

# One-pot synthesis of Ag–Fe<sub>3</sub>O<sub>4</sub> nanocomposite: a magnetically recyclable and efficient catalyst for epoxidation of styrene†

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Received (in Cambridge, UK) 4th April 2008, Accepted 21st April 2008

First published as an Advance Article on the web 15th May 2008

DOI: 10.1039/b805737k

**With the assistance of PVP, a novel magnetically recyclable Ag-based catalyst has been synthesized in one pot, and it is found that this catalyst is highly efficient in selectively catalyzing styrene conversion to styrene oxide.**

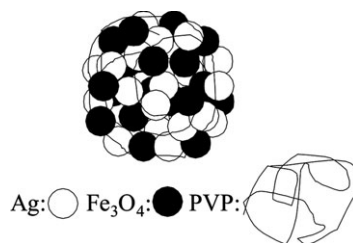
Heterogeneous catalysts play key roles in liquid-phase catalytic processes that are important in the fine and speciality chemicals industry.<sup>1</sup> It has been extensively demonstrated that nanometre-sized catalysts exhibit much higher activities than their bulk counterparts.<sup>2</sup> However, the problem with very small particles is that they cannot be efficiently recovered from the catalytic reaction systems with traditional methods such as filtration and centrifugation. Nanometre-sized magnetically recyclable catalysts (MRCs) developed in recent years allow the catalysts to be recycled conveniently through applying an external magnetic field, and hence high activity and easy separation are integrated in nanometre-sized MRCs. Many efforts have been made to synthesize this kind of catalyst. However, all the MRCs preparation processes reported so far are multi-step and employ rather sophisticated procedures. Generally, in order to complex catalytically active components, the magnetic components (Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, etc.) should be modified with layers of rigid materials (SiO<sub>2</sub>, carbon, etc.) and/or functional organic agents (amines, oleate, etc.) in advance.<sup>3</sup> For example, Hyeon and co-workers<sup>3</sup> synthesized an MRC by depositing a dense layer of silica on the surface of Fe<sub>2</sub>O<sub>3</sub> followed by formation of a mesoporous silica shell, impregnation in the catalyst precursor and finally treatment of the composite in a reducing atmosphere. Thus, the invention of facile and rapid methods for the preparation of efficient MRCs is rather challenging.

Styrene oxide, an important and versatile intermediate for fine chemicals and pharmaceuticals, is the expected product when styrene is epoxidized.<sup>4</sup> It has been proved that metallic silver is capable of catalyzing epoxidation reactions. Though various modified silver catalysts have been obtained and their performances in epoxidizing styrene have been assessed,<sup>5,11</sup> to the best of our knowledge, no silver-based MRC has been reported so far. In this communication, we present a simple one-pot synthesis of a silver-based MRC, Ag–Fe<sub>3</sub>O<sub>4</sub> nano-

composite, with the assistance of polyvinylpyrrolidone (PVP). Furthermore, it is found that the as-synthesized MRC is efficient for the epoxidation of styrene in toluene with *tert*-butyl hydroperoxide (TBHP) as oxidant, and no deactivation is observed after the catalyst is recycled for at least five times.

In a typical synthesis, silver nitrate was added into a solution of ethylene glycol (EG) containing iron(III) chloride, PVP and anhydrous sodium acetate, leading to a suspension of AgCl with Fe<sup>III</sup> cations in EG. The suspension mixture was stirred and sealed in a PTFE-lined stainless steel autoclave, followed by successive thermal treatments at 180 °C and 200 °C. By doing so, an Ag–Fe<sub>3</sub>O<sub>4</sub> nanocomposite material was produced in one pot (see ESI† for details). In the reaction, Ag<sup>0</sup> was generated through reduction of Ag<sup>+</sup> by the solvent molecules,<sup>6</sup> whereas Fe<sup>2+</sup> species were formed *via* reduction of a fraction of the Fe<sup>3+</sup> cations.<sup>7</sup> Reduction of metal ions by EG molecules in solvothermal reaction systems has been commonly observed.<sup>6,7</sup> In our synthesis, Fe<sup>3+</sup> and Ag<sup>+</sup> were both reduced by the EG molecules (see Table S1†), and the presence of EG prevented the re-oxidation<sup>8</sup> of the formed Ag<sup>0</sup> by Fe<sup>3+</sup>. On the basis of the powder X-ray diffraction (XRD) patterns recorded for the samples collected at different reaction times (Fig. S1†), Ag<sup>+</sup> is reduced to Ag first by EG and aggregates with the subsequently crystallized Fe<sub>3</sub>O<sub>4</sub> particles into Ag–Fe<sub>3</sub>O<sub>4</sub> nanocomposites with the assistance of PVP. Ag and Fe<sub>3</sub>O<sub>4</sub> primary particles are randomly distributed throughout the nanocomposite. Fig. 1 illustrates the schematic structure of the as-synthesized Ag–Fe<sub>3</sub>O<sub>4</sub> nanocomposite.

