Effects of the ratio of Cu/Co and metal precursors on the catalytic activity over Cu-Co/Al$_2$O$_3$ prepared using the polyol process

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ABSTRACT

Cu-Co bimetallic catalysts were prepared using a simple polyol process. The effects of various metal precursors (nitrate, acetate, and chloride) and Cu/Co ratios on the activities of the catalysts were evaluated for toluene oxidation and NO reduction. The results indicated that the use of the metal precursor Cu-Co acetate in preparing the bimetallic catalysts resulted in good metal dispersion and high catalytic activity. When the atomic Cu/Co ratio was 0.21 in the Al$_2$O$_3$-supported catalyst, the dispersion of active sites was promoted by the Cu, and the catalytic activity was stable over the reaction time. CuO and Cu^0 species and large particle sizes (20 nm) formed when the Co loading weight in the catalyst increased, and conversion decreased. When the reaction temperature was 300 °C, NO and toluene were able to be simultaneously removed with high conversion rates (83% and 98%).

1. Introduction

The polyol process is an easy and chemical reduction agent-free method for preparing nanoscale metal powder that employs the potential difference (ΔE) between a high-boiling-point alcohol reducing agent (e.g., ethylene glycol [EG], diethylene, tetraethylene glycol, or glycerol) and a metallic precursor (e.g., metal alkoxide or metal salts) [1–4]. The polyol process is an effective, simple, and inexpensive method for reduction of a large quantity of metallic powder with a uniform size and shape, and involves adjustment of the reaction time and temperature, pH, and concentration of the protective reagent (polyvinylpyrrolidone [PVP]). Moreover, it has been shown that various catalysts (e.g., PdO/Al$_2$O$_3$, Ag/Al$_2$O$_3$, Pd-Ag/Al$_2$O$_3$, Ru/Al$_2$O$_3$, Pt/C, Pd/C, Pt/CNT, Pt-Ru/CNT, PtSn/C, PtSnNi/C, and Ni-Pd/SWNT) prepared using the polyol process have active sites at nanoscale sizes and disperse well onto the supports [1–7]. Thus, the polyol process has been used to prepare catalysts for a wide range of uses, including energy, combustion, pollution control, and medicine.

In a recent study [8], the authors prepared transition metal catalysts supported on activated carbon (AC) using the polyol process; subsequently, VOC oxidation activity of these catalysts was evaluated. The results indicated that the polyol process can generate well-dispersed metallic nanoparticles on AC. For VOC oxidation, the activities of the catalysts followed the sequence Cu > Co > Fe > Ni. To increase the activity of the catalysts and maximize the advantages of the polyol process, bimetallic catalysts comprising IB (Cu, Ag, Au) and VIIIB (Co, Rh, Ir) metals were considered. Tyurkin et al. [9] indicated that a mixture of metals is capable of forming mutual interactions with complex crystals (spinel- or perovskite-type). Sales et al. [1], Bonet et al. [3], and Shaheen and Ali [10] found that bimetallic catalysts had stronger catalytic activity and higher selectivity than monometallic catalysts. The advantages of these bimetallic catalysts were suggested to be due to both electronic and geometric effects [11]. Interaction between the reactants and the d-band of the active sites was promoted by an electronic effect, and new active sites were produced due to geometric effects when the secondary metal was added to the catalyst.

Although there have been several studies on bimetallic catalysts, most of the studies have focused on noble metal-transition metal bimetallic catalysts prepared using the polyol process. Few studies have evaluated transition metal-transition metal bimetallic catalysts prepared by using the polyol process for controlling air pollution emissions (i.e., NO$_x$, CO, volatile organic compounds [VOCs], and SO$_2$); moreover, few studies have analyzed the activity of bimetallic catalysts prepared using various metal precursors. Therefore, it is necessary to study the activity of bimetallic catalysts prepared with various metal precursors using a simple method such as the polyol process. In this study, bimetallic (Cu-Co) catalysts were synthesized using the polyol process, and these Cu-Co catalysts were subsequently employed for VOC oxidation. To elucidate

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the catalytic activity of the Cu-Co bimetallic catalyst for VOC conversion under various reaction conditions, the effects of space velocity, reaction temperature, and reactant concentrations were studied.

