

REGULAR ARTICLE

Highly efficient epoxidation of alkenes with *m*-chloroperbenzoic acid catalyzed by nanomagnetic Co(III)@Fe₃O₄/SiO₂ salen complex

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MS received 25 August 2016; revised 7 November 2016; accepted 29 December 2016

Abstract. A new type of heterogeneous Co(III) complex was synthesized by covalent grafting of homogeneous Co(III) salen complex onto the surface of Fe₃O₄/SiO₂ nanoparticle (NP). The heterogeneous nanocatalyst was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR), atomic absorption spectroscopy (AAS), vibrating sample magnetometer (VSM) and nitrogen adsorption–desorption isotherm (BET). The catalytic activity was investigated for the epoxidation of alkenes using *m*-chloroperbenzoic acid as oxidant at room temperature and the corresponding epoxide was achieved with excellent yields and selectivity. In addition, the effect of axial ligand was studied on the epoxidation reaction and pyridine *N*-oxide (PNO) was chosen as an excellent axial ligand in dichloromethane. Furthermore, the heterogeneous catalyst showed good stability and the magnetic properties (which made possible the easy recovery of catalyst with external magnet) without significant decrease in the activity in the epoxidation reaction.

Keywords. Co (III) salen complex; Fe₃O₄/SiO₂; Olefins; epoxidation; *m*-chloroperbenzoic acid.

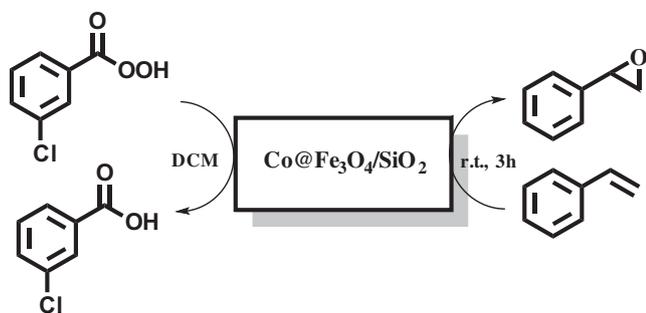
1. Introduction

Epoxidation of terminal alkenes to the corresponding epoxides is especially interesting because epoxides are valuable intermediates for the synthesis of fine chemicals, pharmaceuticals and agrochemicals.^{1,2} Schiff bases and their stable complexes with most of transition metals have a key role in coordination chemistry.^{3–6} They can be prepared simply and cheaply for industrial applications. A number of homogeneous and heterogeneous Schiff base complexes were developed for the oxidation reactions and, in particular, epoxidation of alkenes. Although, great attention was shown to the epoxidation of alkenes using Mn(III) salen complex,^{7–14} several investigations have reported that Co(III) complexes are good catalysts for the epoxidation of alkenes.^{15–18} Covalent attachment of Co(III) complexes on a solid support such as polymer, zeolite and silica have recently been reported as innovation in the catalytic properties of such compounds.^{19–23}

Recently, magnetic nanoparticles with special properties, such as ease of separation by external magnet,

high catalyst loading capacity due to high surface area, high dispersion, convenient recycling of catalyst and outstanding stability, have been extensively employed as a good candidate for catalyst supports.^{24,25} In addition, they possess attractive properties (low toxicity and high biocompatibility, super paramagnetism, high magnetic susceptibility and saturation magnetization) that could potentially be used in catalysis, magnetic resonance imaging contrast enhancement, drug delivery, data storage, magnetic bioseparation, gene manipulation, targeted drug carrier, enzyme immobilization, immunoassay and environmental remediation.^{26–33} However, pure magnetic particles such as Fe₃O₄ NPs usually suffer from a large aggregation which alters magnetic properties. To overcome this problem, an appropriate coating material such as silica was applied to avoid such limitations.³⁴ Several types of functionalized Fe₃O₄ NPs and studies on immobilization of organo-catalysts and metal on silica-coated Fe₃O₄ NPs have also been recently reported.^{26,35–37} In continuation of the study of metal salen complexes,^{38,39} herein, we synthesized Co(III) salen complex anchored onto the Fe₃O₄/SiO₂ NPs (Co@Fe₃O₄/SiO₂). The heterogeneous catalyst was used in the epoxidation of alkenes using *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant in dichloromethane (Scheme 1).

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Scheme 1. Schematic illustration for the epoxidation of alkenes.

