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Au–Cu alloy nanoparticles supported on silica gel as catalyst for CO oxidation: Effects of Au/Cu ratios

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ABSTRACT

Au–Cu bimetallic catalysts with Au/Cu ratios ranging from 3/1 to 20/1 were prepared on silica gel support by a two-step method. The catalysts were characterized by ICP, XRD and TEM. The results showed that, irrespective of Au/Cu ratios, all the bimetallic nanoparticles had significantly reduced particle sizes (3.0–3.6 nm) in comparison with monometallic gold catalysts (5.7 nm). Both CO oxidation and PROX reactions were employed to evaluate the catalytic activities of Au–Cu bimetallic catalysts. For CO oxidation, the alloy catalysts show non-monotonic temperature dependence showing a valley in the intermediate temperature range. The catalyst with Au/Cu ratio of 20/1 gave the highest activity at room temperature, but its activity showed the deepest valley with increasing the reaction temperature. On the other hand, the catalyst with Au/Cu ratio of 3/1 exhibited the best performance for PROX reaction. For the Au/Cu ratios investigated, the bimetallic catalysts showed superior performance to monometallic gold catalysts, demonstrating the synergy between gold and copper.

1. Introduction

Gold nanocatalysts have been intensively studied since the pioneering work of Haruta in the 80 s of last century [1–3]. It has been reported that the optimized size of gold nanoparticles in CO oxidation reaction is ∼3 nm [4–6]. Generally, highly dispersed gold nanoparticles can be facilely obtained by a deposition-precipitation (DP) method on “active” metal oxide supports (e.g., TiO_2, Fe_2O_3, etc.) with iso-electronic points (IEP) between 6 and 9 [7,8]. However, it remains challenging to obtain small gold nanoparticles on “inert” supports with acidic surfaces (e.g., silica, IEP = 2.0) and without anchoring sites (e.g., defects, F centers) [9,10]. At the same time, silica is appealing as a support for its large surface area, good thermal stability, high resistance against corrosion, and availability. Therefore, it would be attractive to synthesize highly dispersed and highly active gold nanocatalysts supported on silica.

It has been demonstrated theoretically that the electronic and structural properties of gold nanoparticles can be modified by doping with a second metal [11]. Supported bimetallic catalysts containing gold is becoming an emerging research subject recently, especially Au–platinum group metals (PGMs). It has been reported that supported Au–Pt bimetallic catalysts showed enhanced activity in methanol electrooxidation [12], oxygen reduction [13], CO tolerance for hydrogen activation [14] and biomass conversion [15]. Supported Au–Pd catalysts also showed superior activity compared to Au and Pd nanocatalysts in the acetoxylation of ethylene to vinyl acetate [16], alcohol oxidation [17] and direct synthesis of hydrogen peroxide [18]. Recently, supported Au–Ir bimetallic catalysts were reported to exhibit higher activity in CO oxidation than the monometallic ones [19]. However, alloying gold with the other two coinage metals (silver and copper) has received relatively less attention.

The group IB metals (gold, silver and copper) have the same face center cubic (fcc) crystal structure and similar lattice spacing, so they can form alloy very easily. In our previous work [20–23], we designed a one-pot method to prepare Au–Ag alloy nanoparticles supported on MCM-41. Gold and silver showed obvious synergetic effect in CO oxidation reaction. However, the particle size was not well controlled (∼30 nm) and the Au–Ag@MCM-41 catalyst showed no activity when H_2 was present. Recently, we developed a general two-step method to prepare highly dispersed Au–Ag alloy nanoparticles on silica gel [24] and on MCM-41 [25] and Au–Cu alloy nanoparticles on SBA-15 [26]. It has been shown that alloying gold with silver or copper is a good way to obtain highly active, sintering-resistant nanoparticles on inert supports. For the Ag–Au alloy, the Au/Ag ratio was found to be a determining factor in the catalysts for the activity of CO oxidation [21]. The effect of Au/Cu ratios has not been investigated in details, in particular for large Au/Cu ratios. In this work, we prepared Au–Cu bimetallic catalysts

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with different Au/Cu ratios, from 3/1 to 20/1, with a focus on the effect of Au/Cu ratios on the particle size and catalytic activity for both CO oxidation and PROX reactions.

2. Experimental

2.1. Catalyst preparation

The Au–Cu alloy nanoparticles were supported on silica gel (provided by Qingdao Ocean Chemical Plant, $S_{BET} = 467\,m^2\,g^{-1}$) by a two-step method which was reported in our previous works [24–26]. Briefly, 1.0 g of the silica gel was dispersed in 50 mL ethanol containing 2.5 g of APTES ($H_2N(CH_2)_3Si(OEt)_3$) under stirring, and the mixture was then refluxed at 80 °C for 24 h. The recovered solid was dried at 60 °C overnight to obtain APTES-functionalized silica gel (APTES-SiO_2). To synthesize Au–Cu alloy nanoparticles supported on silica gel, in the first step, 1.0 g of the as-prepared APTES-SiO_2 was dispersed in 15 mL of H_2O, to which 5 mL of a 1.89 wt% $HAuCl_4$ aqueous solution was added. After continuous stirring at room temperature for 30 min, the mixture was recovered by filtration and washing, and was then redispersed in 20 mL of an aqueous solution of $NaBH_4$ (0.1 M) and stirred for another 20 min. After that, the solid was recovered by filtering and washing until there was no Cl^- detected by $AgNO_3$, thus obtaining Au/APTES-SiO_2. In the second step, Cu was deposited on the Au/APTES-SiO_2 using $Cu(NO_3)_2$ as the precursor with the same procedure as that for Au deposition in the first step. Finally, the solid was dried at 110 °C, calcined at 500 °C in air for 6 h, and reduced at 550 °C in pure H_2 for 1 h to obtain the Au–Cu/SiO_2 catalysts. The atomic ratio of gold to copper was varied from 3/1 to 20/1, and the total metal loading was fixed at 6 wt%. According to the nominal Au/Cu atomic ratios, the catalysts are designated as $Au_{20}Cu_1/SiO_2$, $Au_{10}Cu_1/SiO_2$, Au_6Cu_1/SiO_2, Au_3Cu_1/SiO_2, as well as Au/SiO_2 and Cu/SiO_2.

