Formation of Amorphous Pt Oxides: Characterization and Their Catalysis

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Keywords: am-PtOx, TPD, BET, CO oxidation

Amorphous Pt oxides (am-PtOx) were formed by the leaching of copper from a Cu3Pt alloy in concentrated HNO3 at 323 K for 12 h. The resulting am-PtOx was characterized using synchrotron X-ray powder diffraction, hard X-ray photoelectron spectroscopy, thermal analysis (TG-DTA, TPD) and the BET method. This material had a high specific surface area with micropores (61.7 m²/g) and decomposed to form Pt and O₂ at approximately 720 K. The catalytic performance of the am-PtOx during CO oxidation was superior to that of a conventional Pt black catalyst. This study demonstrated a novel method of preparing am-PtOx with applications as a catalyst. [doi:10.2320/matertrans.MF201410]

(Received January 6, 2015; Accepted January 28, 2015; Published March 6, 2015)

1. Introduction

Recently, a leaching process using the selective dissolution of the less-noble metal from an alloy in bulk form has been used to fabricate nano- or mesoporous metals with high specific surface areas (~10 m²/g) as well as unique structural characteristics. This leaching technique can generate nanoporous metals with extraordinary structural characteristics. Interestingly, Zielasek et al.2) and Xu et al.3) reported that the nanoporous gold obtained by leaching silver from Au-Ag solid solutions exhibits an unexpectedly high catalytic activity for CO oxidation even under ambient conditions. Independent of the Au-Ag system, leaching from intermetallic compounds (IMCs) such as Cu₃Au and Al₂Au was found to produce homogeneous mesoporous Au. IMCs, in which atoms are located at defined positions in an orderly manner, generally have specific stoichiometric compositions. This characteristic ensures homogeneity on the atomic level, as opposed to solid solutions wherein atoms are located randomly at lattice points. In spite of its relatively low specific surface area (~1 m²/g) mesoporous Au has exhibited high activity for CO oxidation, comparable to that of the standard catalyst Au/TiO₂. This result implies that the combination of nano-sized Au and oxide supports in standard catalysts may not be the only means of achieving high activity, and suggests that mesoporous Au has the potential to act on its own as an unsupported catalyst.

In order to fabricate novel catalytic materials with unique structural characteristics, we have investigated the leaching of a diverse range of binary alloys, including Au-TM and Pt-TM (TM = Fe, Co, Ni, Cu and others). During the course of this study, an amorphous Pt oxide (am-PtOx) phase was obtained by selective leaching of copper from a Cu₃Pt alloy using concentrated nitric acid at 323 K. We report herein the characterization of this am-PtOx using synchrotron X-ray powder diffraction (SXRD), hard X-ray photoelectron spectroscopy (HXPS), thermal analysis (thermogravimetry-differential thermal analysis: TG-DTA, temperature-programmed decomposition: TPD) and the Brunauer-Emmet-Teller (BET) method. The catalytic properties of the am-PtOx for CO oxidation were also investigated and are reported.

2. Experimental

Cu₃Pt alloy was prepared from pure Pt and Cu (both 99.9% pure) in an electric arc furnace under an Ar atmosphere. A ribbon-shaped sample of the resulting Cu₃Pt (thickness: ca. 0.02 mm, width: ca. 2.0 mm) was fabricated by the single-roller melt spinning method in an Ar atmosphere. This Cu₃Pt ribbon was subsequently leached in concentrated HNO₃ for 12 h at 323 K, following which the solution was filtered and the remaining solid material was thoroughly washed with distilled water until the filtrate was no longer acidic. The composition (in at%) of the sample after leaching was determined by inductively couple plasma (ICP) analysis. For comparison, Pt black (Wako 168-11121) was also studied. The sample designations are given in Table 1. The specific surface areas of samples were determined by BET analysis (BELSORP-mini). SXRD and HXPS analyses were carried out using high brilliance synchrotron radiation generated by NIMS undulator beam line BL15XU (λ = 0.065297 nm for SXRD, hv = 5.951 keV for HXPS) at the SPring-8 facility in Japan.6,7) The morphologies and microstructures of samples were observed using a field-emission scanning electron microscope (SEM, HITACHI S-5500) with an acceleration voltage of 10 kV. The TG-DTA and TPD

Table 1 Results of composition of Pt (at%) and Cu (at%) in Cu₃Pt sample before and after leaching and surface areas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ICP analysis*</th>
<th>Dissolved*</th>
<th>S_BET (m² g⁻¹ cat⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃Pt-BL</td>
<td>25.0</td>
<td>75.0</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cu₃Pt-AL</td>
<td>85.4</td>
<td>14.6</td>
<td>61.7 (14.3)*²</td>
</tr>
<tr>
<td>Pt black</td>
<td>100</td>
<td>—</td>
<td>29.0 (2.2)*⁵</td>
</tr>
</tbody>
</table>

