active catalysts are also required for reforming, shift reaction, preferential oxidation, electrode reaction, etc. [4–12]. Precious metals are generally deposited on oxide or carbon supports which possess high surface area to maintain highly dispersed active reaction sites. In most of the cases, these supports do not contribute to reactions because they are inert. However, a series of oxide supports exhibit chemical interaction with metals and affect the catalytic activity [13–21]. This phenomenon is well known as strong metal–support interaction (SMSI), and many studies have been conducted in this field. This metal–support effect not only promotes the reaction but also suppresses poison or deactivation factors. However, the mechanism has not been elucidated sufficiently for several catalyst systems.

Palladium and platinum based catalysts are generally the most active for flameless combustion. Tin oxide is widely used as a gas sensing device and the catalysts of oxidation reaction [22–26]. Accordingly, synergistic effects are expected by combining these two materials. We have previously reported the palladium-oxide system for methane catalytic combustion, whose catalytic activity strongly depended on the support materials [27–29]. When the palladium–tin oxide system was employed, the catalytic activity significantly improved regardless of extremely small surface area compared to palladium–alumina system. This enhancement can be explained as the result of the metal–support interaction. In the case of electrodes for polymer electrolyte fuel cells, platinum is widely used because of high electrocatalytic activity for hydrogen oxidation. However, its activity drastically deteriorates in the presence of carbon monoxide. Therefore, new electrodes with high CO tolerance are required, and several platinum-oxide systems such as Pt/MoOx, NbOx, and TaOx were reported [12,30,31]. The role of oxides was proposed to relax the strong CO adsorption on Pt, which originates in the modification of the electronic band structure of Pt and the interaction between Pt and metal oxides. These kinds of chemical interaction would be applied to other catalytic systems.

In this review, we summarized our recent researches on chemical interaction between platinum and tin oxide. Tin oxide supported platinum catalysts were heat-treated under oxidizing or reducing atmospheres at various temperatures, and its effect on the catalytic activity for methane combustion and electrochemical oxidation of CO was investigated.

2. Experimental

2.1. Catalyst preparation

Platinum catalysts supported on tin oxide were prepared by the impregnation method. An aqueous solution of Pt(NO3)2(NH3)2 (Tanaka Kikinzoku Kogyo) and tin oxide (SnO2, Wako Pure Chemical Industries Ltd.) were used as Pt source and support, respectively. After calcination at 800 °C for 5 h, SnO2 powder (BET surface area: 5.0 m² g⁻¹) was impregnated with a desired amount of an aqueous solution of Pt(NO3)2(NH3)2. The Pt loadings on SnO2 were 1 and 20 wt%; lightly loaded catalysts were used for methane combustion experiments. The mixture was kept on a steam bath at 80 °C until the solution evaporated. The resulting powders were heat-treated under various conditions prior to the characterization and catalytic reaction, as summarized in Table 1.

2.2. Characterization of the catalysts

The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). XRD patterns were recorded by using Cu-Kα radiation on a RIGAKU Rint 2500 diffractometer for phase identification in the samples. XPS measurements were conducted on a Shimadzu ESCA-850 using a Mg-Kα source. Catalysts heat-treated under various conditions were analyzed by on-line non-dispersive infrared (NDIR, CGT-7000) to measure the concentration of CH4 and CO2.

2.3. Catalytic activity for methane oxidation

In this experiment, catalysts of 1 wt% Pt/SnO2 were used. Catalytic activity for methane combustion was investigated by using a fixed bed flow reactor of quartz tubing at atmospheric pressure. A gaseous mixture of 1 vol% CH4, 20 vol% O2, and N2 as balance was fed to the catalytic reactor at a space velocity of 30,000 l kg⁻¹ h⁻¹. The catalytic performance was measured by raising the reaction temperature from room temperature to 400 °C at the heating rate of 150 °C h⁻¹. The effluent gas was analyzed by on-line non-dispersive infrared (NDIR, CGT-7000) to measure the concentration of CH4 and CO2.

