



Selective oxidation of styrene catalyzed by cerium-doped cobalt ferrite nanocrystals with greatly enhanced catalytic performance



Jinhui Tong^{a,*}, Wenyan Li^a, Lili Bo^b, Huan Wang^b, Yusen Hu^b, Zhixia Zhang^b, Abdulla Mahboob^{c,*}

^a College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, People's Republic of China

^b College of Science, Gansu Agricultural University, Lanzhou 730070, People's Republic of China

^c Department of Chemistry, School of Science and Technology, Nazarbayev University, 53 Kabanbay Batyr Avenue, Astana 010000, Kazakhstan

ARTICLE INFO

Article history:

Received 21 July 2016

Revised 1 October 2016

Accepted 3 October 2016

Available online 12 November 2016

Keywords:

Sol–gel autocombustion

Magnetic nanocrystals

Rare-earth-doped ferrites

Styrene oxidation

Hydrogen peroxide

ABSTRACT

The rare earth metal Ce-doped cobalt ferrite samples $Ce_xCo_{1-x}Fe_2O_4$ ($x = 0.1, 0.3, 0.5$) were prepared by the sol–gel autocombustion route. The as-prepared samples were characterized by X-ray diffractometry, scanning electron microscopy, transmission electron microscopy, ICP–atomic emission spectroscopy, and N_2 physisorption. Their catalytic performance was evaluated in oxidation of styrene using hydrogen peroxide (30%) as oxidant. Compared with pristine $CoFe_2O_4$, the Ce-doped samples were found to be more efficient catalysts for the oxidation of styrene to benzaldehyde, with greatly enhanced catalytic performance. Especially, when $Ce_{0.3}Co_{0.7}Fe_2O_4$ was used as catalyst, 90.3% styrene conversion and 91.5% selectivity for benzaldehyde were obtained at 90 °C for 9 h reaction. The catalyst can be magnetically separated easily for reuse, and no obvious loss of activity was observed when it was reused in five consecutive runs.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Nanospinel ferrites with the general formula AB_2O_4 , as a class of chemically and thermally stable materials, are of great fundamental and technological importance due to their structural, electronic, magnetic, and catalytic properties [1–4]. The complex metal oxides have been widely used in diverse areas such as magnetic recording and separation [5], ferrofluids [6], magnetic resonance imaging (MRI) [7], biomedicine [8], gas sensors [9], high-quality ceramics [10,11], and superparamagnetic materials [12–14]. Especially, they have been widely used as catalysts in liquid phase reactions due to their redox and magnetic recovery properties [15]. As a matter of fact, these catalysts can be separated from a reaction medium by simply placing a magnetic field on the surface of a flask. Spinel ferrites are found to be highly active toward a number of industrial processes, such as oxidative dehydrogenation of hydrocarbons [16,17], decomposition of hydrogen peroxide [18], treatment of automobile-exhaust gases [19], oxidation of various compounds such as chlorobenzene [20], phenol hydroxylation [21], alkylation reactions [22–24], hydrodesulfurization of crude petroleum [20], and catalytic combustion of methane [25,26].

The physical and chemical properties of the ferrites are strongly dependent on their shapes, sizes, and constituents, which are closely related to the method of preparation [27–29]. A widely adopted strategy for synthesizing new ferrites with various constituents and properties is doping other elements in the pristine ferrites [30–35]. As for preparation methods, a most popular one is the sol–gel autocombustion method. This method combines the advantages of chemical sol–gel and combustion processes and gives rise to a thermally induced anionic redox reaction. The energy released from the reaction between oxidant and reductant is adequate to form a desirable phase within a very short time. The process exhibits the advantages of inexpensive precursors and a simple preparation process and can produce highly reactive nano-sized powder [36,37].