*BL and AL mean before leaching and after leaching, respectively.
*²Provided by Wako Chemical Co.
*Elemental composition of whole sample analyzed by ICP.
*⁵Amount of extracted Cu (%) from original Cu₃Pt.
*BET surface area (S_BET) after CO oxidation.
measurements were carried out using 50 mg samples heated from room temperature to 1000 K at a rate of 10 K/min under an inert gas flow (Ar or He). The TPD analysis was performed by quadrupole mass spectrometry (QMS, m/e = 32) under the He flow. Reaction trials were performed in a standard fixed-bed flow reactor by passing a gaseous mixture of CO (1 vol%) and O₂ (0.5 vol%) in He flow at a space velocity (SV) of 20,000 h⁻¹ (total pressure: 1 atm). All catalytic experiments were conducted on fresh specimens without any pretreatment. The reaction products were monitored by an on-line gas chromatograph (Shimadzu GC-8A) equipped with a Molecular Sieve 5A (for O₂ and CO) and a Porapak Q column (for CO₂). The catalytic activity during the oxidation of CO with O₂ was evaluated by calculating the percentage conversion of CO to CO₂. The data used for the catalytic activity measurements were recorded at the point at which the reaction had reached a steady state after 30 min.

3. Results and Discussion

Figure 1 shows the SXRD patterns of the Cu₃Pt alloy before and after leaching in concentrated HNO₃ at 323 K (hereafter denoted as Cu₃Pt-BL and Cu₃Pt-AL, respectively). All the diffraction peaks present in the BL sample can be attributed to an fcc Cu₃Pt alloy before leaching (Cu₃Pt-BL), whereas these peaks disappear completely after leaching. Surprisingly, the post leaching sample does not generate any diffraction peaks implying that amorphous phases were formed by the leaching treatment. ICP analysis of the leaching solution determined that only copper ions were present, indicating the selective dissolution of copper from the original Cu₃Pt alloy. However, some residual copper was also detected in the leached sample by ICP analysis (Table 1), which showed a Cu content in the Cu₃Pt-AL specimen of 14.6 at%.

Figures 2(A) and 2(B) present SEM micrographs of Cu₃Pt-AL obtained with different magnifications, showing a structure consisting of fine nanoparticles. The BET surface area of
the Cu3Pt-AL was determined to be 61.7 m²/g, a value more than three orders larger than that of the original Cu3Pt-BL.

Figure 3 shows the Pt 4f, Cu 2p3/2 and O 1s HXPS spectra obtained from the Cu3Pt-BL and Cu3Pt-AL samples. The Pt 4f photoemission spectrum from Cu3Pt-BL shows sharp peaks at almost the same binding energies (BEs, 4f7/2: 74.4 eV, 4f5/2: 71.1 eV) as that from the Pt foil (4f7/2: 74.5 eV, 4f5/2: 71.2 eV), whereas the Cu3Pt-AL reveals a broad spectrum which consists of multiple components located at the same or higher BEs. In the case of the Cu 2p3/2 spectra, although the BE of Cu 2p3/2 of Cu3Pt-BL (2p3/2: 932.5 eV) was almost the same as that of the Cu foil (2p3/2: 932.6 eV), only a very weak Cu 2p3/2 peak was observed for the Cu3Pt-AL (2p3/2: 932.2 eV). The O 1s spectrum of the Cu3Pt-AL exhibits a broad peak at around 530.4 eV, while only a trace level peak is seen in the vicinity of 531.4 eV for the Cu3Pt-BL. Compared to the BEs obtained for the Cu3Pt-BL, the Pt 4f peaks of the Cu3Pt-AL are shifted to higher BEs, whereas the O 1s peak of the Cu3Pt-AL is shifted to a lower BE. From these results, the Pt species in the Cu3Pt-AL believed to have been in the PtO state, and the BE values are in good agreement with literature values (Pt 4f7/2: 77.4–74.5 eV, Pt 4f5/2: 74.1–71.2 eV; O 1s: 530.5–530.2 eV).9–11