The formation of Ag and Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the nanocomposite is confirmed by powder XRD (Fig. 2). The XRD pattern is indexable on the basis of face-centered cubic silver (JCPDS No. 87-0720) and face-centered cubic magnetite (JCPDS No. 19-0629). The diffraction peaks of Ag appear to be much stronger than those for Fe<sub>3</sub>O<sub>4</sub>, suggesting that the crystallization of Fe<sub>3</sub>O<sub>4</sub> nanoparticles is not as good as that of Ag nanoparticles. Fig. 3a and b show the scanning electron microscope (SEM) and low-magnification transmission

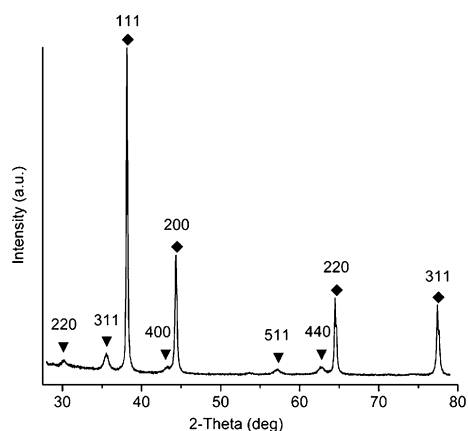


**Fig. 1** Schematic representation of the structure of the as-synthesized Ag–Fe<sub>3</sub>O<sub>4</sub> nanocomposite.

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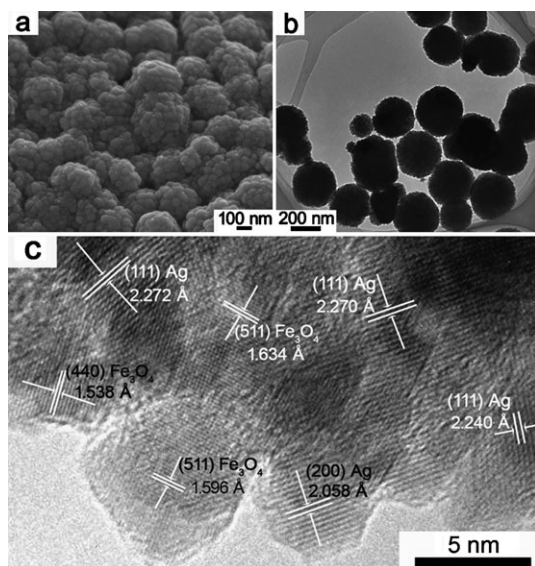
† Electronic supplementary information (ESI) available: Detailed experimental procedures, spectroscopic characterizations, SEM images and catalysis testing. See DOI: 10.1039/b805737k



**Fig. 2** XRD pattern of the as-synthesized Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. ◆: peaks of Ag, ▼: peaks of Fe<sub>3</sub>O<sub>4</sub>.