2.2. Characterization

The actual metal loadings of the catalysts were determined by inductively coupled plasma spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The wide-angle X-ray diffraction (XRD) patterns were recorded on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu K_α radiation source ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. A continuous mode was used for collecting data in the 2θ range from 20° to 80° at a scanning speed of 5°/min. TEM images were obtained on a Tecnai G^2 Spirit FEI Transmission Electron Microscope operating at 120 kV. The particle size distribution of the catalysts was obtained by measuring more than 300 nanoparticles in each sample. The HRTEM images and the lattice parameters of the Au–Cu nanoparticles were observed with a Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan GIF100 imaging filter.

2.3. Activity measurement

The catalytic testing was conducted with a continuous flow fixed-bed reactor system. Prior to the reaction, the catalyst was pretreated with H_2 at 550 °C for 1 h, and then cooled to the reaction temperature under He. For CO oxidation, the feed gas containing 1.0 vol% CO and 1.0 vol% O_2 balanced with He was allowed to pass through 60 mg (20–40 mesh) of a catalyst sample at a flow rate of $20\,mL\,min^{-1}$ (corresponding to a space velocity of $20,000\,mL\,h^{-1}\,g_{cat}^{-1}$). For preferential CO oxidation in rich H_2, the feed stream was composed of 1.0 vol% CO, 0.5 vol% O_2 and 50 vol% H_2 balanced with He, and the total flow rate was $40\,mL\,min^{-1}$ (corresponding to a space velocity of $40,000\,mL\,h^{-1}\,g_{cat}^{-1}$). The inlet and outlet gas compositions were analyzed on-line by a gas chromatograph (HP 6890, TDX-01 column).

3. Results and discussion

3.1. Actual Au/Cu molar ratios

In order to investigate the effect of Au/Cu ratios on the catalytic performance, we prepared four Au–Cu bimetallic catalysts with different Au/Cu atomic ratios according to our previously developed two-step approach [24–26]. As shown in Table 1, when the nominal Au/Cu ratios were 20/1 and 10/1, the actual Au/Cu ratios were almost exactly the same as the nominal values. However, for the nominal Au/Cu ratios of 6/1 and 3/1, the actual Au/Cu atomic ratios were somewhat larger than the nominal values. The deviation of the actual Au/Cu ratios from their nominal values at low Au/Cu ratios indicates that the loading of Cu on the support is more difficult than that of Au. Actually, comparing the metal loadings of Au/SiO_2 and Cu/SiO_2, one can see that the actual Cu loading is only one-third that of Au although their nominal loadings were all at 6 wt%. Apparently, the interaction between the amine ($-NH_2$) on the support surface and copper is weaker than with gold species.

3.2. Wide-angle XRD patterns

Fig. 1 presents the XRD patterns of the four bimetallic samples before and after the reduction treatment. Irrespective of the Au/Cu ratios, the four samples before the reduction treatment show the same XRD patterns as Au/SiO_2. None of any copper species, either copper oxides or metallic Cu, were detected by XRD. It is noted that even for the Cu/SiO_2 catalyst, not any copper crystal species were detected, suggesting that copper may exist as highly dispersed particles or amorphous species that could not be detected by XRD. On the other hand, upon reduction treatment with H_2, the XRD peaks slightly shift toward high angles with decreasing Au/Cu ratios, and this shift became more discernable at the Au/Cu ratio of 3/1. The d spacings, which were calculated according to the (1 1 1) reflection peak, also reflect such a tendency (Table 1). This is an indication of the formation of Au–Cu alloy after the reduction treatment [27]. The

Table 1
Chemical compositions, average particle sizes and the lattice spacings of Au–Cu/SiO_2 with various Au/Cu atomic ratios.

Catalysts	Au/Cu [a]	Total metal loading (wt%) [a]	D_{XRD} (nm)[b]	d spacing (nm)	D_{TEM} (nm) [c]	Specific rate ($mol_{co}\ g_{Au}^{-1}\ h^{-1}$)	Contact time ($g_{cat}\ h\ mol_{co}^{-1}$)	TOF (s^{-1})
Au/SiO_2	1/0	5.72	4.3	0.235	5.7	0.10	4.3	0.018
$Au_{20}Cu_1/SiO_2$	19.55/1	5.55	2.6	0.233	3.6	0.21	4.3	0.036
$Au_{10}Cu_1/SiO_2$	10.14/1	5.52	2.4	0.232	3.5	0.14	4.3	0.023
Au_6Cu_1/SiO_2	7.09/1	5.74	2.5	0.231	3.2	0.14	4.3	0.020
Au_3Cu_1/SiO_2	3.99/1	5.35	2.6	0.229	3.0	0.18	4.3	0.023
Cu/SiO_2	0/1	1.91	–	0.208	–	–	–	–

[a] Atomic ratios of Au to Cu determined by ICP.
[b] Average particle sizes estimated from Scherrer's equation according to XRD.
[c] Average particle sizes estimated by TEM images.