Formation of Amorphous Pt Oxides: Characterization and Their Catalysis

Satoshi Kameoka^{1,*}, Masahiko Shimoda², Yoshitaka Matsushita^{2,3}, Yoshiyuki Yamashita^{2,3},
 Yoshio Katsuya³, Masahiko Tanaka³ and An-Pang Tsai^{1,2}

¹*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan*

²*National Institute of Materials Science (NIMS), Tsukuba 305-0047, Japan*

³*Synchrotron X-ray Station at SPring-8, NIMS, Sayo, Hyogo 679-5148, Japan*

Amorphous Pt oxides (am-PtO_x) were formed by the leaching of copper from a Cu₃Pt alloy in concentrated HNO₃ at 323 K for 12 h. The resulting am-PtO_x 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-PtO_x during CO oxidation was superior to that of a conventional Pt black catalyst. This study demonstrated a novel method of preparing am-PtO_x with applications as a catalyst. [doi:10.2320/matertrans.MF201410]

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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.¹⁾ 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.^{4,5)} 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/TiO₂.⁴⁾ 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-PtO_x) 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-PtO_x using synchrotron X-ray powder diffraction (SXRD), hard X-ray photoelectron spectroscopy (HXPES), thermal analysis (thermogravimetry-differential thermal analysis: TG-DTA, temperature-programmed decomposition: TPD) and the Brunauer-Emmett-Teller (BET)

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

Sample	ICP analysis ^{*3}		Dissolved ^{*4} (%)	S _{BET} (m ² g ⁻¹ -cat)
	Pt (at%)	Cu (at%)		
Cu ₃ Pt-BL ^{*1}	25.0	75.0	—	<0.1
Cu ₃ Pt-AL ^{*1}	85.4	14.6	94.3	61.7 (14.3) ^{*5}
Pt black ^{*2}	100	—	—	29.0 (2.2) ^{*5}

^{*1}BL and AL mean before leaching and after leaching, respectively.

^{*2}Provided by Wako Chemical Co.

^{*3}Elemental composition of whole sample analyzed by ICP.

^{*4}Amount of extracted Cu (%) from original Cu₃Pt.

^{*5}BET surface area (S_{BET}) after CO oxidation.

method. The catalytic properties of the am-PtO_x 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 HXPES analyses were carried out using high brilliance synchrotron radiation generated by NIMS undulator beam line BL15XU (λ = 0.065297 nm for SXRD, hν = 5.951 keV for HXPES) 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

*Corresponding author, E-mail: kameoka@tagen.tohoku.ac.jp

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. Figure 2(C) presents the isotherm curve obtained during N₂ adsorption-desorption on Cu₃Pt-AL at 77 K. This conforms to a type I plot, typically generated by microporous solids having relatively small external surfaces.⁸⁾ The BET surface area of

Fig. 1 SXRD patterns of Cu₃Pt samples before leaching (BL), after leaching (AL) and after CO oxidation reaction (AL+AR), as well as of Pt powder, obtained using high brilliance synchrotron radiation (SPring-8 BL15XU, $\lambda = 0.065297$ nm).

Fig. 2 SEM images of a Cu₃Pt-AL sample under (A) low and (B) high magnification and (C) an isotherm obtained from the Cu₃Pt-AL sample.

Fig. 3 Pt 4f, Cu 2p_{3/2} and O 1s HXPS spectra obtained from Cu₃Pt-BL and Cu₃Pt-AL samples. For comparison, the Pt 4f_{5/2} and Pt 4f_{7/2} spectra of Pt foil and the Cu 2p_{3/2} spectrum of Cu foil are also shown.

