Copper ferrite supported gold nanoparticles as efficient and recyclable catalyst for liquid-phase ethanol oxidation

Wenjia Hu [a], Deping Li [a], Yang Yang [a], Tao Li [a,b,*], Hanping Chen [b], Peng Liu [a,b,*]

[a] Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

ABSTRACT

Copper-containing spinel-supported gold nanoparticle catalysts are optimized toward high activity and stability in liquid-phase aerobic oxidation of aqueous bioethanol to acetic acid under mild hydrothermal conditions (3 MPa O_2, 140 °C). In this work, we investigate the structure–performance relationships of supported gold catalysts by changing the composition and calcination temperature of spinel supports to gain insight into the gold-support interaction. The support effect specially acts on the rate-controlling ethanol activation step, with ferrite-spinel outperforming aluminate and chromite-spinels, and the activity increasing with the copper content in the spinels. Moreover, support calcination at 700 °C results in the optimal $Au/CuFe_2O_4$ catalyst, which can be magnetically separated and reused at least five times. The improved reusability is likely attributed to the alloying between AuNPs and Cu^0 on the partially reduced $CuFe_2O_4$. The presence of negatively charged $Au^{\delta-}$ and redox active Fe^{2+} species in the spent $Au/CuFe_2O_4$ catalyst points to a specific $Au^{\delta-}$-Fe^{2+} synergy for the enhanced activation of O_2 and ethanol. With the help of negatively charged AuNPs, heterogeneous Fenton-like reaction is suggested to provide hydroxyl radicals for the C—H bond activation of ethanol.

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1. Introduction

With increased annual production (over 100 billion liters) and reduced cost, bioethanol is holding considerable promise as a renewable and versatile platform molecule for the production of a variety of value-added chemicals to decrease the use of fossil energy reserves [1,2]. Crude bioethanol is produced by biomass fermentation and contains up to 90% water, which usually needs to be removed before use [3]. Because water-removing is an energy-consuming process, it is with great interest that bioethanol could be converted to chemicals through reactions that are not sensitive to the water content. Consequently, aqueous bioethanol has been tested for producing valuable products such as acetic acid [4–15]. Although acetic acid is mainly synthesized by carbonylation of methanol catalyzed by a Rh complex catalyst [16], the direct catalytic oxidation of aqueous bioethanol to acetic acid is strongly desired.

Various heterogeneous catalysts have been demonstrated to be active in the formation of acetic acid by ethanol oxidation in gas phase and in liquid phase [16]. In contrast to the need of high temperatures for the gas phase oxidation, the processing of ethanol oxidation in aqueous phase largely proceeds at lower temperatures (<200 °C). Ruthenium-, palladium-, platinum-, and gold-based catalysts are effective in the liquid-phase oxidation of aqueous ethanol with molecular oxygen [4–15]. Among these noble metal catalysts, supported gold nanoparticles (AuNP) have drawn more attention due to the higher resistance to oxidation [4–11]. Christensen and co-workers firstly reported the aerobic oxidation of ethanol in water over $MgAl_2O_4$-supported Au, Pt and Pd catalysts [4], finding that the AuNP catalyst shows similar catalytic activity but much higher acetic acid selectivity than the Pd or Pt catalyst. The subsequent studies confirmed that the catalytic performance of supported Au catalysts depend on the size of AuNP [6] and the nature of support [5,7,11]. For instance, AuNPs supported on reducible TiO_2 exhibited similar performance as $Au/MgAl_2O_4$, whereas Au/C showed inferior performance [5]. Haruta and his group screened various unitary oxide-supported AuNP catalysts, demonstrating that NiO was the preferable support and Cu doping could further improve the selectivity to acetic acid [11]. However,

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* Corresponding authors at: Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

E-mail addresses: taoli@hust.edu.cn (T. Li), pengliu@hust.edu.cn (P. Liu).

catalyst stability remains a challenge in this aqueous oxidation due to the facile AuNP aggregation under hydrothermal conditions.

In aerobic oxidation with AuNPs, the strong interactions between metal and support usually result in the enhanced catalytic performance [17–23]. For instance, Au/CuO [22,23] catalysts showed good activity and better stability than bimetallic AuCu/SiO$_2$ catalyst [24] in the liquid-phase oxidation of alcohols. One of the present authors discovered that Au/MgCuCr$_2$O$_4$ outperformed Au/MgAl$_2$O$_4$ and Au/CuO-SiO$_2$ catalysts in the gas-phase oxidation of ethanol to acetaldehyde, without gold sintering and deactivation during 500 h on-stream [25]. Its exceptional performance is attributed to a specific Au-Cu interaction at the interface of Au/MgCuCr$_2$O$_4$ for O$_2$ and ethanol activation [26–28]. Since the activation of O$_2$ and ethanol is crucial for both the gas-phase and liquid-phase ethanol oxidation, it would be interesting to know whether the beneficial Au-Cu interaction also works in the liquid-phase ethanol oxidation. Herein, we focus on aerobic oxidation of aqueous ethanol by using Cu-containing spinel-supported AuNP catalysts. The scope of support was expanded to chromite, aluminate and ferrite spinels to screen the most efficient gold-support interaction. The results evidently show that magnetically separable copper ferrite (CuFe$_2$O$_4$) is the best choice when high catalytic activity and reusability are desired. The effects of calcination temperature of CuFe$_2$O$_4$ and reaction conditions were also investigated to optimize the catalytic performance. Kinetic studies, controlling experiments and characterization of the spent catalysts evidence that the superior performance of Au/CuFe$_2$O$_4$ catalyst is primarily due to a specific Au$^{\delta-}$-Fe^{2+} synergy for the enhanced activation of O$_2$ and ethanol.