Catalytic oxidation of styrene at side chains is of great interest for both academic research and utilization in the industry, because the products styrene oxide and benzaldehyde are important and versatile synthetic intermediates in chemical industries [38]. Especially, benzaldehyde is a very valuable chemical that has widespread applications in perfumery, pharmaceuticals, dyestuffs, and agrochemicals [39]. Traditionally, this reaction has been carried out in both homogeneous and heterogeneous catalyst systems [40–42]. However, homogeneous catalysts have recently become less attractive because of difficulty in separating products and catalysts. Thus, heterogeneous catalysts have currently been paid much attention [43]. Various kinds of catalysts have been

* Corresponding authors. Fax: +86 931 7971533 (J. Tong).

E-mail address: jinhuitong@126.com (J. Tong).

employed to catalyze styrene oxidation [44]. From the viewpoint of environmental protection, molecular oxygen was used as a green and cheap oxidant, for which MOF-74(Cu/Co) [45], bulk Au particles [46], and gold nanoparticles supported on dendrimer resin [47], sulfur-doped graphene [48], and hollow iron oxide nanoshells [49] have been reported to be active catalysts. However, as a mild oxidant, molecular oxygen is usually less efficient, with a low reaction rate at ambient pressure. Compared with molecular oxygen, H₂O₂ is a green and more efficient alternative. Various catalysts have been used to catalyze styrene oxidation using H₂O₂ as oxidant, such as N₄O₄-type bis(diazoimine) complexes supported on silica [50], platinum nanoclusters supported on TiO₂ anatase [51], phosphomolybdic acid supported on ionic-liquid-modified MCM-41 [52], zinc phthalocyanine supported on multiwalled carbon nanotubes [53], Ag-WO₃ catalyst [54], V-MCM-48 [55], Ti-containing mesoporous silica [56], and iron oxide nanoparticles supported on mesoporous silica-type materials [57]. Based on the mentioned advantages of ferrites, several examples have been reported for oxidation of styrene using ferrites as catalysts, such as nickel and zinc ferrites [26], SrFe₂O₄ [28], Mg_xFe_{3-x}O₄ [29], CaFe₂O₄ [58], Ni-Gd ferrites [59], spinel Mg-Cu ferrites [60], and supported noble metals [1,54,61]. Being a terminal olefin, styrene is difficult to oxidize, and most of these oxidation reactions were limited by complicated preparation procedures, high costs, harsh conditions, or low efficiency.

In our previous work [62], CoFe₂O₄ nanocrystals synthesized by sol-gel autocombustion were proved to be a highly active and easily recovered catalyst for the oxidation of cyclohexane by molecular oxygen without addition of solvents or reductants. As part of our interest in hydrocarbon oxidation catalyzed by spinel ferrites, we are reporting here that rare earth metal Ce-doped cobalt ferrites synthesized by a sol-gel autocombustion method can efficiently catalyze the oxidation of styrene to produce benzaldehyde, and their catalytic activities can be greatly enhanced when compared with those of pristine CoFe₂O₄ and CeO₂.

2. Experimental

2.1. Materials and equipment

All reagents were of analytical grade and were used as received. X-ray diffraction (XRD) patterns of the samples were collected using a PANalytical X'Pert Pro diffractometer with CuK α radiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs were obtained using a JSM-5600LV and a Hitachi H-600 microscope, respectively. Metal content was determined by inductively coupled plasma (ICP) on a Perkin-Elmer ICP/6500 atomic emission spectrometer. BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. The oxidation products were determined by an HP 6890/5973 GC/MS instrument and quantified by a Shimadzu GC-2010 gas chromatograph using toluene as internal standard.

