



Highly active gold catalysts loaded on NiAl-oxide derived from layered double hydroxide for aerobic alcohol oxidation

Jianbo Zhao^{a,b}, Guiyun Yu^a, Kaiyang Xin^a, Lei Li^a, Teng Fu^a, Yuming Cui^a, Hong Liu^a, Nianhua Xue^a, Luming Peng^a, Weiping Ding^{a,*}

^a Key Lab of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

^b Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, China

ARTICLE INFO

Article history:

Received 13 February 2014

Received in revised form 25 May 2014

Accepted 29 May 2014

Available online 5 June 2014

Keywords:

Au catalysts

Layered double hydroxide

Mixed oxide

Alcohol oxidation

Synergistic effect

ABSTRACT

Highly active aerobic oxidation of alcohols under mild conditions is achieved by using the catalyst constituted of Au nanoparticles supported on mixed NiAl-oxide derived from its corresponding layered double hydroxide. Besides the contribution of electronic interaction, the enhanced catalytic property of the Au catalyst is mainly attributed to the synergistic effect between the Au and the support on reaction mechanism. The unique support with loading Au nanoparticles comes through structural interconversion between the mixed oxide and the layered double hydroxide upon the water exchange during the reaction, which is beneficial to the fast removal of water from the Au surface and then accelerates the restore of the active sites of Au for oxidation of alcohols.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The selective oxidation of alcohols to the corresponding aldehydes or ketones is one of the most fundamental transformations in the manufacture of fine chemicals and highly valuable intermediates [1]. Such oxidation reactions are traditionally carried out using stoichiometric oxidants such as chromate or permanganate [2], which are toxic and/or expensive and always lead to environmental problems. The green processes involving the use of molecular oxygen (O₂) in the presence of effective heterogeneous catalysts under mild conditions, thus producing water as the only by-product, have received growing interest [3–5]. A number of platinum group metals (PGMs) such as Pd [6–8] and Pt [9,10] have been reported as catalysts for aerobic oxidation of alcohols, which, however, often exhibit poor selectivity with complex substrates [11–13]. Besides, as their resources become scarcer and more expensive, the high cost of PGM-based catalysts has hampered the widespread implementation of many chemical processes [14,15]. Therefore, the findings that more abundant gold has shown the unexpectedly higher activity and selectivity than PGM catalysts in many important reactions are of particular significance [13,16].

Catalysis by gold has been the subject of intensive research interest in the past decades since the breakthrough discovery by Haruta et al. [17]. In comparison with the PGM catalysts, supported Au nanoparticles are emerging as new and highly selective catalysts for the aerobic oxidation of alcohols [18–20]. A further increase in the activity can be achieved by alloying gold with another metal such as Pd, Pt and Cu [21–23]. Hutchings et al. have reported that Au-Pd/TiO₂ exhibited higher activity and selectivity than Au/TiO₂ and Pd/TiO₂ for the oxidation of a variety of alcohols [21]. It has been also known that the catalytic property of gold nanoparticles is highly dependent on the nature of support and the interaction between them [24–26]. Cao et al. have reported the high performance of Au/Ga₃Al₃O₉ for the aerobic alcohol oxidation, due to the unique property of Ga-based mixed oxide for alcohol dehydrogenation [27]. Xu et al. have showed that gold nanoparticles supported on ceria {1 1 0} crystal planes were more reactive than on the {1 1 1} and {1 0 0} crystal planes for the oxidative dehydrogenation of alcohols [28]. It has been also demonstrated that when Au and oxide supports such as NiO or FeO_x were both in the nanometer scale, the catalytic performance of the resulting catalysts was dramatically enhanced for the aerobic oxidation of alcohols [29,30]. And even the product distribution could be tuned by the proper selection of oxide supports for gold nanoparticles [31]. For these documented investigations, the oxide supports play an important role in enhancing the catalytic activity and selectivity of the Au catalysts. To develop gold catalysts with the high performance for the alcohol oxidation

* Corresponding author. Tel.: +86 2583595077.