2. Experimental

2.1 Materials

Tetraethoxysilane (TEOS), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, styrene, α -methylstyrene, 4-chlorostyrene, cyclooctene, indene, cis & trans stilbene, cyclohexene, 1-octene, pyridine *N*-oxide (PNO), pyridine (Py), *N*-methylmorpholine *N*-oxide (NMNO), 1-methyl imidazole (MI), imidazole (IM), ethylacetate (EtOAc), dichloromethane (DCM), CH_3CN , toluene, CHCl_3 , ethanol (EtOH), tetrahydrofuran (THF), *m*-chloroperbenzoic acid (*m*-CPBA), NaIO_4 , NH_4OAc , *tert*-butylhydrogenperoxide (TBHP), $\text{PhI}(\text{OAc})_2$, H_2O_2 (30%), (R,R)-1,2-cyclohexanediamine, 2,4-dihydroxybenzaldehyde and oxone were purchased from Merck Company and used without purification.

The IR spectra were recorded on a Perkin-Elmer 783 Infrared spectrophotometer in a KBr pellet, scanning from 4000 to 600 cm^{-1} at room temperature. The XRD measurements were recorded using a Bruker D₈-advance X-ray diffractometer with Cu K_α radiation ($k = 1.5406 \text{ \AA}$). The TEM images were obtained using the Philips CM10 instrument. Magnetization measurements were carried out at 300 K on a vibrating sample magnetometer (VSM Leak shore 7200). TGA curves were obtained using a Perkin-Elmer Diamond TG/DTA thermal analyzer by heating the samples in an Argon flow at a rate of 100 mL min^{-1} with a heating rate of $10^\circ\text{C min}^{-1}$. The yields and selectivity of the products were obtained by GC-17A Shimadzu with capillary column (Shimadzu, CBP5, $30\text{ m} \times 25\text{ mm} \times 0.25\text{ }\mu\text{m}$).

2.2 Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanocatalyst

Black powder of magnetic Fe_3O_4 NPs was synthesized as described in the literature.⁴⁰ The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs were synthesized by the Stober method with some modification.⁴¹ Briefly, 0.5 g of Fe_3O_4 (2.1 mmol) was dispersed in the solution containing the mixture of ethanol/deionized water (80:20 mL), followed by the addition of 3 mL of NH_3 . Then, 1.5 mL of TEOS was added dropwise to the mixture and stirred mechanically for 20 h at room temperature. The core-shell $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was separated by an external magnet, washed with deionized water and ethanol three times and dried at 80°C for 8 h. Fe_3O_4 : IR/ cm^{-1} : 3446, 580; XRD:

$2\theta = 30.2^\circ, 35.4^\circ, 43.3^\circ, 53.6^\circ, 57.5^\circ, 63.1^\circ$. $\text{Fe}_3\text{O}_4/\text{SiO}_2$: IR/ cm^{-1} : 3446, 1059, 954, 755, 580; XRD: $2\theta = 15\text{--}27^\circ, 30.2^\circ, 35.4^\circ, 43.3^\circ, 53.6^\circ, 57.5^\circ, 63.1^\circ$.

2.3 Synthesis of ligand salen

N,N'-Bis(2,4-di-hydroxybenzaldehyde)-1,2-cyclohexanediamine was synthesized as described in the literature.⁴² *N,N'*-Bis(2,4-di-hydroxybenzaldehyde)-1,2-cyclohexanediamine: Light brown Solid, yield 85%, M.p. = $187\text{--}189^\circ\text{C}$, IR/ cm^{-1} : 2600–3450(br, OH), 2920(CH₂), 2880(CH₂), 1615(vs, C=N), 1496(s), 1425(s), 1380(vs), 1247(m), 1170(s, C–O), 970(s), 925(m), 835(s), 780(m), 730(vs). ¹H-NMR (DMSO, 250 MHz) ppm: 1.5 (4H, CH₂), 1.8 (4H, CH₂), 3.1 (2H, CH), 6.37–7.43 (C, 6H, CH_{arom}), 8.43 (s, 1H, CH=N), 8.50 (s, 1H, CH=N), 9.8–10.20 (br, 2H, OH), 12.72 (s, 1H, OH), 13.16(s, 1H, OH); ¹³C-NMR(DMSO, 62.7 MHz) ppm: 23.6, 29.2, 71.8, 104.5, 109.2, 118.1, 133.0, 161.0, 162.5, 163.1; Ms, *m/z* (%), 355.16($\text{M}^+ + 1$, 2), 354.16(M^+ , 20), 277(10), 262(38), 227(41), 183(39), 122(base peak), 109(29), 77(55).

2.4 Synthesis of Co(III) salen complex

Co(III) salen complex was synthesized as described in the literature.⁴³ Co(III) salen complex: Dark brown Solid, yield 90%, IR/ cm^{-1} , 2600–3450(br, OH), 2920(CH₂), 2880(CH₂), 1590(vs, C=N), 1496(s), 1425(s), 1380(vs), 1247(m), 1170(s, C–O), 970(s), 925(m), 835(s), 780(m), 730(vs).

