



Synthesis of magnetically recyclable Fe₃O₄@NiO nanostructures for styrene epoxidation and adsorption application

Tianyong Li, Chao Yang, Xuehui Rao, Feng Xiao, Jide Wang, Xintai Su*

Ministry Key Laboratory of Oil and Gas Fine Chemicals, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

Received 21 August 2014; received in revised form 26 September 2014; accepted 1 October 2014

Available online 12 October 2014

Abstract

A solvothermal method combining a calcination process was conducted to synthesize Fe₃O₄@NiO core-shell hierarchical nanostructures. First, Fe₃O₄ microspheres were synthesized through a solvothermal method by using ethylene glycol as solvent. Second, Fe₃O₄@Ni(OH)₂ core-shell hierarchical nanostructures were prepared through an in situ growing procedure. Third, Fe₃O₄@NiO core-shell hierarchical nanostructures were obtained from the Fe₃O₄@Ni(OH)₂ precursors by a simple calcination procedure. The results showed that the Fe₃O₄ core was about 250 nm in diameter and the NiO shell was around 30 nm in thickness. The Fe₃O₄@NiO core-shell nanostructures were used as a magnetically separable adsorbent for the removal of Congo red (CR) dye from aqueous solution, which exhibited a high adsorption capacity of ~128.9 mg g⁻¹. Moreover, the Fe₃O₄@NiO core-shell nanostructures displayed a superior catalytic property for the epoxidation of styrene with an extremely high selectivity (100%), conversion (99%) and yield (99%). Such Fe₃O₄@NiO catalyst could be conveniently recycled from the reaction system by using a magnet and without any noticeable catalytic deactivation even after five cycles. The results indicate that the as-prepared core-shell materials can be used as a recyclable catalyst for the epoxidation of styrene.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Fe₃O₄@NiO composite; Core-shell nanostructures; Adsorption; Magnetically recyclable; Olefin epoxidation

1. Introduction

Over the last several decades, considerable researches have taken place into the metal oxide nanomaterials owing to their potential applications in the fields of electronics, magnetics, biomedicine, and catalysis [1–5]. As a typical metal oxide, nickel oxide (NiO) is a particularly interesting and promising transition-metal oxide because of its excellent chemical thermal stability and environmental benignity. There are numerous potential attractive applications of NiO in various fields, such as catalysts [6–8], gas sensors [9,10], battery materials [11–13], supercapacitors [14–16], active optical fibers and fuel cell electrodes [17]. Recent studies have shown that the NiO nanoparticles demonstrate remarkable adsorption performance in the removal of organic dye from aqueous solution and outstanding catalytic activity in many organic catalytic reactions [18,19]. Furthermore,

according to the recent studies and our previous work [20,21], the NiO showed a superior catalytic performance in olefin epoxidation among the transition metal oxides. However, the nanocatalysts are easily lost in the process of the reaction, and the separation and recycling problem may also confine its applications.

Recently, magnetic core-shell nanostructures with a magnetic core and a catalytic shell have drawn a great deal of attention due to the facile recycle process of the catalyst by an external magnetic field [22–26]. Moreover, the interactions between a variety of ingredients of the core and shell can significantly enhance the overall performance of the core-shell materials and even produce beneficial synergistic effects [22,23]. For instance, Li et al. reported a method to fabricate magnetically recoverable Fe₃O₄@C@Cu₂O nanocomposites for the dye water treatment by using amorphous carbon [24]. Xuan et al. assembled multifunctional Fe₃O₄@polyaniline@Au hybrid nanocomposites by using polyaniline (PANI) as a linker coated on an Fe₃O₄ core for the reduction of RhB [25]. Piao et al. reported a magnetically recyclable and efficient nanocomposite catalyst for the

*Corresponding author. Tel./fax: +86 991 8581018.

E-mail address: suxintai827@163.com (X. Su).

epoxidation of olefins by using SiO_2 as a linker. [26]. In spite of some success of these approaches, there are still many problems to date. They are often limited by complicated procedures, time-consuming experiment techniques, nonessential waste of energy and time, as well as some linker shells (e.g. carbon, silica, polymers). In addition, the complicated synthetic process may increase the cost for widespread industrial use and decrease the saturation magnetization of composite materials.

Herein, we report a facile straightforward strategy to prepare $\text{Fe}_3\text{O}_4@ \text{NiO}$ core-shell hierarchical structures without any linker shell. Scheme 1 shows the synthesis and application of the $\text{Fe}_3\text{O}_4@ \text{NiO}$ core-shell composites. The obtained composite microspheres showed good adsorption performance for the removal of Congo red (CR) from aqueous solution and exhibited excellent catalytic activity for the styrene epoxidation. Moreover, its catalytic activity does not change significantly even after five cycles of catalytic reaction.

