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A recyclable Mn-porphyrin catalyst for enantioselective epoxidation of unfunctionalized olefins using molecular dioxygen

Afsaneh Farokhi^a and Hassan Hosseini-Monfared^a

A magnetically separable chiral catalyst, $Fe_3O_4/tart/Mn(TCPP)CI$, was prepared by the synthesis and immobilization of manganese-tetra(4-carboxyphenyl)porphyrin, Mn(TCPP)CI, onto the chiral surface of magnetite nanoparticles ($Fe_3O_4/tart-NPs$; tart = L-tartaric acid) through the carboxylate groups. The solid catalyst was characterized with a variety of methods including XRD, FE-SEM, FT-IR and UV-Vis spectroscopy. The catalytic activity was tested in epoxidation reactions of prochiral olefins with molecular oxygen. The reactions carried out in acetonitrile as solvent with molecular oxygen in the presence of isobutyraldehyde as the stoichiometric oxidant. The method showed consistently high conversion, epoxide selectivity and enantioselectivity to epoxide formation for a variety of terminal, cyclic and aromatic olefins oxidation. The catalyst showed little deactivation with time and is easily recovered by magnetic filtration and could be reused four times with little or no loss in activity and selectivity.

Introduction

Enantioselective synthesis represents one of the biggest challenges in synthetic chemistry^{12,3,4} because of the increasing trend towards the application of single enantiomers of chiral compounds especially for pharmaceuticals, agrochemicals, flavors and fragrances.^{5,6} Chiral compounds are very important in our daily life, especially in medicinal chemistry, because different configurations have different drug activities.^{7,8}

For producing enantiopure or enantio-enriched compounds the most elegant approach is enantioselective catalysis, where prochiral starting materials are transformed to enantiomerically pure products with the help of chiral catalysts.^{9,10,11} The application of enantioselective catalysis to the fine chemicals industry has great potential both from economic and ecological points of view.¹² Since the early 1980s, numerous catalysts have appeared, the most recognizable ones being the seminal work of Katsuki and Sharpless on the asymmetric epoxidation of allylic alcohols¹³ which followed by the development of manganese-salen complexes by Katsuki et al.¹⁴ and Jacobsen et al.¹⁵ for the epoxidation of certain unfunctionalised olefins. A chiral epoxide is a valuable intermediate, containing one or two stereogenic centers, which can be used in further transformations through asymmetric ring opening reactions.^{16,17}

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Numerous asymmetric catalysts have been designed for producing enantioenriched compounds in the past four $\mbox{decades}^{18,19,20}$ and the main emphasis has been on ligand design to control the reactant approach to the active center, so that the reaction occurs at only one face of the approaching prochiral substrate. This has led to the design of libraries of chiral ligands with varying degrees of steric bulk that can control the enantioselection, for example C_2 symmetric ligands: salen, bis(oxazoline) and BINAP (2, 2' bis(diphenylphosphino)-1,1'-binaphthyl).¹⁸ However. their applications in industrial processes have often been hindered due to the high costs⁹ of both the precious metals and chiral ligands typical of these catalysts, as well as difficulties in removing trace amounts of toxic metals from the organic products. Due to these intrinsic shortcomings, many heterogenization approaches, including adsorption. encapsulation, tethering using a covalent bond.^{21,22,23,24,25,26,27} and via cation exchange,²⁸ have been explored to overcome these problems. However, the heterogenized catalysts obtained from these methods are often less effective in terms of both activity and enantioselectivity than their homogeneous counterparts and their preparations are often difficult. There is thus a need to develop more efficient and easy to synthesis immobilization strategies for the heterogenization of homogeneous asymmetric catalysts.

On the other hand, magnetic nanoparticles (MNPs) application as catalyst supports show unique properties such as high surface area, good dispersion, superparamagnetic behavior as well as low toxicity.²⁹ The most attractive feature of MNP-supported catalysts is that they can be recycled by simple magnetically driven separation, thereby eliminating the requirement of catalyst filtration and centrifugation. Furthermore, improved activity is usually achieved in the

Department of Chemistry, University of Zanjan 45195-313, Zanjan, I.R. Iran. Corresponding author. Tel.: +98 24 33052576; fax: +98 241 33583203. E-mail address: monfared@znu.ac.ir (H. Hosseini-Monfared)

