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CO Oxidation Over a Fine Porous Gold Catalyst Fabricated by Selective Leaching from an Ordered $AuCu_3$ Intermetallic Compound

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Abstract A fine porous gold catalyst has been fabricated by selective leaching of Cu from an ordered $AuCu_3$ intermetallic compound with 50%HNO_3 aqueous solution at 50 °C. This catalyst exhibited comparable areal rate (mol min^{-1} m^{-2}-cat) with the Au/TiO_2 catalyst for CO oxidation. The present study demonstrates that high catalytic activity of gold is originated neither from the presence of fine dispersed Au particles nor from Au-support perimeter interface.

Keywords CO oxidation · Porous gold · Leaching · Ordered $AuCu_3$ · Intermetallic compound

1 Introduction

Gold has been generally considered catalytically inactive. However, Haruta et al. [1] reported that nanosized gold particles supported on oxides show high catalytic activity for CO oxidation. In the last decade, supported gold nanoparticles have been extensively investigated where most of the studies have focused on the activity for CO oxidation at low temperatures [2]. Although the catalytic performances of gold nanoparticles have been correlated with electronic, structural and support effects, e.g., quantum size effect, oxidation state, defects and perimeter interface etc., an unified consensus has not yet been reached. In order to get insight in the origin of the exceptional catalytic behavior, study on unsupported gold catalysts is highly required. Iizuka et al. have studied kinetics of the CO oxidation over an unsupported fine Au powder (mean particle size, ~100 nm) [3, 4]. Matarrese and Rossi et al. reported high activities for colloidal gold for glucose oxidation [5] and Davis et al. reported high activities for particulate gold under high alkaline conditions for both CO and glycerol oxidation [6]. However, few detailed works with respect to catalytic behavior of unsupported gold catalysts have been performed.

Recently, Erlebacher and co-workers [7] presented an analytical atomistic model to understand the underlying physics of porosity evolution during dealloying and showed that the nanoporous gold with a spongelike morphology formed through the selective leaching of silver from Au–Ag alloy. Zielasek et al. [8] and Xu et al. [9] reported that the nanoporous gold obtained by dealloying of silver from Au–Ag solid solutions exhibits an unexpectedly high catalytic activity for CO oxidation even at ambient condition. Independent to these studies, we have been developing new processes for synthesizing high catalytic performance catalysts where intermetallic compounds were used either as precursors for leaching [10–12] or as the replacement for a definite catalytic element [13]. An intermetallic compound, in which atoms orderly sit at definite positions, generally has a sharp stoichiometric composition. These characteristics ensure homogeneity of intermetallic compounds at atomic level, being different from solid solution in which atoms randomly sit at lattice points. A stoichiometric compound only has a definite structure but a solid solution may have indefinite structures depending on fabrication conditions. Therefore, an intermetallic compound is a promising precursor for obtaining a homogeneous porous structure by selective leaching. In this study, we used two precursors with same composition but different structure, namely an

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ordered AuCu$_3$ which is an intermetallic compound and a disordered AuCu$_3$ which is a solid solution. This enables us to make a comparison in microstructure generated by leaching and its corresponding catalytic properties for two precursors leached under the same condition without taking composition into account. The AuCu$_3$ exhibits complete solid solubility at high temperatures (>390 °C), but show a well-known prototype of ordered structure based on the fcc structure below 390 °C [14], which has been studied for a long time as a typical system of order–disorder phase transformations [15]. During the course of this study, a fine porous gold catalyst obtained by selective leaching of copper from an ordered AuCu$_3$ intermetallic compound, which performs effectively for the CO oxidation, was found to show comparable areal rate (mol min^{-1} m^{-2}-cat) with the Au/TiO$_2$ catalyst. We show here that the ordered AuCu$_3$ intermetallic compound can use as a precursor for fabricating a fine porous gold catalyst with high catalytic activity.