2.5 Synthesis of $\text{Co}@Fe_3O_4/\text{SiO}_2$ nanocatalyst

Homogeneous Co(III) salen complex was chemically immobilized onto the $\text{Fe}_3\text{O}_4/\text{SiO}_2$. In brief, 2 g of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was dispersed in 100 mL of dry toluene under magnetic stirring followed by the addition of 0.5 g of homogeneous Co(III) complex (Scheme 1) and refluxed for 24 h under inert atmosphere. After the completion of the reaction, the heterogeneous catalyst ($\text{Co}@Fe_3O_4/\text{SiO}_2$) was washed in turn with dry toluene, EtOH and extracted repeatedly on a Soxhlet extractor with methanol and dichloromethane until the washing became colorless. The heterogeneous catalyst was dried at 70°C under vacuum for 6 h. The $\text{Co}@Fe_3O_4/\text{SiO}_2$ was characterized by FT-IR, TEM, XRD, VSM, BET and TGA.

2.6 General procedure for the epoxidation of alkenes

Typically, 2.5 mol% of $\text{Co}@Fe_3O_4/\text{SiO}_2$ as catalyst (based on Co element) was dispersed in dichloromethane (3 mL) for 20 min. Styrene (1 mmol), toluene (internal standard, 40 μL), *m*-CPBA (2 mmol) as oxidant and PNO (0.5 mmol) as additive were added to the mixture. The reaction mixture was stirred at room temperature for appropriate times and the progress of the reaction was monitored by TLC.

After the completion of the reaction, the catalyst was separated using external magnet and the solution was washed with NaOH (1 M, 8 mL) and brine (8 mL) and dried over MgSO₄. Finally, the solution was concentrated to 1 mL and the yield and selectivity of products were determined by GC. The heterogeneous catalyst was washed with ethanol and reused.

3. Results and Discussion

Co@Fe₃O₄/SiO₂ NPs was synthesized according to the procedure illustrated in Scheme 2. Initially, Fe₃O₄ NPs was synthesized and coated with silica (Fe₃O₄/SiO₂). The homogeneous Co(III) salen complex was immobilized onto the Fe₃O₄/SiO₂ NPs afforded the desired Co@Fe₃O₄/SiO₂ nanoparticle.

3.1 Characterizations of the catalyst

The magnetic properties of the Fe₃O₄, Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ NPs were investigated by different techniques (FT-IR, TEM, VSM, XRD, BET, AAS and TGA). The IR spectrum of Fe₃O₄ NPs shows important vibration bands in 560–590 and 3400 cm⁻¹ which are due to Fe–O and O–H, respectively (not listed). Salen ligand shows important band at 3450 cm⁻¹ which belongs to the O–H group (Figure 1a). Also, the bands at 2920 and 2880 cm⁻¹ are assigned to the aliphatic CH bond. Furthermore, the band at 1615 cm⁻¹ corresponds to the C=N bond. This band shifts to the lower position (25 cm⁻¹) in homogeneous Co(III) salen complex, which suggests the coordination of Co through C=N bond (Figure 1b). In Figure 1(d) which belongs to the Fe₃O₄/SiO₂ NPs, several important vibration bands at 560–590, 954, and 3400 cm⁻¹ are observed.

These vibration bands are due to Fe–O, Si–OH, and O–H, respectively. Also, the vibration bands at 755 and 1100 cm⁻¹ are due to Si–O–Si. The vibration bands at 755, 954 and 1100 cm⁻¹ confirmed that the silica shell was coated on the surface of the Fe₃O₄ NPs. The IR spectra of Co@Fe₃O₄/SiO₂ NPs showed a strong vibration band at 1595 cm⁻¹. This vibration band is assigned coordination to Co through C=N functional groups (Figure 1c). Furthermore, new stretching, vibration bands at 1590, 2880 and 2920 cm⁻¹ confirmed the immobilization of homogeneous Co(III) salen complex on the Fe₃O₄/SiO₂ NPs (Figure 1c).

The TGA curves of Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ NPs are shown in Figure 2. In the TG cure of Fe₃O₄/SiO₂ NPs, a weight loss over the range of 90–165°C was observed (3%). This weight loss is attributed to the loss of adsorbed water and dehydroxylation of