FT-IR, UV-Vis and NMR spectra, XRD pattern, comparison of the activity of the catalyst with reported chiral Mn-porphyrin catalysts, particles size distribution. See DOI: 10.1039/x0xx00000x

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nanometre-sized supported catalyst due to the high surface area and good dispersion properties. In the past few years, several transition-metal catalysts have been successfully immobilized on MNPs with good catalytic activity and reusability. 30,31,32,33

Porphyrin-based catalysts show remarkable potential for the enantioselective epoxidation of unfunctionalized terminal olefins with high enantiomeric excess (ee) and turnover numbers.^{34,35} They give better ee values than those obtained with other catalytic systems such as the much studied Mn(salen) derivatives.³⁴ However, several crucial challenges still remain. First, it is important to develop the synthesis of the catalysts using inexpensive and easy-to-prepare ligands. Second, an ultimate achievement would involve the use of molecular dioxygen. Among various oxidants, molecular dioxygen is a cheap, clean and readily available oxidant.^{36,37}

Herein we report on a highly efficient chiral catalyst derived from inexpensive raw materials via a convenient immobilization of a manganese-porphyrin on magnetite stabilized nanoparticles by chiral L-tartaric acid (Fe₃O₄/tart/Mn(TCPP)Cl) as shown in Fig. 1. We aimed to obtain a nanoparticles displaying asymmetric catalytic activity. The catalytic activity of the synthesized Fe₃O₄/tart/Mn(TCPP)Cl was evaluated in the oxidation of prochiral olefins by molecular dioxygen. We also describe the recovery and reuse of the heterogeneous catalyst. Supported metalloporphyrins are provided significant protection under oxidizing conditions, avoiding the approximation of two porphyrins planes that can promote a self-destruction of the macrocycle ring or a dimerization by a μ -oxo bonding between manganese. These effects lead to an inactivation of the catalyst behavior and are commonly reported in homogeneous catalysis studies. In our previous studies, it was found that Fe₃O₄/tart-NPs were efficient catalyst for asymmetric oxidation.³⁰ However, the Fe₃O₄/tart-NPs generally showed limited epoxide selectivity for aromatic olefins.

Experimental section

Materials and equipments

4-Carboxybenzaldehyde (99.5%, Merck), propionic acid (99%, Merck,), nitrobenzene (99%, Merck), pyrrole (97%, Merck), manganese(II) chloride tetrahydrate (99%, Merck), ferric chloride hexahydrate (99%, VWR,), urea (99 %, Merck), diethylene glycol (DEG) (99%, Merck), (2R,3R)(+)-tartaric acid (L-(+)-tartaric acid, 99%, Merck,) and isobutyrlaldehyde (98%. Merck,) used as received. Solvents and other reagents of the highest grade were purchased from Merck and Fluka and used without further purification.



Fig. 1 Representation of (a) Mn(TCPP)Cl structure and (b) schematic representation of the immobilized Mn(TCPP)Cl on Fe₃O₄/tart-NPs, a chiral nanocatalyst (see the next section).

The reaction products of the oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenyl methyl siloxane 30 m \times 320 μm \times 0.25 $\mu m)$ with flame-ionization detector. The enantiomeric excess (ee) was determined by chiral GC (HP 6890-GC) using a SGE-CYDEX-B capillary column (25 m \times 0.22 mm ID× 0.25 μ m). ¹H- and ¹³C-NMR spectra of the reaction mixtures (without purification) were run on a Bruker 250 MHz spectrometer using CDCl₃ as solvent. UV-Vis spectra of solutions were obtained on a Shimadzu 160 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer 597 spectrophotometer after making pellets with KBr powder. Powder X-ray diffraction patterns were collected at the Bruker, D8ADVANCE, Germany, wavelength 1.5406 Å (Cu K α), voltage: 40 kV, current, 40 mA. The size and morphology of solid compounds were recorded by using a Hitachi F4160 scanning electron microscope (SEM) operated at an accelerating voltage of 10 KV. The magnetization measurement was performed at room temperature using a vibrating sample magnetometer (VSM) device in the Development Centre of the University of Kashan (Kashan, Iran).

