



Investigation of hollow bimetal oxide nanomaterial and their catalytic activity for selective oxidation of alcohol



Wenbin Gao^{a,b}, Feng Li^{a,b}, Hongfei Huo^{a,b}, Yuanyuan Yang^{a,b}, Xiang Wang^{a,b}, Yu Tang^{a,b}, Pengbo Jiang^{a,b}, Shuwen Li^{a,b}, Rong Li^{a,b,*}

^a State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, PR China

^b Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, PR China

ARTICLE INFO

Keywords:

Metal oxide
Hollow nanoparticles
Liquid phase
Kinetic law
Alcohol oxidation

ABSTRACT

The aerobic oxidation procedure utilized sustainable non-noble-metal catalysts has been a long-standing objective in laboratory and industrial research. The synthesized hollow bimetal oxide nanoparticles catalysts (HNPs) as a stable and efficient catalyst, which was applied to the selective oxidation of alcohols with molecular oxygen as oxidant, is reported. The catalytic performance of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4@\text{C}$ HNPs was tested via selective aerobic oxidation catalytic reaction of cinnamyl alcohol in the liquid phase. The results prove that the $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4@\text{C}$ HNPs exhibit ~ 90% yield for alcohol oxidation, which can be conveniently separated and recycled from reaction system by an external magnetism. Furthermore, the catalyst can be reutilized for at least 5 runs without a distinct activity reduction. A feasible reaction mechanism over the bimetal catalyst for the alcohol oxidation was proposed. The surface effect between metal oxide nanoparticle and carbon support, and relatively high and easy reducibility grant favorable catalytic activity of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4@\text{C}$ HNPs. This makes the $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4@\text{C}$ HNPs a very significant catalyst for aerobic catalytic oxidation reaction of alcohols in the liquid phase for industrial manufacture.

1. Introduction

Selective aerobic oxidation of alcohol to the corresponding aldehyde or ketone has turned out to be a very pivotal reaction process in the current of laboratory and chemical industry. Utilization of corresponding products as diverse intermediates for synthesis of key fine chemicals is emerging as a complementary alternative to the current energetically inefficient and/or environmentally unfriendly multi-step reactions such as pharmaceuticals, agrochemicals and polymers [1,2]. Traditionally, many toxic stoichiometric oxidative reagents are performed for this oxidation process, which fabricate a lot of waste and pollutants, and are unsanctioned in viewpoint of green and environmental chemistry [3]. From both green and sustainable standpoints, there are a strongly moving toward searching and developing the environmental-friendly and green oxidant in this chemosynthesis, such as the air or O_2 being the ideal oxidant from the environmental point of view [4]. Since these oxidants are readily securable, inexpensive, vast pollution-free natural gas, and water is the main byproduct, that catalytic process is industrially promising alternatives for available alcohol oxidation [5].

In recent years, noble metal nanoparticles have shown a high activity to effect alcohol oxidation using molecular oxygen under moderate temperatures and pressures [1–3]. The heterogeneous precious metal catalysts have been abundantly employed in aerobic oxidation catalysis reaction of alcohols owing to their perfect catalytic property [6], for example, many efficient catalysts based on gold [7,8], palladium [9,10], and platinum [8,11], have been extensively reported and obtained a good result. However, these catalysts possess obvious drawbacks used in practical application, which are expensive cost, limited availability and toxic properties [12,13]. Therefore, considering the drawbacks of noble metal catalysts, it would be still desirable to develop non-noble metal catalysts to affect alcohol oxidation. Moreover, a more significant shortcoming with some of these catalysts in solid-liquid state reaction using molecular oxygen as the oxidant are sensitive for the deactivation of alcohol oxidation due to substrates overoxidation, and a basic condition is needed to activate and enhance catalyst for reaction process [14–16].

Based on the reports of the above, and considered the past study of the non-noble metal and non-noble oxides due to their properties such as non-toxicity, lower cost, fine chemical stability and environmentally

* Corresponding author at: State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, PR China.

E-mail address: liyirong@lzu.edu.cn (R. Li).

<https://doi.org/10.1016/j.mcat.2018.01.028>

Received 28 October 2017; Received in revised form 23 January 2018; Accepted 23 January 2018

2468-8231/© 2018 Elsevier B.V. All rights reserved.

friendly [17–22], for example Co_xO_y [23], Fe_xO_y [24], Mn_xO_y [25–28], CeO_x [29], VO_x [22], and many bimetal oxides, including $\text{Co}_2\text{Mn}_3\text{O}_8$ [30], Co-Mn-Al complex oxides [31], Co-Mn oxides [32], Mo-Fe bimetal oxides [33] and others. Meanwhile, cobalt oxide and iron oxide are excellent catalyst for dehydrogenation [24,34,35], CO oxidation [36], CO_2 conversion [37], alcohol oxidation reaction [38], and others. carbon materials due to low density, abundant surface functional groups, well-diffusion performances and higher specific surface area, are a widely-applied support for plentiful catalytic nanoparticles, and hollow nanoparticles with low density, higher surface-to-volume, their prospective applications in catalysis and others based on nanoscale Kirdendall effect are also proven to be fascinating catalytic support for numerous reaction [39,40]. In addition, the experiments have demonstrated that the iron oxide and carbon support have special interaction, the negatively charged surface oxygen functional groups of the carbon support serve as strongly active sites for anchoring positively charged Fe^{3+} ions and lead to high dispersion of iron oxide species. These oxygen functional groups also provide a suitable coordinate environment to increase the electron density of iron centres and form efficient active sites for the oxidation of alcohols with molecular oxygen [41].

