羟基磷灰石包覆 γ -Fe₂O₃ 担载氧化钼: 一种新型磁性可回收的 烯烃环氧化多相催化剂

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摘要: 制备了羟基磷灰石 (HAP) 包覆纳米 γ -Fe₂O₃ 颗粒复合材料 (HAP- γ -Fe₂O₃), 并进一步采用浸渍法担载氧化钼 (MoO_x/HAP- γ -Fe₂O₃). 高分辨透射电镜结果表明, γ -Fe₂O₃ 纳米颗粒被包覆于 HAP 当中, 平均粒径为 1~3 nm. 所制备催化剂对以叔丁基过氧化氢为氧化剂的烯烃环氧化反应显示了良好的催化活性. 此外, 催化剂的可磁力分离特性为反应后催化剂的分离回收提供了一种方便、快捷的途径. 催化剂可重复使用至少 5 次以上而没有显著的活性下降.

关键词: 羟基磷灰石; 环氧化; 叔丁基过氧化氢; 负载型钼基催化剂; 磁力分离

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Molybdenum Oxide Supported on Hydroxyapatite-Encapsulated γ -Fe₂O₃: A Novel Magnetically Recyclable Catalyst for Olefin Epoxidation

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Abstract: Hydroxyapatite-encapsulated magnetic γ -Fe₂O₃ (HAP- γ -Fe₂O₃) was synthesized and used as catalyst support. Molybdenum oxide nanoparticles were supported on HAP- γ -Fe₂O₃ by incipient wetness impregnation (MoO_x/HAP- γ -Fe₂O₃). High-resolution transmission electron microscopy characterization demonstrated the formation of γ -Fe₂O₃ nanocrystallites with a mean diameter of 1–3 nm within the HAP matrix. The molybdenum oxide dispersed on the surface of HAP- γ -Fe₂O₃ showed good catalytic activities for the epoxidation of various olefins with *tert*-butyl hydroperoxide as oxidant. The magnetism of MoO_x/HAP- γ -Fe₂O₃ provided a convenient route for the separation of the catalyst from the reaction mixture by a magnet. The catalyst was recycled at least five times without appreciable loss of catalytic activity.

Key words: hydroxyapatite; epoxidation; *tert*-butyl hydroperoxide; supported molybdenum catalyst; magnetic separation

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Olefin epoxidation is an important reaction because epoxides are very useful intermediates in the organic synthesis of fine chemicals [1]. Molybdenum (VI) solid catalysts are widely used for the epoxidation of olefins [2–8]. However,

the catalysts can only be recycled by tedious procedures using filtration and centrifugation, which inevitably leads to the loss of catalyst in the separation processes. Recently, magnetic nanoparticles of iron oxides have received grow-

ing attention due to their unique properties and potential application in various fields, such as magnetic resonance imaging (MRI) contrast agents, magnetically assisted drug delivery, hyperthermia, magnetic separation of biomolecules, and isolation and recycling of catalysts [9–12]. Magnetic separation is a convenient method for separating magnetic solid catalysts for recycling. However, bare nanoparticles of iron oxides tend to aggregate into large clusters and lose their single-domain and magnetic nanostructures. Therefore, a suitable passive material such as a polymer, carbon, or silica has to be coated on the surface of the iron oxide nanoparticles to prevent aggregation and improve their chemical stability [13–15].

Hydroxyapatites (HAPs) with the molecular formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ are of considerable interest for their structural stability, ionic substitution, and adsorption capacity [16]. The hexagonal apatite structure is composed of Ca^{2+} sites surrounded by tetrahedral PO_4^{3-} units. OH^- ions occupy columns parallel to the hexagonal structure. HAP has these unique advantages as a catalyst support: (1) a high ion-exchange ability and adsorption capacity, which are good for immobilizing active species; (2) a nonporous structure to avoid the problem of mass transfer limitation; and (3) weak acid-base properties that reduce side reactions induced by the support itself. HAP-encapsulated magnetic nanocrystallites as the catalyst support for olefin oxidation, alcohol oxidation, and dehalogenation reactions have been reported [17–19].

