J. Chem. Sci. © Indian Academy of Sciences.
DOI 10.1007/s12039-017-1229-y

REGULAR ARTICLE

Highly efficient epoxidation of alkenes with m-chloroperbenzoic acid catalyzed by nanomagnetic Co(III)@Fe_3O_4/SiO_2 salen complex

ALI ALLAHRESANI* and MOHAMMAD ALI NASSERI
Department of Chemistry, Faculty of Sciences, University of Birjand, P. O. Box 97175-615, Birjand, Iran
Email: a_allahresani@birjand.ac.ir; manaseri@birjand.ac.ir

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 Fe_3O_4/SiO_2 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; Fe_3O_4/SiO_2; Olefins; epoxidation; m-chloroperbenzoic acid.

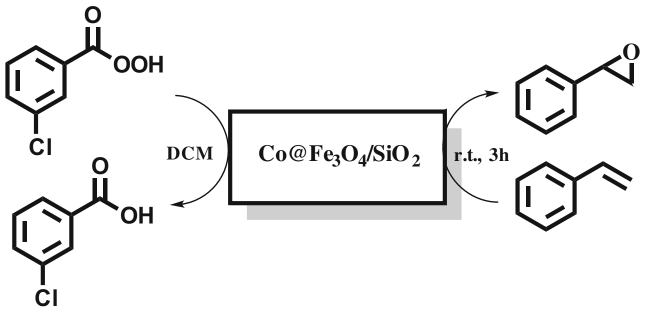
1. Introduction

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 Fe_3O_4 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 Fe_3O_4 NPs and studies on immobilization of organo-catalysts and metal on silica-coated Fe_3O_4 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 Fe_3O_4/SiO_2 NPs (Co@Fe_3O_4/SiO_2). The heterogeneous catalyst was used in the epoxidation of alkenes using *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant in dichloromethane (Scheme 1).

---

*For correspondence



Scheme 1. Schematic illustration for the epoxidation of alkenes.

2. Experimental

2.1 *Materials*

Tetraethoxysilane (TEOS), $FeCl_3·6H_2O$, $FeCl_2·4H_2O$, 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), $PhI(OAc)_2$, 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 D_8-advance X-ray diffractometer with Cu K_α radiation (k = 1.5406 Å). 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°C min^{-1}. The yields and selectivity of the products were obtained by GC-17A Shimadzu with capillary column (Shimadzu, CBP5, 30 m × 25 mm × 0.25 μm).

2.2 *Synthesis of Fe_3O_4/SiO_2 nanocatalyst*

Black powder of magnetic Fe_3O_4 NPs was synthesized as described in the literature.[40] The Fe_3O_4/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 Fe_3O_4/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: $2\theta = 30.2°, 35.4°, 43.3°, 53.6°, 57.5°, 63.1°$. Fe_3O_4/SiO_2: IR/cm^{-1}: 3446, 1059, 954, 755, 580; XRD: $2\theta = 15–27°, 30.2°, 35.4°, 43.3°, 53.6°, 57.5°, 63.1°$.

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. = 187–189°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). ^{1}H-NMR (DMSO, 250 MHz) ppm :1.5 (4H, CH2), 1.8 (4H, CH2), 3.1 (2H, CH), 6.37–7.43 (C, 6H, CHarom), 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); ^{13}C-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($M^+ + 1$, 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 Co@Fe_3O_4/SiO_2 nanocatalyst*

Homogeneous Co(III) salen complex was chemically immobilized onto the Fe_3O_4/SiO_2. In brief, 2 g of Fe_3O_4/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 (Co@Fe_3O_4/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 Co@Fe_3O_4/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 Co@Fe_3O_4/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 $MgSO_4$. 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@Fe_3O_4/SiO_2 NPs was synthesized according to the procedure illustrated in Scheme 2. Initially, Fe_3O_4 NPs was synthesized and coated with silica (Fe_3O_4/SiO_2). The homogeneous Co(III) salen complex was immobilized onto the Fe_3O_4/SiO_2 NPs afforded the desired Co@ Fe_3O_4/SiO_2 nanoparticle.