electron microscope (TEM) images of the as-synthesized Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. It is seen that uniform spherical particles are composed of smaller units that aggregate together tightly. The average size of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite spheres is 230 nm (calculated on the basis of 127 nanospheres from TEM images). The lattice fringes for both Ag and Fe<sub>3</sub>O<sub>4</sub> nanocrystals can be clearly determined in an individual spherical particle in a high-resolution TEM (HRTEM) image (Fig. 3c). In the absence of Fe<sup>3+</sup> in the reaction system, the Ag particles grown under identical conditions are larger than the Ag-Fe<sub>3</sub>O<sub>4</sub> composite spheres (Fig. S2†). Obviously, the formation of Fe<sub>3</sub>O<sub>4</sub> restricts the growth of the Ag particles in the nanocomposite.‡

The control experiment also demonstrates that the PVP molecules are indispensable to the aggregation of the Ag and Fe<sub>3</sub>O<sub>4</sub> particles to form the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. In the absence of PVP, the formed Ag particles are separated from the Fe<sub>3</sub>O<sub>4</sub> ones, and the formation of Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite fails (Fig. S3†). As is known, PVP can adsorb on some



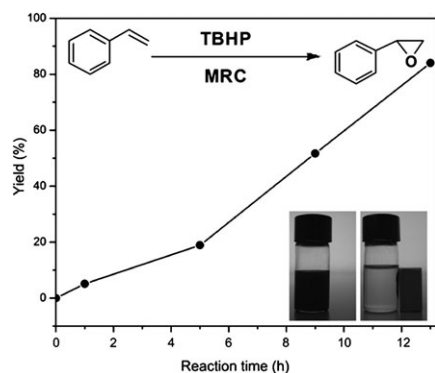
**Fig. 3** SEM (a), TEM (b) images of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite, and HRTEM (c) image of an individual spherical particle.

particular facets of nanoparticles and is a powerful surfactant in the synthesis of both Ag<sup>6</sup> and Fe<sub>3</sub>O<sub>4</sub><sup>9</sup> nanoparticles. Furthermore, PVP enables the assembly of Fe<sub>3</sub>O<sub>4</sub> primary nanoparticles into spherical aggregates.<sup>9</sup> In our reaction system, it is believed that the PVP molecules assist Ag and Fe<sub>3</sub>O<sub>4</sub> primary particles to gather together to form the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite spheres in a way similar to that for the Fe<sub>3</sub>O<sub>4</sub> aggregate formation.<sup>9</sup> The infrared (IR) spectrum of the nanocomposite shows characteristic absorptions of PVP (Fig. S4†), confirming the existence of PVP molecules in the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. The thermogravimetric analysis (TGA) curve of the composite material in N<sub>2</sub> atmosphere exhibits a total weight loss of 4.16 wt% (Fig. S5†), corresponding to the decomposition of the PVP molecules in the composite.

The magnetic properties of the composite have been elucidated (Fig. S6†). At 4 K, the material gives rise to a typical hysteresis loop, whereas this loop disappears at 300 K, indicating that the nanocomposite is superparamagnetic at room temperature. This phenomenon is consistent with the small size of primary magnetite particles in the spherical aggregates.<sup>7</sup> The saturation magnetization of the sample is 15.7 emu g<sup>-1</sup>, which is distinctly smaller than that of bulk magnetite (90 emu g<sup>-1</sup>). The reduced saturation magnetization is caused by both the small particle size effect and the presence of a nonmagnetic silver component in the nanocomposite.<sup>10</sup> The superparamagnetic behaviour of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite allows the particles to gather together rapidly in the presence of an external magnetic field and to disperse easily in solutions when the external magnetic field is removed.

The catalytic performance of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite for the epoxidation of styrene has been evaluated. Fig. 4 shows the yield of styrene epoxide *versus* reaction time. Increase in yield is observed as the reaction proceeds. Upon reaction for 13 h, the conversion of styrene reaches 100%. The yield of styrene epoxide is 84.0%, with a turnover frequency (TOF) of 1473.3 mmol mol<sup>-1</sup> h<sup>-1</sup>. Five reaction cycles have been tested for the same catalyst, and no deactivation of the catalyst has been observed. The catalyst particles can be attracted to one side of the reaction vial within one minute by a magnetic bar placed near the vial after each cycle of catalytic reaction (inset in Fig. 4). Li and co-workers<sup>11</sup> have investigated the catalysis performances of silver nanoparticles with three different morphologies. Their catalytic reaction conditions are identical to ours, but on average, the TOF value in our case is about eight times higher than that obtained in their experiment (Table S2†).