In this paper, we report the fabrication of molybdenum oxide nanoparticles dispersed on a hydroxyapatite shell that was coated on magnetic iron oxides particles. This was a highly active and magnetically recyclable catalyst for the epoxidation of alkene with *tert*-butyl hydroperoxide (TBHP).

1 Experimental

1.1 Catalyst preparation

The synthesis procedure is represented in Scheme 1. HAP-encapsulated γ -Fe₂O₃ (HAP- γ -Fe₂O₃) was prepared according to a previously reported method [18]. The detailed procedure was as follows. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.85 mmol)

and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.7 mmol) were dissolved in deionized water (30 ml) under an Ar atmosphere at room temperature. The resulting solution was added to a 25 wt% NH_4OH solution (10 ml) under vigorous mechanical stirring (300 r/min). A black precipitate of Fe_3O_4 was produced. In order to get small and uniform Fe_3O_4 particles, the drop rate of NH_4OH was controlled precisely by a constant dropper. The drop time was 10 min. After 15 min, 100 ml of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (33.7 mmol, 0.5 mol/L) and $(\text{NH}_4)_2\text{HPO}_4$ (20 mmol, 3.0 mol/L) solutions with their pH adjusted to 11 were added dropwise to the precipitate over 30 min under mechanical stirring. The resulting milky solution was heated to 90 °C. After 2 h, the mixture was cooled to room temperature and aged overnight. The dark brown precipitate formed was filtered, washed repeatedly with deionized water until the water was neutral, and then air dried under vacuum at room temperature. The synthesized sample was calcined at 300 °C for 3 h. The color of the powder changed from deep black to reddish-brown after calcination, indicating the transformation of the magnetite (Fe_3O_4) cores to hematite (Fe_2O_3).

The $\text{MoO}_x/\text{HAP}-\gamma\text{-Fe}_2\text{O}_3$ catalyst was prepared by incipient wetness impregnation. The required amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water. HAP- γ -Fe₂O₃ (1.0 g) was added into the stirred solution at 80 °C, and the water was completely evaporated. The $\text{MoO}_x/\text{HAP}-\gamma\text{-Fe}_2\text{O}_3$ catalyst was obtained after the solid material was calcined at 550 °C for 3 h in air.

1.2 Catalyst characterization

X-ray diffraction (XRD) was carried out on a PANalytical X'pert Pro diffractometer. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB 210 spectrometer. All binding energies were calibrated using the C 2p peak at 285.0 eV. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 electron microscope. High-resolution TEM (HRTEM) micrographs were obtained with a JEM-2010 electron microscope. BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. Magnetic properties were characterized by a VSM by Lakeshore 7304. The magnetism of HAP- γ -Fe₂O₃ was investigated using a superconducting quantum interface device magne-

Scheme 1. Synthesis of $\text{MoO}_x/\text{HAP}-\gamma\text{-Fe}_2\text{O}_3$.

tometer.

1.3 Catalytic tests

The activity of the $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst was tested with the epoxidation of olefin. In a typical experiment, a mixture of substrate (5 mmol), TBHP (70 wt%, 5 mmol), and 25 mg of $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ in 6 ml chloroform was introduced into a 50 ml glass reactor with vigorous stirring. The reaction was maintained for 8 h to get a high conversion. Qualitative analysis was conducted with a HP 6890/5973 GCMS with Chemstation and the NIST mass spectral database. Quantitative analysis was conducted with an Agilent 6820 GC equipped with an FID.

The reusability of the catalyst was tested as follows. After the reaction, a bar magnet was used to keep the $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst on the side wall of the reactor while the reaction solution was removed. The catalyst was washed repeatedly with chloroform. Alkene, chloroform, and TBHP were then added to start the next run.

2 Results and discussion

2.1 Characterization results

2.1.1 Textural, chemical, and physical properties

Figure 1 shows the nitrogen adsorption-desorption isotherms of the samples. All samples showed a Type IV isotherm with a Type H2 hysteresis loop, indicating the presence of well-developed mesoporosity in all the samples.