3.1 *Characterizations of the catalyst*

The magnetic properties of the Fe_3O_4, Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 NPs were investigated by different techniques (FT-IR, TEM, VSM, XRD, BET, AAS and TGA). The IR spectrum of Fe_3O_4 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 Fe_3O_4/SiO_2 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 Fe_3O_4 NPs. The IR spectra of Co@Fe_3O_4/SiO_2 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 Fe_3O_4/SiO_2 NPs (Figure 1c).

The TGA curves of Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 NPs are shown in Figure 2. In the TG cure of Fe_3O_4/SiO_2 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

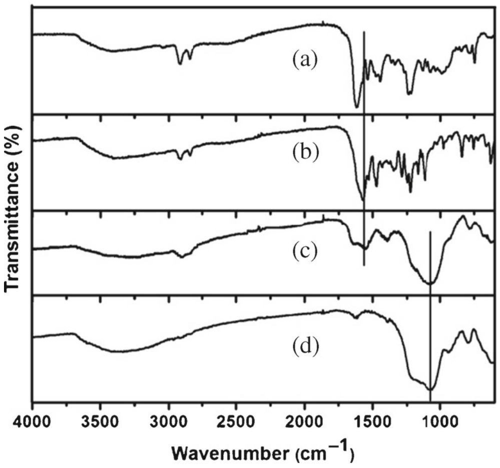
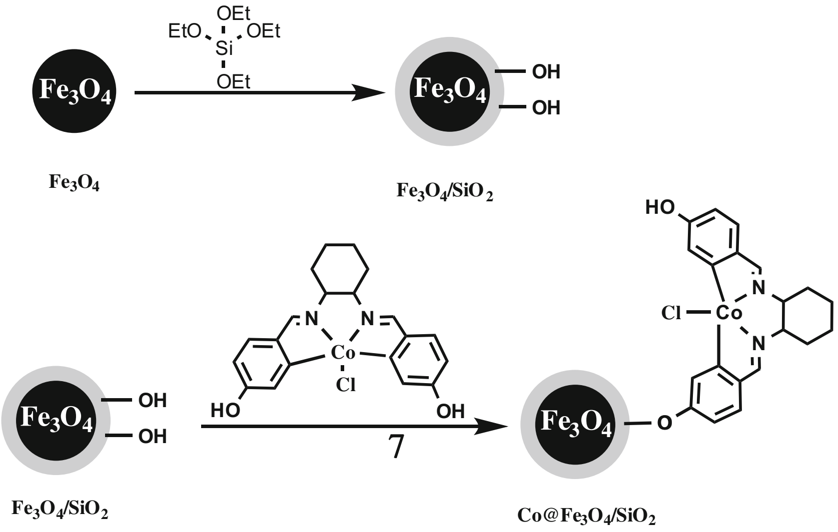


Figure 1. FT-IR spectra. (a) salen, (b) Co complex, (c) Co@Fe_3O_4/SiO_2, and (d) Fe_3O_4/SiO_2 NPs.



Scheme 2. Schematic illustration for the preparation of Co@Fe_3O_4/SiO_2 catalyst.

internal $^{-}$OH groups. The second weight loss over the range 250–590°C wa 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 Fe_3O_4/SiO_2 NPs which indicated that the Co(III) salen complex has been successfully immobilized onto the Fe_3O_4/SiO_2. The TGA curve of Co@Fe_3O_4/SiO_2 has two weight losses over the range of 90–160°C and 250–650°C which are similar to the Fe_3O_4/SiO_2. 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 Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2.

The vibrating sample magnetometer (VSM) recordings of Fe_3O_4, Fe_3O_4/SiO_2 NPs and Co@Fe_3O_4/SiO_2 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 Fe_3O_4, Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 NPs catalyst are 70.495, 38.30 and 34.30 emu/g, respectively. By immobilization of SiO_2 and Co(III) salen complex onto Fe_3O_4, the saturation magnetization values of Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 catalyst were decreased. Despite the considerable decrease in the magnetization of Co@Fe_3O_4/SiO_2, this heterogeneous catalyst can still be separated from the solution by using an external magnetic field on the side wall of the reactor.

