

A Magnetically Recyclable Nanocomposite Catalyst for Olefin Epoxidation**

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Olefin epoxidation is an important reaction because epoxides are widely used in the production of epoxy resins, paints, and surfactants and are also intermediates in many organic syntheses.^[1] Many catalytic epoxidation reactions using transition-metal compounds of molybdenum, tungsten, and vanadium have been successfully demonstrated,^[2] although homogeneous catalysts have proved to be of somewhat limited use owing to the difficulties in separating the products and contamination by residual catalyst. The immobilization of homogeneous catalysts has therefore attracted a lot of attention. Polymer-supported catalysts are now frequently used,^[3] although they often suffer from instability at high reaction temperatures, give poor selectivity, and have low activity for high-molecular-weight olefins.^[4]

Inorganic nanoporous materials have recently been utilized as catalyst supports for many homogeneous catalysts.^[5] Nanoparticles of metals and metal oxides have been extensively used as catalysts in many organic reactions because of their high surface area and facile separation.^[6] Among the various nanostructured materials, magnetic nanoparticles have attracted growing interest owing to their unique properties and potential applications in various fields, such as magnetically assisted drug delivery, magnetic resonance imaging (MRI) contrast agents, hyperthermia, magnetic separation of biomolecules, and especially the isolation and recycling of expensive catalysts.^[7]

Magnetic separation provides a convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. This approach may prevent the agglomeration of the catalyst particles during recovery and can increase the durability of the catalysts. For example, magnetic nanoparticles have been immobilized on various catalyst supports, including polymers, carbons, and silicas,^[8] and novel nanocomposite catalyst supports have been syn-

thesized by combining mesoporous materials with a high surface area and well-defined pore size with magnetic nanoparticles.^[9] Magnetic nanoparticles have also been incorporated into the pores of mesoporous silicas, such as MCM-41 and SBA-15.^[10] Unfortunately, these types of magnetic nanoparticle-based catalytic materials cannot be used for epoxidation reactions because of the corrosive and drastic reaction conditions required. To circumvent this drawback an impermeable dense silica layer has been coated on the core magnetic nanoparticles^[11] to protect them from erosion during the harsh epoxidation reactions. Herein we report the fabrication of molybdenum oxide nanoparticles incorporated into a mesoporous silica shell that are coated on dense silica-coated magnetite nanoparticles and demonstrate a magnetically recyclable epoxidation catalyst.

The overall synthetic procedure is represented in Figure 1. Uniform hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles with an average diameter of 400 nm were synthesized in a hydrothermal

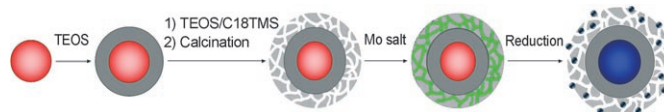


Figure 1. Synthetic procedure leading to the magnetic nanocomposite catalyst from hematite nanoparticles.

reaction by aging an aqueous $4.0 \times 10^{-2} \text{ M}$ FeCl_3 solution in an autoclave (PARR-5500) at 180°C for 24 h.^[12] The resulting hematite particles (200 mg) were stabilized with 2 g of poly(vinylpyrrolidone) (PVP) in water and then a dense silica layer of the desired thickness (50 nm) was deposited on their surface. In a typical procedure, hematite particles were added to a solution containing 50 mL of ethanol, 5 mL of distilled water, and 2 g of aqueous ammonia at room temperature and the resulting solution was vigorously stirred for 30 min. Tetraethoxysilane (TEOS; 0.4 mL) was then rapidly added and the solution aged at room temperature for 15 h. After being separated by centrifugation, the dense silica-coated hematite particles were well dispersed in a mixture of 50 mL of ethanol and 2 g of aqueous ammonia. The mesoporous silica shell was formed by the simultaneous sol-gel polymerization of a mixture of TEOS and *n*-octadecyltrimethoxysilane (C18TMS) with a molar ratio of 4:7 for 2 h at room temperature. The nanocomposite was then calcined at 500°C for 5 h to remove the organic groups. Finally, ammonium molybdate (weight ratio: 1:10) was introduced into the mesopores of the mesoporous silica shell/dense silica inner shell/hematite particles (MS/DS/HP) by impregnation