Table 1 summarizes the physicochemical parameters of the catalysts. As compared with $\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$, the BET

Fig. 1. N_2 adsorption-desorption isotherms of $\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ (1), 5 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ (2), 10 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ (3), 20 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ (4), and 30 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ (5).

Table 1 Textural parameters of the catalyst samples

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
$\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$	119	0.43	14.3
5 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$	59	0.39	26.2
10 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$	48	0.36	28.7
20 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$	40	0.29	29.9
30 wt% $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$	16	0.14	34.3

surface area and specific pore volume of $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ were obviously smaller while the pore diameter was increased. This was because molybdenum oxide particles have blocked some of the pores when they were deposited, which suggested that molybdenum oxide can be easily fixed on the surface of $\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ by conventional incipient wetness impregnation. It should be noted that the changes in BET surface area, specific pore volume, and pore diameter increased abruptly when the Mo loading exceeded 20 wt%, which was attributed to the agglomeration of molybdenum oxide.

2.1.2 XRD

The powder XRD patterns of HAP, $\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$, $\text{Mo}/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$, and MoO_3 samples are shown in Fig. 2. Seven well-resolved diffraction peaks of pure HAP ($2\theta = 25.9^\circ, 31.8^\circ, 32.9^\circ, 34.1^\circ, 39.8^\circ, 46.7^\circ$, and 49.5°) were

Fig. 2. XRD patterns of HAP, $\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$, $\text{MoO}_x/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$, and MoO_3 .

clearly observed with HAP- γ -Fe₂O₃ and all the MoO_x/HAP- γ -Fe₂O₃ catalysts, confirming the formation of the HAP phase. The diffraction peaks of HAP- γ -Fe₂O₃ were weak, which was probably due to the small size of the particles [18]. As compared with pure γ -Fe₂O₃ [20,21], HAP- γ -Fe₂O₃ exhibited clear diffraction peaks at $2\theta = 30.2^\circ$, 35.7° , and 43.6° , which were assigned to the (220), (311), and (400) reflections of γ -Fe₂O₃, respectively. Other iron oxide phases such as α -Fe₂O₃ ($2\theta = 24.1^\circ$, 33.1° , 35.6° , 40.8° , 54.1° , and 63.9°) were not detected. The diffraction line of MoO₃ was absent in the diffractograms of the catalysts with Mo content lower than 30 wt%. It is worth noting that two new diffraction peaks at $2\theta = 18.5^\circ$ and 28.7° appeared with all the MoO_x/HAP- γ -Fe₂O₃ catalysts, which were not seen with HAP- γ -Fe₂O₃ and MoO₃. The appearance of these two new peaks indicated that molybdenum oxide phases that were different from MoO₃ were formed on the surface of the MoO_x/HAP- γ -Fe₂O₃ catalysts. As compared with the fresh catalyst, there was no change in the characteristic diffraction peaks of the spent MoO_x/HAP- γ -Fe₂O₃ catalyst after six recycles, indicating the high stability of the catalyst.

2.1.3 XPS

XPS binding energies and intensities of the surface elements provide information on the chemical states and relative quantities of the surface compounds. Figure 3 shows the Mo 3d spectra of the MoO_x/HAP- γ -Fe₂O₃ catalysts as a function of molybdenum content. Assignment of the Mo on the supports was possible using the spectra of pure MoO₃ as reference. The Mo binding energies in MoO₃ ($E_b(\text{Mo } 3d_{5/2}) = 233.1 \text{ eV}$, $E_b(\text{Mo } 3d_{3/2}) = 236.2 \text{ eV}$) were similar to that of the MoO_x/HAP- γ -Fe₂O₃ catalysts. As compared with pure MoO₃, the Mo binding energies of all the MoO_x/HAP-

Fig. 3. XPS spectra of the Mo 3d region for different MoO_x/HAP- γ -Fe₂O₃ catalysts and MoO₃.

