



Short communication

A simple route to magnetically separable mesoporous silica with high surface area and large pore: A recyclable catalyst for aldol reaction



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ABSTRACT

Magnetic mesoporous silica composites were prepared by embedding magnetic oxide nanoparticles into abundance of host silica matrix. The resultant composites possess ordered hexagonal mesopores, very high surface area of up to 1124 m²/g, large pore volume (1.324 cm³/g), and large mesopore (>10 nm), as well as good magnetic response. After aminoalkylsilylation, the magnetic SBA-15 composites were demonstrated to be recyclable heterogeneous catalysts for efficient catalytic aldol reaction inside the nanochannels.

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1. Introduction

Ordered mesoporous silica (OMS) such as SBA-15 [1,2] has attracted much attention because of their distinctive properties [3,4]. In particular, OMSs are promising candidates as large-molecule delivery vehicles and catalyst support materials. In the latter case, the ordered uniform mesopores serve as support materials to immobilize homogeneous catalysts. In such heterogeneous catalysis, the separation of catalysts from multiphase complex systems often requires tedious, time-consuming separation processes involving filtration or centrifugation step. To overcome this issue, considerable effort has been devoted to combining a mesoporous structure with magnetic property in order to achieve magnetic response, high pore volume, and large surface area simultaneously. So far, several strategies have been proposed for preparation of magnetic OMS nanocomposites, including the incorporation of magnetic nanoparticles inside the mesopore via a post-impregnation or infiltration [5–8], embedding of magnetic nanoparticles into the silica framework [9], grafting cobalt nanoparticles on the outer surface of SBA-15 via mesopore prefilling [10,11], and preparation of core-shell magnetic composites consisting of magnetic core and mesoporous silica shell [9,12,13]. Very often, however, the post-deposition method causes a significant decrease in surface area [14–16], and seldom reports were found regarding the synthesis of magnetic mesoporous composites with large pore size (>7 nm) [17], which is one of the great obstacles limiting their extensive applications for adsorption, separation and immobilization of large molecules [18,19].

Following our continuous research efforts in the zeolite and molecular sieve-based catalysts [20–23], herein, we demonstrate the preparation of magnetic SBA-15 composites with very high surface area (up to 1124 m²/g), large mesopore (9–11 nm), and uniform and large pore volume (up to 1.324 cm³/g). This was realized by first coating the magnetic nanocrystals with a layer of amorphous silica then embedding the encapsulated magnetic core into abundance of host silica matrix. The magnetic SBA-15 composites were then functionalized by amine-containing organic groups and demonstrated as a recyclable heterogeneous catalyst for efficient catalytic aldol reaction.

2. Experimental

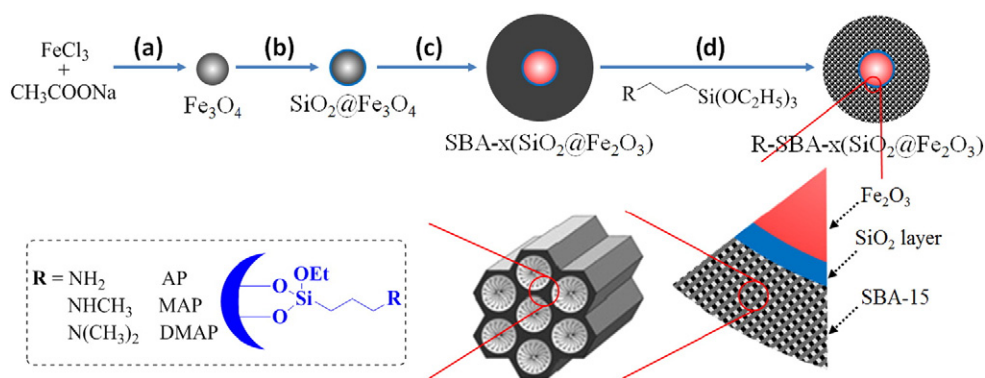
More detailed version of this section is given in the Supporting information.

2.1. Preparation of catalysts

For the preparation of Fe₃O₄ nanoparticles, solvothermal synthesis [24] at 200 °C for 8 h was carried out starting from 9.97 mmol of FeCl₃·6H₂O and 87.7 mmol of sodium acetate in 100 mL of ethylene glycol. The coating of SiO₂ over the Fe₃O₄ nanoparticle was performed by adding aqueous solution of 6.5 mmol of sodium silicate into the water suspension of 1.0 g of Fe₃O₄ nanoparticles at 40 °C, followed by the addition of 0.3 M H₂SO₄ aqueous solution to keep the pH at 9.5. After maintaining the temperature at 40 °C for 3 h, water was removed from the suspension at 95 °C over the period of 1 h, and then washed with de-ionized water and dried at room temperature under vacuum to give black powder (denoted SiO₂@Fe₃O₄) [25].

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Scheme 1. Synthesis route to the composite of magnetic particles and ordered mesoporous silica.

