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Synergistic effect on Au-Pd bimetallic catalyst during oxidation of benzyl alcohol to sodium benzoate

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ABSTRACT

A series of AuPd/CeO$_2$ bimetallic catalysts with different Au/Pd molar ratios were investigated and their catalytic performance in the oxidation of benzyl alcohol to sodium benzoate and benzoic acid under solvent-free conditions was studied. The supported catalysts were characterized by X-ray diffraction, UV-Vis diffuse reflectance spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The Au-Pd nanoparticles were successfully deposited onto CeO$_2$ as a homogeneous alloy. The activity of the bimetallic catalysts was superior to that of the corresponding monometallic catalysts. This improvement was attributed to the synergistic effect between Au and Pd. The catalyst with an Au/Pd molar ratio of 3/1 showed the best catalytic performance (the yield of benzoic acid reached 92%), and it could be easily recovered and reused for more than seven successive reactions without significant loss of activity.

1. Introduction

Supported bimetallic nanoclusters have generated much interest for decades owing to their unique bifunctional and synergistic properties [1–4]. Compared with monometallic systems, the activity and stability of bimetallic catalysts are drastically improved upon addition of the second metallic element, which can affect both the geometry and electronic properties of the pure metal clusters [5–8]. Supported Au-Pd bimetallic catalysts are used to catalyze a number of reactions with outstanding activity such as oxidative elimination of toluenes [9], nitroarene reduction to imine [10], oxidation of primary carbon-hydrogen [11–13], and oxidation of alcohols [14,15]. Recently, the beneficial effect of Au-Pd alloy exerted on Au and Pd catalysts has attracted much attention [16–18]. For example,

Goodman and co-workers [19] examined the surface structure of model catalysts, such as Pd/Au(111) and Pd/Au(100), via the synthesis of vinyl acetate, and demonstrated that Au on Pd resulted in catalysts with greatly improved activity and selectivity. Keane and co-workers [20] examined a significant increase in activity of AuPd/Al$_2$O$_3$ when compared with Au/Al$_2$O$_3$ towards the hydrogenation of *p*-chloronitrobenzene. Hao's group [21] demonstrated that the addition of Pd to Au/SBA-15 catalysts could decrease the size of the gold nanoparticles, resulting in higher activity towards the selective aerobic oxidation of benzyl alcohol. Additionally, Huang's group [22] has reported the effect of the Au/Pd molar ratio of bimetallic AuPd/MgO on the liquid phase oxidation of benzyl alcohol to benzaldehyde. Regardless, to date, the application of Au-Pd bimetallic catalysts in the oxidation of benzyl alcohol to sodium

benzoate and benzoic acid has rarely been reported.

Cerium oxide (CeO_2) is an effective catalyst employed in various organic reactions such as transamidation of amides [23], selective synthesis of esters from nitriles and alcohols [24], preparation of organic carbamates [25], synthesis of *N*-alkyl amides [26], and reduction of NO_x [27]. Because CeO_2 has acid-base and redox properties that are expected to facilitate and promote catalysis performance [28,29], CeO_2 has been used to support Au [30,31], Cu [32], Ru [33,34], Pt [35], and Pd [36] to catalyze diverse inorganic and organic reactions. Moreover, Au/CeO_2 catalyst has been reported to exhibit better catalytic performance than Au/TiO_2 and Au/Fe_2O_3 towards CO oxidation [30]. Therefore, CeO_2 is considered a promising support candidate to load gold and other noble metals.

Sodium benzoate and benzoic acid are important commodity chemicals with wide use as food additives, preservatives, spices, plasticizers, and mordants. As reported, sodium benzoate and benzoic acid can be prepared upon oxidation of benzyl alcohol in a one-pot solvent-free synthesis method that is environmentally friendly, non-toxic, and energy-efficient [37]. A novel efficient $AuAg/TiO_2$ bimetallic catalyst with a high stability was employed in this reaction. The catalyst that was prepared with an Au/Ag molar ratio of 1/3 produced the best catalytic performance. To further improve the catalytic activity and evaluate the synergistic effect between Au and Pd, herein, we report the preparation of $AuPd/CeO_2$ bimetallic catalysts and investigate their catalytic properties towards the oxidation of benzyl alcohol to sodium benzoate and benzoic acid. A series of $AuPd/CeO_2$ catalysts with different Au/Pd molar ratios were obtained and structurally characterized by UV-Vis diffuse reflectance spectroscopy (DRS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). It was found that the Au-Pd nanoparticles were mainly present as homogeneous alloys and the catalyst prepared with an Au/Pd ratio of 3/1 displayed optimum catalytic performance.