γ -Fe₂O₃ catalysts with different Mo loadings were shifted to lower binding energies, indicating that there was electron transfer from the support to the Mo species on the surface of the catalysts. This result also confirmed that there existed chemical interactions between Mo and the HAP- γ -Fe₂O₃ support, which was consistent with the XRD result. The energy of the Mo 3d_{5/2} signal from the MoO_x/HAP- γ -Fe₂O₃ catalyst was 232.5 eV, which agreed with that of MoO₄²⁻ reported previously [22]. Therefore, the main Mo peak of this catalyst was explained by the presence of a mixture of MoO₃ and MoO₄²⁻. In addition, as seen from Fig. 3, the XPS signal intensity of Mo 3d increased with Mo content.

2.1.4 HRTEM

Figure 4 shows the HRTEM images. Figure 4(a) showed a clear image that γ -Fe₂O₃ was coated with a layer HAP. The γ -Fe₂O₃ nanocrystallites were uniformly distributed within the host HAP matrix with diameters of 1–3 nm, which were smaller than those in the results reported by Mori et al. [18]. The micrograph of 20 wt% MoO_x/HAP- γ -Fe₂O₃ is shown in Fig. 4(b). Dark amorphous nano-particles of molybdenum oxide with a size distribution of 20–50 nm existed on the surface of HAP, which was consistent with the XRD result. The diffraction pattern (the inset in Fig. 4(a)) exhibited atomic lattice fringes corresponding to the (220), (311), and (400) planes of γ -Fe₂O₃,

Fig. 4. HRTEM images of HAP- γ -Fe₂O₃ (a) and 20 wt% MoO_x/HAP- γ -Fe₂O₃ (b).

which was in good agreement with those obtained from XRD described earlier [23].

2.1.5 Magnetic hysteresis loop

Figure 5 shows the magnetic hysteresis loop of HAP- γ -Fe₂O₃. As shown in Fig. 5, the isothermal magnetization curve of HAP- γ -Fe₂O₃ displayed a rapid increase with increasing applied magnetic field, with a saturation magnetization (M_s) value of 7 emu/g. Taken into consideration the γ -Fe₂O₃ content in the sample (12 wt%), the M_s value of 58 emu/g for γ -Fe₂O₃ encapsulated in the mesoporous titanium-silica shell was smaller than the theoretical M_s value of 76 emu/g for bulk γ -Fe₂O₃ [24], which can be explained by the size effect degradation of the magnetic properties of iron oxide nanocrystallites [25].

Fig. 5. Magnetic hysteresis loop of HAP- γ -Fe₂O₃.

2.2 Catalytic test

The catalytic activities of the various catalysts for the epoxidation of cyclohexene under different reaction conditions are shown in Table 2. In the absence of a catalyst (entry 1), cyclohexene gave only 27.1% conversion and no

epoxide was found. Since the carrier of HAP- γ -Fe₂O₃ gave a similar result to that with no catalyst, the carrier was not active (entry 2).

MoO₃/HAP- γ -Fe₂O₃ gave very high conversion and epoxide selectivity, which indicated that molybdenum oxide was the active component and confirmed the existence of molybdenum oxide on the surface of MoO₃/HAP- γ -Fe₂O₃. The catalytic performances over various molybdenum-containing catalysts with different molybdenum content were tested (entries 3–6). When the molybdenum content increased from 5 wt% to 20 wt%, the cyclohexene conversion and epoxide selectivity increased gradually. However, when the molybdenum content was > 20 wt%, the epoxide selectivity decreased, which was probably due to the increase of side reactions caused by the agglomeration of molybdenum oxide. 20 wt% MoO₃/HAP- γ -Fe₂O₃ showed 90.8% cyclohexene conversion and 98.7% epoxide selectivity, which were higher than those reported previously for this reaction using Mo-based catalysts [2–6]. Taking into account the cyclohexene conversion as well as the epoxide selectivity, 20 wt% MoO₃/HAP- γ -Fe₂O₃ was the best for the epoxidation of cyclohexene.

Various solvents were examined to find the appropriate conditions for the reaction (entries 5, 7–9). The performance of this catalyst was significantly solvent dependent, with CHCl₃ giving the best result.

