Electronic Supplementary Information

One-pot Synthesis of Ag-Fe₃O₄ Nanocomposite: A Magnetically Recyclable and Efficient Catalyst for Epoxidation of Styrene

Dong-Hui Zhang, Guo-Dong Li, Ji-Xue Li and Jie-Sheng Chen

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People’s Republic of China. Fax: (+86)-431-8516-8624; E-mail: chemcj@jlu.edu.cn

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China. E-mail: chemcj@sjtu.edu.cn

Synthesis of Ag-Fe₃O₄ nanocomposite

FeCl₃·6H₂O (2.975 mmol), PVP (8.925 mmol K₃₀ Mr = 10 000), CH₃COONa (29.75 mmol), AgNO₃ (2.975 mmol) were successively added to 35 mL EG in a 50 mL beaker. The mixture was stirred in dark until a homogeneous suspension was formed. The resulting suspension was then transferred to a 50 mL PTFE-lined stainless steel autoclave and sealed. After heating at 180 °C for 1 h and 200 °C for 8 h, the autoclave was allowed to cool to room temperature naturally. Finally, the reaction product was magnetically collected and washed thoroughly with distilled water and absolute ethanol, followed by drying under vacuum at room temperature. To reveal the role played by the PVP molecules in the formation of the composite material, the synthesis was also performed in the absence of PVP, and magnetic and non-magnetic parts were found to form in the reaction product.

Synthesis of Ag nanoparticles for catalysis comparison

The synthesis process was the same as that for the Ag-Fe₃O₄ nanocomposite, except that no FeCl₃·6H₂O was added into the reaction system. The final product was obtained by centrifugation and washed with acetone and ethanol, and then dried under vacuum at room temperature. The nanoparticles formed were metallic silver as confirmed by powder XRD.

Synthesis of Fe₃O₄ nanoparticles for catalysis comparison

The synthesis process was the same as that for the Ag-Fe₃O₄ nanocomposite, except that no AgNO₃ was added into the reaction system. The nanoparticles formed were magnetite as confirmed by powder XRD.

Catalytic testing

100 mg as-synthesized Ag-Fe₃O₄ nanocomposite and 10 mmol styrene (distilled under reduced pressure) were added to 10 mL toluene (distilled under atmospheric pressure) and refluxed for 0.5 h in a three-necked flask under magnetic stirring. The catalytic reaction was initiated by adding freshly extracted anhydrous TBHP (about 6 mL TBHP in 4 mL toluene) dropwise to the mixture in the flask. Samples (about 0.5 mL) were taken from the reaction system at various time intervals using a glass syringe, and analyzed on gas chromatograph. After each cycle of catalytic reaction, the catalyst was collected magnetically, washed with toluene for several times and dried under vacuum overnight for re-use. Control experiments were also carried out, and the yield of styrene oxide was below
0.2 % in the absence of catalyst under otherwise identical conditions after 9 h.

The assessment for the catalytic performance of Ag (or a mixture of Ag and Fe$_3$O$_4$) nanoparticles was the same as that for the Ag-Fe$_3$O$_4$ nanocomposite, except that 100 mg Ag (or a mixture of Ag and Fe$_3$O$_4$) instead of 100 mg Ag-Fe$_3$O$_4$ nanocomposite was used.

**Table S1** Times needed for reduction of Fe$^{3+}$ and Ag$^+$ by EG in the synthetic system.

<table>
<thead>
<tr>
<th>Chemical reactions</th>
<th>Time needed (h)</th>
<th>Confirmed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO$_3$ $\xrightarrow{\text{EG NaCl}}$ Ag</td>
<td>0.5 0</td>
<td>XRD</td>
</tr>
<tr>
<td>FeCl$_3$ $\xrightarrow{\text{EG NaAc PVP}}$ Fe$_3$O$_4$</td>
<td>1 2</td>
<td>XRD</td>
</tr>
</tbody>
</table>

The results in Table S1 indicate that EG plays the role of reductant in the solvothermal process, and Fe$^{3+}$ and Ag$^+$ were both reduced by the EG molecules.

**Fig. S1** XRD patterns of the products obtained at different reaction times. Only the peaks of Ag appear after heating at 180 °C for 1 h and 200 °C for 1 h (◆: peaks of Ag) and the peaks of Fe$_3$O$_4$ appear after heating at 180 °C for 1 h and at 200 °C for 2 h, and become stronger at 3 h (▼: peaks of Fe$_3$O$_4$).
**Fig. S2** SEM images of Ag and Ag-Fe$_3$O$_4$ products obtained at different reaction times.

**Fig. S3** Energy dispersive spectrum (EDS) for the non-magnetic part of the product synthesized in the absence of PVP. The atomic ratio of Ag/Fe is 7.3, much higher than the ratio (1.3) for the sample synthesized in the presence of PVP, suggesting that the particles are mainly composed of Ag. Therefore it is believed that most of the Ag and Fe$_3$O$_4$ primary nanoparticles are separated and cannot gather together to form Ag-Fe$_3$O$_4$ nanocomposite under this circumstance. The signals of carbon, silicon and chlorine arise from the carbon spray, the silicon plate and the reactant FeCl$_3$·6H$_2$O.
**Fig. S4** IR spectra of the as-prepared nanocomposite and PVP.

**Fig. S5** TGA curve in N₂ for Ag-Fe₃O₄ nanocomposite.

**Fig. S6** Magnetization curves for Ag-Fe₃O₄ nanocomposite at 4 K and at 300 K.
Table S2 Comparison of the TOF values for epoxidation of styrene reported in ref.11 using various Ag nanoparticles as catalysts and the corresponding value obtained in this work using Ag-Fe$_3$O$_4$ as the catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>triangular</th>
<th>spherical</th>
<th>cubic</th>
<th>average</th>
<th>Ag-Fe$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>this work</td>
</tr>
<tr>
<td>TOF (mmol mol$^{-1}$ h$^{-1}$)</td>
<td>109.4</td>
<td>170.1</td>
<td>280.4</td>
<td>186.6</td>
<td>1473.3</td>
</tr>
</tbody>
</table>

Fig. S7 SEM images of the as-prepared Ag (left), Fe$_3$O$_4$ (middle) particles and the Ag-Fe$_3$O$_4$ nanocomposite (right) after five cycles of catalytic reaction.

Fig. S8 XPS of Ag3d pattern of the as-synthesized nanocomposite.