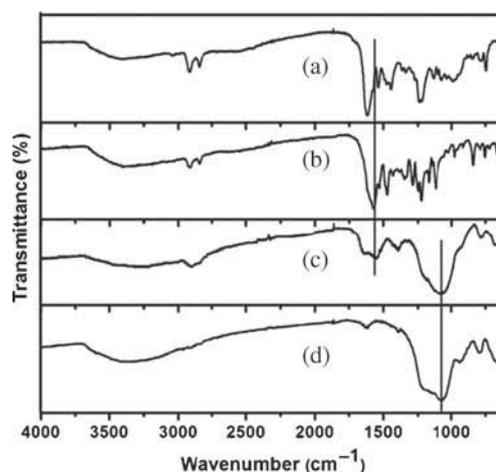
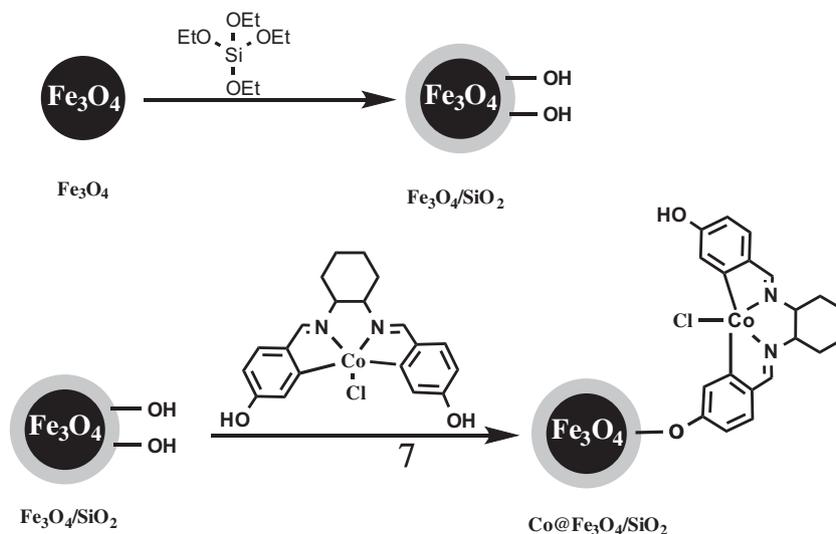


Figure 1. FT-IR spectra. (a) salen, (b) Co complex, (c) Co@Fe₃O₄/SiO₂, and (d) Fe₃O₄/SiO₂ NPs.



Scheme 2. Schematic illustration for the preparation of Co@Fe₃O₄/SiO₂ catalyst.

internal -OH groups. The second weight loss over the range 250–590°C was observed. This weight loss is ascribed to even further decomposition of the material. The total weight losses were approximately 10% (Figure 2a). As shown in Figure 2b, the first step of weight loss is decreased after the immobilization of Co(III) salen complex onto the Fe₃O₄/SiO₂ NPs which indicated that the Co(III) salen complex has been successfully immobilized onto the Fe₃O₄/SiO₂. The TGA curve of Co@Fe₃O₄/SiO₂ has two weight losses over the range of 90–160°C and 250–650°C which are similar to the Fe₃O₄/SiO₂. The total weight losses were approximately 13% (Figure 2b). The loading of Co(III) salen complex is 0.40 mmol g⁻¹ based on the difference in the weight losses for Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂.

The vibrating sample magnetometer (VSM) recordings of Fe₃O₄, Fe₃O₄/SiO₂ NPs and Co@Fe₃O₄/SiO₂ are shown in Figure 3. As obvious in Figure 3, all the nanoparticles have superparamagnetism property at 300 K and no hysteresis phenomenon was observed. The values of saturation magnetization for Fe₃O₄, Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ NPs catalyst are

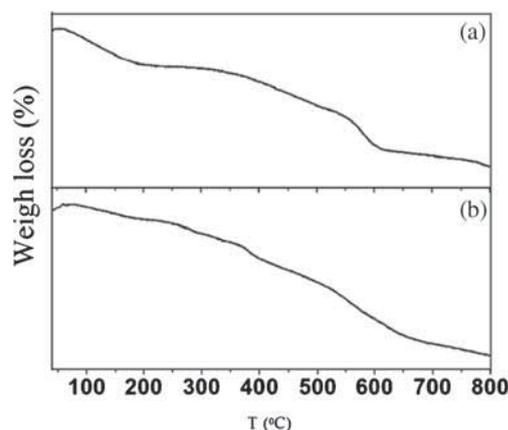


Figure 2. Thermogravimetric weight loss pattern of (a) Fe₃O₄/SiO₂ NPs and (b) Co@Fe₃O₄/SiO₂ with temperature raised of 10°C/min.

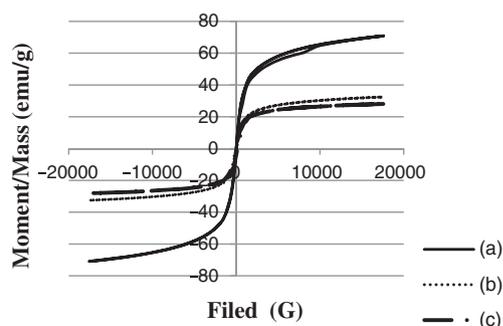


Figure 3. Magnetization curves of (a) Fe₃O₄, (b) Fe₃O₄/SiO₂ NPs, (c) Co@Fe₃O₄/SiO₂ NPs at 300 K.