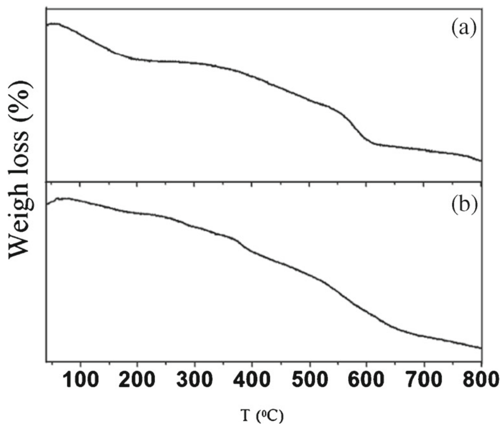


Figure 2. Thermogravimetric weight loss pattern of (a) Fe_3O_4/SiO_2NPs and (b) Co@ Fe_3O_4/SiO_2 with temperature raised of 10°C/min.

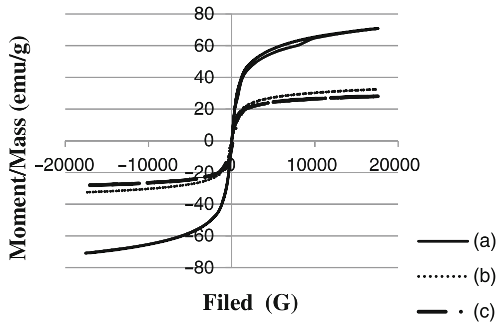


Figure 3. Magnetization curves of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2 NPs, (c) Co@Fe_3O_4/SiO_2 NPs at 300 K.

Figure 4 shows the XRD patterns of Fe_3O_4, Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 NPs which were determined by powder X-ray diffraction (XRD). The XRD pattern of Fe_3O_4 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 $2\theta = 15$–27° in the XRD patterns of Fe_3O_4/SiO_2 and Co@Fe_3O_4/SiO_2 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).

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

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 Fe_3O_4 NPs was 15 nm, while the diameter of Fe_3O_4/SiO_2 NPs was about 20 nm which is due to the agglomeration of Fe_3O_4 inside nanosphere and surface growth of silica on the shell.

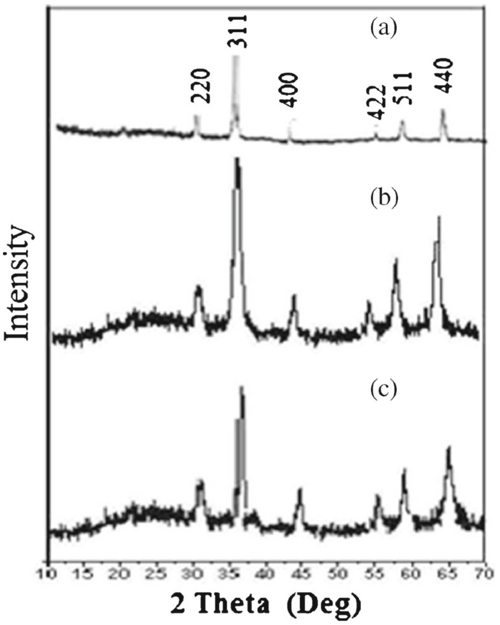


Figure 4. XRD pattern of (A) Fe_3O_4, (B) Fe_3O_4/SiO_2 NPs and (C) Co@Fe_3O_4/SiO_2 NPs.