Synthesis of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP)

Manganese(III) and metal-free tetrakis(4carboxyphenyl)porphyrin (H₂TCPP) were synthesized according to the methods described in the literature.^{38,39} Fig. 1 represents the porphyrin structure. To synthesize the metalfree porphyrin (H₂TCPP), pyrrole (0.11 mL, 1.66 mmol) was added to a mixture of 4-carboxybenzaldehyde (0.25 g, 1.66 mmol), propionic acid (5.8 mL) and nitrobenzene (2.5 mL) with stirring at room temperature. The mixture was heated at 120 °C for 1 h. After cooling and solvent removal under vacuum, porphyrin was dissolved in 14 mL of 0.1 M NaOH solution. H₂TCPP was precipitated with a 1 M HCl solution, filtrated, redissolved in ethanol and recrystallized by solvent evaporation. Yield 37% (0.12 g). UV-Vis in ethanol: λ_{max} (log $\epsilon,$ dm³ mol⁻¹ cm⁻¹): 418 (4.55), 514 (3.65), 548 (3.53), 588 (3.45) and 645 (3.38). FT-IR (KBr, cm⁻¹): 3440 (s, br, O-H), 3125 (w, N-

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Synthesis of Mn(TCPP)Cl

The free-base porphyrin was metallated with MnCl₂, by modifying the conventional methodology reported by Kobayashi, using 0.082 mmol of porphyrin dissolved in 20 mL of N,N-dimethylformamide (DMF) and an excess of 10 times of the metal salt.⁴¹ The mixture was refluxed for 2 h. DMF was removed by distillation and Mn(TCPP)Cl precipitated by adding water. The precipitate was dissolved in 0.1 M NaOH solution and reprecipitated by adding 1 M HCl solution. Mn(TCPP)Cl was dissolved in ethanol and recrystallized by solvent evaporation. Finally, Mn(TCPP)Cl was dried at room temperature. Yield 80%. Manganese(II) was oxidized to Mn(III) by air during the reaction.

The porphyrins H₂TCPP and Mn(TCPP)Cl have shown the absorptions by UV-Vis spectroscopy. The porphyrins spectra are due to π - π * transitions. For H₂TCPP the bands were obtained at 417 nm (Soret) and 514, 547, 591 and 644 nm (Q-bands) whereas in Mn(TCPP)Cl the number of bands were reduced to two (565 and 599 nm) in the visible region and Soret band appeared at 465 nm. Thus, successful insertion of metal in porphyrin was confirmed by disappearance of 644 nm band⁴² and reduction in number of Q bands as compared to H₂TCPP.

FT-IR (KBr, cm $^{-1}$): 3440 (s, br, O-H), 2921 (w), 2851 (w), 1713 (shoulder, -CO_2), 1606 (s, C=C). 40

Synthesis of magnetite nanoparticles with chiral stabilizer (Fe $_{3}O_{4}$ /tart-NPs)

Magnetite nanoparticles stabilized with chiral tartaric acid (Fe₃O₄/tart-NPs) was synthesized according to our previously reported procedures.^{30,31} In a typical experiment, FeCl₃·6H₂O (0.81 g, 3 mmol), L-(+)-tartaric acid (0.075 g, 0.5 mmol) and urea (1.80 g, 30 mmol) were completely dissolved in diethylene glycol (30 mL) by vigorous mechanical stirring. The obtained yellow clear solution was sealed in a Teflon lined stainless steel autoclave (23 mL capacity) and then heated at 200 °C for 4 h. After cooling down to room temperature, the black magnetite were separated magnetically and washed with ethanol for several times to eliminate organic and inorganic impurities, and then dried at 60 °C for 6 h.

Immobilization of Mn(TCPP)Cl on Fe₃O₄/tart-NPs

Mn(TCPP)Cl was adsorbed on Fe₃O₄-tart NPs surface (Fe₃O₄/tart/Mn(TCPP)Cl) by a method similar to the previously reported procedure.⁴³ Typically, 0.25 g Fe₃O₄/tart-NPs was added to 250 mL of 0.2 mM Mn(TCPP)Cl ethanolic solution. The mixture was stirred overnight at 60 °C. The solid was filtered, washed with ethanol in order to remove the unadsorbed metalloporphyrin and dried at 60 °C for 6 h.

 $Fe_3O_4/tart/Mn(TCPP)CI$ is a stable catalyst without leaching of Mn-porphyrin during the oxidation reaction. The supernatant solution of the oxidation reaction of tetralin catalyzed by $Fe_3O_4/tart/Mn(TCPP)CI$ (see the next section) showed no absorption peak of Mn(TCPP)CI at 465 nm.