Variable amount (0.2–0.8 g) of the SiO₂@Fe₃O₄ were added into 3.21 mmol HCl (0.1 M) and ultrasonicated for 20 min. 0.38 mmol Pluronic P123 was then added to the suspension and stirred at 40 °C for 4 h. After that, 20.3 mmol TEOS was added to the solution and stirred at 40 °C for 20 h. Then, the mixture was put into an oven (100 °C) for hydrothermal reaction for 20 h. After that, the mixture was filtered off, washed thoroughly with water, and dried overnight. The sample was calcined at 550 °C for 10 h (heating rate = 1.4 °C/min), resulting in a brick red powder, these materials are denoted as SBA-*x*(SiO₂@Fe₂O₃) where *x* = 0.2–0.8, depending on the SiO₂@Fe₃O₄ content incorporated. For comparison, the pristine SBA-15 was also prepared under the same conditions.

The composites (*x* = 0.6, 1.0 g) were silylated with various silylating agents (2.8 mmol) having 3-aminopropyl (AP), 3-methylaminopropyl (MAP), and 3-dimethylaminopropyl (DMAP) groups following the known procedure [21]. The products were denoted as AP-SBA-0.6(SiO₂@Fe₂O₃), MAP-SBA-0.6(SiO₂@Fe₂O₃), and DMAP-SBA-0.6(SiO₂@Fe₂O₃), respectively. The content of amino group was estimated based on thermogravimetric and elemental analyses: AP 2.46 mmol/g-cat, MAP 2.28 mmol/g-cat, and DMAP 1.11 mmol/g-cat.

2.2. Catalytic reaction and the characterization of catalysts and products

Aldol reaction of aromatic aldehyde (1.0 mmol) with excess amount of aliphatic ketone was carried out over 50 mg of solid catalyst at 30 °C for 22 h unless otherwise noted. Further details of the reaction procedure as well as the characterization of catalysts and products are shown in the Supporting information.

3. Results and discussion

Through the routes in Scheme 1, uniform Fe₃O₄ microspheres with a mean diameter of ca. 400 nm (Fig. 1a), silica-Fe₃O₄ composites (SiO₂@Fe₃O₄), and SBA-*x*(SiO₂@Fe₂O₃) where *x* = 0.2–0.8 were successfully prepared. The adjustment of pH value is essential to the final successful fabrication of magnetic SBA-15. As shown in Fig. S1, both the low-angle XRD patterns and FE-SEM images revealed that the ordered mesoporous structure of SBA-*x*(SiO₂@Fe₂O₃) was greatly developed with increasing the acid amount, due to the acid-promoted hydrolysis/condensation of TEOS. For example, when 0.05 M HCl was used, the resultant magnetic composite (SBA-0.6(SiO₂@Fe₂O₃)) exhibited only a

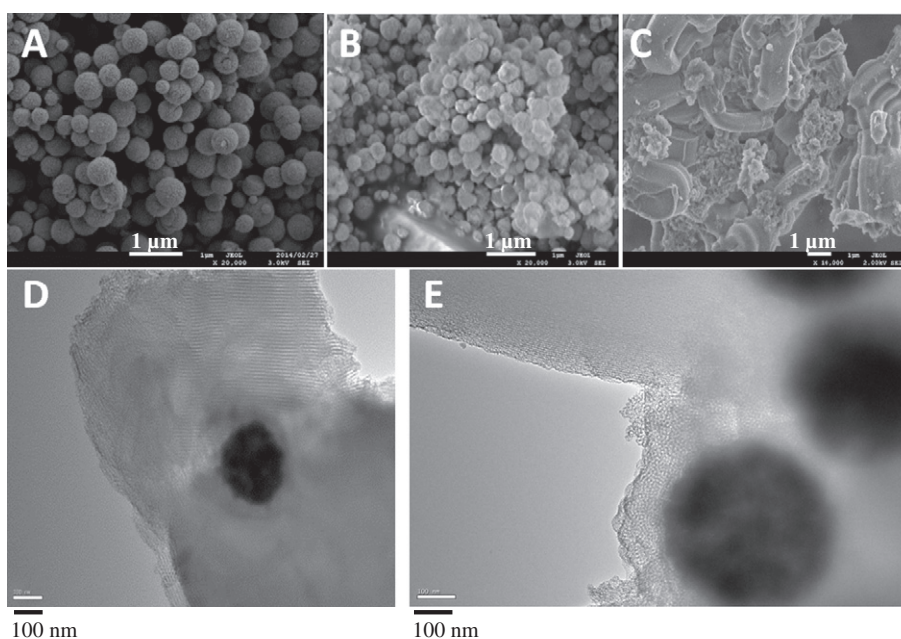


Fig. 1. FE-SEM images of (A) Fe₃O₄, (B) SiO₂@Fe₃O₄, (C) SBA-0.6(SiO₂@Fe₂O₃) nanoparticles, and (D and E) HRTEM images of SBA-0.6(SiO₂@Fe₂O₃).

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