



Efficient low-temperature selective hydrogenation of esters on bimetallic Au–Ag/SBA-15 catalyst

Jianwei Zheng, Haiqiang Lin, Ya-nan Wang, Xinlei Zheng, Xinping Duan, Youzhu Yuan*

Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry for Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:

Received 7 August 2012

Revised 26 September 2012

Accepted 27 September 2012

Available online 30 October 2012

Keywords:

Gold

Silver

Alloy

Hydrogenation

Dimethyl oxalate

Methyl glycolate

Ethylene glycol

ABSTRACT

Gold (Au)–silver (Ag) bimetallic catalyst supported on ordered mesoporous silica SBA-15 exhibits unprecedentedly high activity and superior stability for the selective hydrogenation of dimethyl oxalate to methyl glycolate at a low temperature of 418 K. By contrast, monometallic Au/SBA-15 and Ag/SBA-15 catalysts are almost inactive under identical conditions. A combined tuning of particle dispersion and its surface electronic structure is shown as a consequence of the changes in the size and valence band structure of Au and Ag, which leads to significantly enhanced synergy. Considerably reduced apparent activation energies indicate that special active sites with the ability to activate substrate molecules more efficiently are generated in Au–Ag alloy nanoparticles. The Au–Ag bimetallic catalyst also displays excellent activity for the selective hydrogenation of some other unsaturated or saturated esters and acetic acid.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The selective hydrogenation of esters to corresponding alcohols is an important chemical transformation that is gaining both academic and industrial interests [1–4]. For example, the hydrogenation of oxalates such as dimethyl oxalate (DMO) to ethylene glycol (EG) is known to consist of two sequential reactions, that is, DMO hydrogenation to methyl glycolate (MG) and MG hydrogenation to EG [5]. The reaction is key connection to the process of indirect synthesis of EG from coal [6,7]. In fact, apart from the importance of EG, MG is also extensively used in the synthesis of pharmaceutical products, fine chemicals, and perfumes [8]. Compared to ketones and aldehydes, esters are relatively resistant to reduction. In the industrial sector, the heterogeneous hydrogenation of some fatty esters is conducted at relatively high temperatures (473–573 K) and high hydrogen pressures (20–30 MPa) using transition-metal catalysts [9,10]. Global energy consumption growth and a serious lack of energy resources restrict the progress and development of modern industries. Therefore, catalysts should have high activity and selectivity under mild conditions to realize clean and efficient energy utilization.

On the other hand, although Bond and coworkers reported in 1973 the hydrogenation of olefins over supported gold catalysts

* Corresponding author.

E-mail address: zyuan@xmu.edu.cn (Y. Yuan).

[11], the catalysts have been received tremendous attention only after the pioneering work of Haruta et al. [12] and Hutchings [13] in CO oxidation and hydrochlorination. Up to date, except the successful application of nanosized Au catalysts in oxidation reactions [14], their applications to chemoselective hydrogenation reactions, such as transformation of α,β -unsaturated aldehydes to α,β -unsaturated alcohol [15,16], selective partial hydrogenation of alkyne, alkadiene and alkene [17], methanol synthesis from CO and CO₂ [18], water–gas shift reaction [19] and like, are also of great potential. Nonetheless, Au catalysts possess relatively low activity to activate and dissociate dihydrogen compared with other metals, such as Ni, Pd, and Pt [20,21]. In addition, pure Au also generally exhibits poor stability and lifetime because of the ready aggregation of Au nanoparticles (NPs).