70.495, 38.30 and 34.30 emu/g, respectively. By immobilization of SiO₂ and Co(III) salen complex onto Fe₃O₄, the saturation magnetization values of Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ catalyst were decreased. Despite the considerable decrease in the magnetization of Co@Fe₃O₄/SiO₂, this heterogeneous catalyst can still be separated from the solution by using an external magnetic field on the side wall of the reactor.

Figure 4 shows the XRD patterns of Fe₃O₄, Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ NPs which were determined by powder X-ray diffraction (XRD). The XRD pattern of Fe₃O₄ NPs (Figure 4A) indicates a crystalline structure at 2θ: 30.2°, 35.4°, 43.3°, 53.6°, 57.5° and 63.1° which are assigned to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystallographic faces of magnetite. A broad peak at 2θ = 15–27° in the XRD patterns of Fe₃O₄/SiO₂ and Co@Fe₃O₄/SiO₂ NPs are assigned to amorphous silica Figure 4(B, C). Using Debye–Scherrer equation (1), the size of these particles could be estimated by determining the width of the (3 1 1) Bragg reflection (1).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where, λ is the wavelength of the X-ray, k is the Scherrer constant, β is the half-width of the peak and θ is half of the Bragg angle. Therefore, the size (D) of the particles could be estimated. The average diameter of Fe₃O₄ NPs was 15 nm, while the diameter of Fe₃O₄/SiO₂ NPs was about 20 nm which is due to the agglomeration of Fe₃O₄ inside nanosphere and surface growth of silica on the shell.

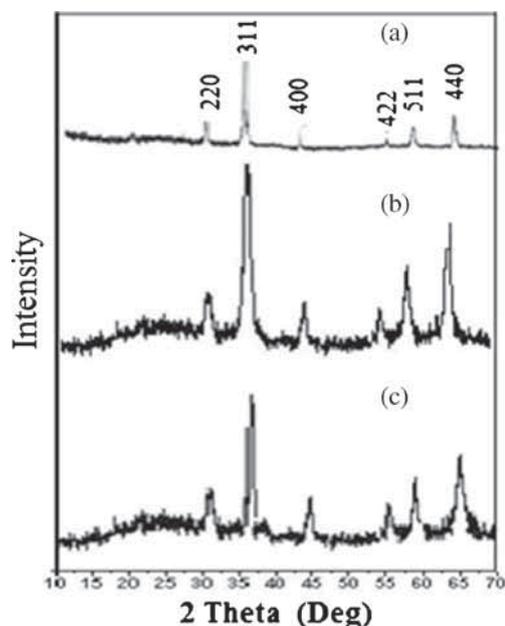


Figure 4. XRD pattern of (A) Fe₃O₄, (B) Fe₃O₄/SiO₂ NPs and (C) Co@Fe₃O₄/SiO₂ NPs.

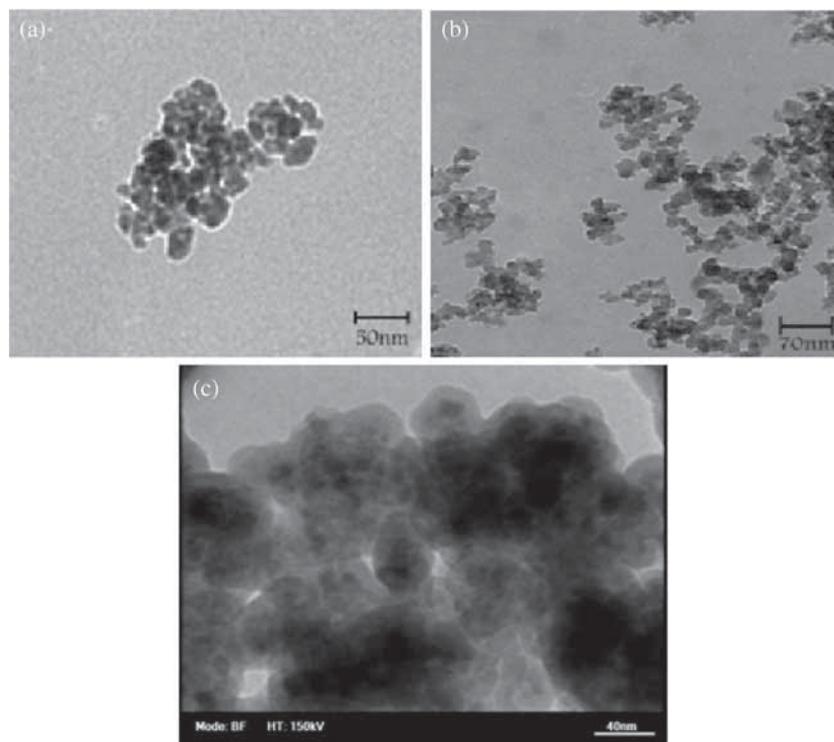


Figure 5. TEM images of (a) Fe₃O₄, (b) Fe₃O₄/SiO₂ and (c) Co@Fe₃O₄/SiO₂.