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 2p_{3/2} 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, 4f_{5/2}: 74.4 eV, 4f_{7/2}: 71.1 eV) as that from the Pt foil (4f_{5/2}: 74.5 eV, 4f_{7/2}: 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 2p_{3/2} spectra, although the BE of Cu 2p_{3/2} of Cu₃Pt-BL (2p_{3/2}: 932.5 eV) was almost the same as that of the Cu foil (2p_{3/2}: 932.6 eV), only a very weak Cu 2p_{3/2} peak was observed for the Cu₃Pt-AL (2p_{3/2}: 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_x state, and the BE values are in good agreement with literature values (Pt 4f_{5/2}: 77.4–74.5 eV, Pt 4f_{7/2}: 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 process. Additionally, the TPD (m/e = 32) shows that O₂ was desorbed under a He flow (Fig. 4(B)), in good agreement with the TG-DTA results. The proportional mass loss of the Cu₃Pt-AL (before and after the TG-DTA process) was *ca.* 0.854, a value that indicates the decomposition of PtO₂ to Pt (PtO₂ → Pt + O₂ (g)) since the Pt/PtO₂ mass ratio is 0.859.

The catalytic properties of the Cu₃Pt-AL were assessed using the oxidation of CO as a model reaction, and Fig. 5(A) summarizes the catalytic performance of both the Cu₃Pt-AL

Fig. 4 (A) TG-DTA and (B) TPD profiles of a Cu₃Pt-AL sample.

and the Pt black during CO oxidation. In the case 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

Fig. 5 (A) Catalytic activities of $\text{Cu}_3\text{Pt-AL}$ and Pt black for CO conversion as a function of reaction temperatures and (B) SXRD patterns of Pt black before (BR) and after (AR) the CO oxidation reaction (SPring-8 BL15XU, $\lambda = 0.065297$ nm).

11.9 and 20.0 (BR: 9.2) [nm], respectively. Interestingly, the decrease in the BET specific surface area of the $\text{Cu}_3\text{Pt-AL}$ was much less than that of the Pt black catalyst (Table 1). Values of the areal rate [$\mu\text{mol}_{\text{CO}} \cdot \text{min}^{-1} \cdot \text{m}^{-2} \cdot \text{cat}^{-1}$] at 373 K (2nd run) of the $\text{Cu}_3\text{Pt-AL}$ and the Pt black are 21.9 and 0.06, respectively. Assuming all of surface Pt atoms play as active sites and 1.25×10^{19} Pt atoms per square meter ($20.8 [\mu\text{mol}_{\text{Pt}} \cdot \text{m}^{-2}]$), apparent TOF values of the $\text{Cu}_3\text{Pt-AL}$ and the Pt black can be estimated at 1.23×10^{-3} and $2.19 \times 10^{-5} [\text{s}^{-1}]$, respectively. Interestingly, the TOF value of the $\text{Cu}_3\text{Pt-AL}$ is much larger than that of the Pt black. Therefore, it is suggested that am- PtO_x is very effective as a precursor of the unsupported Pt catalyst. Recently, Murao *et al.* investigated the structure of $\text{Cu}_3\text{Pt-AL}$ using high-energy XRD coupled with anomalous X-ray scattering (AXS) and reported that the $\text{Cu}_3\text{Pt-AL}$ was composed of a fine nanocomposite $\text{Pt}(\text{Cu})\text{-Pt}(\text{Cu})\text{O}_x$.¹²⁾ 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.¹³⁾ Therefore, we cannot exclude the possibility that the presence of residual copper in the $\text{Cu}_3\text{Pt-AL}$ 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 ($\text{PtO}_2 \cdot \text{H}_2\text{O}$) material employed during organic syntheses involving hydrogenation and hydrogenolysis.¹⁴⁾ 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 H_2PtCl_6 or ammonium chloroplatinate $(\text{NH}_4)_2\text{PtCl}_6$ with sodium nitrate at high temperatures (583–973 K).^{14–16)} However, some sodium and chlorine 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 Cu_3Pt alloy readily reacted with HNO_3 to generate PtO_x even at 323 K. Although a detailed mechanism by which amorphous PtO_x is formed during the leaching process is not presently known, it is nonetheless evident that amorphous PtO_x 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- PtO_x) are formed by the selective leaching of copper from a Cu_3Pt alloy in concentrated HNO_3 at 323 K for 12 h. The resulting amorphous Pt oxides were characterized using SXRD, HXPS and thermal analysis. The catalytic performance of am- PtO_x for the CO oxidation was found to be superior to that of a Pt black catalyst. Interestingly, the catalytic behavior of the am- PtO_x 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.

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