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and was then reduced in a flowing mixture of H_2 and N_2 (1:1) at $500^\circ C$ for 12 h to produce MoO_3 nanoparticles (designated as the Mag-Mo-Nano catalyst). The color of the powder changed from red to deep black after the reduction process, thereby indicating the reduction of the hematite cores to magnetite.

The intermediates and the final Mag-Mo-Nano catalyst were characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), and nitrogen adsorption/desorption isotherms. The TEM image of the hematite particles (Figure 2a) shows that

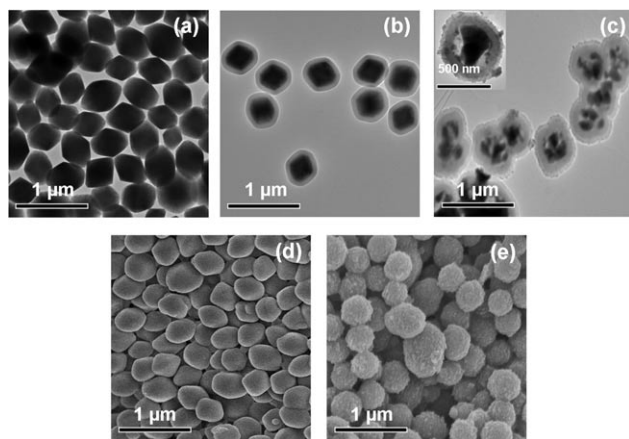


Figure 2. TEM images of a) hematite nanoparticles, b) dense silica-coated nanoparticles, c) the Mag-Mo-Nano catalyst, and FE-SEM images of d) dense silica-coated nanoparticles and e) the Mag-Mo-Nano catalyst.

they are relatively uniform with an average size of 400 nm. The TEM image of the dense silica-coated hematite particles reveals that the silica coating is uniform, with a thickness of about 50 nm (Figure 2b). The TEM image of the Mag-Mo-Nano catalyst shows that the iron oxide particle in the core part has shrunk and has broken into two or three smaller particles (Figure 2c), although the dense silica coating remains intact even after the harsh reduction process, which is very important for subsequent catalytic applications. The fragmentation of the hematite core into smaller magnetite particles seems to be due to a reduction of volume during the thermal treatment and the strong interaction of the iron oxide species with the silica inner wall. Gösele et al. have reported that a strong interaction between the inner wall of alumina and metal species during annealing induces adhesion of metal nanostructures to the inner wall.^[13]

The SEM images show that the Mag-Mo-Nano catalyst with the mesoporous shell exhibits a rough surface whereas the dense silica-coated hematite particles have a smooth surface (Figures 2d,e). The thickness of both the dense silica coating and the mesoporous silica shell can be easily tuned from 30–80 nm by varying the relative amounts of TEOS and the mixture of TEOS and C18TMS, respectively.

The energy dispersive X-ray spectrum (EDX) of the Mag-Mo-Nano catalyst shows that the Mo species are successfully immobilized in the mesoporous shell (see Supporting Information). The molybdenum loading in the Mag-Mo-Nano

catalyst, as measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), was found to be 1.0 wt %.

Representative nitrogen adsorption/desorption isotherms and the corresponding pore size distribution of the mesoporous silica shells after calcinations obtained from analysis of the adsorption branch using the BJH (Barett–Joyner–Halenda) method are shown in Figure 3. The BET surface area and single point total pore volume are $352\text{ m}^2\text{ g}^{-1}$ and $0.37\text{ cm}^3\text{ g}^{-1}$, respectively. The pore size distribution (PSD) curve, shown in the inset of Figure 3, shows a single peak centered at 3 nm.

