Structure and formation process of the water-pretreatedPt/FeOx-Al2O3 catalyst capable of CO oxidation below room temperature

A Tomita1, K Shimizu2, K Kato3 and Y Tai1

1 Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan
2 Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan
3 Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan

Email: tai.y@aist.go.jp

Abstract. Structure and formation process of water-pretreatedPt/FeOx-Al2O3 catalyst capable of CO oxidation below room temperature has been investigated using Pt L-IIIX-ray absorption fine structure (XAFS) measurement and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Before the water-pretreatment, Pt monomers and small clusters were detected while formation of Pt nanoparticles (PtNPs) having an average diameter of ≈1.3 nm and Pt-O-Fe interaction were confirmed after the pretreatment, implying that Pt monomers and small clusters aggregated at FeOx on alumina upon the pretreatment. The present results seem to indicate that the formation of Pt monomers and small clusters prior to the water-pretreatment is important for the high mobility of the Pt species and the contact formation between the Pt particles and FeOx on the resultant catalyst which is a key to the high CO oxidation activity at low temperatures.

1. Introduction

The use of additives to promote catalytic reactions over platinum group metals (PGMs) is employed in various applications such as the three-way catalyst (TWC) for purification of automotive exhaust. To optimize interactions between PGMs and promoters, it is necessary for uniform contacts to exist between them. We have recently reported that in Pt/Fe-containing alumina catalysts prepared and treated with water under moderate conditions, Pt nanoparticles (PtNPs) and iron oxides form intimate contacts with each other and as a result, the catalyst exhibited CO oxidation activity even at temperatures below 0 °C [1].

Obviously, the key process for the catalyst preparation is the hydrogen treatment with water at ≈200 °C prior to measurement of CO conversions (water-pretreatment). From transmission electron microscopy (TEM), it was confirmed that on the water-pretreated catalysts, mobility of Pt species was enhanced and larger NPs were formed. However, the growth of the PtNPs was suppressed when the catalyst support contained small amount of FeOx. These results suggest that PtNPs were formed at FeOx sites upon the water-pretreatment.

Although, the effect of the water-pretreatment on the catalyst structure has been clarified to a certain extent, the role of each step in the catalyst preparation is not clarified. In this paper, we will analyze the structure of the catalyst at each step of the catalyst preparation in detail using Pt L-IIIX-ray...
absorption fine structure (XAFS) measurement and high-angle annular dark-field scanning TEM (HAADF-STEM).

2. Experimental

2.1. Catalyst Preparation

The method of catalyst preparation has been described elsewhere; thus, is described here only briefly. γ-alumina sample containing small amount of Fe [ALO-5 (Fe content: 0.48 wt%, Japan Reference Catalyst (JRC))] was used as a catalyst support. A HNO₃ solution of Pt(NH₃)₂(NO₃)₂ (Tanaka precious metals, Pt content: 50 g/L) was added to a slurry containing the γ-alumina (1 g). The mixture was then heated on a steam bath, with stirring, to evaporate water. The resultant solid was (I) calcined at 200 °C for 2 h in a flow of dry air (300 mL/min) and then (II) it was reduced at 200 °C in a flow of H₂/Ar (1:1, 50 mL/min). The catalysts (100 mg) were wetted with deionized water at room temperature and (III) heat-treated under a flow of H₂ (33.3 mL/min) in a Pyrex tube at 200 °C for 30 min prior to measurement of CO conversions. We denote the final treatment, the water addition and the following H₂ reduction, as “water-pretreatment”. In addition to this preparation procedure, the water addition was examined at the steps (I) and (II). For the measurement of catalytic activity, the reactant gas [CO (1%), O₂ (0.5%), N₂ (98.5%)] was passed through the catalytic bed at a flow rate of 33.3 mL/min [hourly gas space velocity (HGSV) = 20,000 mL/(h·g-cat.)]. The specific surface area, pore diameter, and chemical compositions of the ALO-5 alumina have also been described previously [2].

2.2. Catalyst Characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were recorded using a Hitachi HD-2700 electron microscope with a Cs corrector operated at an accelerating voltage of 200 kV. For the STEM observations, an ethanol dispersion of the ground catalysts was dried on a carbon-coated microgrid.

Pt L₃ XAFS measurements for the catalysts (2.5wt % Pt/ALO-5) prior to the water-pretreatment have been performed in air at the BL11 in the SAGA-LS (Saga, Japan, Proposal No.100657N). The catalysts after the water-pretreatment have been measured at the BL01B1 in SPring 8 (Hyogo, Japan, Proposal No.2011B1337) in the in situ transmission QXAFS mode. A pelletized catalyst was water-pretreated in a flow cell with kapton windows, and then measured under He atmosphere at room temperature. The k³χ(k) functions in the range of values of k typically from 3.0 to 16.0 Å were Fourier-transformed using Hanning windows to obtain FTs.