2. Experimental

2.1. Materials

Gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O) was purchased from Sigma-Aldrich. Metal nitrates (Cu(NO$_3$)$_2$·3H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O), sodium hydroxide (NaOH), ethanol (absolute, >99.8%), acetaldehyde, acetic acid and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl (TEMPO, 98%), diphenylamine (Ph$_2$NH, 99%), and bromotrichloromethane (CBrCl$_3$, 97%) were purchased from Adamas Reagent Co., Ltd. All chemicals were used as received.

2.2. Catalyst preparation

All spinels were prepared by a co-precipitation method [25]. Typically, a mixed metal nitrate solution in the molar ratio Mg(NO$_3$)$_2$/Cu(NO$_3$)$_2$/Fe(NO$_3$)$_3$ = 3/1/8 was prepared. To this solution was added dropwise 1 M NaOH solution to bring the pH to 11 in order to ensure full precipitation. The precipitate was filtered and washed until the pH of filtrate was neutral. The solid was dried at 110 °C overnight and grinded, then the solid was further calcined at 700 °C in air for 6 h to yield a Mg$_{0.75}$Cu$_{0.25}$Fe$_2$O$_4$ spinel support. Except for the aluminate spinels (MgAl$_2$O$_4$, Mg$_{0.75}$Cu$_{0.25}$Al$_2$O$_4$ and CuAl$_2$O$_4$), which were calcined at 900 °C in air for 6 h, all chromite (MgCr$_2$O$_4$, Mg$_{0.75}$Cu$_{0.25}$Cr$_2$O$_4$ and CuCr$_2$O$_4$) and ferrite (MgFe$_2$O$_4$, Mg$_{0.75}$Cu$_{0.25}$Fe$_2$O$_4$, Mg$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$, Mg$_{0.25}$Cu$_{0.75}$Fe$_2$O$_4$, and CuFe$_2$O$_4$) spinels were calcined at 700 °C in air for 6 h unless otherwise stated. Spinel supported AuNP (Au/spinel) catalysts were prepared by homogeneous deposition–precipitation of HAuCl$_4$ using urea as the precipitation agent. The targeted gold loading was 1.0 wt%. The catalysts were finally calcined in air at 300 °C for 5 h.

2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on an Empyrean apparatus using Cu K$_\alpha$ radiation (40 kV and 30 mA). Nitrogen physisorption was done on a Tristar 3000 automated gas adsorption system. Scanning electron microscopy (SEM) images were taken using a FEI Nova NanoSEM 450 microscope. Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai G2 20 electron microscope at an acceleration voltage of 200 kV. The average size of AuNP was calculated by measuring ∼300 metal particles from several images. The gold loading was determined by a Perkin Elmer AA-300 atomic absorption spectrometer (AAS) after extracting the metal in aqua regia. The magnetization and coercivity of the ferrite spinel-supported AuNP catalysts were measured by using a Model 3472-70 GMW vibrating sample magnetometer (VSM) with a maximum magnetic field of 15 kOe. Temperature-programmed reduction (TPR) experiments were performed on Micrometrics AutoChem 2920II instrument. Typically, 20 mg of the sample was loaded in a U-shape quartz tube and pretreated in argon at 350 °C for 1 h. After cooling to room temperature in flowing Ar, the sample was reduced in 10 vol% H$_2$ in Ar at a flow rate of 10 mL/min, while it was heated from room temperature up to 800 °C at a ramp rate of 10 °C/min. The outlet gas was detected by the thermal conductivity detector. X-ray photoelectron spectroscopic (XPS) measurements were conducted on an AXIS-ULTRA DLD-600 W spectrometer with Al Kα irradiation and the binding energies were calibrated by using the C 1s peak of contaminant carbon at 284.5 eV as an internal standard.

2.4. Catalytic tests

Catalytic oxidation of ethanol in aqueous phase was performed in a stainless steel autoclave with Teflon liner (20 mL) and magnetic stirring. Typically, the autoclave was charged with 2 mL of 5 wt% ethanol aqueous solution and a certain amount of gold catalyst, with the molar ratio of ethanol to gold (ethanol/Au) being 2000, then the autoclave was sealed and pressurized with O$_2$ to 3.0 MPa at room temperature. When the temperature of the autoclave reached 140 °C, the reaction was initiated by switching on the magnetic stirring (800 rpm). After a certain reaction time, the reaction was stopped by cooling the autoclave in an ice-water bath. The catalyst was separated and reused up to five times. The liquid products were analyzed on a Fuli-9070 GC with a KB-5 capillary column and a FID detector. The gas phase carbon-containing by-products were analyzed on another GC with a TDX-01 packed column and a TCD detector. In all cases, the selectivity of CO$_2$ was below 3% by carbon calibration.

3. Results and discussion

3.1. Characterization of spinel-supported AuNP catalysts

We firstly studied the physico-chemical properties of spinel-supported AuNP catalysts. The chromite, aluminate and ferrite supports with different Mg/Cu molar ratio basically had the same structure as MgCr$_2$O$_4$ (JCPDS 10-0351), MgAl$_2$O$_4$ (JCPDS 21-1152), and MgFe$_2$O$_4$ (JCPDS 17-0464) spinels, respectively, as confirmed by XRD analysis. The Mg-free supports showed identical structure as CuCr$_2$O$_4$ (JCPDS 34-0424), CuAl$_2$O$_4$ (JCPDS 33-0448), and CuFe$_2$O$_4$ (JCPDS 34-0425) spinels. The XRD patterns did not change upon gold loading (Fig. 1), except for a small peak at ∼38.2° originating from the (1 1 1) plane of gold visible in some samples.

SEM was used to study the morphology of ferrite spinel-supported AuNP catalysts (Fig. S1 in the Supporting Information).