The addition of a second metal is found to restrain the aggregation of monometals [22,23]. The physical and chemical properties of alloy particles usually differ from those of monometallic particles and significantly vary as a function of the composition and particle sizes. The nanoalloy catalysts usually show complementary advantages and synergistic effects. It has been reported that a number of Au-containing bimetallic catalysts like Au–Cu [23,24], Au–Ag [25–30], Au–Pt [31], and Au–Pd [32] can exhibit improved catalytic performances in a variety of reactions. Among them, Ag, an IB element, holding highly analogous cell parameters and high affinity for Au atoms, can readily form homogeneous bimetallic Au–Ag alloy without phase segregation. Introduction

of Ag atoms into Au NPs provides a simple and feasible mean to tune the electronic and geometric features of Au-based catalysts. The synergistic effect and improved activity via Au–Ag alloying have been obtained in particularly for low-temperature CO oxidation [25–28]. As for the chemoselective hydrogenation of carbonyl group [29] and the selective hydrogenation of acetylene [30], the combination of Au and Ag can also exhibit enhanced performance. Unlike Au, Ag lacks affinity toward CO but interacts more strongly with hydrogen than Au [33], particularly after proper pretreatment [34,35]. Recently, Wittstock et al. reported that a nanoporous Au catalyst by dealloying of Au–Ag alloys showed high efficiency in oxidative coupling of methanol, and they evidenced that the residual amount of Ag could regulate the availability of reactive oxygen species and promote the catalytic activity [36,37]. However, to the best of our knowledge, the catalytic properties of supported Au–Ag bimetallic catalysts for the gas-phase selective hydrogenation of ester have not yet been studied.

The current study reports an ordered mesoporous silica SBA-15-supported Au–Ag catalyst (Au–Ag/SBA-15) for the selective hydrogenation of esters. The Au–Ag/SBA-15 catalyst displayed excellent performance in the selective hydrogenation of DMO to MG at a temperature as low as 418 K. To determine the underlying reason for the promoting and stabilizing effect between Au and Ag, detailed investigations on the catalyst structures were conducted. Nitrogen sorption, X-ray diffraction (XRD) patterns, and transmission electron microscopy (TEM) were employed to observe the crystal grain size, morphology, architecture, and dispersion of the NPs on the support. UV–visible diffuse reflectance spectroscopy (UV–vis DRS) was used to study the structure and the electronic interactions of the resultant Au–Ag system. The electronic property modifications of the Au–Ag catalysts were monitored using the binding energy (BE) derived from X-ray photoelectron spectroscopy (XPS). These characterizations elucidate the key role of modified surface chemistry and the synergistic effect on bimetallic Au–Ag catalysts, showing the electronic properties and possible mechanism of Au–Ag alloy NPs on inert silica supports for selective hydrogenation.

2. Experimental

2.1. Catalyst preparation

The ordered mesoporous silica SBA-15 was synthesized according to a procedure described in literature [38]. Amino-functionalized SBA-15 was prepared with 3-aminopropyltrimethoxysilane (APTES, Sigma–Aldrich) according to a method described in literature [39]. About 3.0 g of SBA-15 and 5.0 g of APTES were mixed together with 100 mL of ethanol. The mixture was refluxed at 363 K for 24 h, and the resultant solid (denoted as NH₂-SBA-15) was collected by filtration, washed with ethanol, and dried at 333 K.

The Au–Ag/SBA-15 catalyst was prepared using a sequential deposition–reduction method. The required amount of 0.0025 mol L⁻¹ HAuCl₄ solution, 50 mL of deionized water, and 1.0 g of NH₂-SBA-15 were placed in a 500 mL beaker. Then, 20 mL of 0.066 mol L⁻¹ NaBH₄ solution was subsequently added dropwise to the beaker under vigorous stirring. The solution was further stirred for 15 min, and then, the solid was filtered and thoroughly washed with a large quantity of water to generate the Au/NH₂-SBA-15. Next, a required amount of 0.0012 mol L⁻¹ AgNO₃ solution was added to the Au/NH₂-SBA-15 in a beaker. Subsequently, 20 mL of the 0.066 mol L⁻¹ NaBH₄ solution was added dropwise to the beaker under vigorous stirring. The solution was further stirred for 15 min, and then, the solid was filtered and thoroughly washed with a large quantity of water. The solid was dried overnight, calcined at 773 K for 6 h, and then reduced in a 5%H₂–95%N₂ atmo-

sphere at 623 K for 4 h to produce the final catalyst labeled as xAu–yAg/SBA-15 (x and y denote the weight percentage loading of Au and Ag; the percentage sign was removed for naming simplicity). The monometallic catalysts Au/SBA-15 and Ag/SBA-15 were prepared by the same procedure described above.