Herein, considering the previous reported catalysts employed in basic condition and expensive cost limited availability, the catalytic property of the $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4@\text{C}$ HNPs catalysts was employed in the selective oxidation of alcohol with molecular oxygen in the liquid phase, which shows > 95% alcohol conversion and ~ 90% aldehyde yield without any promoter (eg., NaOH). In addition, the catalyst can be reused after at least 5 runs with a good activity and recycled with external magnetic. This catalyst is a useful and a meaningful candidate for aerobic catalytic oxidation reaction of alcohols in the liquid phase system.

2. Experimental

2.1. Reagents and chemicals

All reagents and chemicals were analytical grade and used as received without any further purification. Ferric (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5%) was purchased from Chengdu Kelong Chemical Reagents Co., Ltd. Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.0%) was purchased from Shanghai Zhongqin Chemical Reagents Co., Ltd. Sodium hydroxide (NaOH, 96.0%) was purchased Chemical Reagents Manufacturing Co., Ltd. Sodium oleate ($\text{C}_{17}\text{H}_{33}\text{COONa}$ or NaOA, 99.5%) was purchased from Tianjin Guangfu Chemical Reagents Co., Ltd. Absolute ethanol and hexane was purchased from Lianlong Bohua (Tianjin) Pharmaceutical Chemical Co., Ltd.

2.2. Preparation of the catalyst

In brief, 1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.404 g), 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 g) and 5 mmol NaOA (1.522 g) were dissolved in the solution with 10 mL of deionized water, 20 mL absolute ethyl alcohol, and 30 mL of hexane. The mixture solution was heated to 70 °C with magnetic stirring for about 30 min. Then 5 mmol of NaOH (0.200 g) was added to the solution and the mixture solution was stirred for 4 h. After cooled down, the mixture solution was dried at 80 °C for 12 h and a precipitate was obtained. The precipitate mixed with 10 g of Na_2SO_4 was grind to form the homogeneous power, which was heated to 500 °C under nitrogen at heating rate of 10 °C min^{-1} and kept the temperature for 3 h. After cooled down, the black product was washed with deionized water and absolute ethanol, and it was dried at 60 °C for 12 h. Finally the metal nanoparticles (MNPs) loaded on the carbon (MNPs/C) nanocomposites was prepared, which was heated in air 400 °C for 2 h at heating rate of 5 °C min^{-1} , the metal oxide nanoparticles (MONPs) loaded on the carbon (MOHNPs@C) nanocomposites was obtained.

2.3. Catalyst characterization

The crystal phase of the materials was evaluated by X-ray diffractometer (XRD) with a Rigaku D/max-2400 diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Running condition of XRD and current are 40 kV and 40 mA and the X-ray source in the 2 theta range of 20–90°. The full width at half maximum (FWHM) of the XRD line can be used the Schere's formula to estimate the crystallite size from the following equation:

$$D_{\text{XRD}} = K\lambda/\beta\cos\theta$$

Where is the observed angular width at half maximum intensity of the peak, K is a dimension less number (equal to 0.89), is the x-ray wavelength (1.5418 Å for Cu K α) and θ is the diffraction angle. And Inductive coupled plasma optical emission spectrometer (ICP-OES) analysis was carried out with Perkin Elmer (Optima-4300DV) to measure the metal content.

Scanning electron microscopy (SEM) was utilized to observe the image of the samples daubing Carbon double-sided conductive tape with MIRA3 TESCAN. The morphology of the synthesized catalyst was investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) with a field emission gun transmission electron microscopy Tecnai G²TF²⁰ operating at 300 kV and EDX was measured on a Tecnai G²TF²⁰ microscope. The specimens were dispersed in ethanol and on a holed carbon-coated Cu grid. Nitrogen physisorption isotherms were carried out at –195.8 °C on a static volumetric instrument (TriStar II 3020 V1.04). The specific surface area was calculated by the Brunauer–Emmett–Teller method.

A physical magnetic quality of the sample was researched by a Quantum Design vibrating sample magnetometer (VSM) at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on the PHI-5702 instruments with an Mg anode (Mg K α $h\nu = 1253.6 \text{ eV}$) at a base pressure of 5×10^{-8} mbar). The revision of the binding energies (BE) was implemented with the C1 s peak of extraneous C at 284.6 eV.

2.4. Catalytic tests

The reaction was tested in a 25 mL, a three-necked batch reactor with a suitable reflux condenser, oil bath, and thermocouple at atmospheric pressure. Typically, 4 mmol of substrates, 10 mL of o-xylene and 20 mg of catalyst were mixed with stirring at 393.15 K oxygen (20 mL/min) was continuously brought in bottle and reaction time is 3 h. In addition, the reaction catalyst can be recycled and collected by the external magnetic force, and then it was washed with deionized water and absolute ethanol several times, and following by a heat treatment before next time. Our reaction sample was analyzed by GC–MS (Agilent 6,890N/5,937N).

The catalytic activity was calculated as follows: % conversion = $100 \times ([C_0 - C_1]/[C_0])$, and % Yield = $100 \times [C']/[C_0]$, based on the initial $[C_0]$ and the final $[C_1]$ concentrations of organic substrate and the reaction $[C']$ concentrations of aldehyde. Turnover Frequency (TOF) = mol number of substrate converted/[moles number of active sites \times reaction time].

3. Result and discussion

3.1. Characterizations catalyst

To characterize and prove the morphology of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ HNPs@C, the TEM, HRTEM-mapping and EDX were carried out. Fig. 1a presents a typical TEM image of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ HNPs@C, which clearly exhibits a hollow structure metal oxide nanoparticles of the catalyst, and the sample of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ HNPs@C was successfully obtained. Fig. 1b showed a part of a HNSs with HRTEM and the corresponding morphology sketch. It was observed that the shell of a thin layer of

Download English Version:

<https://daneshyari.com/en/article/8916895>

Download Persian Version:

<https://daneshyari.com/article/8916895>

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