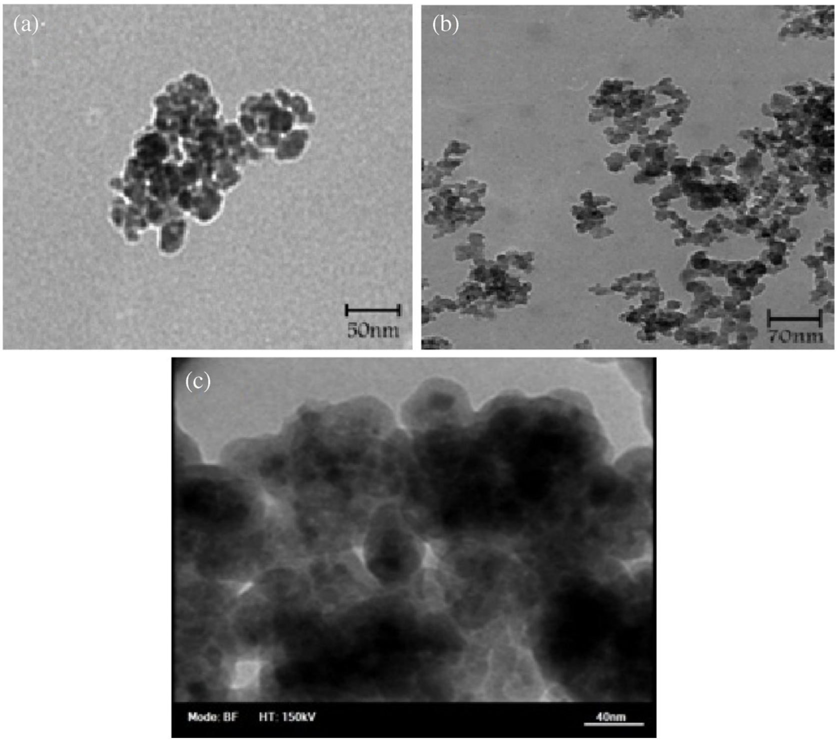


Figure 5. TEM images of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2 and (c) Co@Fe_3O_4/SiO_2.

Figures 5a and 5b show the TEM images of Fe_3O_4 and Fe_3O_4/SiO_2 NPs. Considering the TEM of Fe_3O_4 and Fe_3O_4/SiO_2, the average size of 16 and 21 nm were obtained which are similar to the results of XRD patterns. The TEM images of Fe_3O_4/SiO_2 NPs indicated the successful coating of silica shell on the magnetic Fe_3O_4 NPs (Figure 5b).

The TEM image of Co@Fe_3O_4/SiO_2 showed the successful immobilization of Co(III) salen complex on the Fe_3O_4/SiO_2 NPs (Figure 5c). The BET specific surface area of the Co@Fe_3O_4/SiO_2 was measured at room temperature by nitrogen physisorption and the surface area of was found to be 20 m^2/g. The loading of Co(III) salen complex on the Fe_3O_4/SiO_2 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@Fe_3O_4/SiO_2 was studied for the epoxidaton of terminal alkenes. The activity and selectivity of Co@Fe_3O_4/SiO_2 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@Fe_3O_4/SiO_2*: To optimize the amount of catalyst, different amounts of Co@Fe_3O_4/SiO_2 (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@Fe_3O_4/SiO_2 is the optimum amount of catalyst (Table 1, entry 5). The epoxidation reaction of styrene was carried out over parent of Co@Fe_3O_4/SiO_2 (Fe_3O_4 and Fe_3O_4/SiO_2) to determine which part of the Co@Fe_3O_4/SiO_2 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@Fe_3O_4/SiO_2*: 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@Fe_3O_4/SiO_2 (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 yiled 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@Fe_3O_4/SiO_2 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

[a]Reaction conditions: substrate (1 mmol), DCM (3 mL), oxidant (2 mmol) and Co@Fe_3O_4/SiO_2 (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_2O	13
2	EtOH:H_2O	22
3	MeOH	28
4	EtOH	30
5	THF	40
6	$CHCl_3$	50
7	CH_3CN	65
8	EtOAc	80
9	DCM	95