2 Experimental

AuCu$_3$ was prepared from pure elements with purities of 99.9% Au and Cu in an electric arc furnace in Ar atmosphere. The ribbon samples of AuCu$_3$ (thickness: ca. 0.02 mm, wideness: ca. 2.0 mm) were fabricated by single-roller melt spinning method in an Ar atmosphere. The samples were heat-treated at 600 °C for 24 h and then quenched in ice water, in order to obtain a disordered AuCu$_3$. The ordered AuCu$_3$ was obtained by annealing the samples at 350 °C for 100 h and then slowly cooled in vacuum sealed in quartz ampoules. The sample ribbons were leached in a 50%HNO$_3$ aqueous solution, kept in the aqueous solution for 12 h at 50 °C, and then filtered out and thoroughly washed with distilled water until no acid was detected in the filtrate. The composition (at%: atomic percent) of the sample after leaching treatment was determined by ICP analysis. For comparison, porous copper (CDT-60) and Au/TiO$_2$ (1.5 wt% Au) catalysts were also studied, which were supplied by Kawaken Fine Chemical Co. and World Gold Council [16], respectively. Surface area of particle was determined by BET analysis. The crystal structure of each sample was confirmed by X-ray diffraction (Mac science M03XHF22) using Cu Kα (λ = 1.543 A) radiation. The morphology of the sample was observed in a field-emission SEM (HITACHI S-5500) equipped with an energy dispersion X-ray analyzer (EDAX). The reaction was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of CO (4 vol%) and O$_2$ (2 vol%) in He flow at a total flow rate of 50 cm^3 min^{-1} (total pressure: 1 atm; space velocity (SV): 120,000 h^{-1}). The sample was supported on quartz wool in a straight quartz tube with a 4 mm inside diameter in which 50 mg or 10 mg (for the Au/TiO$_2$) catalyst was used. All the catalytic experiments have been performed in the temperature range at 60–350 °C on the fresh materials without any pretreatment. The products were monitored by an on-line gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A (O$_2$, CO) and Porapak Q (CO$_2$). The catalytic activity for the oxidation of CO with O$_2$ was evaluated by the percentage conversion of CO to CO$_2$. The data in the catalytic activity measurements were recorded when the reaction reached steady state after 30 min.

3 Results and Discussion

Figure 1 shows the XRD patterns of an ordered and a disordered AuCu$_3$ before and after leaching in the 50%HNO$_3$ aqueous solutions. The peaks responsible for the fundamental and/or the superlattice reflections of AuCu$_3$ phase were observed before leaching (Fig. 1a, c). As shown in Fig. 1b and d, the original diffraction peaks of ordered AuCu$_3$ disappear completely after leaching, while the original diffraction peaks of disordered AuCu$_3$ are still visible even after leaching. Clearly, leaching on intermetallic compound reveals more homogeneous structure than that on solid solution. Only broad diffraction peaks from Au came up after leaching and no diffraction peaks related to copper or copper oxides were observed for the ordered

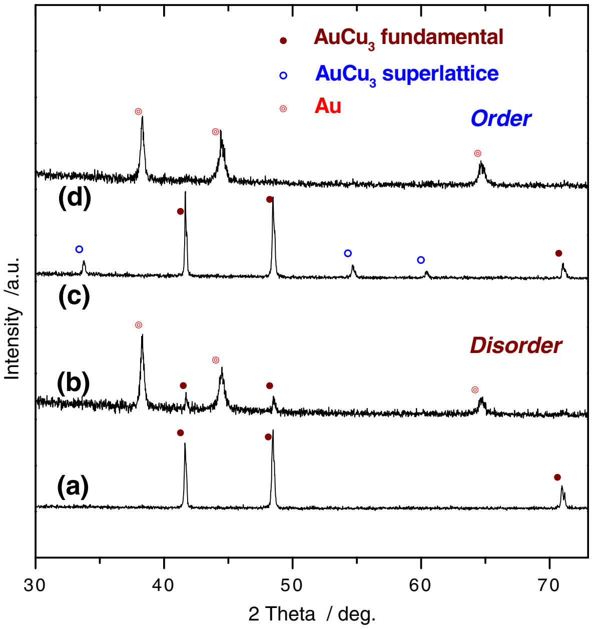

Fig. 1 Powder XRD patterns for AuCu$_3$ samples before and after leaching with 50%HNO$_3$ aq. at 50 °C for 12 h; the disordered AuCu$_3$ before (**a**) and after (**b**) leaching, the ordered AuCu$_3$ before (**c**) and after (**d**) leaching