Table 1

| Sample | Heat treatment |
|--------|----------------|
| S-1    | Pyrolysis at 400 °C in air |
| S-2    | Pyrolysis at 400 °C in air, followed by reduction at 400 °C in 10% H2/N2 |
| S-3    | Pyrolysis at 400 °C in air, followed by reduction at 90 °C in 10% H2/N2 |
| S-4    | Pyrolysis at 200 °C in 10% H2/N2 |
| S-5    | Reoxidized S-2 at 400 °C in air |
2.4. Evaluation of electrochemical properties

The electrochemical measurements of the catalysts in 1 M HClO₄ solution were conducted at 25 °C. A suspension containing the catalyst in water was ultrasonically dispersed for 30 min, and then was dropped onto the glassy carbon disk electrode (0.196 cm²) to be 14 μg-Pt cm⁻². After the water evaporated, the electrode surface was covered with 10 μl of Nafion® solution (Aldrich, diluted to 1 wt% solution with ethanol). The conventional three-electrode cell with reversible hydrogen electrode (RHE) was used. Oxidation of pre-adsorbed CO was measured by CO stripping voltammetry with a scan rate of 20 mV s⁻¹. Gaseous CO was purged into the cell for 30 min while maintaining a constant voltage of 0.1 V vs. RHE, and then the excess CO in the electrolyte was purged out with Ar for 40 min before the measurement. The potentiodynamic oxidation curves of pure CO were also measured with a scan rate of 20 mV s⁻¹. Equilibrium was achieved by bubbling CO for 30 min at an electrode potential of 0.1 V at an electrode rotation rate of 2000 rpm before the measurement.

For the evaluation of the power generation with a fuel cell, Pt/SnO₂ catalysts were employed as a fuel electrode. A commercial 5 wt% Nafion® solution was mixed with n-butyl acetate and water; then the catalyst powder was added to the solution to form a suspension. Commercial 40 wt% Pt/C (Johnson-Matthey) was used for the cathode. In the case of Pt/SnO₂ catalysts, carbon black (Valcan®, X72R) was also added to increase the overall electrical conductivity of the anode. The suspension thus prepared was applied onto carbon paper (R50 T, Ballard) until the final Pt level of 1 mg cm⁻² was attained. The dried carbon paper with the active catalytic layer was attached to a proton exchange membrane (Nafion® 117, Aldrich) by hot-pressing. Current–voltage characteristics were measured by using the cell housing for an electrode area of 5 cm². The gaseous mixture of hydrogen (70%) and water (30%) with or without CO (100 ppm) was supplied to the anode. Humidified oxygen was used as an oxidant. The power generation was tested at 75 °C.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction patterns of 20 wt% Pt/SnO₂ after various heat treatments are shown in Fig. 1. The pattern after heating at 400 °C in air (S-1) consisted of lines from SnO₂, whereas no lines ascribable to Pt have been observed. Platinum species in this case appear to stay as metallic state, indicating that the sample was in the amorphous state, although the oxidation state could not be judged from the phase. The sample was subjected to reduction treatment after heating in air at 400 °C. After heat treatment in H₂ at 90 °C (S-3), the pattern consisted of metallic Pt and SnO₂ phases. When the reduction temperature was raised to 400 °C (S-2), the diffraction pattern was significantly changed. The pattern contained the new phases attributed to PtSn₂ and PtSn₄, accompanied with the disappearance of Pt. Thus the Pt/SnO₂ in reducing atmosphere gives rise to the formation of the intermetallic compounds which are formed due to solid state reactions between platinum and tin. However, after the reoxidation treatment at 400 °C in air (S-5), the diffraction pattern corresponded with that of S-2. The sample of S-4, directly reduced at 200 °C, exhibited the similar pattern of S-3. Considering that the intensities of the Pt lines were slightly stronger than S-3, this sample was in the intermediate state between those reduced at 90 and 400 °C.