E-mail address: Dingwp@nju.edu.cn (W. Ding).

reactions under mild conditions, a novel support needs to be suitably designed in consideration of the catalytic cooperation of the two moieties of the catalyst in reaction mechanism.

Layered double hydroxide (LDH) as a kind of unique materials known to all has already attracted considerable attention because its properties can be finely tuned through changing its composition in reserved layered structure. Gold nanoparticles loaded on MgAl-LDH support have been found promising for catalytic oxidation [32,33] and their performances strongly depended on the Mg/Al molar ratio of the support [34]. Li et al. have observed that gold nanoparticles supported on transition metal-containing LDH instead of MgAl-LDH exhibited higher activity in the aerobic oxidation of alcohols due to the promotion of the transition metal on alcohol dehydrogenation [35]. Interestingly, Zhang et al. have reported that Au nanoparticles preferentially deposited on the lateral {1 0 1 0} faces of MgAl-LDH platelets efficiently catalyzed the epoxidation of styrene [36]. It should be mentioned that the LDH materials possess a unique property of structural “memory effect”, which causes the mutual transformation between the mixed oxide and corresponding layered double hydroxide with water absorption and dehydration processes and thus would probably be helpful to further enhance the Au catalytic property for the aerobic oxidation of alcohols by removing the water produced on the metallic sites. Herein, we report that Au catalysts with the mixed NiAl-oxide derived from its LDH precursor as a novel support show high performances for the aerobic oxidation of alcohols under mild conditions. The structural characterization on the mutual transformation and the NMR measurement on isotopic water exchange suggest that the synergistic effect between Au and the support which promotes the removal of water be important to enhance the activity of the catalyst for aerobic oxidation of alcohols.

2. Experimental

2.1. Preparation of supports

The NiAl-LDH with varied composition was prepared by a coprecipitation method as described in the literature with some modifications [37,38]. A mixed aqueous solution of nickel nitrate and aluminum nitrate with a certain molar ratio of Ni to Al, and an aqueous NaOH solution were separately added to 100 mL distilled water at room temperature under vigorous stirring. The pH of the solution was controlled at about 9.0 during the process. The resultant gel-like material was transferred to an autoclave and aged at 100 °C for 48 h. After washed with distilled water, the slurry was mixed with an aqueous Na₂CO₃ solution and stirred at 100 °C for 2 h. The resultant suspension was separated by filtration, washed with distilled water and dried at 80 °C for 24 h. Thus NiAl-LDH-2.0, NiAl-LDH-2.5 and NiAl-LDH-3.0 were obtained in this manner. Similarly, MgAl-LDH with the Mg/Al molar ratio of 2.0 (MgAl-LDH-2.0) was obtained. The mixed NiAl-oxide was obtained from the calcination of the corresponding layered double hydroxide in flowing air at 375 °C for 3 h, denoted as NiAlO-2.0, NiAlO-2.5 and NiAlO-3.0, respectively.

2.2. Preparation of catalysts

The Au/NiAlO-*x* catalysts were prepared by a deposition-precipitation method with some modifications [39]. Typically, 0.8 g of NiAlO-*x* was added to 80 mL of deionized water and the obtained mixture was stirred at room temperature for 2 h. 2.0 mL of aqueous HAuCl₄ (0.024 mol/L) was then added and stirred for 2 h. After the addition of 0.2 g of urea, the mixture was increased to 80 °C and maintained for a period of time. After cooled to room temperature, the suspension was centrifugated, thoroughly washed with

deionized water and dried at 60 °C for 12 h. Finally, the solid was reduced in H₂ at 200 °C for 2 h, denoted as Au/NiAlO-*x*. The reference catalysts, e.g., Au/MgAl-LDH-2.0, Au/Al₂O₃ and Au/TiO₂, were prepared following the same procedure, employing MgAl-LDH-2.0, Al₂O₃ and TiO₂ (P25) as supports, respectively.