Figures 5a and 5b show the TEM images of Fe₃O₄ and Fe₃O₄/SiO₂ NPs. Considering the TEM of Fe₃O₄ and Fe₃O₄/SiO₂, the average size of 16 and 21 nm were obtained which are similar to the results of XRD patterns. The TEM images of Fe₃O₄/SiO₂ NPs indicated the successful coating of silica shell on the magnetic Fe₃O₄ NPs (Figure 5b).

The TEM image of Co@Fe₃O₄/SiO₂ showed the successful immobilization of Co(III) salen complex on the Fe₃O₄/SiO₂ NPs (Figure 5c). The BET specific surface area of the Co@Fe₃O₄/SiO₂ was measured at room temperature by nitrogen physisorption and the surface area of was found to be 20 m²/g. The loading of Co(III) salen complex on the Fe₃O₄/SiO₂ was 0.42 mmol/g based on Co elemental analysis by AAS.

3.2 Catalytic activity studies

3.2a Epoxidation of unfunctionalized alkenes: The catalytic activity of Co@Fe₃O₄/SiO₂ was studied for the epoxidation of terminal alkenes. The activity and selectivity of Co@Fe₃O₄/SiO₂ was compared with the respective homogeneous Co salen complex. Initially, the reaction of styrene as the test reaction was investigated using *m*-CPBA as the oxidant and PNO as axial ligand at room temperature in dichloromethane (DCM) as solvent. In search of optimal reaction conditions to achieve maximum selectivity and yield of styrene

oxide, the effects of different amounts of catalyst, oxidant, axial ligand, solvent, temperature and time were investigated for the test reaction.

3.2b The effect of catalyst amount on the epoxidation of styrene catalyzed by Co@Fe₃O₄/SiO₂: To optimize the amount of catalyst, different amounts of Co@Fe₃O₄/SiO₂ (0.5–3 mol% based on Co element) were studied in the epoxidation of styrene (1 mmol) with *m*-CPBA (2 mmol) at room temperature in 3 mL DCM and the results showed that 2.5 mol% of Co@Fe₃O₄/SiO₂ is the optimum amount of catalyst (Table 1, entry 5). The epoxidation reaction of styrene was carried out over parent of Co@Fe₃O₄/SiO₂ (Fe₃O₄ and Fe₃O₄/SiO₂) to determine which part of the Co@Fe₃O₄/SiO₂ has catalytic activity and the results showed that low yields were observed (20 and 42%, respectively) (not listed). In the absence of catalyst, since there are no active sites, negligible conversion was found which demonstrates that the epoxidation reaction is a catalytic process (Table 1, entry 8). The effect of axial ligand (PNO) was also investigated and the results showed that in the absence of PNO an obvious decrease in the yield (70%) was observed (not listed). Also, in the homogeneous phases, the Co(III) complex was used under the same reaction conditions and the time of reaction is shortened to 2 h (Table 1, entry 8).

3.2c The effect of different solvents and time on the epoxidation of styrene catalyzed by Co@Fe₃O₄/SiO₂: The selected solvents should be stable and dissolve the substrate and oxidant. So, different types of solvent with a range of polarity were investigated in the reaction under the same conditions. Considering the results, the polarity of solvents was effective on the catalytic activity of Co@Fe₃O₄/SiO₂ (Table 2). Under the mentioned conditions, the reaction did not proceed well in water which can be due to the low dispersion of the catalyst and collision with the substrate (Table 2, entry 1).⁴⁴ In the case of ethanol and methanol, the low yield of styrene oxide was observed which may be because of the coordination of solvent with Co(III) ions and competing with the oxidation reaction.^{45,46} Furthermore, poor conversion of styrene oxide was observed in the nonpolar media (Table 2, entry 5). Finally, the excellent yield of the styrene oxide was observed in DCM (Table 2, entry 9).

Table 1. Optimization of different amount of Co@Fe₃O₄/SiO₂ nanocatalyst on the reaction of styrene with *m*-CPBA as a model reaction.^a

Entry	Catalyst amount (mol%)	Yield ^b (%)
1	0.5	20
2	1.0	41
3	1.5	64
4	2.0	80
5	2.5	95
6	3.0	97
7	homogeneous Co (III) complex (2.5 mol%)	98
8	–	0

^aReaction conditions: substrate (1 mmol), DCM (3 mL), oxidant (2 mmol) and Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co) at r.t. Duration: 3 h. ^b Determined by GC with a Shimadzu CBP5 column (30 m × 0.32 mm × 0.25 mm).