The thermal characteristics of the Cu3Pt-AL were subsequently investigated and Figs. 4(A) and 4(B) show the TG-DTA and the TPD profiles obtained for this material. The TG-DTA (Fig. 4(A)) indicates a change in mass with an onset at around 720 K, accompanied by an endothermic peak of the Cu3Pt-AL, the catalytic activity exhibited on cooling was significantly higher than the activity seen while increasing the temperature. As shown in Fig. 5(A), the hysteresis of the catalytic activity of the Cu3Pt-AL sample contrasts with that observed for the Pt black catalyst. In general, the application of rising temperatures leads to sintering and a significant loss of catalytic activity in the case of unsupported metal catalysts, and the Cu3Pt-AL applied in this study generated, clear diffraction peaks corresponding to fcc Pt following its use in the CO oxidation reaction (Fig. 1: Cu3Pt-AL+AR). Sharpening of the Pt diffraction peaks was also observed for both the Cu3Pt-AL and the Pt black (Fig. 1 and Fig. 5(B)) following the oxidation reaction, since the Pt particles readily undergo crystal grain growth as the temperatures applied during the reaction are increased up to 500 K. Crystallite sizes of the Cu3Pt-AL (AR) and the Pt black (AR), which are estimated from the XRD line broadening analysis using the Scherrer equation for the Pt(111) reflection, are estimated
11.9 and 20.0 (BR: 9.2) [nm], respectively. Interestingly, the decrease in the BET specific surface area of the Cu₃Pt-AL was much less than that of the Pt black catalyst (Table 1). Values of the areal rate [µmolCO·min⁻¹·m⁻²·cat] at 373 K (2nd run) of the Cu₃Pt-AL and the Pt black are 21.9 and 0.06, respectively. Assuming all of surface Pt atoms play as active sites and 1.25×10¹² Pt atoms per square meter (20.8 [µmolPt·m⁻²]), apparent TOF values of the Cu₃Pt-AL and the Pt black can be estimated at 1.23×10⁻³ and 2.19×10⁻⁵ [s⁻¹], respectively. Interestingly, the TOF value of the Cu₃Pt-AL is much larger than that of the Pt black. Therefore, it is suggested that am-PtOₓ is very effective as a precursor of the unsupported Pt catalyst. Recently, Murao et al. investigated the structure of Cu₃Pt-AL using high-energy XRD coupled with anomalous X-ray scattering (AXS) and reported that the Cu₃Pt-AL was composed of a fine nanocomposite Pt(Cu)–Pt(Cu)Oₓ. When studying the preferential oxidation (PROX) of CO in hydrogen, Komatsu et al. found that the Cu atoms in a PtCu IMC plays an important role in supplying the oxygen necessary for the reaction to CO molecules adsorbed on neighboring Pt atoms. Therefore, we cannot exclude the possibility that the presence of residual copper in the Cu₃Pt-AL may contribute to the catalytic properties of this material as well as to its thermal stability.

On the other hand, Adams’s catalyst is a well-known platinum dioxides (PtO₂·H₂O) material employed during organic syntheses involving hydrogenation and hydrogenolysis. The oxide itself is not originally an active catalyst, but becomes active after exposure to hydrogen, whereupon it converts to platinum black, which is responsible for the catalytic activity. Adams’s catalyst is typically prepared in molten sodium nitrate by the reaction of chloroplatinic acid H₂PtCl₆ or ammonium chloroplatinate (NH₄)₂PtCl₆ with sodium nitrate at high temperatures (583–973 K). However, some sodium and chloride are strongly retained in the final product, leading to deactivation and poisoning of the Pt catalyst. In order to mitigate this problem, therefore, it is necessary to devise improved method of preparing the catalyst, such as using Cl-free reagents as precursors. In the present study, it was determined that the Cu₃Pt alloy readily reacted with HNO₃ to generate PtOₓ even at 323 K. Although a detailed mechanism by which amorphous PtOₓ is formed during the leaching process is not presently known, it is nonetheless evident that amorphous PtOₓ species were effectively formed under mild conditions when applying this technique. Consequently, the method described herein shows promise as a novel means of preparing such materials.

4. Conclusions

This study demonstrated that amorphous Pt oxides (am-PtOₓ) are formed by the selective leaching of copper from a Cu₃Pt alloy in concentrated HNO₃ at 323 K for 12 h. The resulting amorphous Pt oxides were characterized using SXRD, HXPS and thermal analysis. The catalytic performance of am-PtOₓ for the CO oxidation was found to be superior to that of a Pt black catalyst. Interestingly, the catalytic behavior of the am-PtOₓ exhibited a hysteresis different from that observed for the Pt black catalyst. This process represents a facile, non-thermal method for the preparation of amorphous Pt oxides that show promise as a novel, sodium and chlorine-free Adams’s catalyst.

Acknowledgements

The authors are grateful to Dr. Reiko Murao and Prof. Dr. Kazunasa Sugiyama (IMR, Tohoku University) for helpful discussions. The authors would like to thank Dr. S. Ueda and Mr. Ishimaru for improving HXPS in BL15XU at SPring-8. Synchrotron analyses were performed with the approval of NIMS synchrotron X-ray station at SPring-8 facility, Japan (proposal nos. 2012A4500, 2012B4502, 2013A4900,
2013A4902, 2013B4901 and 2013B4903). This work was supported in part by Grant-in-Aid for Scientific Research (A) 23247117, (B) 24360329 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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