In addition, three metal salts (nitrate, chloride, and acetate) were selected as potential Cu-Co metal precursors for the polyol process due to the low dissolution of metal alkoxides; further, the effects of the metal precursors and the Cu/Co ratio of the bimetallic catalyst were evaluated. Moreover, Burch and Ottery [12] and Lu and Wey [13] have examined the reduction of NO by hydrocarbons and found that hydrocarbons can act as a reductant. Therefore, because gaseous NO and VOCs (toluene) coexist in reaction gases, the efficiency of their simultaneous removal over a Cu-Co bimetallic catalyst was assessed.

2. Experimental

2.1. Preparation of catalysts

Cu-Co bimetallic catalysts were prepared using the polyol process. A given amount of the Al_2O_3 was added to an EG–PVP–metal precursor solution (Cu, Co), and agitated with a magnetic stirrer. $Cu(CH_3COO)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, and $CuCl_2 \cdot 2H_2O$ were chosen as copper precursors, and $Co(CH_3COO)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $CoCl_2 \cdot 6H_2O$ were used as cobalt precursors. The concentration of PVP $((C_6H_9NO)_x)$ was 5×10^{-3} M, and the ratio of [precursors]/[EG] was 0.1 in the solution. Ammonia (1 M, 3 mL) was added to promote formation of the Cu-Co colloid in solution (pH 10). The suspension was then heated to a given temperature to reduce the Cu-Co ions and form Cu-Co metals on the Al_2O_3 in a closed Teflon bottle. At the end of the reaction, the preparation was rapidly cooled to room temperature in an ice-water bath. The catalyst thus obtained was separated by filtration, and subsequently washed several times with ethanol to remove the organic phase. Afterwards, the metal-loaded Cu-Co bimetallic catalyst was dried in a furnace. Before activity test, the catalyst was calcined at 450 °C for 4 h in H_2. The catalysts prepared with different precursors and various Cu/Co ratio were denoted as $Cu_{(a)}Co_{(b)}/Al_2O_3$-(c) where (a) and (b) refer to the percentage of Cu-Co loading weight over catalyst, and (c) refers to the three kinds of metal precursors (A for acetate, N for nitrate, Cl for chlorate). The preparation conditions for the various Cu-Co bimetallic catalysts are shown in Table 1.

2.2. Characterization of catalysts

The loading weight of copper on the support was determined using an inductively coupled plasma-mass spectrometer (ICP-MS, SCIEX ELAN 5000; PerkinElmer, Waltham, MA, USA). The metal loading efficiency was defined as (nominal loading weight – actual loading weight)/nominal loading weight. Transmission electron microscope (TEM) observations were conducted with a Philips 400T microscope operated at 120 keV to observe the dispersion of active sites on the support surface. The samples were crushed in an agate mortar and suspended in ethanol. After ultrasonic dispersion, a

droplet was deposited on a copper grid supporting a perforated carbon film.

The surface area of the Cu-Co bimetallic catalysts was measured at 77 K using gravimetric methods with an ASAP 2010 vacuum microbalance, providing area comparisons for catalysts prepared with different reduction times. N_2 adsorption–desorption on the surface was used to determine textural properties. The Brunauer–Emmett–Teller (BET) surface area and average pore diameter were calculated from the adsorption isotherm.

An X-ray powder diffractometer (XRD, SIEMENS D5000) was used to identify the crystalline species of the Cu-Co bimetallic catalysts. A Cu tube serving as the X-ray source was employed to estimate the active site phase, and the working voltage and current was 30 kV and 20 mA, respectively. The powdered samples were pressed onto suitable holders. The scanning range of 2θ was 20–80° with a scanning speed of 2°/min. Diffraction patterns were manually analyzed using the Joint Committee of Powder Diffraction Standard (JCPDS) card.

