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Oxidation behavior and catalytic property of intermetallic compound AuCu

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Abstract

Catalytic activity of CO oxidation reaction in relation to oxidation for an ordered AuCu intermetallic compound is studied. Oxidation performed at temperatures above 400 °C on the AuCu intermetallic compound leads to the formation of a composite consisted of Au and CuO, accompanied by a large increase in the surface area and significant enhancement of the activity. The oxidation performed at 600 °C yields a unique composite structure where an Au layer is sandwiched by two porous CuO layers, revealing a maximum in the surface area and the activity. The porous CuO layer is found to be key factor dominating catalytic activity. We show in this study that the oxidation of the intermetallic compound AuCu is a novel and an effective way to prepare metal/oxide composite for catalyst.

Keywords: AuCu; Intermetallic compound; Selective oxidation; Metal/oxide composite; CO oxidation

1. Introduction

Gold has been long believed to be catalytically inactive. Recently, this belief has been broken by an observation that nanosized gold particles supported on oxides revealed high catalytic activity for the CO oxidation reported by Haruta et al. [1]. However, active gold catalysts cannot readily prepare by conventional methods such as an impregnation method, being a major drawback for practical applications [1,2]. To overcome this problem, several preparation methods such as a coprecipitation and a deposition–precipitation method for obtaining ultrafine gold particles have been proposed [2]. Gold-containing alloys used as precursors for preparing fine gold catalysts have been reported [3–6]. Although the gold-containing alloys themselves have too small surface areas to use as catalysts, effective composite gold catalysts with considerable surface areas can be obtained by the oxidative decomposition. In order to prepare fine gold catalysts, direct oxidation of bulk alloys for the limited systems such as Zr–Au [3–5], Zr–Au–Ag and Zr–Au–Fe [6] alloys have been studied so far.

The stoichiometric AuCu alloy has been known for a long time as a typical system of order–disorder phase transformations [7]. The Au–Cu alloys have complete solid solubility at high temperatures, but show different phase formation at low temperatures [8]. The AuCu alloy is a disordered face centered cubic phase above 410 °C, which transforms into an ordered phases below this temperature. As shown in Fig. 1, AuCu I ordered structure ($L1_0$, face centered tetragonal structure) reveals alternating (0 0 2) stacking of Au and Cu layers along the *c*-axis is stable below 385 °C, which is regarded as an intermetallic compound. The AuCu II ordered structure (orthorhombic structure) exists in the temperature range between 385 and 410 °C, which is a superstructure with periodic anti-phase domain boundaries derived from the ordered AuCu I phase [7]. Structures of the Au–Cu alloys have been well studied in relation to order-disordering transition and change in physical properties during the transition [9–11]. Additionally, oxidation behaviors of Au–Cu alloys have been examined so far [12–14]. However, the Au–Cu alloys such as intermetallic compound AuCu have never been studied from viewpoint of catalyst materials.

In order to develop a novel preparation method of catalyst by direct oxidation of bulk alloys, we examined oxidation behavior and catalytic activity of CO oxidation on an intermetallic compound AuCu. We propose that the oxidation of the

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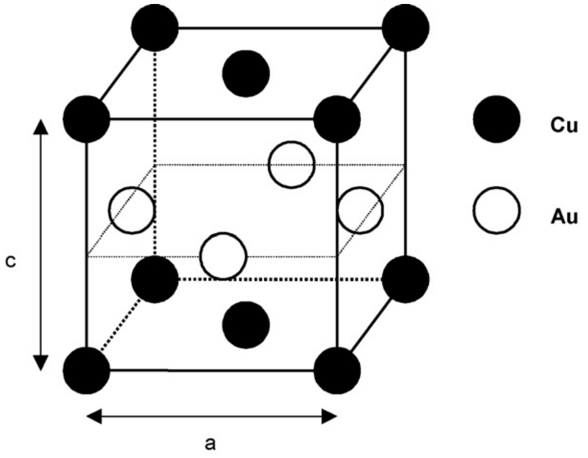

Fig. 1. Illustration of the tetragonal superlattice of AuCu alloy (AuCu I phase: $c/a = 0.92$).

intermetallic compound AuCu is a novel and an effective way to prepare metal/oxide composite for catalyst.