3.2. Surface analysis

From the binding energy of Pt on oxide support, the oxidation state was evaluated (Table 2). The binding energy of the Pt signal for S-1 was larger than those in metallic state, indicating that the sample was in the oxidation state. On the other hand, remaining samples commonly demonstrated almost identical binding energies to those for metallic Pt. In the case of Pt alloys, it was reported that the positive shift of the binding energy for Pt 4f and Pt 4d led to an increase in d-vacancy and a small contribution of Pt 5d electrons to the CO 2p⁰ orbital, resulting in the suppression of CO coverage [32]. Thus, for all reduction-treated samples, it is difficult to expect the suppression of CO chemisorption on Pt. The shift of tin signal was insensitive to the reduction treatment, since the formation of intermetallic compound appears to have partially proceeded in overall tin species at or below 400 °C. In the case of S-5, reoxidized S-2 at 400 °C, metallic and oxidized platinum species co-existed on the surface. Therefore, partial oxidation of intermetallic compounds or
platinum species proceeds in oxidizing atmosphere. Considering that there were no diffraction lines of platinum oxide, the resulting species should be in amorphous state. These results indicate that intermetallic compounds do not recover to the initial state of S-1, regardless of the oxidizing treatment.

The composition of catalyst at the surface was estimated from the intensity ratio of Sn and Pt signals, and the results are also listed in Table 2. It is noted that the surface composition has been significantly changed with heat treatments. The sample of S-1 exhibited the smallest Sn/Pt value among the heat-treated catalysts. The surface Sn/Pt ratio increased as the higher reduction temperature was employed. In the samples of S-2, significant enrichment of Sn species was observed. This implies that the surface of Pt grains was homogeneously mixed with Sn or covered with Sn species. The composition ratio of Sn/Pt for S-4 is located in between the samples for S-2 and S-3. This result corresponds to the result of XRD pattern. Thus, the oxidation pre-treatment does not affect the final state after the reduction.

### 3.3. Microscopic observation

Textural microstructures were investigated from TEM observation. For S-1, highly dispersed Pt particles were observed on the surface of tin oxide support. Reduction of platinum easily proceeds on subsequent exposure to hydrogen, resulting in the grain growth (Fig. 2(a)). After the subsequent severe reduction treatment at 400 °C in hydrogen, as shown in Fig. 2(b), peculiar microstructure with core/shell morphology has appeared. The surface of Pt was covered with a shell of tin oxide. Considering the results of XRD pattern, this core–shell microstructure is related with the formation of intermetallic compounds of PtSn2 and PtSn4. Although the homogeneous compound would be formed after the reduction at elevated temperature, the surface was inevitably oxidized on exposure to air for TEM observation. Accordingly, the tin oxide is deposited on the topmost surface as a result of preferential oxidation of surface tin species. Thus, the reduction–oxidation treatment contributed to the surface rearrangement of atoms and to the characteristic tailored structure.

### 3.4. Catalytic activity for methane oxidation

Catalytic combustion of methane over S-1 and S-2 are shown in Fig. 3. The reduction treatment significantly deteriorated the catalytic activity: even at 400 °C, the CH4 conversion for S-2 did not reach 50% whereas S-1 achieved...
99%. The ignition temperature for S-2 at a conversion level of 10%, \( T_{10} \), was ca. 100 °C higher than that of S-1. Thus, the formation of intermetallic compound gave rise to the deactivation. At this stage, however, it is difficult to evaluate whether the intermetallic compounds themselves or the peculiar core–shell structure mainly affects the deactivation. Time course of the catalytic activity at 400 °C is shown in Fig. 4. In the case of S-2, it was expected that the catalytic activity would improve with time because of the coexistence of platinum oxide species on the surface in oxidizing atmosphere as is observed in S-5. However, both catalysts exhibited stable behaviors for 30 h. Thus, it was found that the reoxidized surface of S-2 appeared to be less active.