2.3. Activity test

Fig. 1 depicts the activity test system used in this experiment. Catalytic activity measurements for the activity test were conducted at atmospheric pressure in a micro-catalytic reactor under steady-state conditions. In this study, the activity tests were carried out under various reaction atmospheres ($NO/N_2/O_2$/toluene). A toluene/nitrogen mixture was chosen to represent one of the VOC pollutants. The toluene vapor (250–1000 ppm) was carried by nitrogen from a saturator filled with liquid toluene. The catalyst reactor was a 9-mm ID quartz tube, and the catalysts (0.20–3.70 g) were placed on a quartz filter board. A thermocouple was placed in the center of the catalyst bed to record reaction temperature and also to control the furnace. Both reactants and products were monitored using a gas chromatograph/flame ionization detector (GC-6890N; Agilent) and an online flue gas analyzer (PG-250; Horiba). Thus, conversion was calculated as toluene and NO consumption based on the inlet and outlet concentrations of toluene. Operating conditions for the activity tests are shown in Table 2.

3. Results and discussion

3.1. ICP-MS of Cu-Co loading weights on catalysts

In this study, acetate, nitrate, and chloride were chosen as three potential Cu-Co precursors for preparing Al_2O_3-supported Cu-Co bimetallic catalysts using the polyol process. As is well known, the metal loading weight on the catalyst is an important parameter indicating catalytic activity. In theory, activity is enhanced by increasing the proportion of the active phase. Table 3 shows the ICP-MS analysis results for the Cu-Co loading weights on the Cu-Co/Al_2O_3 catalysts with the three different precursors. It can be seen that the actual loading weight on $Cu_{0.23}Co_{1.45}/Al_2O_3$-Cl (1.68 wt.%) is lower than the nominal value (5 wt.%), whereas the actual loading weights on $Cu_{1.14}Co_{1.95}/Al_2O_3$-N and $Cu_{1.68}Co_{1.49}/Al_2O_3$-A were 3.09 and 3.17 wt.%, respectively. However, there is no linear correlation and these results are affected by the precursors. The actual loading ratios of Cu/Co on $Cu_{1.14}Co_{1.95}/Al_2O_3$-N, $Cu_{0.23}Co_{1.45}/Al_2O_3$-Cl, and $Cu_{1.68}Co_{1.49}/Al_2O_3$-A were 33.6%, 61.8%, and 63.4%, respectively. The actual atomic Cu/Co ratios on three catalysts were 0.54, 0.15, and 1.05, respectively. These results indicate that the efficiencies of the Al_2O_3-supported Cu-Co bimetallic catalysts prepared using the polyol process were significantly affected by the choice of metal precursor; acetate had the best Cu/Co ratio and actual metal loading weight on the catalyst.

Table 1
Preparing condition of various Cu-Co bimetallic catalysts.

Catalyst	Cu precursor	Co precursor	Reduction temperature (°C)
$Cu_{1.14}Co_{1.95}/Al_2O_3$-N	$Cu(NO_3)_2 \cdot 2.5H_2O$	$Co(NO_3)_2 \cdot 6H_2O$	140
$Cu_{0.23}Co_{1.45}/Al_2O_3$-Cl	$CuCl_2 \cdot 2H_2O$	$CoCl_2 \cdot 6H_2O$	180
$Cu_{1.68}Co_{1.49}/Al_2O_3$-A	$Cu(CH_3COO)_2 \cdot H_2O$	$Co(CH_3COO)_2 \cdot 4H_2O$	130
$Cu_{0.54}Co_{2.43}/Al_2O_3$-A	$Cu(CH_3COO)_2 \cdot H_2O$	$Co(CH_3COO)_2 \cdot 4H_2O$	130
$Cu_{1.02}Co_{0.91}/Al_2O_3$-A	$Cu(CH_3COO)_2 \cdot H_2O$	$Co(CH_3COO)_2 \cdot 4H_2O$	130
$Cu_{2.59}/Al_2O_3$	$Cu(CH_3COO)_2 \cdot H_2O$	$Co(CH_3COO)_2 \cdot 4H_2O$	130
$Co_{2.93}/Al_2O_3$	$Cu(CH_3COO)_2 \cdot H_2O$	$Co(CH_3COO)_2 \cdot 4H_2O$	130