Catalysis Today 175 (2011) 404–410

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Superior catalytic properties in aerobic oxidation of alcohols over Au nanoparticles supported on layered double hydroxide

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ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form 10 February 2011
Accepted 16 March 2011
Available online 31 May 2011

Keywords:
Au nanoparticles
Layered double hydroxide (LDH)
Oxygen
Aerobic oxidation
Primary and secondary alcohols

ABSTRACT

Extremely small-size Au nanoparticles mainly distributed at 1–5 nm were successfully prepared on layered double hydroxide by ion-exchange and reduction procedures (Au/LDH). This catalyst showed superior catalytic properties in aerobic oxidation of a wide range of secondary and primary alcohols under very mild conditions (e.g. 1 atm pressure of oxygen and even at room temperature). In addition, this catalyst is stable and recyclable during oxidations. These advantages are reasonably attributed to the interaction between Au sites and basic LDH.

1. Introduction

The oxidation of alcohols to the corresponding aldehydes or ketones is greatly important for the production of fine chemicals [1–3]. Conventionally, these oxidations are carried out using metallic salts as oxidants including permanganate, chromate and bromate. These processes are typically environmentally unfriendly because of the production of undesirable wastes and consequently high costs [3b,4,5]. In recent years, environmentally benign oxidants such as molecular oxygen with high atom efficiency have been used [6]. However, heterogeneous oxidations with molecular oxygen under very mild conditions (1 atm O_2 and even at room temperature) without additives is still a great challenge [7].

It is well known that a lot of metal ions and metal nanoparticles are catalytically active for alcohol oxidations using molecular oxygen as oxidants. For example, ruthenium, copper, cobalt, and palladium have been proved to be active for this kind of reactions [6d,8–11]. Recently, gold catalysts have been paid much attention because of their unprecedented catalytic properties, since the works of Hutchings and Haruta [12–15]. One of the most important findings is that Au nanoparticles are able to catalyze the oxidation of alcohols [7,16–19]. Compared with Pd and Pt catalysts, Au nanoparticles on supports show superior catalytic properties under mild conditions. In these cases, the activities are strongly dependent on Au nanosizes and support types [16,17]. For example, compared with silica, CeO_2 supported Au nanoparticles have improved activity and selectivity for the desired products in the aerobic oxidation of alcohols due to the synergetic electronic interactions between Au sites and CeO_2 [16a]. The use of Au/$Ga_3Al_3O_9$ could effectively promote the conversion of alcohol oxidations, since the $Ga_3Al_3O_9$ support might substantially facilitate the crucial alcohol-dehydrogenation step [16b].

More recently, we reported a communication that layered double hydroxide supported Au nanoparticles (Au/LDH) were active for aerobic oxidation of a few alcohols at 80 °C [17b]. Herein, we showed a systematical study on catalytic oxidations of a wide range of primary and secondary alcohols over Au/LDH catalyst under very mild conditions such as room temperature.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of LDH

As a typical run, 30.76 g of $Mg(NO_3)_2 \cdot 6H_2O$ (AR, Beijing Chem Co.) and 15 g of $Al(NO_3)_3 \cdot 9H_2O$ (AR, Beijing Chem Co.) were dissolved in 400 ml of water, followed by the addition of 72 g of urea (AR, Beijing Chem Co.) under stirring at room temperature. After heating to boiling point, a white precipitate was formed. After boiling for 8 h and precipitating at room temperature for 12 h, the solid LDH was collected by filtration and washing with water.

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doi:10.1016/j.cattod.2011.03.040

2.1.2. *Preparation of Au/LDH*

Au/LDH was prepared by ion-exchange and $NaBH_4$ reduction. For a typical run, 0.22 g of hydrochloroauric acid ($HAuCl_4 \cdot 4H_2O$, AR, Shanghai Chem Co.) was dissolved in 80 ml of water, followed by the addition of 6 g of LDH and stirring for overnight. After filtrating, washing and drying, the sample was transferred to 50 ml of toluene (AR, Beijing Chem Co., dried by P_2O_5), followed by the addition of $NaBH_4$ (AR, Beijing Chem Co.). After stirring for 10 min, 15 ml of ethanol was added and the mixture was stirred for 6 h. Au/LDH with Au loading at 1.8% was collected by filtration and washing with ethanol and water. The Au loading was analyzed by inductively coupled plasma (ICP) technique.

2.1.3. *Preparation of Pd/LDH*

For a typical run, 0.38 g $PdCl_2$ (AR, Shanghai Chem Co.) and NaCl (molar ratio of $PdCl_2$/NaCl is 1:2.3) were dissolved in 80 ml of water, followed by the addition of 6 g of LDH and stirring for overnight. The following ion-exchange and reduction procedures were the same as the preparation of Au/LDH. The Pd loading analyzed by ICP was 1.8%.

2.1.4. *Preparation of Au/TiO_2, Au/MgO, Au/Fe_2O_3 and Au/SiO_2*

As typical run, solid supports such as TiO_2 was added to the solution of hydrochloroauric acid. After stirring at 80 °C for overnight (pH = 9.0), filtrating and washing at room temperature, drying at 100 °C for 12 h, and calcination at 400 °C for 4 h, the sample was obtained. The Au loading analyzed by ICP was 1.8%.