### 3.5. Electrochemical properties

The CO-stripping voltammograms of Pt/SnO2, Pt/C, and PtRu/C catalysts in 1 M HClO4 solution are shown in Fig. 5. Solid and dotted lines show first and second cycles, respectively. The anodic peak potentials of CO oxidation and the electrochemical surface area for each catalyst are summarized in Table 3. The electrochemical surface area of precious metal determined by the COad oxidation assuming a monolayer of linearly adsorbed CO. For all samples, voltammograms in second cycle coincided with that in Ar saturated solution. The order of the electrochemical surface area corresponded to that of surface atomic ratio: the surface area decreased with an increase in Sn/Pt. In the first cycle, both S-3 and S-4 exhibited almost the same peak potential as Pt/C catalyst, whereas the significant negative
shift was observed for PtRu/C catalyst (0.51 V vs. RHE). However, the onset potential of CO oxidation was below 0.4 V, indicating the possibility of the improvement in CO tolerance. In the second cycle, there were no the double layer region (ca. 0.3–0.7 V) and the peaks attributed to Pt-oxide layer formation/reduction (over 0.8 V) identical to Pt/C catalysts, whereas the peaks related with hydrogen adsorption/desorption on Pt were observed (0–0.3 V). Alternatively, the anodic current gradually increased from 0.35 V up to ca. 0.7 V, and a corresponding cathodic current peak was observed at ca. 0.5–0.6 V. Similar redox peaks were reported for the Sn-modified Pt electrodes, which were attributed to the Sn(II)/Sn(IV) redox couple for tin oxide/hydroxide species [33,34]. Accordingly, there should be partially reduced tin oxide on the surface, and the redox couple might promote the stripping removal of adsorbed CO on Pt. On the other hand, in the case of S-2, a quite different result was obtained: the first cycle coincided with the second one and there were no peaks attributed to hydrogen adsorption/desorption. Thus, this sample suppressed CO adsorption completely and had no electrocatalytic activity for hydrogen oxidation. This should also originate from the formation of intermetallic compounds.

To investigate the intrinsic CO tolerance of catalysts, the potentiodynamic oxidation of CO was also conducted in CO saturated solution. The current density was normalized by the amount of loaded precious metal, and results are shown in Fig. 6. For both S-3 and S-4, the onset potential of CO oxidation shifted negatively compared to Pt/C and PtRu/C, and the anodic current increased at two regions, 0.35–0.9 V and over 0.9 V. At the former region, the current density was higher than that of the Pt/C catalyst, regardless of the extremely small electrochemical surface area. The latter region of over 0.9 V should be attributed to the CO oxidation on Pt, which is not affected by tin oxide. Taking into account that the electronic band structure of Pt showed no change, these results also indicate that the Sn(II)/Sn(IV) redox couple should promote the CO oxidation.

The $I-V$ characteristics of the hydrogen oxygen fuel cell with the Pt/SnO$_2$ (20 wt% Pt) anode and Pt/C cathode were compared with the fuel cell with Pt/C electrodes. Fig. 7 shows the $I-V$ characteristics of two kinds of fuel cells with different anode catalysts. At a given current, the terminal voltage was higher for the cell with Pt/C than that with S-3 in H$_2$. This difference is ascribed to the higher surface area and dispersion of Pt on carbon support. When the gaseous mixture of 100 ppm CO/H$_2$ was supplied, the generation performance was deteriorated for both cells. It is well known that carbon monoxide at this concentration level strongly suppresses electrode reaction because of the strong adsorption of CO molecule on the Pt surface. The extent of the deterioration was much smaller for S-3 anode

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**Table 3**

Peak potential of CO oxidation and electrochemical surface area for 20 wt% Pt/SnO$_2$ catalysts

| Sample | Peak potential of CO oxidation vs. RHE/V | Electrochemical surface area ($m^2 g^{-1}$-Pt(Ru)) |
|--------|-----------------------------------------|-----------------------------------------------|
| S-2    | —                                       | —                                             |
| S-3    | 0.70                                    | 11.2                                          |
| S-4    | 0.74                                    | 6.11                                          |
| Pt/C   | 0.74                                    | 36.4                                          |
| PtRu/C | 0.51                                    | 91.4                                          |

*Electrochemical surface area was determined by CO$_{ad}$ oxidation.
This review has shown examples of strong chemical interaction of a precious metal catalyst system. Tin oxide supported platinum catalysts were sensitive to the reduction–oxidation pretreatments. The changes in the morphology, microstructure and composition on the surface resulted in the striking effect on the catalytic activity, such as the catalytic combustion of methane and electrocatalytic oxidation of CO. Especially, the formation of intermetallic compounds gave rise to the peculiar structure and catalytic activity. This kind of interaction may appear for other catalyst systems and be a useful guide to design the active catalysts.

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