[a]Reaction conditions: substrate (1 mmol), *m*-CPBA (2 mmol) and Co@Fe_3O_4/SiO_2 (2.5 mol% based on Co element) at r.t. duration: 3 h. [b]Determined 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), $NaIO_4$, Oxone, H_2O_2, $PhI(OAc)_2$, 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, H_2O_2, PhIO, $PhI(OAc)_2$, low yield of products was observed (Table 3, entries 2–5). Oxone and $NaIO_4$ (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

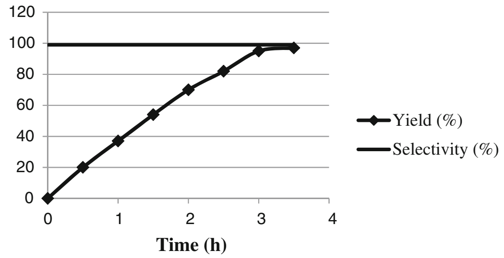


Figure 6. Change of conversion with reaction time for the model reaction catalyzed by fresh Co@Fe_3O_4/SiO_2 catalyst.

Table 3. The effect of different oxidants on the epoxidation of styrene catalyzed by Co@Fe_3O_4/SiO_2.[a]

Entry	Oxidant	Yield (%)
1	–	0
2	H_2O_2	25
3	PhIO	27
4	$PhI(OAc)_2$	22
5	UHP	30
6	$NaIO_4$	50
7	Oxone	60
8	TBHP	85
9	*m*-CPBA	95

[a]Reaction conditions: Styrene (1 mmol), Oxidant (2 mmol), PNO (0.5 mmol) and Co@Fe_3O_4/SiO_2 (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 NH_4OAc, 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 in Table 4, poor conversion was observed in the presence of NH_4OAc (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).

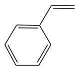
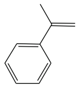
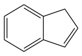
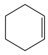
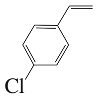
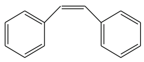
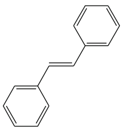
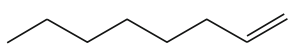
Table 4. The effect of different axial ligand on the epoxidation of styrene catalyzed by Co@Fe_3O_4/SiO_2.[a]

Entry	Axial ligand	Yield (%)
1	NH_4OAc	15
2	Py	45
3	MI	56
4	imidazole	65
5	NMNO	80
6	PNO	95

[a]Reaction conditions: Styrene (1 mmol), *m*-CPBA (2 mmol), axial ligand (0.5 mmol) and Co@Fe_3O_4/SiO_2 (2.5 mol% based on Co) at r.t.

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@Fe_3O_4/SiO_2, 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@Fe_3O_4/SiO_2. 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@Fe_3O_4/SiO_2.[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

[a]Reaction conditions: Substrate (1 mmol), DCM (3 mL), Oxidant (2 mmol), PNO (0.5 mmol) and Co@Fe_3O_4/SiO_2 (2.5 mol% based on Co). [b]Determined by GC with a Shimadzu CBP5 column (30 m × 0.32 mm × 0.25 mm). [c]Selectivity based on alkene conversion. [d]TON = mmol of converted alkene/mmol Co; [e]TOF = TON/time of reaction.

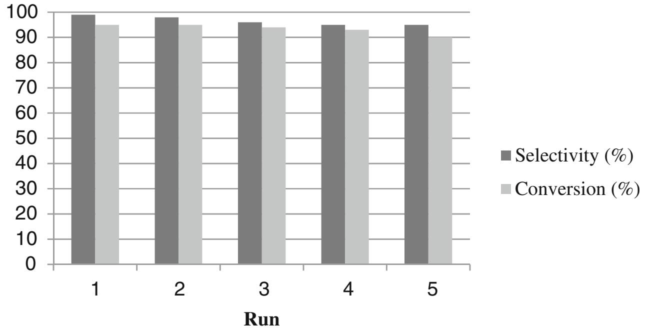


Figure 7. The recycles of the catalyst for the epoxidation styrene with m -CPBA (2 mmol) and PNO (0.25 mmol) in DCM (3 mL) catalyzed by Co@Fe_3O_4/SiO_2 (2.5 mol% based on Co elemental content) at r.t.