2.2. Preparation of the catalysts

The rare earth metal cerium-doped cobalt ferrite samples Ce_xCo_{1-x}Fe₂O₄ ($x = 0.1, 0.3, 0.5$) were prepared by a sol-gel autocombustion route under optimized conditions reported in our previous work [62]. In a typical procedure, stoichiometric amounts of Co(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O, and citric acid were completely dissolved in distilled water with a 1:1 molar ratio of metals to citric acid and a 0.1 mol L⁻¹ concentration of metals. Concentrated ammonia (25–28%) was added slowly under constant stirring to adjust the solution to neutral. The solution was

evaporated in an oil bath at 80 °C under continuous stirring until a brown gel formed. After the reaction, the formed gel was dried at 120 °C until a foamy xerogel was obtained. Then the produced xerogel was ignited at 650 °C, a self-propagating combustion process occurred, and an olive brown product was obtained after it combusted completely. The Ce-doped samples were prepared as described above and were designated as **CFO-Ce_{0.1}**, **CFO-Ce_{0.3}**, and **CFO-Ce_{0.5}**, respectively. For comparison, pristine CoFe₂O₄ was also prepared and was designated as **CFO-A**. The samples were ground finely and screened by a 300 mesh sieve before characterization and employment as catalysts for oxidation of styrene with hydrogen peroxide.

2.3. Oxidation of styrene

The selective oxidation of styrene was carried out in a 25 mL Schlenk tube. In a typical procedure, 0.06 mmol (ca. 15.0 mg, based on the given formula Ce_xCo_{1-x}Fe₂O₄) of catalyst, 2.0 mL (17.4 mmol) of styrene, 10 mL of solvent, and 2.7 mL of hydrogen peroxide (30%), styrene:H₂O₂ molar ratio of 2:3, were added successively into the flask. The flask was then immersed in an oil bath at a desired temperature for a desired reaction time under stirring with an optimum stirrer speed of 1200 rpm, at which the highest conversion rate could be obtained (Fig. S1; see the Supporting Information). It is clear from Fig. S1 that the reaction is effected by diffusion limitation. Under the above conditions, the atmosphere in the tube included mainly air, vapor of substrate, water, and solvent, and oxygen from decomposition of H₂O₂. The pressure in the tube ranged from 1.1 to 1.2 atm. After the reaction, the tube was cooled to room temperature. The gas-phase mixture was collected and analyzed by gas chromatography (GC) equipped with a 5A molecular sieve column and a thermal conductivity detector (TCD). Liquid-phase aliquots were identified by GC-MS and quantified by GC equipped with an SE-54 capillary column and a hydrogen flame ionization detector (FID) using toluene as internal standard. The detected products in the liquid phase included the main product benzaldehyde and byproducts phenylacetaldehyde, styrene oxide, benzoic acid, phenylacetic acid, and formaldehyde. Trace of CO was detected in the gas phase. The amount of residual H₂O₂ was determined by iodometric titration [63,64] and the H₂O₂ utilization efficiency was defined as follows: H₂O₂ utilization efficiency = [(mol (benzaldehyde + phenylacetaldehyde + styrene oxide) + 2 × mol (benzoic acid + phenylacetic acid))/mol (H₂O₂)_{consumed}] × 100%.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. The XRD characterization

The XRD patterns of the Ce-doped samples are shown in Fig. 1. The average particle sizes (based on the Scherrer equation) and lattice parameters (based on the formula $a = d\sqrt{h^2 + k^2 + l^2}$, $2d \sin \theta = n\lambda$) based on the most intense diffraction peaks of the spinel phase of the samples are shown in Table 1. It can be confirmed from Fig. 1 that the main phase in Ce-doped samples is spinel (JCPDS No. 22-1086). It can also be confirmed that the minor new phases of CeO₂ (PDF No. 801792) formed and their contents increased with increasing Ce content.

Table 1 shows that the lattice parameters of the Ce-doped samples increased from 8.3812 to 8.3870 Å with increase of Ce from 0 to 0.5. This confirms that Ce⁴⁺, with a larger radius of 0.101 nm, partly replaced Co²⁺ or Fe³⁺, with small radii of 0.082 and 0.067 nm, respectively.

Download English Version:

<https://daneshyari.com/en/article/6455859>

Download Persian Version:

<https://daneshyari.com/article/6455859>

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