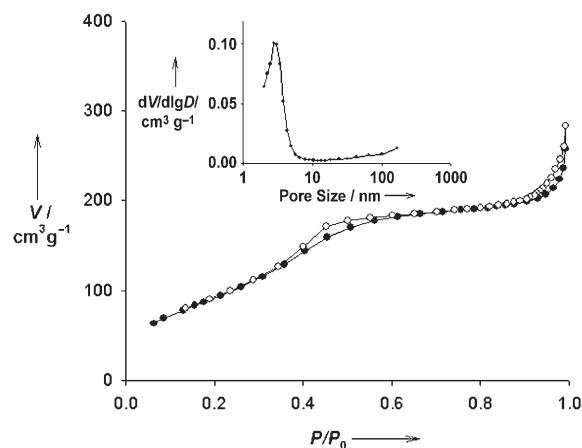


Figure 3. N_2 adsorption/desorption isotherms of the mesoporous silica shell/dense silica inner shell/hematite particles. The inset shows the corresponding pore size distribution.

Several magnetic nanostructured materials have recently been used as catalyst supports to facilitate the recovery and recycling of catalysts from the reaction mixture.^[14] The magnetic behavior of the Mag-Mo-Nano catalyst was investigated using a superconducting quantum interference device (SQUID) magnetometer. The field-dependent magnetization curve at 300 K reveals that the catalyst is ferromagnetic with a saturation magnetization of 1.32 emu g^{-1} (Figure 4).

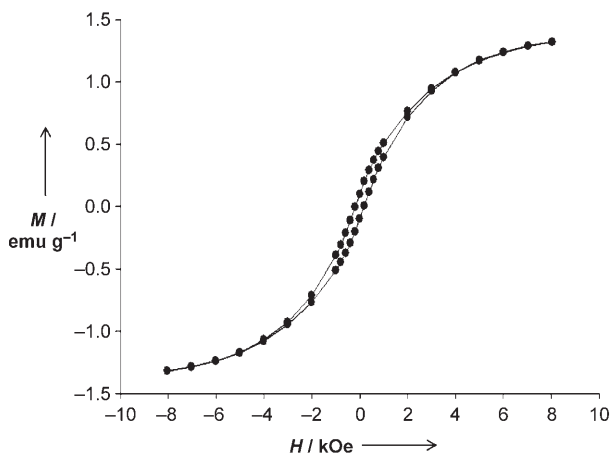


Figure 4. Field-dependent magnetization of the Mag-Mo-Nano catalyst at 300 K.

The activity of the Mag-Mo-Nano catalyst was tested for the epoxidation of *cis*-cyclooctene. Various solvents were examined in order to find the appropriate conditions for the reaction with 1 mol% of the catalyst. The yield of this heterogeneous catalytic reaction proved to be significantly solvent-dependent, with carbon tetrachloride (CCl₄) giving the best results (see Supporting Information).

We also screened various oxidants, including *tert*-butyl peroxide (*t*BuOOH), *meta*-chloroperoxybenzoic acid (MCPBA), cumene hydroperoxide (CHHP), hydrogen peroxide (H₂O₂), sodium periodate (NaIO₄), sodium hypochlorite (NaOCl), and oxone (potassium peroxydisulfate). *t*BuOOH and MCPBA gave the best results and we selected *t*BuOOH as the oxidant for the epoxidation reactions because it is much cheaper than MCPBA.