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@Fe_3O_4/SiO_2 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@Fe_3O_4/SiO_2, 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 a 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 Fe_3O_4 or the leaching of silica.

4. Conclusions

Novel Co@Fe_3O_4/SiO_2 was synthesized by grafting hemogeneous Co(III) salen complex onto the Fe_3O_4 @SiO_2NPs. The characterization results confirmed that hemogeneous Co(III) salen complex has been successfully incorporated onto Fe_3O_4@SiO_2 NPs. This nanocatalyst has strong magnetic responsivity due to a high saturation magnetization value (34.3 emu g^{-1}). Themagnetic 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@Fe_3O_4/SiO_2 showed comparable conversion and selectivity as that of homogeneous counterpart for the epoxidation of several alkenes. In addition, the heterogeneous Co@Fe_3O_4/SiO_2 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.

References

1. Xia Q H, Ge H Q, Ye C P, Liu Z M and Su K X 2005 Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation *Chem. Rev.* **105** 1603
2. Lane B S and Burgess K 2003 Metal-catalyzed epoxidations of alkenes with hydrogen peroxide *Chem. Rev.* **103** 2457
3. Dede B, Karipcin F and Cengiz M 2009 Novel homo- and hetero-nuclear copper (II) complexes of tetradentate schiff bases: Synthesis, characterization, solvent-extraction and catalase-like activity studies *J. Hazard. Mater.* **163** 1148
4. Ghosh T and Pal S 2015 Synthesis and characterization of dodecahedral cerium (IV) and gadolinium (III) complexes with a tetradentate schiff base *J. Chem. Sci.* **127** 1201
5. Gupta M, Sharma P, Gupta M and Gupta R 2015 Silica functionalized Cu (II) catalysed selective oxidation of benzyl alcohols using TEMPO and molecular oxygen as an oxidant *J. Chem. Sci.* **127** 1485
6. Sandaroos R, Taghi Goldani M, Damavandi S and Mohammadi A 2012 Efficient asymmetric Baeyer–Villiger oxidation of prochiral cyclobutanones using new polymer-supported and unsupported chiral Co (salen) complexes *J. Chem. Sci.* **124** 871
7. Zhang W, Loebach J L, Wilson S R and Jacobsen E N 1990 Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes *J. Am. Chem. Soc.* **112** 2801
8. Liao S and List B 2010 Asymmetric counteranion-directed transition-metal catalysis: Enantioselective epoxidation of alkenes with manganese (III) salen phosphate complexes *Angew. Chem. Int. Ed. Engl.* **49** 628