Table 2. The effect of different solvents on the epoxidation of styrene.^a

Entry	Solvent	Yield ^b (%)
1	H ₂ O	13
2	EtOH:H ₂ O	22
3	MeOH	28
4	EtOH	30
5	THF	40
6	CHCl ₃	50
7	CH ₃ CN	65
8	EtOAc	80
9	DCM	95

^aReaction conditions: substrate (1 mmol), *m*-CPBA (2 mmol) and Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co element) at r.t. duration: 3 h. ^bDetermined by GC with a Shimadzu CBP5 column (30 m × 0.32 mm × 0.25 mm).

The progress of the conversion of styrene was also investigated at different times (Figure 6). As shown in the Figure 6, the conversion increased linearly with the reaction time and reached up to 70% at 2 h. Increasing the time of reaction to 3 h gradually increased the yield of styrene oxide to 95% with constant selectivity of 99%.

3.2d The effect of different oxidants/additives in the epoxidation of styrene: Co(III) is a good Lewis acid, which makes it able to withdraw electron from the peroxidic oxygen and susceptible to be attacked by nucleophilic alkene in DCM medium. The conversion and selectivity of the reaction were investigated in the presence of various oxidants (*m*-CPBA, urea hydrogen peroxide (UHP), NaIO₄, Oxone, H₂O₂, PhI(OAc)₂, PhIO and TBHP). As can be seen from Table 3, in the absence of oxidant, no yield was observed (Table 3, entry 1). In the presence of some oxidants, such as UHP, H₂O₂, PhIO, PhI(OAc)₂, low yield of products was observed (Table 3, entries 2–5). Oxone and NaIO₄ (for both of them, the 2:1 mixture of acetonitrile: water was used as the solvent) gave better yields (Table 3, entries 6, 7). The best yields were observed in the presence of *m*-CPBA (Table 3, entry 9). Different amount of the oxidant was also tested and the best result was obtained

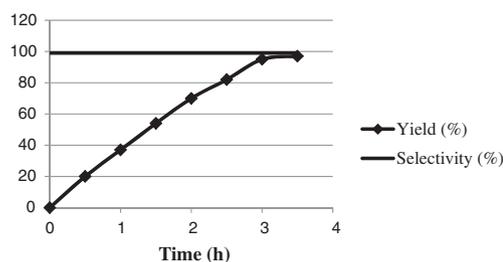


Figure 6. Change of conversion with reaction time for the model reaction catalyzed by fresh Co@Fe₃O₄/SiO₂ catalyst.

Table 3. The effect of different oxidants on the epoxidation of styrene catalyzed by Co@Fe₃O₄/SiO₂.^a

Entry	Oxidant	Yield (%)
1	–	0
2	H ₂ O ₂	25
3	PhIO	27
4	PhI(OAc) ₂	22
5	UHP	30
6	NaIO ₄	50
7	Oxone	60
8	TBHP	85
9	<i>m</i> -CPBA	95

^aReaction conditions: Styrene (1 mmol), Oxidant (2 mmol), PNO (0.5 mmol) and Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co) at r.t. duration: 3 h.

with 2 equivalents of the *m*-CPBA which provides moderate source of oxygen for the catalytic reaction (not listed). Consequently, the optimum molar ratio of olefin to oxidant is 1:2.

The effect of different axial ligands such as NH₄OAc, PNO, NMNO, Py, MI and imidazole was investigated in the epoxidation of styrene in DCM/*m*-CPBA system (Table 4). Despite of some reports which stated that axial ligands decrease the yield of reaction, our results showed that some axial ligands obviously increased the yields and shortened the time of reaction. As shown

Table 4. The effect of different axial ligand on the epoxidation of styrene catalyzed by Co@Fe₃O₄/SiO₂.^a

Entry	Axial ligand	Yield (%)
1	NH ₄ OAc	15
2	Py	45
3	MI	56
4	imidazole	65
5	NMNO	80
6	PNO	95

^aReaction conditions: Styrene (1 mmol), *m*-CPBA (2 mmol), axial ligand (0.5 mmol) and Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co) at r.t.

in Table 4, poor conversion was observed in the presence of NH₄OAc (Table 4, entry 1). Using some axial ligand such as Py, MI, imidazole and NMNO, the yield increased up to 45, 56, 68 and 80%, respectively (Table 4, entries 2–5). Finally, the best yield was observed in the presence of PNO as axial ligand (Table 4, entry 6, yield: 95%). Under the same conditions, a new reaction was carried out in the presence of homogeneous Co(III) complex and styrene was converted to the styrene oxide in 2 h with 97% yield (not listed).