2. Experimental

Stoichiometric AuCu (Au/Cu = 1) alloy ribbon was prepared from the pre-mixed melt of the pure metals by using a single roller melt-spinning apparatus. The obtained AuCu ribbons were annealed at 350 °C (AuCu I phase: intermetallic compound AuCu) in Ar and then quenched into ice brine. Each oxidized sample was obtained by the oxidation for 5 h in air at 300–1000 °C. The phase identification of samples was performed by X-ray diffraction using Cu Kα ($\lambda = 1.543$ Å) radiation. The temperature-programmed oxidation (TPO) measurement was carried out using 50 mg of the sample from room temperature to 1000 °C at a heating rate of 4 °C/min in air. The TPO profile was obtained using thermal analyzer (Rigaku Thermoplus TG8120). The micrographs and elemental profiles of samples were measured by SEM and EDS, respectively. Surface areas of samples were determined by BET analysis. 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 ml/min over 50 mg of catalyst (total pressure: 1 atm; space velocity (SV): 120,000 h^{-1}). All the catalytic experiments have been performed 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

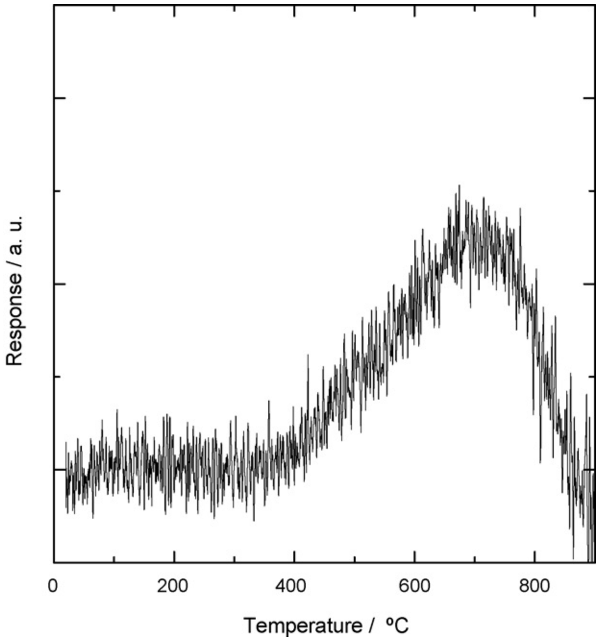

Fig. 2. TPO profile of the AuCu sample, TPO condition: heating rate 4 °C/min in air.

To examine the oxidation behavior of AuCu intermetallic compound, we performed TPO measurement. Fig. 2 shows the TPO profile of the AuCu up to 1000 °C in air. A broad peak above 400 °C corresponding to oxidation of the AuCu was observed. Fig. 3 shows the XRD patterns of AuCu intermetallic compound before and after oxidation in air at different temperatures. As shown in Fig. 3, all the diffraction peaks could be identified from the ordered AuCu (*i.e.*, AuCu I phase) before oxidation whereas those disappeared after oxidation at 450 °C in air. Subsequently, diffraction peaks from CuO and Au were clearly observed after oxidation above 600 °C. Thus, it is clear that broad oxidation peak in Fig. 2 is responsible for the oxidative decomposition of AuCu to CuO and Au (Eq. (1)). The change in XRD patterns in a series of oxidation is well