9. Zhang H, Wang Y M, Zhang L, Gerritsen G, Abbenhuis H C, Van Santen R A and Li C 2008 Enantioselective epoxidation of β-methylstyrene catalyzed by immobilized Mn (salen) catalysts in different mesoporous silica supports *J. Catal.* **256** 226
10. Qi B, Wang Y, Lou L, Huang L, Yang Y and Liu S 2013 Solvent-free aerobic oxidation of alcohols over palladium supported on MCM-41 *J. Mol. Catal. A*: *Chem.* **370** 95
11. Kureshy R I, Roy T, Khan N-uH, Abdi S H, Sadhukhan A and Bajaj H C 2012 Reusable chiral macrocyclic Mn (III) salen complexes for enantioselective epoxidation of nonfunctionalized alkenes *J. Catal.* **286** 41
12. Maity N C, Abdi S H, Kureshy R I, Khan N-u H, Suresh E, Dangi G P and Bajaj H C 2011 Chiral macrocyclic salen Mn (III) complexes catalyzed enantioselective epoxidation of non-functionalized alkenes using NaOCl and urea-H$_2$O$_2$ as oxidants *J. Catal.* **277** 123
13. Ren W, Fu X, Bao H, Bai R, Ding P and Sui B 2009 Enantioselective epoxidation of unfunctionalized olefins catalyzed by chiral salen Mn (III) catalyst immobilized on zirconium oligostyrenylphosphonate-phosphate *Catal. Commun.* **10** 788
14. Barbaro P and Liguori F 2009 Ion exchange resins: Catalyst recovery and recycle *Chem. Rev.* **109** 515
15. Tang Q, Zhang Q, Wu H and Wang Y 2005 Epoxidation of styrene with molecular oxygen catalyzed by cobalt(II)-containing molecular sieves *J. Catal.* **230** 384
16. Tang Q, Wang Y, Liang J, Wang P, Zhang Q and Wan H 2004 Co^{2+}-exchanged faujasite zeolites as efficient heterogeneous catalysts for epoxidation of styrene with molecular oxygen *Chem. Commun.* 440
17. Sebastian J, Jinka K M and Jasra R V 2006 Effect of alkali and alkaline earth metal ions on the catalytic epoxidation of styrene with molecular oxygen using cobalt (II)-exchanged zeolite X *J. Catal.* **244** 208
18. Cui H, Zhang Y, Zhao L and Zhu Y 2011 Adsorption synthesized cobalt-containing mesoporous silica SBA-15 as highly active catalysts for epoxidation of styrene with molecular oxygen *Catal. Commun.* **12** 417
19. Jinka K M, Pai S M, Newalkar B L, Choudary N V and Jasra R V 2010 Co-SSZ-51 as a catalyst for styrene epoxidation using molecular oxygen *Catal. Commun.* **11** 638
20. Jain S and Reiser O 2008 Immobilization of cobalt(II) schiff base complexes on polystyrene resin and a study of their catalytic activity for the aerobic oxidation of alcohols *Chem. Sus. Chem.* **1** 534
21. Kowalski G, Pielichowski J and Jasieniak M 2003 Polymer supported cobalt (II) catalysts for alkene epoxidation *Appl. Catal. A*: *Gen.* **247** 295
22. Jin C, Fan W B, Jia Y J, Fan B B, Ma J H and Li R F 2006 Encapsulation of transition metal tetrahydro-schiff base complexes in zeolite Y and their catalytic properties for the oxidation of cycloalkanes *J. Mol. Catal. A*: *Chem.* **249** 23
23. Bhunia S, Jana S, Saha D, Dutta B and Koner S 2014 Catalytic olefin epoxidation over cobalt(II)-containing mesoporous silica by molecular oxygen in dimethylformamide medium *Catal. Sci. Technol.* **4** 1820
24. Amarasekara A S, Oki A R, McNeal I and Uzoezie U 2007 One-pot synthesis of cobalt-salen catalyst immobilized in silica by sol–gel process and applications in selective oxidations of alkanes and alkenes *Catal. Commun.* **8** 1132
25. Ko S and Jang J 2006 A Highly efficient palladium nanocatalyst anchored on a magnetically functionalized polymer-nanotube support *Angew. Chem. Inter. Edit.* **45** 7564
26. Polshettiwar V, Luque R, Fihri A, Zhu H, Bouhrara M and Basset J-M 2011 Magnetically recoverable nanocatalysts *Chem. Rev.* **111** 3036
27. Cai W and Wan J Q 2007 Facile synthesis of superparamagnetic magnetite nanoparticles in liquid polyols *J. Colloid. Interf. Sci.* **305** 366
28. Yan F, Li J, Zhang J J, Liu F Q and Yang W S 2009 Preparation of Fe$_3$O$_4$/polystyrene composite particles from monolayer oleic acid modified Fe$_3$O$_4$ nanoparticles *via* miniemulsion polymerization *J. Nanopart Res.* **11** 289
29. Gu S C, Onishi J Y, Kobayashi Y, Nagao D and Konno M 2005 Preparation and colloidal stability of monodisperse magnetic polymer particles *J. Colloid. Interf. Sci.* **289** 419
30. Wang X, Ji H, Zhang X, Zhang H and Yang X 2010 Hollow polymer microspheres containing a gold nanocolloid core adsorbed on the inner surface as a catalytic microreactor *J. Mater. Sci.* **45** 3981
31. Liao Z, Wang H, Lv R, Zhao P, Sun X, Wang S, Su W, Niu R and Chang J 2011 Polymeric liposomes-coated superparamagnetic iron oxide nanoparticles as contrast agent for targeted magnetic resonance imaging of cancer cells *Langmuir* **27** 3100
32. Weertman J R and Koch C C 2002 In *Nanostructured materials: processing, properties and applications* (Norwich, NY: William Andrews Publishing)
33. Nakayama H, Arakaki A, Maruyama K and Takeyama H 2003 Single-nucleotide polymorphism analysis using fluorescence resonance energy transfer between DNA-labeling fluorophore, fluorescein isothiocyanate, and DNA intercalator, POPO-3, on bacterial magnetic particles *Biotechnol. Bioeng.* **84** 96
34. Jia H F, Zhu G Y and Wang P 2003 Catalytic behaviors of enzymes attached to nanoparticles: The effect of particle mobility *Biotechnol. Bioeng.* **84** 406
35. Lei Z, Li Y and Wei X 2008 A facile two-step modifying process for preparation of poly (SStNa)-grafted Fe$_3$O$_4$/SiO$_2$ particles *J. Solid. State. Chem.* **181** 480
36. Shylesh S, Schunemann V and Thiel W R 2010 Magnetically separable nanocatalysts: Bridges between homogeneous and heterogeneous catalysis *Angew. Chem. Inter. Edit.* **49** 3428
37. Govan J and Gun'ko Y K 2014 Recent advances in the application of magnetic nanoparticles as a support for homogeneous catalysts *Nanomater.* **4** 222
38. Nasseri M A, Allahresani A and Raissi H 2014 Grafting of a chiral Mn (III) complex on graphene oxide nanosheets and its catalytic activity for alkene epoxidation *RSC Adv.* **4** 26087
39. Allahresani A and Nasseri M A 2014 A magnetically recyclable Fe$_3$O$_4$@SiO$_2$/Mn (III) chiral salen complex as a highly selective and versatile heterogeneous nanocatalyst for the oxidation of olefins and sulfides *RSC Adv.* **4** 60702
40. Gawande M B, Branco P S and Varma R S 2013 Nano-magnetite (Fe$_3$O$_4$) as a support for recyclable catalysts in the development of sustainable methodologies *Chem. Soc. Rev.* **42** 3371