For comparison, the Ag/SBA-15-IMP catalysts were prepared using a volumetric immersion method. For example, 1.0 g of SBA-15 was dissolved in 3 mL of 0.145 mol L⁻¹ AgNO₃ solution under stirring. The mixture was aged at room temperature for 10 h without light. After filtration, the solid was dried at 383 K, calcined at 623 K for 4 h in air, and then reduced in a 5%H₂–95%N₂ at 623 K for 4 h to produce the 4.5Ag/SBA-15-IMP catalyst.

The Au and Ag loadings of the samples were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) using a Thermo Elemental IRIS Intrepid II XSP. The sample was treated by aqua regia at 363 K for 30 min, and the resultant solution was heated until it evaporated. The residue was diluted with 5% HNO₃ and filtrated to a 25 mL volumetric flask before ICP-OES measurement.

2.2. Catalyst characterizations

N₂ sorption isotherm was measured at 77 K using a Micromeritics TriStar II 3020 porosimetry analyzer. The samples were degassed at 573 K for 3 h prior to the measurements. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The average pore diameter and pore size distributions were determined using the Barret–Joyner–Halenda method according to desorption isotherm branch. The total pore volume depended on the absorbed N₂ volume at a relative pressure of approximately 0.99.

Powder XRD patterns were obtained using a Philips PANalytical X'pert Pro diffractometer equipped with a graphite monochromator and Cu K_α radiation (40 kV and 30 mA). The diffraction lines were identified by matching them with reference patterns in the JCPDS database.

The measurements of TEM and energy-dispersive X-ray spectroscopy (EDX) operated in scanning TEM (STEM) mode were performed on a Philips Analytical FEI Tecnai 30 electron microscope operated at an acceleration voltage of 300 kV. The catalyst powders were lightly ground and ultrasonically dispersed in ethanol at room temperature. The as-obtain solution was then dropped into copper grids supported by holey carbon films.

XPS was performed using a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) equipped with an Al K_α X-ray radiation source ($h\nu = 1486.6$ eV). A flood gun with variable electron voltage (from 6 eV to 8 eV) was used for charge compensation. The raw data were corrected for substrate charging with the BE of the Si_{2p} peak (103.4 eV), as shown in the XPS handbook. The measured spectra were fitted using a least-squares procedure to a product of Gaussian–Lorentzian functions after removing the background noise. No trace of chlorine or sodium was detected on the reduced catalyst samples using XPS. The concentration of each element was calculated from the area of the corresponding peak and calibrated with the sensitivity factor of Wagner.

The UV–vis DRS of as-reduced catalysts were collected on a UV–vis–NIR Spectrophotometer CARY 5000 scan spectrophotometer. Prior to UV–vis measurements, all catalyst precursors were freshly reduced in a 5%H₂–95%N₂ atmosphere at 623 K. The reduced samples were directly used for the UV–vis measurement.

CO adsorption by FTIR was conducted on a Nicolet 6700 spectrometer using a stainless steel cell with CaF₂ windows, which allowed in situ treatment for the sample up to 873 K under different atmospheres or high vacuum. Briefly, 30 mg of dried catalyst was compressed into a self-supporting wafer and carefully loaded into the in situ cell. The catalyst wafer was reduced under a flow of

Download English Version:

<https://daneshyari.com/en/article/6527784>

Download Persian Version:

<https://daneshyari.com/article/6527784>

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