2. Experimental

2.1. Synthesis of $\text{Fe}_3\text{O}_4@ \text{NiO}$ core-shell composites

First, the magnetic Fe_3O_4 cores were synthesized by a solvothermal reaction, then the uniform magnetite particles were coated with the nickel hydroxide layer through an in situ growing procedure [27]. Finally, the above $\text{Fe}_3\text{O}_4@ \text{Ni}(\text{OH})_2$ precursors were transformed to magnetic $\text{Fe}_3\text{O}_4@ \text{NiO}$ core-shell composites by a low-temperature calcination techniques.

A typical process for the preparation of Fe_3O_4 particles was as follows: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.65 g) was dissolved in ethylene glycol (50 mL) to form a stable orange solution, followed by the addition of sodium acetate (3.0 g), trisodium citrate (0.65 g) under vigorously magnetic stirring until completely dissolved. The obtained homogeneous solution was sealed in a Teflon-lined stainless-steel autoclave (100 mL). The autoclave was heated to and maintained at 200°C for 10 h. After cooling to room temperature, the obtained products were washed several times with deionized water and absolute ethanol in sequence, and then dried in a vacuum at 60°C for 12 h [28].

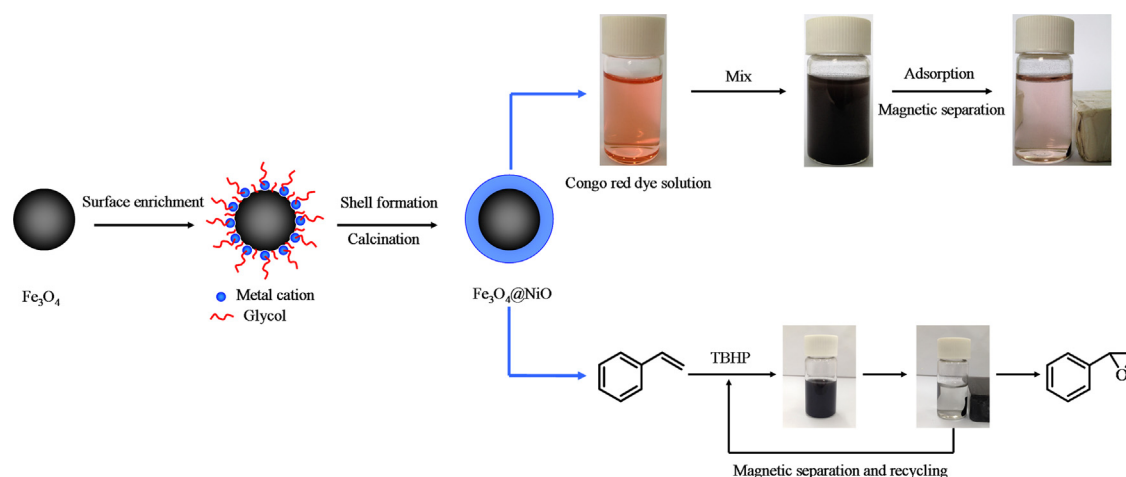
The hierarchical core-shell structured $\text{Fe}_3\text{O}_4@ \text{NiO}$ microspheres were fabricated via a facile solvothermal coating and calcination method. In a typical process, 150 mg of the above magnetic Fe_3O_4 particles were dispersed in a mixture solution that contained ethanol (30 mL), ethylene glycol (20 mL), and then sonicating for 30 min. Afterward, 2 mmol of $\text{Ni}(\text{NO}_3)_2$ was added to the resulting black solution. Next, after sonicating for another 30 min, the above mixed solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL) and heated to a temperature of 160°C for 6 h, and then allowed to cool to room temperature naturally. The obtained $\text{Fe}_3\text{O}_4@ \text{Ni}(\text{OH})_2$ precursors were washed several times with deionized water and absolute ethanol in sequence, as well as dried in a vacuum at 60°C overnight. With the protection of N_2 , the as-prepared magnetite particles were calcined at 350°C for 2 h at a ramping rate of 1°C min^{-1} to yield the black $\text{Fe}_3\text{O}_4@ \text{NiO}$ hierarchical architectures.

2.2. Characterization of samples

The obtained sample was characterized by X-ray diffractometer (XRD) using a Rigaku *D/max-ga* X-ray diffractometer at a scanning of 2°min^{-1} in 2θ ranging from 10° to 80° with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 with an accelerating voltage of 100 kV. The scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS) analysis was conducted with the use of a LEO 1450 VP microscope.

2.3. Removal of the selected organic pollutant

CR, an anionic dye, was selected as a model organic pollutant in the wastewater. To estimate the adsorption capacity, 10 mg of the $\text{Fe}_3\text{O}_4@ \text{NiO}$ composite were added to 50 mL of the CR solutions varied in the range of $10\text{--}500 \text{ mg L}^{-1}$. After stirring for 12 h to reach the adsorption equilibrium, the solid and liquid were separated and the CR concentrations in the remaining solutions were analyzed by UV-visible (UV-vis) spectroscopy



Scheme 1. Schematic illustration of the synthesis and application of the $\text{Fe}_3\text{O}_4@ \text{NiO}$ core-shell composites.

Download English Version:

<https://daneshyari.com/en/article/1459236>

Download Persian Version:

<https://daneshyari.com/article/1459236>

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