Table 1 Results of composition of Au (at%) and Cu (at%) in the leached samples and extraction of Cu (%) from original $AuCu_3$ samples

Sample	ICP analysis[a]		Extracted Cu from $AuCu_3$[b] (%)
	Au (at%)	Cu (at%)	
Ordered $AuCu_3$	87.9	12.1	95.4
Disordered $AuCu_3$	72.9	27.1	87.6

[a] Elemental composition of whole sample after leaching treatment analyzed by ICP

[b] Amount of extracted Cu (%) from original $AuCu_3$ sample during leaching treatment calculated from ICP analysis

$AuCu_3$. According to the ICP analysis of the leaching solution, only copper ions were detected, indicating that selective dissolution of copper from $AuCu_3$ takes place during the leaching in the HNO_3 aq. solution (Eq. 1). However, residual copper in the leached samples was detected by ICP analysis (Table 1). The Cu content in the leached-ordered and -disordered $AuCu_3$ catalysts was 12.1 and 27.1 at%, respectively. The amount of residual copper of the disordered $AuCu_3$ was larger than that of the ordered $AuCu_3$ (Table 1).

$$AuCu_3 + 8HNO_3 \rightarrow Au^* + 3Cu(NO_3)_2 + 4H_2O + 2NO \uparrow \quad (1)$$

Figure 2 shows the SEM micrographs of the ordered and the disordered $AuCu_3$ after the leaching treatment. The SEM images show a structure consisting of a uniform three-dimensional network of fine ligaments. As shown in Fig. 2, porous morphology generated from the ordered $AuCu_3$ is more homogeneous than that from the disordered $AuCu_3$. Selective dissolution of copper from the disordered $AuCu_3$ does not proceed efficiently probably because copper and gold atoms sit randomly at lattice points [15]. This corresponds to the residual fundamental peaks observed in the XRD (Fig. 1b). After the leaching, both the ordered and the disordered $AuCu_3$ are replaced by a gold fcc phase as verified by the XRD (Fig. 1b, d). This indicates that the formation of fine porous gold (i.e., Au* in Eq. 1) was achieved by selective leaching of copper from the $AuCu_3$ and the subsequent rearrangement of gold atoms.

Figure 3 shows the CO conversion as a function of reaction temperature for the CO oxidation over different catalysts. Leaching on the $AuCu_3$ samples promotes drastic increase in catalytic activities. The porous gold catalyst generated from the ordered $AuCu_3$ was more active than that from the disordered $AuCu_3$ at low temperature range (below 150 °C). The $AuCu_3$ samples are activated by leaching due to the increase of the surface area and the formation of activated surfaces. Surprisingly, the catalytic activities for CO oxidation with respect to areal rate (mol min^{-1} m^{-2}-cat) of the porous Au catalysts are comparable with that of Au/TiO_2 reference catalyst, as shown in Table 2. Assuming that the gold particles of the Au/TiO_2 reference catalyst are homogeneously dispersed with uniform hemispherical shape and with a mean diameter of 3.5 nm [16], the surface area of the gold particles on the TiO_2 was estimated to be 1.33 m^2_{Au}/g-cat. Values of the areal rate were estimated by assuming that all of surface gold atoms play as active sites. The areal rates of CO oxidation over the porous Au catalysts are more than three orders of magnitude higher than that over porous copper. Clearly the fine porous structure forms by the selective leaching of copper from $AuCu_3$ is responsible for high catalytic activity.