The temperature dependence of cyclohexene epoxidation was also investigated (entries 5, 10, and 11). Cyclohexene conversion and epoxide selectivity strongly depended on the reaction temperature, which was consistent with the results in a previous report [26]. When the reaction was performed at 30 °C, the conversion of cyclohexene and selectivity for epoxide were very low. As the temperature increased, both the conversion of cyclohexene and selectivity for epoxide increased. A cyclohexene conversion of 90.8% and epoxide selectivity of 98.7% were obtained at 70 °C.

The present catalyst afforded a simple way for separating

Table 2 Epoxidation of cyclohexene under various reaction conditions

Entry	Catalyst	Solvent	Temperature (°C)	Conversion (%)	Epoxide selectivity (%)
1	blank	CHCl ₃	70	27.1	—
2	HAP- γ -Fe ₂ O ₃	CHCl ₃	70	33.9	—
3	5 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	70	46.1	51.8
4	10 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	70	68.9	89.0
5	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	70	90.8	98.7
6	30 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	70	93.4	95.6
7	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	C ₆ H ₁₄	70	25.7	43.4
8	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CH ₃ CN	70	no reaction	—
9	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CH ₃ OH	70	no reaction	—
10	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	30	10.3	11.2
11	20 wt% MoO ₃ /HAP- γ -Fe ₂ O ₃	CHCl ₃	50	59.4	83.7

Reaction conditions: cyclohexene 5 mmol, TBHP 5 mmol, catalyst 25 mg, solvent 6 ml, 8 h. Conversion and selectivity for olefins were determined by GC using an internal standard (decane) technique.

the catalyst from the reaction mixture due to the heterogeneous nature and magnetic properties of the catalyst. This is shown in Fig. 6. The catalyst was easily recoverable by using an external permanent magnet.

Fig. 6. Magnetic separation and recycling of the $\text{MoO}_3/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst.

We also investigated the recycling of the catalyst. It was successfully recycled and reused six times in the epoxidation of cyclohexene with no significant loss of activity, as shown in Fig. 7. As can be seen, the conversion of cyclohexene and selectivity to epoxide were almost unchanged after six reaction cycles. ICP analysis of the filtrate confirmed that the metal contents in it were negligible ($\text{Mo} < 5 \mu\text{g/L}$, $\text{Fe} < 3 \mu\text{g/L}$).

Fig. 7. Reuse of the 20 wt% $\text{MoO}_3/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst. Reaction conditions: cyclohexene 5 mmol, TBHP 5 mmol, catalyst 25 mg, CHCl_3 6 ml, 70°C , 8 h.

To extend the scope of the catalyst, the $\text{MoO}_3/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst was applied for the oxidation of a wide range of cyclic and linear alkenes with TBHP under the optimized conditions. As shown in Table 3, all of the olefins were converted into the corresponding epoxides with excellent conversions and epoxide selectivities.

Table 3 Epoxidation of olefins catalyzed by the 20 wt% $\text{MoO}_3/\text{HAP-}\gamma\text{-Fe}_2\text{O}_3$ catalyst

Substrate	Product	X/%	S/%
		72.8	97.2
		98.4	100
		79.2	86.4
		91.5	94.2
		53.8	100
		48.7	100

Reaction conditions: olefin 5 mmol, TBHP 5 mmol, catalyst 25 mg, CHCl_3 6 ml, 70°C , 8 h. Conversion and selectivity for olefins were determined by GC using an internal standard (decane) technique.

3 Conclusions

We have developed a new magnetically recyclable and efficient nanocomposite catalyst for the epoxidation of olefins using molybdenum oxide nanoparticles supported on hydroxyapatite-encapsulated $\gamma\text{-Fe}_2\text{O}_3$ nanocrystallites. This catalyst showed several attractive features for practical applications. First, $\gamma\text{-Fe}_2\text{O}_3$ nanocrystallites were dispersed within the HAP matrix. Second, the magnetic core was protected by hydroxyapatite, which makes its use under harsh reaction conditions possible. Third, the magnetic core allowed the easy recovery and recycling of the catalyst with no significant loss of catalytic activity. This magnetic nanocomposite catalyst should find applications in many other industrially important catalytic processes.

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