The Au/Fe₂O₃ and Au/NiO were prepared according to a coprecipitation method [40,41]. In a typical preparation, 5.24 g of Fe(NO₃)₃·9H₂O and 2.0 mL of aqueous HAuCl₄ (0.024 mol/L) were mixed and added to 16 mL deionized water. After stirring for 10 min, 0.5 mol/L Na₂CO₃ solution was added dropwise to the above mixture until the pH of the solution was adjusted to 8.2. The resulting mixture was stirred at room temperature for 2 h, and the suspension was centrifugated and thoroughly washed with deionized water to obtain the precipitate, which was dried at 80 °C and then calcined at 350 °C for 3 h in static air.

The Al₂O₃-NiO-2.5 with the Ni/Al molar ratio of 2.5 was purposely prepared by impregnating NiO with aqueous solution of Al(NO₃)₃·9H₂O. The resulted slurry was stirred to evaporate water completely, dried and then calcined at 450 °C for 3 h. The solid was crushed and denoted as Al₂O₃-NiO-2.5. The Au/Al₂O₃-NiO-2.5 was also fabricated by the deposition of Au nanoparticles on Al₂O₃-NiO-2.5 according to a deposition-precipitation method [39].

The reference Au/CeO₂ catalyst was prepared by a deposition-precipitation method employing NaOH [26]. Typically, 10 mL of aqueous HAuCl₄ (0.024 mol/L) solution and 30 mL deionized water were mixed, and the pH of the resulting mixture was adjusted to 10.0 by adding 0.2 mol/L aqueous NaOH solution. After the addition of 0.8 g of self-made CeO₂ nanoparticles, the pH of the suspension decreased dramatically and was again adjusted to 10.0 by adding aqueous NaOH solution. After stirred at room temperature for 18 h, the suspension was filtrated, thoroughly washed with deionized water and dried at 100 °C for 16 h.

2.3. Characterization

X-ray Diffraction patterns were recorded on a Shimadzu XRD-6000 using a Cu K α radiation operated at 40 kV and 30 mA. TEM micrographs were recorded on a JEOL JEM-2010 transmission electron microscope. The average sizes of Au nanoparticles and their distribution were estimated by counting more than 200 particles. The Brunauer-Emmett-Teller (BET) specific surface areas of the samples were measured by nitrogen adsorption at 77 K using a Micromeritics tristar ASAP 2020. XPS spectra were obtained under ultrahigh vacuum (<10⁻⁶ Pa) on an UIVAC-PHI 5000 Versa Probe spectrometer with an Al anode (Al K α = 1486.6 eV). All binding energies were calibrated using contaminant carbon (C1s = 284.6 eV) as a reference. The gold loadings and the molar ratio of Ni (Mg) to Al were determined by ICP-AES on an Optima 5300DV.

2.4. Exchange of heavy water

The exchange between D₂O in solvent and H₂O in catalysts was as follows. A certain amount of D₂O and the catalysts were quantitatively put in a closed Teflon-lined autoclave. The resulting mixture was stirred at 80 °C for a period of time. Then, the amount of H₂O exchanged into the solvent was quantitatively measured by ¹H NMR.

2.5. Catalytic test

The aerobic oxidation of alcohols was carried out using a 25 mL three-necked round bottle flask with a reflux condenser. Typically, the reactor was charged with 0.12 g of catalyst (0.006 mmol Au), 1 mmol (or 0.5 mmol) of substrate, 10 mL of *o*-xylene and 0.5 mmol of mesitylene (the internal standard). Molecular oxygen (flow rate = 20 mL/min) was bubbled through the reaction mixture,

Download English Version:

<https://daneshyari.com/en/article/39611>

Download Persian Version:

<https://daneshyari.com/article/39611>

[Daneshyari.com](https://daneshyari.com)