Catalytic aerobic oxidation of hydrocarbons

The oxidation of hydrocarbons with O₂ was performed in a 25mL round-bottom flask. The catalyst was used without any pretreatments. In a typical experiment the flask was charged with the suspension of $Fe_3O_4/tart/Mn(TCPP)Cl$ (1.0 mg; contains 0.17 µmol Mn, 0.01 mol% Mn) in 5 mL acetonitrile, 0.1 g chlorobenzene as internal standard, substrate (2 mmol, 1 mmol for cis-stilbene, 0.5 mmol for trans-stilbene) and 5 mmol isobutyraldehyde. The flask was conditioned by purging with oxygen for 5 min and re-filled with oxygen. Dioxygen, as oxidant, was filled in the system by using an oxygen balloon. The reaction mixture was stirred at 25 °C for 8 h. At appropriate intervals, aliquots were removed and analyzed by GC-FID. The products were identified with authentic samples and/or ¹H- and ¹³C-NMR spectroscopic data. The reaction products were quantified by gas chromatography using the following equation:

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A = peak area in GC chromatogram

Running the reaction when chlorobenzene was used as substrate resulted to no oxidation product. This finding confirmed that chlorobenzene as internal standard is innocent under the oxidation conditions. Control experiments in the absence and presence of chlorobenzene were also confirmed that it did not involve in the oxidation of a substrate.

Catalyst recycling

In order to investigate the possibility of several recycling runs for $Fe_3O_4/tart/Mn(TCPP)Cl$, the solid catalyst was separated from the reaction mixture at the end of the reaction. In the presence of a magnetic stirrer bar, $Fe_3O_4/tart/Mn(TCPP)Cl$ moved onto the stirrer bar steadily and the reaction mixture turned clear within 30 s. The catalyst was isolated by simple decantation. After washing with 2 mL CH₃CN and drying at 60 °C for 6 h, the catalyst was reused as fresh catalyst for the oxidation of 1,2,3,4-tetrahydronaphthalene.

Results and discussion

Synthesis and characterization

In order to heterogenize the Mn-porphyrin for ease of separation and recycling, we synthesized a tetraphenylporphyrin with the carboxyl functional groups in the *p*-position of the phenyl rings. The reaction conditions used to prepare the free-base porphyrin H₂TCPP were adapted from literature procedure³⁸ and metallated it using the manganese(II) salt (Scheme 1). The metallation process was confirmed by employing UV–Vis and FT-IR spectroscopies (see the Experimental section).

A chiral support of the catalyst (Fe₃O₄/tart-NPs) was prepared by stabilizing magnetite nanoparticles by L-(+)-tartaric acid³⁰ and Mn(TCPP)Cl immobilized on it to obtain Fe₃O₄/tart/Mn(TCPP)Cl nanoparticles (Fig. 1b). According to

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the	UV-Vis	analysis, ⁴⁴	the	Mn(TCPP)Cl	loading	in
Fe ₃ O ₄ /tart/Mn(TCPP)Cl was 0.17 μmol/g catalyst.						

$\xrightarrow{C_2H_5CO_2H, C_6H_5NO_2}_{120 \text{ °C}, 1 \text{ h}} H_2\text{TCPP}$		
DMF Mn ^{III} (TCPP)CI		
EtOH ► Fe ₃ O₄/tart/Mn(TCPP)Cl		

Scheme 1 Synthetic route of the heterogeneous catalyst $Fe_3O_4/tart/Mn(TCPP)Cl$

On the basis of our recent studies on the functionalization of magnetite Fe₃O₄-NPs with different carboxylic acids,³¹ we chose Fe_3O_4 /tart-NPs as a support to immobilize the prepared Mn(TCPP)Cl. We obtained the Fe₃O₄/tart-NPs through the polyol method and used it without any further functionalization.³⁰ Among the variety of methods for synthesizing magnetic nanoparticles, 45,46,47,48 the polyol method has been paid more attention.⁴⁹ The polyols in this method often serve as reducing agent and stabilizer to prevent interparticle aggregating. Presence of L-tartaric acid enhances further the stabilization of Fe_3O_4 nanoparticles. The carboxyl group in L-tartaric acid can provide coordination to the nanoparticles and thereby the NPs are stabilized. It is wellknown that sodium citrate can attach to Au and provides a negatively surface charged for Au nanoparticle stabilization. 50,51