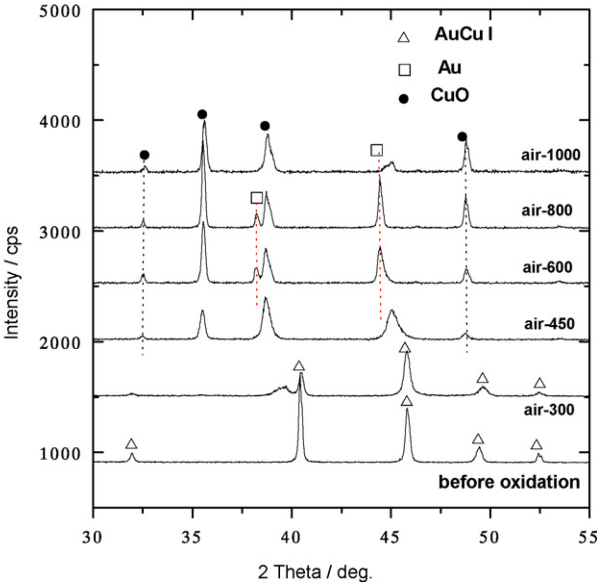

Fig. 3. Powder X-ray diffraction patterns for the AuCu samples after oxidation at various temperatures in air.

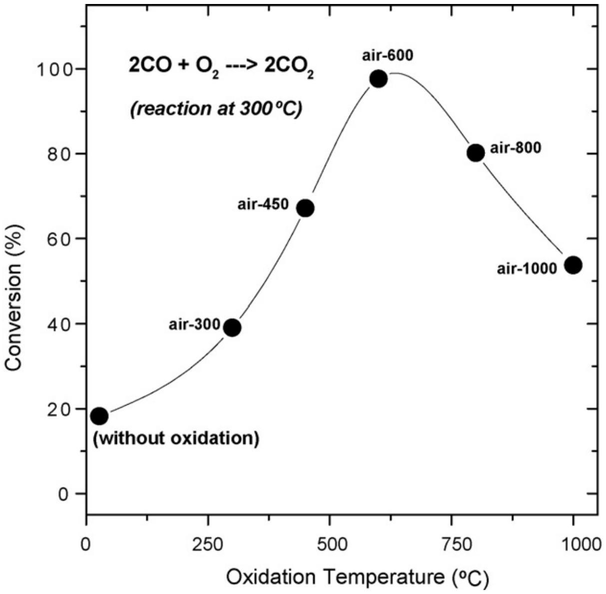

Fig. 4. CO conversion as a function of oxidation temperatures on the CO oxidation at 300 °C for samples given in Fig. 3.

interpreted with the TPO profile for the AuCu. These results indicate that the AuCu I ordered structure collapses at very early stage of the oxidation process due to selective oxidation of copper.

$$\mathrm{AuCu} \xrightarrow{\text{in air}} \mathrm{Au} + \mathrm{CuO} \quad (>400\,^{\circ}\mathrm{C}) \tag{1}$$

Fig. 4 shows the conversion of CO oxidation reaction at 300 °C over the AuCu intermetallic compound as a function of oxidation temperature. The CO conversion varied with oxidation temperature of the AuCu. Although the AuCu without oxidation exhibited only very low activity, the catalytic activity increased with increasing oxidation temperature. Maximum of the CO conversion was observed around the oxidation temperature of 600 °C. On the other hand, Fig. 5 shows the SEM images of surface of the AuCu ribbon before and after oxidation treatment at 600 °C in air. Surface of the alloy before oxidation reveals flat structure with several polycrystalline of the AuCu ordered phase grains (Fig. 5(A)), while the surface of the alloy after oxidation at 600 °C in air consists of porous structure (Fig. 5(B)). From this result, the low activity of the AuCu without oxidation is due to the low surface area ($<0.05\ \mathrm{m^2/g}$). The BET surface area of the oxidized sample at 600 °C is $8.3\ \mathrm{m^2/g}$, which is more than two orders larger than that of the sample without oxidation. Degradation of the activities for the samples treated at oxidation temperature at 800 and 1000 °C is ascribed to the decrease in surface area where the specific surface area is $7.2\ \mathrm{m^2/g}$ for the former and $5.4\ \mathrm{m^2/g}$ for the latter, respectively. Therefore, it is indicated that the formation of porous structure on the surface after oxidation at 600 °C leads to drastic increase in the surface area and the activity. We discuss the active phase for the catalytic activity in the next paragraph.