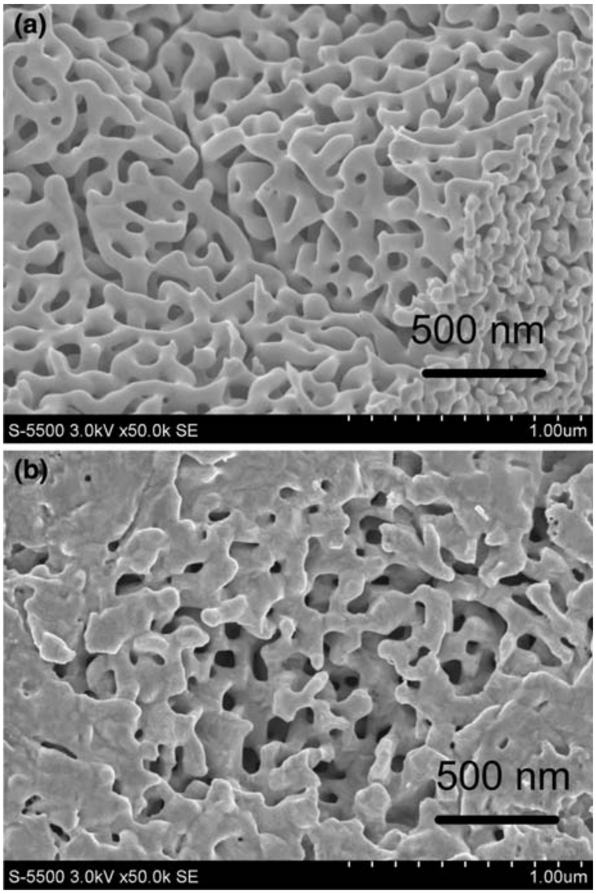

Fig. 2 SEM images of porous gold samples; (**a**) the ordered $AuCu_3$ after leaching with 50%HNO_3 aq. at 50 °C for 12 h, (**b**) the disordered $AuCu_3$ after leaching with 50%HNO_3 aq. at 50 °C for 12 h

Figure 4 shows Arrhenius plots for the CO oxidation over different catalysts. Apparent activation energies E_a estimated from Arrhenius plots are given in Table 2. The values of activation energies over the porous Au catalysts fabricated from the ordered and the disordered $AuCu_3$ are around 5–6 kJ/mol. These values are the same level as that of the Au/TiO_2 catalyst, while the porous Cu catalyst

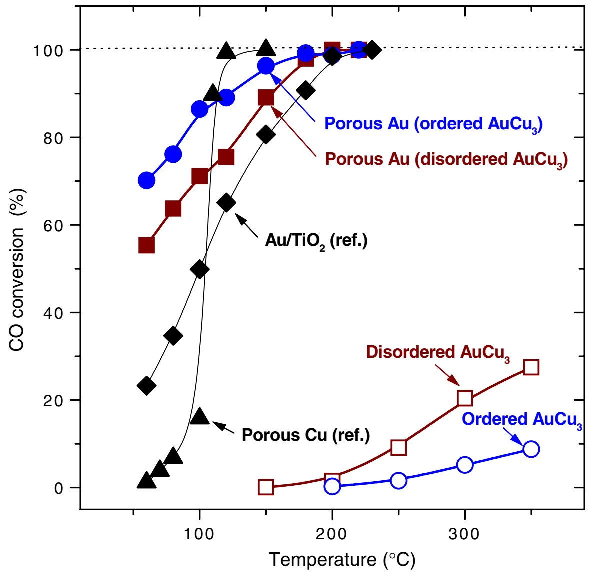

Fig. 3 CO conversions of CO oxidation as a function of temperature over different catalysts. Reaction conditions: CO (4 vol%) + O_2 (2 vol%) in He balance; flow rate: 50 cm^3 min^{-1}; space velocity (SV): 120,000 h^{-1}

shows much higher activation energy. The reaction mechanism of CO oxidation over the gold catalyst is much different from that over the copper catalyst. This indicates that the porous Au catalysts are inherently gold catalyst for the CO oxidation and contribution of residual copper species on the activity is negligible. This is also evidenced in Fig. 3 where the porous Au catalyst fabricated from disordered $AuCu_3$ contains higher concentration of copper but in contrast shows lower activity than that from ordered $AuCu_3$.

Several groups have reported that the role of the perimeter interfaces of Au particles with oxide support as the sites for reactions is important [17, 18]. However, the present study reveals that high catalytic activity of gold is originated neither from the presence of fine dispersed Au