UV–Vis absorption spectrum of the H_2TCPP in ethanol showed a typical Soret band at 417 nm and four Q bands at 514, 547, 591 and 644 nm (Fig. 2). The Soret and Q bands are assigned to constructive and destructive mixing of electron transitions between the HOMO (a_2u, π)/HOMO-1 (a_{1u}, π) and LUMO (e_g, π^*) molecular orbitals, respectively.⁵² The manganese porphyrin, Mn(TCPP)Cl, was obtained by metallation of the free ligand H₂TCPP with the Mn(II) salt. During the metallation process, the Mn(II) oxidation took place and the Mn(III)-porphyrin was obtained. The insertion of Mn(III) in the porphyrin ring proves a significant modification of the macrocycle symmetry. Distortions or reduction in the electronic structure of the porphyrin molecule changes the frontier orbital symmetry and acts to decrease their free electron box and raises their energies.⁵³ The free basic porphyrin with D_{2h} symmetry and four bands in the 500–800 nm region, changes to D_{4h} resulting in a reduction to two bands (α and β) in this region, and a Soret band red shift for manganese.⁵⁴ The UV-Vis spectrum observed for Mn(TCPP)CI in ethanol presented the Soret band at 465 nm and, in the visible region, the bands at 565, 599 nm (Fig. 2). The groups of the observed bands confirm the metallation process.

The absorption spectrum of the immobilized Mn(TCPP)Cl on chiral magnetite nanoparticles is similar to that of Mn(TCPP)Cl by a small red shift to 469 nm due to the interaction between the carboxylate groups of the porphyrin and Fe₃O₄/tart-NPs.



Fig. 2 UV–Vis spectra of H_2TCPP , Mn(TCPP)Cl and Fe₃O₄-tart/Mn(TCPP)Cl in ethanol; Fe₃O₄-tart/Mn(TCPP)Cl was dispersed in ethanol by using an ultrasound.

XRD analysis was used to investigate the crystalline structure of the synthesized catalyst. The XRD pattern of Fe₃O₄/tart/Mn(TCPP)Cl nanoparticles (Fig. 3) shows a pattern similar to those of Fe₃O₄ and Fe₃O₄/tart nanoparticles which indicates the stability of the crystalline phase of the magnetic nanoparticles during the subsequent surface modification.



Fig. 3 XRD patterns of the synthesized (a) Fe_3O_4-NPs, (b) Fe_3O_4/tart-NPs and (c) Fe_3O_4/tart/Mn(TCPP)Cl nanoparticles

In the case of Fe₃O₄/tart/Mn(TCPP)Cl, using intense peak at 2theta = 35.837, FWHM = 0.236, we get crystallite size of 35.3 nm by X'Pert program. Characteristic peaks ($2\theta = 18.3^{\circ}$, 30.4° , 35.8° , 43.5° , 54.2° , 57.6° , 63.1 and 74.7°) corresponding to (111), (220), (311), (400), (422), (511), (440) and (533) planes of cubic inverse spinel Fe₃O₄ are obtained.⁵⁵ The positions and relative intensities of all diffraction peaks for all the Fe₃O₄-NPs, Fe₃O₄/tart-NPs and Fe₃O₄/tart/Mn(TCPP)Cl-NPs match well with those expected for Fe₃O₄. This conclusion was confirmed by their FT-IR spectra (see below) which proved the mainly magnetite nature of the catalyst core.^{56,57}

The FT-IR spectra of Mn(TCPP)Cl, Fe_3O_4 /tart-NPs and Fe_3O_4 /tart/Mn(TCPP)Cl nanoparticles are shown in Fig. 4. Strong absorption bands at 587 and 630 cm⁻¹ are related to the