2. Experimental

2.1. Catalyst preparation

Au-Pd bimetallic catalyst with an Au/Pd molar ratio of 1/1 was loaded on different supports, and the synthesis process was as follows. First, Au/support catalyst was prepared by a deposition-precipitation (DP) method using urea as precipitation agent. Then, 1.0 g of support (TiO_2, MnO_2, SnO_2, ZnO, or CeO_2), 9 mL of aqueous $HAuCl_4$ solution (24.3 mmol/L), and 2.6 g of urea were added to 80 mL of H_2O with continuous stirring. The mixture was stirred for 2 h at 353 K, during which the pH value was gradually increased from 3.0 to 8.0. The as-received precipitate was collected by filtration, washed three times with deionized water, and dried overnight at 373 K, followed by calcination for 4 h at 573 K. Then, the Pd species were loaded on the as-synthesized precursor mentioned above using an impregnation (IM) method. Typically, 1.0 g of the as-synthesized precursor was added to 7.2 mL of aqueous $PdCl_2$ solution (56.3 mmol/L) and mixed with 40 mL of H_2O. The resulting slurry was vigorously stirred at 353 K until complete evapora-

tion of water, and the solid material was dried at 373 K, followed by calcination for 4 h at 673 K. The as-synthesized catalyst is denoted as AuPd/MO, where MO represents the support (i.e., TiO_2, MnO_2, SnO_2, ZnO, or CeO_2). It should be noted that the total metal loading and the Au/Pd molar ratio of all AuPd/MO catalysts were controlled at 8 wt% and 1:1, respectively.

Monometallic Au/CeO_2 catalyst was prepared by DP using urea as precipitation agent. First, 1.0 g of CeO_2 (Aldrich), 18 mL of aqueous $HAuCl_4$ solution (24.3 mmol/L), and 5.2 g of urea were added to 80 mL of H_2O with continuous stirring. The mixture was stirred for 2 h at 353 K, during which the pH value was gradually increased from 3.0 to 8.0. The as-received precipitate was collected by filtration, washed three times with deionized water, and dried overnight at 373 K, and calcined for 4 h at 573 K.

Monometallic Pd/CeO_2 catalyst was prepared by IM. First, 1.0 g of CeO_2 was added to 14.5 mL of aqueous $PdCl_2$ solution (56.3 mmol/L) and mixed with 80 mL of H_2O. The resulting slurry was vigorously stirred at 353 K until complete evaporation of water, and the solid material was dried at 373 K, and then calcined for 4 h at 673 K.

The synthesis process of the bimetallic catalysts with different Au/Pd molar ratios was as follows. First, Au/CeO_2 was prepared by DP (similarly to the monometallic Au/CeO_2). Then, $AuPd/CeO_2$ was prepared by IM (similarly to the monometallic Pd/CeO_2), with Au/CeO_2 as the support. The total metal loading was controlled at 8 wt%. The catalysts prepared at varying Au/Pd molar ratios of 3/1, 2/2, and 1/3 are denoted as $3Au1Pd/CeO_2$, $2Au2Pd/CeO_2$, and $1Au3Pd/CeO_2$, respectively.

2.2. Catalyst characterization

The specific surface area of the samples was determined by nitrogen adsorption at 77 K (Micromeritics TriStar ASAP 3000) using the Brunauer-Emmett-Teller (BET) method. The Au and Pd loadings were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo E. IRIS). The XRD patterns were recorded on a Bruker D8 advance diffractometer with Cu K_α radiation (λ = 0.154 nm), operating at 40 mA and 40 kV. The XPS spectra were recorded under ultra-high vacuum (<10^{-6} Pa) at a pass energy of 93.90 eV on a Perkin Elmer PHI 5000C ESCA system equipped with a dual X-ray source using Mg K_α (1253.6 eV) anode and a hemispherical energy analyzer. All binding energy was calibrated using contaminant carbon (C 1s = 284.6 eV) as a reference. The TEM images were obtained on a JOEL JEM 2010 transmission electron microscope. The UV-Vis DRS spectra were collected using a Shimadzu UV-2450 spectrophotometer operating in the scanning range of 200–800 nm using $BaSO_4$ as background.

2.3. Activity test

All the experiments were carried out in a magnetically stirred glass flask under reflux; a mercury thermometer was used to monitor the reaction temperature that was maintained at 453 K using an oil bath. A predetermined quantity of benzyl alcohol (1.08 g) was introduced into the reactor, and then