2.2. *Sample characterization*

Powder X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX 2550 diffractometer with CuKα radiation ($\lambda = 0.1542$ nm). Transmission electron microscopy (TEM) experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The contents of Au and Pd were determined by ICP with a Perkin-Elmer plasma 40 emission spectrometer. XPS spectra were performed a Thermo ESCALAB 250 with Al Kα radiation at $\theta = 90°$ for the X-ray source, the binding energies were calibrated using the C1s peak at 284.9 eV. Temperature programmed surface reaction (TPSR) of adsorbed 2-propanol was carried out as follows: the catalysts were treated at 300 °C for 3 h and cooled down to room temperature, then 2-propanol vapor was introduced into the reaction system for 30 min. After sweeping with Ar for 1 h, the temperature was increased (10 °C/min) from room temperature to 500 °C, and the signals of H_2 ($M/e = 2$) were recorded by mass spectrometer with a thermal conductivity detector (TCD).

2.3. *Catalytic tests*

The oxidation of alcohols was carried out in a 50-ml glass reactor and stirred with a magnetic stirrer. The substrate, solvent and catalyst were mixed in the reactor and heated to the reaction temperature. Then molecular oxygen was introduced at air pressure. After reaction, the product was taken out from the reaction system and analyzed by gas chromatography (GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17 and OV-1. The recyclability of Au/LDH catalyst was carried out by separating the catalyst from the reaction system by centrifugation, washing with a large amount of methanol and drying at 100 °C overnight, then the catalyst was reused in the next reaction.

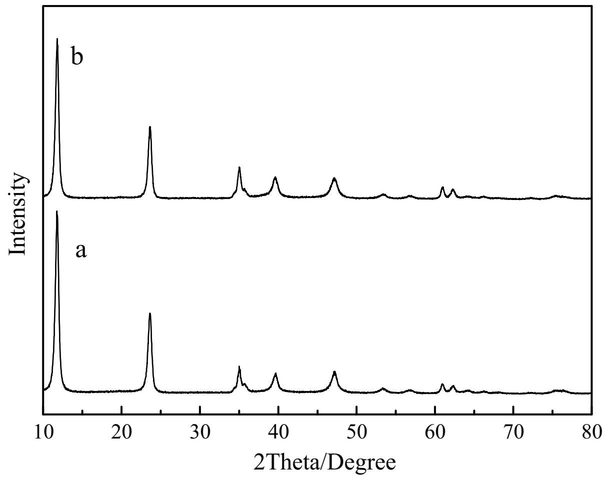

Fig. 1. XRD patterns of (a) LDH support and (b) Au/LDH catalyst.

3. Results and discussion

3.1. *Characterization of Au/LDH catalyst*

Fig. 1 shows XRD patterns of LDH and Au/LDH samples. They exhibited almost the same XRD peaks, indicating that the layered structure of LDH is well remained after loading of Au nanoparticles. Notably, the diffraction peaks associated with Au nanoparticles were not observed, which might be related to high dispersion of Au nanoparticles on LDH. TEM image of Au/LDH (Fig. 1(a)) confirms the presence of very small Au nanoparticles distributed at 1–5 nm.

3.2. *Oxidation of secondary alcohols*

Table 1 presents catalytic activities and selectivities in oxidation of a typical secondary alcohol of 1-phenylethanol to acetophenone with molecular oxygen at an atmospheric pressure over various catalysts. Clearly, Au/LDH catalyst was very active. After reaction at 80 °C for 2 h in toluene, 1-phenylethanol was completely converted (Table 1, entry 1). When the temperature was decreased down to 45 °C, the complete conversion of 1-phenylethanol took for 4 h (Table 1, entry 2). Interestingly, when the reaction was performed at room temperature for 12 h, the conversion still had 96% (Table 1, entry 3). Compared with toluene, the use of water showed relatively low reaction rate. When the reaction was performed at 45 °C for 4 h, the conversion was 40% (Table 1, entry 4). When the reaction time was increased to 16 h, the conversion was 98% (Table 1, entry 5). In contrast, Pd/LDH and the other Au-based catalysts showed very low conversion for this reaction. For examples, Pd/LDH was almost inactive (Table 1, entry 7). A series of Au-based catalysts with similar Au content with Au/LDH (Au/TiO_2, Au/MgO, Au/Fe_2O_3 and Au/SiO_2) exhibited very low conversion (11–26%, Table 1, entries 9–12). Even if the presence of additional Na_2CO_3, Au/SiO_2 still gave a low conversion (19%, Table 1, entry 13). These results indicate that Au/LDH catalyst is very active, compared with Pd/LDH and the other Au-based catalysts.

More importantly, when Au/LDH catalyst was recycled for 6 times, the conversion still have 97% (Table 1, entry 6), which is still comparable with the fresh catalyst (loss of activity less than 3%, Table 1, entry 1). These results indicate that Au/LDH catalyst was stable and reusable in aerobic oxidation of 1-phenylethanol. Sample TEM images (Fig. 2) showed that Au nanoparticle sizes of the recycled catalyst were similar to those of the fresh catalyst, indicating that Au nanoparticles are basically stable during