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vibrations of the Fe-O functional group in Fe₃O₄/tart-NPs and Fe₃O₄/tart/Mn(TCPP)Cl, which shows that the phase of asprepared particles is mainly magnetite.⁵⁸ The absorption band at 630 cm⁻¹ might be assigned to the existence of some amount of oxidized maghemite on the magnetite surface. In the Fe-O range, fine-grained, synthetic maghemite shows broad IR bands at 668, 630, 442 cm^{-1.59,60} The spectrum of magnetite has broad bands at 587 and 400 cm^{-1.59} The stretching vibration of -COOH functional groups of Mn(TCPP)Cl and Fe_3O_4 /tart-NPs is seen at 1731 cm⁻¹. The presence of both the v(C=O) vibrations of the acid COOH functionality at 1731 cm^{-1} and the $v_s(CO_2^{-})$ vibration of the carboxylate group at 1422 cm⁻¹, reveal that the L-tartaric acid is adsorbed as a monotartrate species which is bound to the surface via the deprotonated carboxylate group. L-tartaric acid is adsorbed as a monotartrate species which is bound to the surface via the deprotonated carboxylate group and it is not involved in intermolecular H-bonding interactions with the alcohol groups of neighboring monotartrate species, as shown in Fig. 1.^{30,61} The broad characteristic band at 3424 cm⁻¹ could be assigned to O-H stretching vibration arising from the Fe-OH groups on nanoparticles and adsorbed (2R,3R)(+)-tartaric acid and water. The dominant H-O-H bending vibration of water is seen at 1635 cm⁻¹.⁶² The peaks around 2922 and 2853 cm⁻¹, assignable to asymmetric/symmetric vibrations of C-H in (2R,3R)(+)tartaric acid and intramolecular hydrogen bond derived from OH can be obviously found. The characteristic functional groups of Mn(TCPP)Cl are difficult to see in the FT-IR spectrum of Fe₃O₄/tart/Mn(TCPP)Cl (Fig. 4c) because of low concentration.



Fig. 4 An overlay of the FT-IR spectra of (a) $Fe_3O_4/tart,$ (b) Mn(TCPP)CI and (c) $Fe_3O_4/tart/Mn(TCPP)CI.$

The surface morphology of chiral Fe₃O₄/tart nanoparticles and Fe₃O₄/tart/Mn(TCPP)Cl are shown in Fig. 4(a) and (b). The FE-SEM images of the chiral Fe₃O₄/tart nanoparticles show uniformity and spherical morphology with an average diameter of about 20 nm. The spherical shaped nanoparticles

of Mn(TCPP)Cl/Fe $_3O_4$ /tart are bigger than that of Fe $_3O_4$ /tart-NPs with average size about 61 nm.

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 $Fe_3O_4/tart\text{-NPs};$ average particles size 19.5 \pm 4.2 nm.



 Fe_3O_4 /tart/Mn(TCPP)Cl; average particles size 61 ± 16 nm.

Fig. 5 FE-SEM images and average particle size of (a) $Fe_3O_4/tart-NPs,$ (b) $Fe_3O_4/tart/Mn(TCPP)Cl.$



Fig. 6 shows a typical magnetization curve of the $Fe_3O_4/tar/Mn(TCPP)Cl$ nanoparticles by vibration sample magnetometer (VSM) at room temperature. The hysteresis

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loops of the powdered material showed no magnetic hysteresis, with both the magnetization and demagnetization curves passing through the origin, which clearly indicates the superparamagnetic nature of the material. Moreover, the synthesized heterogeneous nanocatalysts possess strong magnetic responsivity due to a high saturation magnetization value (50.07 emu g⁻¹) which helps the separation of catalyst at the end of catalysis by an external magnet.

Catalytic activities

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With the immobilized Mn(TCPP)Cl catalyst in hand, the oxidation reaction of tetralin was chosen as a model reaction to examine the catalytic activity and reusability. Tetralin is a convenient substance to choose for studying the autoxidation of the CH₂ group.⁶³ The oxidation of tetralin was carried out in acetonitrile at room temperature and in the presence of ≈ 0.01 mol% of catalyst and isobutyraldehyde (ⁱPr-CHO) as co-catalyst with dioxygen as the oxidant. The reaction was evaluated by gas chromatography after 8 h and the results are summarized in Table 1. In the absence of Pr-CHO no conversion was observed (Table 1, entry 1). Although the reaction proceeded very well in the presence of unsupported Mn(TCPP)Cl (conversion 75%); however, as expected, no enantioselectivity was observed (entry 2). The L-tartaric acid as capping agent in Fe₃O₄/tart-NPs affects the enantioselectivity and sterogenic centre configuration of the epoxid.³⁰ The support Fe₃O₄/tart-NPs catalyzes the oxidation of tetralin, but the conversion is low 25% (entry 3).30 To our delight immobilization of Mn(TCPP)Cl on chiral magnetic support Fe₃O₄/tart-NPs resulted to chiral 1-tetralol (ee 74%, entry 4). Additionally, the catalytic activity of Fe₃O₄/tart was increased from 25 to 69% and the only product was 1-tetralol (compare entry 3 and entrv 4). By increasing the concentration of Fe₃O₄/tart/Mn(TCPP)Cl, the activity increased (conversion 74%) without changing enantiomeric excess. The reaction proceeded well in acetonitrile and no activity was observed in methanol or ethyl acetate (entries 6, 7). The possibility of involvement of acetonitrile as co-reactant, through peroxyimidic acid as an oxygen donor, was excluded in the oxidation reactions, since no MeCONH₂ under the catalytic oxidations was detected.⁶⁴ The polarity of acetonitrile (dielectric constant ϵ/ϵ_0 = 37.5 where ϵ_0 is the electric permittivity of free space) is higher than methanol (32.7) and ethyl acetate (6.02).⁶⁵ Probably, the polarity, low coordinating ability and aprotic nature of acetonitrile play the main roles in improving the activity of the catalyst in acetonitrile. Thioanisole and cyclohexane were also examined to explore the scope of the catalytic activity of Fe₃O₄/tart-NPs. Many efforts have been made to develop new catalysts to oxidize cyclohexane under mild conditions.⁶⁶ The main product in the oxidation of cyclohexane was cyclohexanol with 88% selectivity and 25% conversion. This finding shows the nonradical nature of the active intermediate during the oxygen transfer. Thioanisole was oxidized to enantioenriched sulfoxide with 100% selectivity and 88% ee. Immobilized manganese(II) complex, [{Mn(H₂O)₂Cl₂}₂(H₂Btar)], on mesoporous support SBA-15 (H₂L = 2,3-O-4-hydroxybenzhydrazidebenzylidene-D-