For comparison, the catalytic performance of Ag (Fig. S7†) synthesized by treating the reactants free of FeCl<sub>3</sub>·6H<sub>2</sub>O under the same conditions was also evaluated. The Ag catalyst thus obtained shows a styrene conversion similar to that of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite after the catalytic reaction has proceeded for 13 h, but the TOF value of the Ag catalyst is distinctly lower (about three times lower) than the corresponding value of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite (Table 1). A considerable amount of by-products (mainly benzyl alcohol, acetophenone and styrene oligomers) other than styrene oxide and benzaldehyde were detected when the Ag catalyst was used. We also tested the catalytic performance of a simple



**Fig. 4** Yield of styrene epoxide *versus* reaction time catalyzed by Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. The photographs demonstrate the separation of the catalyst by a magnet.

**Table 1** Catalytic performance of Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite, Ag and a simple mixture of Ag and Fe<sub>3</sub>O<sub>4</sub> for the epoxidation of styrene<sup>a</sup>

Catalyst	C <sub>S</sub> (%)	Y <sub>SO</sub> (%)	Y <sub>B</sub> (%)	Y <sub>O</sub> (%)	TOF
Ag-Fe <sub>3</sub> O <sub>4</sub>	100	84.0	11.1	4.9	1473.3
Ag	99.0	64.0	9.8	26.2	539.8
Mixture	95.9	42.8	12.6	44.6	761.6

<sup>a</sup> C<sub>S</sub> = conversion of styrene, Y<sub>SO</sub> = yield of styrene oxide, Y<sub>B</sub> = yield of benzaldehyde, Y<sub>O</sub> = yield of other by-products; TOF = mmol of styrene oxide formed per mol of Ag per hour; reaction time: 13 h.

mixture of Ag and Fe<sub>3</sub>O<sub>4</sub> particles (Fig. S7†) with a composition identical to that of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. The TOF value of the mixture was found to be only about one half of that of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite material (Table 1). These observations indicate that the composition of Ag and Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite enhances the catalytic activity of Ag. It has been reported that oxygen vacancies on the surface of iron oxide assist in supplying reactive oxygen.<sup>12</sup> Similarly, in our catalytic system, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles may assist in providing additional reactive oxygen besides that generated by the Ag particles. This additional reactive oxygen transfers to the surface of the proximate Ag particle in the composite easily, and hence facilitates the epoxidation of styrene molecules adsorbed on the Ag surface. In addition, it is worthwhile to point out that the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite particles are rather robust and remain almost intact after five cycles of catalytic reaction (Fig. S7†). The robustness of the nanocomposite lays the foundation for repeated use of the catalyst.

In summary, a one-pot synthetic route based on PVP-complexing has been reported for the preparation of a unique Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite MRC. This MRC is highly efficient for the epoxidation of styrene to form styrene epoxide, and the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the composite not only function as a magnet for efficient magnetic separation but also enhance the catalytic performance of the Ag nanocrystal component. The

catalyst can be conveniently recycled from the reaction system by using a magnet and no deactivation has been observed after at least five cycles of reaction. The overall synthetic process for the nanocomposite is simple and rapid, and it is envisioned that this synthetic approach may be readily extended to MRCs that contain catalytically active metals other than Ag.

This work was financially supported by the National Natural Science Foundation of China (20731003) and the National Basic Research Program of China (2007CB613303). The authors thank Xuejing Cao for assistance with the SEM measurements.

## Notes and references

† The Brunauer–Emmett–Teller (BET) surface area of the Ag-Fe<sub>3</sub>O<sub>4</sub> nanocomposite material measured using N<sub>2</sub> adsorption and desorption at 77 K is 35.1 m<sup>2</sup> g<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) analysis of Ag3d spectra further confirms that the Ag species on the surface of the nanocomposite is metallic silver (ESI†).

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