We investigated magnetic separation and recycling of the Mag-Mo-Nano catalyst (Figure 5), which was successfully

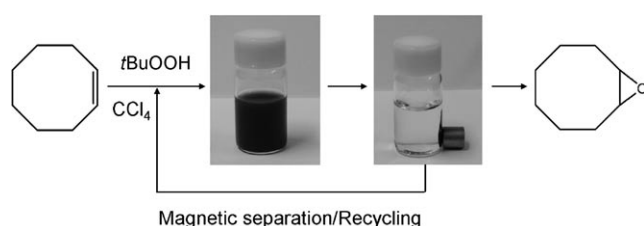


Figure 5. Magnetic separation and recycling of the Mag-Mo-Nano catalyst.

recycled and reused six times in the epoxidation of *cis*-cyclooctene with no major loss of activity (Table 1). As shown in Figure 5, the Mag-Mo-Nano catalyst can be easily sepa-

Table 1: Magnetic separation and recycling of the Mag-Mo-Nano catalyst in the epoxidation of *cis*-cyclooctene.^[a]

Cycle:	1st	2nd	3rd	4th	5th	6th
Yield of epoxide [%] ^[b]	99	99	97	97	95	94

[a] Reaction conditions: 1 mmol *cis*-cyclooctene, 1.2 mmol of *t*BuOOH, 1 mol% of catalyst, 5 mL of CCl₄, 5 h, reflux. [b] The yields were determined by GC-MS with respect to an internal standard (decane).

rated from the reaction mixture. There is a small decrease of the catalytic activity after each recycling of the catalyst, and ICP analysis of the reaction solution after the first cycle of reaction and magnetic separation of the catalyst showed that 1.6% of Mo species remained in the solution. Consequently, the small decrease of catalytic activity seems to result from either incomplete magnetic separation of the catalyst or leaching of Mo species during the reaction.

To extend the scope of this heterogeneous catalytic epoxidation reaction, the epoxidation of various olefins with *t*BuOOH in air was carried out under the optimized conditions. As shown in Table 2, all of the alkenes were converted into the corresponding epoxides with excellent yields within 5 h.

Table 2: Epoxidation of olefins with *t*BuOOH catalyzed by the Mag-Mo-Nano catalyst.^[a]

$\text{>C=C<} \xrightarrow[\text{tBuOOH, 5 h, CCl}_4]{\text{Mo NP Catalyst}} \text{>C(O)-C(O)<}$		
Entry	Alkene	Yield of epoxide [%] ^[b]
1	cyclododecene	85
2	cyclooctene	99
3	cycloheptene	96
4	cyclohexene	87
5	indene	76

[a] Reaction conditions: 1 mmol of *cis*-cyclooctene, 1.2 mmol of *t*BuOOH, 1 mol% of catalyst, 5 mL of CCl₄, 5 h, reflux. [b] The yields were determined by GC-MS with respect to an internal standard (decane).

To evaluate the effect of the silica layer on the catalytic performance, we performed the epoxidation of *cis*-cyclooctene with *t*BuOOH using 1 mol% of a catalyst with two different silica coatings. The dense silica coated magnetite particles gave much lower conversions (37%) than the dense silica/mesoporous silica coated magnetite particles (99%) under the same reaction conditions. These results show that the compound with the mesoporous silica coating and a high surface area (352 m² g⁻¹) is a better catalyst than that with the dense silica coating and a low surface area (23 m² g⁻¹).

In conclusion, we have described a new magnetically recyclable and efficient nanocomposite catalyst for the epoxidation of olefins based on molybdenum oxide nanoparticles incorporated in a mesoporous silica shell that is coated on dense silica-coated magnetite nanoparticles. This catalyst exhibits several attractive features for the synthesis of fine chemicals. Firstly, the magnetic core part is isolated and protected by the dense silica shell, thus making its use under harsh reaction conditions possible. Secondly, the magnetic core can be readily utilized for the easy recovery and recycling of the catalyst with no significant loss of catalytic activity. Thirdly, the high surface area of the mesoporous shell means that it can accommodate large amounts of the catalytic MoO₂ species, thus making the catalyst highly active. We expect this novel magnetic nanocomposite catalyst system to find applications in many other industrially important catalytic processes.

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