41. Tang J, Dong W J, Wang G, Yao Y Z, Cai L M, Liu Y, Zhao X, Xu J Q and Tan L 2014 Efficient molybdenum (VI) modified Zr-MOF catalysts for epoxidation of olefins *RSC Adv.* **4** 42977
42. Qi Y, Luan Y, Yu J, Peng X and Wang G 2015 Nanoscaled copper metal–organic framework (MOF) based on carboxylate ligands as an efficient heterogeneous catalyst for aerobic epoxidation of olefins and oxidation of benzylic and allylic alcohols *Chem. Eur. J.* **21** 1589
43. Yu J, Luan Y, Qi Y, Hou J Y, Dong W J, Yang M and Wang G 2014 Hierarchical PS/PANI nanostructure supported Cu (II) complexes: Facile synthesis and study of catalytic applications in aerobic oxidation *RSC Adv.* **4** 55028
44. Yang Y, Hao S, Zhang Y and Kan Q 2011 Oxovanadium (IV) and dioxomolybdenum (VI) salen complexes tethered onto amino-functionalized SBA-15 for the epoxidation of cyclooctene *Solid State Sci.* **13** 1938
45. Lopez J, Liang S and Bu X R 1998 Unsymmetric chiral salen schiff bases: A new chiral ligand pool from bis-schiff bases containing two different salicylaldehyde units *Tetrahedron Lett.* **39** 4199
46. Vezin H, Lamour E and Catteau J P 2002 Free radical production by hydroxy-salen manganese complexes studied by ESR and XANES *J. Inorg. Biochem.* **92** 177