3. Results and discussion

We examined the addition of water at each step of the catalyst preparation (I, II, and III). Table 1 compares the CO conversions at 25 °C for the catalysts (5wt % Pt) added ≈0.15 mL of deionized water prior to step I, II, and III together with that without water addition. Apparently, only the water addition prior to step III was effective; the conversion for the catalysts prepared with the water additions at other steps were the same as that of the catalyst prepared without the water addition. Accordingly, we investigated the structure of the catalyst at each step in the preparation procedure in which water is added prior to step III using Pt L₃ XAFS spectroscopy and HAADF-STEM observation. We compare Fourier transforms (FTs) of PtL₃ EXAFS oscillations at each step of the catalyst preparation before the water-pretreatment together with that of the HNO₃ solution of Pt(NH₃)₂(NO₃)₂ in Figs. 1 and 2. Interestingly, a few peaks were detected at an R range from 2.4 to 3.8 Å. This result is indicative

| Timing of water addition | STEP I | Step II | Step III | No addition |
|--------------------------|--------|---------|----------|-------------|
| CO conversion at 25 °C (%) | 14     | 27      | 100      | 20          |

Table 1. CO conversions over the catalysts (5wt% Pt)treated with water at each preparation step.
of the formation of second or higher coordination shells in the starting Pt solution. Similar higher shell formation due to oligomerization have been reported for Pt nitrate [3] and Pt(NH$_3$)$_2$(NO$_3$)$_2$ solutions [4]. Thus, oligomerization of Pt(NH$_3$)$_2$(NO$_3$)$_2$ might had been occurred in our starting Pt solution during storage. The impregnated catalyst before calcination exhibited identical FT to that of the starting Pt solution. The FT of the calcined catalyst was also similar to that of the starting solution except for the disappearance of a small peak at $\approx 2.5$ Å. However, after reduction [step (II)], the FT changed significantly as can be seen in Fig. 2. The fitting parameters, $N_{Pt-O}$=4.2, $R_{Pt-O}$=2.01 Å, $N_{Pt-Pt}$=0.8, and $R_{Pt-Pt}$=2.53 Å, were derived. These values can be explained by assuming an ensemble of monomers and very small clusters coordinated with oxygen [5, 6]. Asakura et al. reported that Pt monomers on the (111) surface of $\alpha$-alumina exhibited $N_{Pt-O}$=3±0.5, which indicates that Pt monomers occupy threefold sites on the surface [5]. The present value, $N_{Pt-O}$=4.2, is slightly larger than their value. However, in the present experiment, Pt species are supported on γ-aluminaparticles of which the surfaces may well have some undulations and some of the Pt species are expected to exist at the
boundaries of the γ-aluminaparticles. These factors possibly increase the oxygen coordination number. Short Pt-Pt distances, less than 2.6 Å, have been often reported for small Pt cluster species [6].

To clarify further the state of Pt dispersions, we have observed the catalyst after reduction with HAADF-STEM. Figure 3 displays the results. At low magnification, Pt aggregates with an average diameter of 1~2 nm was observed [Fig.3(a)]. However, the image taken at high magnification [Fig.3(b)] shows a lot of Pt atoms separated from others. Although we cannot identify dimer or other small cluster species unambiguously, these observations seem to be consistent with the EXAFS results. It is known that Pt particles with diameters less than ≈1 nm tend to decay in air [7]. Thus, the aggregated structures seen in Fig. 3(a) probably resulted from the decay of small Pt particles formed in the reduction step [step (II)].

After the water-pretreatment, the formation of Pt particles was evidenced by the fitting parameters due to Pt backscatter, $N_{Pt-Pt}=6.6$, $R_{Pt-Pt}=2.72$ Å (Fig.4). In addition, the best-fit curve was obtained assuming Fe backscatter with $N_{Pt-Fe}=0.7$ and $R_{Pt-Fe}=3.05$ Å. These results seem to indicate that Pt particles having an average diameter of ≈1.3 nm [8] were formed and pinned at FeOx sites, possibly forming thin-layered islands or small clusters on the alumina surface [9], through Pt-O-Fe interaction during the water-pretreatment [1].

As indicated in table 1, the addition of water was effective only when it was done after reduction [step III]. The present results seem to indicate that the formation of atomically dispersed Pt species prior to the water-pretreatment is important for their high mobility and the contact formation between the resultant PtNPs and FeOx.

References

[1] Tomita A, Shimizu K, Kato K, Tai Y, Catal. Commun. 17, 194 (2012).
[2] Okazaki N, Shiina Y, Itoh H, Tada A, Iwamoto M, Catal. Lett. 49, 169 (1997).
[3] Dou D, Liu D-J, Williamson W B, Kharas K C, Robotka H J, Appl. Catal. B-Env. 30, 11 (2001).
[4] Rochon F D, Buculei V, Can. J. Chem. 82, 1606 (2004).
[5] Asakura K, Chun W-J, Shirai M, Tomishige K, Iwasawa Y, J. Phys. Chem. 101, 5549 (1997).
[6] see for example Chun W-J, Tomishige K, Hamakado M, Iwasawa Y, Asakura K, JCS Faraday Trans. 91, 4161 (1995).
[7] Joyner R, J. Chem. Soc. Faraday Trans. I, 76, 357 (1980).
[8] De Graaf J, Van Dillen J, De Jong K P and Konigsberger D C, J. Catal. 203, 307 (2001).
[9] Tomita A, Shimizu K, Kato K, Akita T, Tai Y, submitted to J. Phys. Chem. C.

Figure 4. FT of EXAFS oscillations of the catalyst after the water-pretreatment and the fitting parameters. Open circles represent the experimental data and the solid line indicates the fitting curve.

| BS  | N     | R/Å  | ΔE/eV | DW/Å |
|-----|-------|------|-------|------|
| Pt  | 6.6   | 2.72 | 6.6   | 0.083|
| Fe  | 0.7   | 3.05 | -7.6  | 0.059|

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  |  |  |