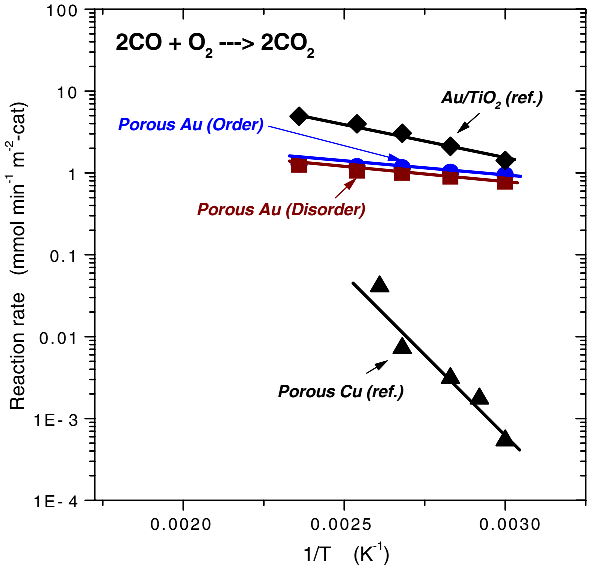

Fig. 4 Arrhenius plots for the reaction rate of CO oxidation over porous Au catalysts fabricated from ordered and disordered $AuCu_3$, porous Cu and Au/TiO_2 catalysts using the data in Fig. 3

particles nor from Au-support perimeter interface. Recently, remarkably high catalytic activity for CO oxidation over unsupported gold catalysts has been reported where the high catalytic activities are associated with the formation of the curved shape of the ligaments of fine porous gold which gives a high density of low-coordinate surface sites such as step and kink atoms [8]. Mavrikakis et al. [19] reported that unusually large catalytic activity of highly dispersed gold particles may in part be due to high step densities on the small particles and/or strain effects due to the mismatch at the Au-support interface. Janssens et al. proposed the gold-support interaction may for instance determine the morphology of the gold particles and thus influence the number of low-coordinated Au atoms or the strain [20]. Therefore, these results support the possibility that the creation of defect sites such as edge,

Table 2 Surface areas, rate values and apparent activation energies for CO oxidation over different catalysts

Sample	Surface area (m^2/g)	Rate[b] (10^{-4} mol_{CO} min^{-1} m^{-2}-cat)	Activation energy (kJ mol^{-1})
Porous Au (Ordered $AuCu_3$)	1.3[a]	9.4	5
Porous Au (Disordered $AuCu_3$)	1.2[a]	7.8	6
1.5wt% Au/TiO_2	45.8 (1.33)[c]	4.1×10^{-1} (14.2)[c]	14
Porous copper[d]	38.8	5.4×10^{-3}	67

[a] BET surface area after leaching with 50%HNO_3 aq. for 12 h at 50 °C. Notes that BET surface areas of both ordered and disordered $AuCu_3$ before leaching are below the experimental accuracy of BET analysis (<0.05 m^2/g)

[b] Reaction at 60 °C

[c] Surface area of supported gold particles (m^2_{Au}/g-cat) was estimated assuming that all of the supported gold particles are uniformly hemispheric shape with the average particle size 3.5 nm [16] and density 19.3 g_{Au}/cm^3

[d] Commercial catalyst (CDT-60; Kawaken Fine Chemical Co.)

step or kink sites on the surface of Au crystallites is responsible for the exceptional catalytic activity for CO oxidation.

The present study reveals the potential of a method to produce such highly active gold catalysts via selective dissolution of copper from an intermetallic compound (ordered $AuCu_3$) with HNO_3 aq. In order to prepare the fine porous gold catalyst, this method can be applied to other gold-containing intermetallic compounds such as $AuAl_2$ [21]. The ease of production of a fine porous gold may make it attractive for possible applications such as catalysts for practical use and high surface area model catalysts for surface science. Further investigation with respect to the detailed adsorption properties of reactants (O_2 and CO) and characterization of active sites are in progress.

4 Conclusions

CO oxidation of the fine porous gold catalysts fabricated by selective leaching of copper from the ordered and the disordered $AuCu_3$ has been studied. The catalytic performance of the fine porous gold catalysts was found to show comparable areal rate (mol min^{-1} m^{-2}-cat) with the Au/TiO_2 catalyst. The role of the perimeter interfaces of Au particles with oxide support as the sites for reactions is believed to be important, but the present study demonstrates that high catalytic activity of gold is not necessarily correlated with the presence of fine dispersed Au particles and/or Au-support perimeter interface. In addition, we show here that the ordered $AuCu_3$ intermetallic compound is more promising as a precursor for fabricating a fine porous gold catalyst with high catalytic activity than the disordered $AuCu_3$ solid solution.

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