The reactions were also performed at 40°C and obvious increase in the conversion was observed while the selectivity of the reaction decreased to 85% (not listed). Therefore, we employed the optimized conditions (Co@Fe₃O₄/SiO₂, 2.5 mol%), *m*-CPBA (2 mmol) and PNO (0.5 mmol) in 3 mL DCM at 25°C for the conversion of several olefins into the corresponding products. Table 5 lists a group of alkenes that were investigated using Co@Fe₃O₄/SiO₂. The catalyst showed excellent activity toward alkene oxidation with an average isolation yield of 93%. The yield and selectivity of the products are 91–95% and 99%, respectively. The efficiency of the catalyst was investigated for the epoxidation of substrates

Table 5. Epoxidation of different alkenes using *m*-CPBA catalyzed by Co@Fe₃O₄/SiO₂.^a

Entry	Alkene	Time (h)	Yield ^b (%)	Selectivity ^c (%)	TON ^d	TOF ^e (h ⁻¹)
1		3	95	99	3800	1266.7
2		3	95	99	3800	1266.7
3		3	93	99	3720	1240.0
4		3	94	99	3760	1253.3
5		3	94	99	3760	1253.3
6		3	92	99	3680	1226.7
7		3	91	99	3640	1213.3
8		3	92	99	3680	1226.7
9		3	90	99	3600	1200.0

^aReaction conditions: Substrate (1 mmol), DCM (3 mL), Oxidant (2 mmol), PNO (0.5 mmol) and Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co). ^bDetermined by GC with a Shimadzu CBP5 column (30 m × 0.32 mm × 0.25 mm). ^cSelectivity based on alkene conversion. ^dTON = mmol of converted alkene/mmol Co; ^eTOF = TON/time of reaction.

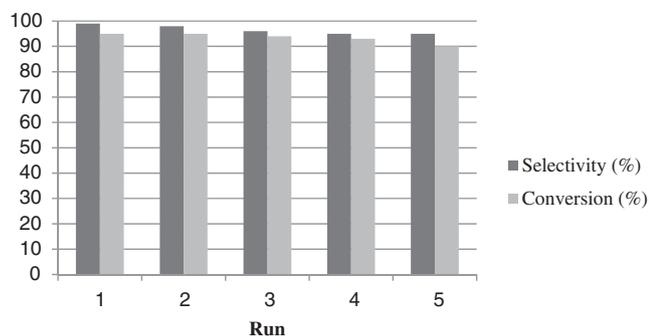


Figure 7. The recycles of the catalyst for the epoxidation styrene with *m*-CPBA (2 mmol) and PNO (0.25 mmol) in DCM (3 mL) catalyzed by Co@Fe₃O₄/SiO₂ (2.5 mol% based on Co elemental content) at r.t.

having sensitive groups (substrates that have electron-withdrawing group likes 2-cyclohexen-1-one) in which lower yields and selectivity were observed. It could be deduced that Co@Fe₃O₄/SiO₂ possessed efficient catalytic activity, when the axial ligand PNO was used. The TON and TOF of the reactions are 3600–3800 and 1213.3–1266.7 h⁻¹, respectively. The conditions used for styrene: injector temperature, 220°C; detector temperature, 250°C, injection volume, 0.2 μL, and the oven temperature program was initially started at 150°C; raised to 220°C at 20°C min⁻¹; and was set at 220°C constantly for 5 min.

To study the reusability of Co@Fe₃O₄/SiO₂, the catalyst was separated by external magnet, washed with ethanol, dried under vacuum and then subjected to a subsequent round of reaction under the same reaction conditions with no significant loss of activity, which validated its recyclability. The yield and selectivity of the final products were comparable to that of the original one (Figure 7). The leaching of Co ion into the solution was checked during the reaction by AAS and no significant Co was detected in the filtrate. As shown in the Figure 7, the catalytic activity did not change significantly after five repeated runs (Yield: from 95 to 90%, Selectivity from 99 to 95%). The slight decrease in the activity and enantioselectivity of products may be due to the aggregation of Fe₃O₄ or the leaching of silica.

4. Conclusions

Novel Co@Fe₃O₄/SiO₂ was synthesized by grafting homogeneous Co(III) salen complex onto the Fe₃O₄@SiO₂NPs. The characterization results confirmed that homogeneous Co(III) salen complex has been successfully incorporated onto Fe₃O₄@SiO₂ NPs. This nanocatalyst has strong magnetic responsivity due to a high saturation magnetization value (34.3 emu g⁻¹).

The magnetic nanocomposite showed excellent catalytic activity toward the epoxidation of alkenes and the best conversion was achieved in the presence of *m*-CPBA as oxidant and PNO as the axial ligand in DCM. The selectivity of the reaction was also investigated and excellent selectivity was observed (99%). Co@Fe₃O₄/SiO₂ showed comparable conversion and selectivity as that of homogeneous counterpart for the epoxidation of several alkenes. In addition, the heterogeneous Co@Fe₃O₄/SiO₂ is relatively stable and can be reused five times with constant catalytic activity and no metal leaching. Therefore, absence of side reactions, short reaction times, high activity and stability, easy recoverability with external magnet and reusability render it a potentially valuable catalyst for industrial applications.

Acknowledgements

The authors are grateful to the University of Birjand for financial support.

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