In order to characterize in more detail, we performed SEM observation of a cross section of the AuCu ribbon. Fig. 6 shows the SEM images and EDS analysis of a cross section before and after oxidation at 600 °C of the AuCu ribbons. As shown in Fig. 6(A), the image is homogeneous over the sample and the composition profile indicates that Cu and Au atoms are uniformly distributed within the alloy before oxidation. The sample oxidized at 600 °C in air exhibits a sandwich structure where a gold layer is between two homogeneous CuO layers, as shown in Fig. 6(B). This result indicates that copper atoms diffused from the AuCu I lattice to the surfaces where copper reacted with oxygen to form CuO. From these findings, it is found that porous structure of the outmost region consists of mainly CuO. Therefore, porous CuO layer rather than Au layer is an important active phase mainly responsible for the activity. It has been reported that the copper oxides such as Cu_2O [15,16] and CuO [17] are the active phases for CO oxidation. Copper oxide is reducible and depending upon the conditions, copper may exist as CuO and/or Cu_2O during the reaction. On the other hand, we do not exclude the possibility that gold atoms remain in the CuO layer which might contribute to the high activity of CO oxidation at present stage. It is well known that nanosized gold supported on oxides exhibits the exceptional catalytic behavior for CO oxidation [18]. Hutchings et al. reported that Au/CuO catalyst gives sustained high catalytic activity for CO oxidation even at ambient temperature [19].

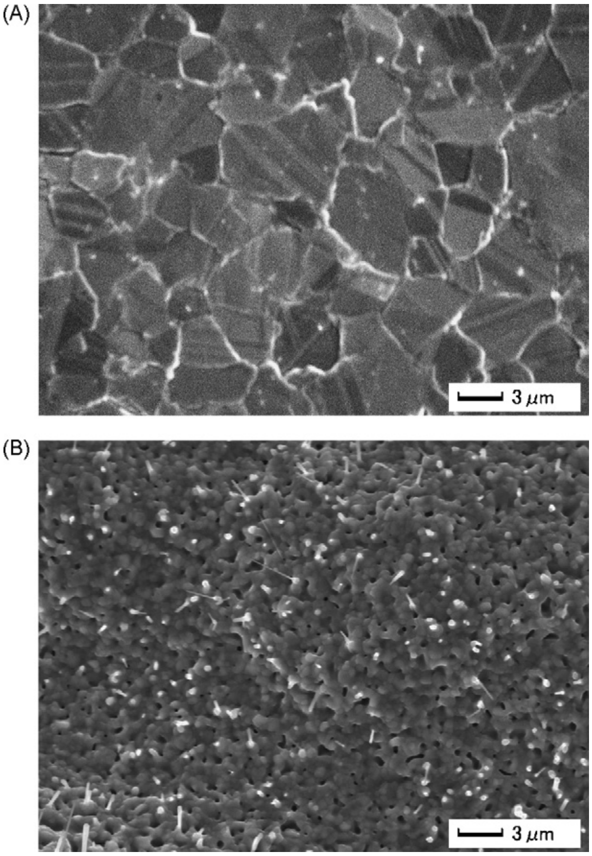

Fig. 5. SEM images of the AuCu sample. (A) Before oxidation in air; (B) after oxidation at 600 °C in air.

To obtain a catalyst with composite metal/oxide structure from a binary alloy, preferential oxidation on either one of components is required. It has been reported that oxidation on

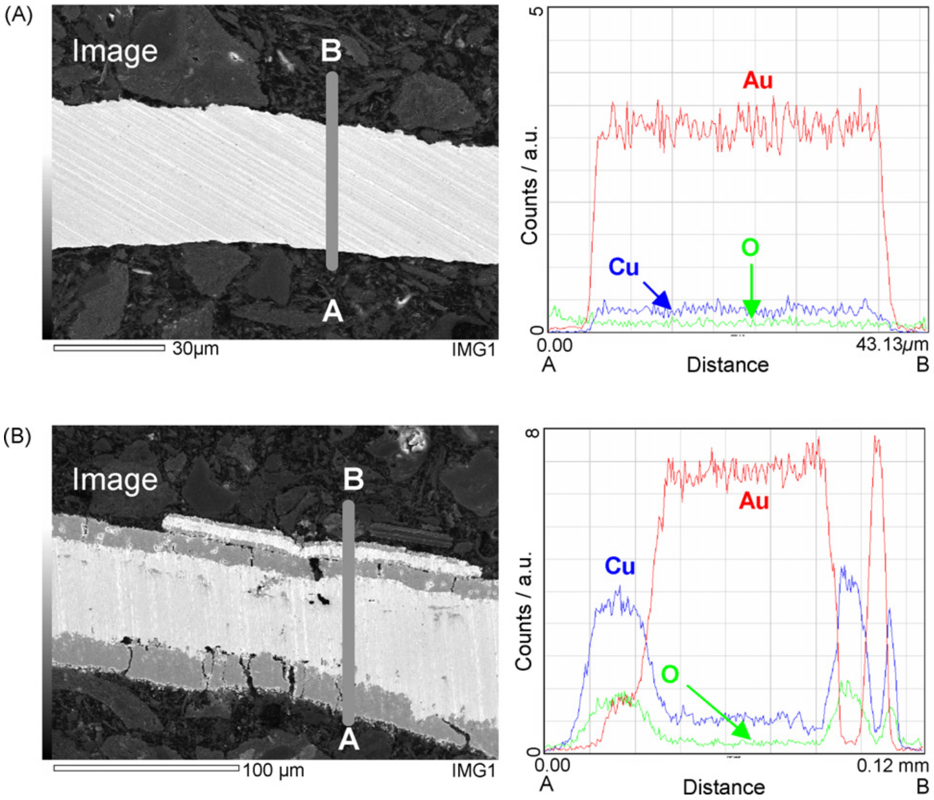

Fig. 6. SEM images and elemental profiles measured by EDS for cross section of the AuCu sample. (A) Before oxidation in air; (B) after oxidation at 600 °C in air.

the Au–Zr alloys led to the formation of an intimate mixture of nanostructured gold and zirconia [5,6,20]. Morphologically, the products of oxidative decomposition of the Au–Zr alloys gave the corresponding zirconia-supported gold catalyst [6], whereas in this study, copper oxide uniformly wrapped over a gold layer at the core after the oxidation (Fig. 6(B)). AuCu and AuZr are both gold alloys but the bonding strength is much larger for Zr–O than for Cu–O. Zirconium is readily oxidized to form zirconia which is very stable, whereas copper oxide is reducible to copper relatively under mild conditions. The difference in bonding nature between Zr–O and Cu–O is a possibility to interpret the difference in morphology between ZrO_2/Au and CuO/Au induced by selective oxidation. For clarification, oxidation process of the alloys should be studied by considering the oxidation conditions and structure of the consequent oxides. It seems that the selective oxidation of copper occurs at surfaces of the AuCu and the oxidation is also the driving force promoting the copper atoms move to the surfaces. Consequently, a homogeneous copper oxide layer forms outside and leaves the gold at the core.

A sandwiched CuO/Au/CuO structure has been fabricated by direct oxidation on the ordered AuCu phase at 600 °C in air. This result suggests that the AuCu intermetallic compound has potential to form a unique composite metal/oxide catalyst by controlling oxidation conditions. Further investigation with respect to the detailed characterization of the AuCu intermetallic compound during the oxidation–reduction processes and the mechanism of oxidation is in progress.

4. Conclusions

Oxidation of the ordered AuCu intermetallic compound and its effect on catalytic activity of CO oxidation reaction have been studied. The oxidation performed at temperatures above 400 °C led to the formation of a composite of CuO and Au, accompanied by the increase in surface area and enhancement of the catalytic activity. The oxidation performed at 600 °C exhibited highest activity in this study, revealing a sandwiched structure where a gold layer is sandwiched by two porous CuO layers. The formation of porous CuO is verified to be the key factor in improving catalytic activity. This study declared that the oxidation of an intermetallic compound is a novel and an effective way to design metal/oxides composites for catalysts.

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