tartrate) oxidaized thioanisole with H_2O_2 in 46% conversion, 29% sulfoxide selectivity and 100% ee.²⁷ Chiral sulfoxides are an important class of compounds as chiral auxiliaries in asymmetric carbon–carbon bond forming reactions,^{67,68} as bioactive ingredients in the pharmaceutical industry⁶⁹ and constitute chiral synthons in organic synthesis for the preparation of biologically active compounds.⁷⁰

 $\mbox{Table 1}$ Conversion and selectivity for catalytic oxidation of tetralin with molecular dioxygen $^{\rm a}$



Entry	Catalyst	Conv.	Product(s) /	Ee %
		(%) ^b	(Yield %) ^b	(Conf.)
1	Fe₃O₄/tart/Mn(TCPP)Cl	0 ^c		
2	Mn(TCPP)Cl	75	1-tatralol (75)	none
3	Fe ₃ O ₄ /tart-NPs	25	1-tetralol (22)	45 (S)
			1-tetralone (3)	
4	Fe₃O₄/tart/Mn(TCPP)Cl	69	1-tetralol (69)	74 (S)
5	Fe₃O₄/tart/Mn(TCPP)Cl ^d	74	1-tetralol (74)	83 (S)
6	Fe₃O₄/tart/Mn(TCPP)Cl	0 ^e		
7	Fe₃O₄/tart/Mn(TCPP)Cl	0 ^f		

^a Reaction conditions: catalyst 1.0 mg (Fe₃O₄/tart/Mn(TCPP)Cl contains 0.17 μ mol Mn-porphyrin; Mn(TCPP)Cl 1.14 μ mol, 6.7 times higher than Fe₃O₄/tart/Mn(TCPP)Cl, tetralin 2 mmol, chlorobenzene 0.1 g, isobutyraldehyde 5 mmol, solvent 5 mL, O₂ balloon, reaction temperature 25 °C, time 8 h. ^b Conversions and yields calculated on the basis of the substrate. ^c No co-catalyst (ⁱPrCHO). ^d Catalyst 3.0 mg, 0.51 μ mol. ^e In CH₃OH as solvent. ^f In ethyl acetate as solvent. Reported results are the average of two experiments.

With the optimized conditions, the substrate scopes were next explored. In the presence of 0.01 mol% of Fe₃O₄/tart/Mn(TCPP)Cl, various olefins including terminal, cyclic and aromatic olefins were oxidized with molecular dioxygen to afford mainly the epoxide with high yields and enantioselectivities (Table 2). Highest enantioselectivity (> 99%) and epoxide selectivity (100%) were obtained in the oxidations of 1-decene with 95% conversion and 1-octene with 68% conversion (Table 2, entries 1 and 2). For 1-decene and 1octene the reaction is almost stopped after the chosen reaction time. There was not any isomerization of the olefins for the Mn catalyst. Considering the chain length of 1-octene and 1-decene, the epoxidation activity of the catalyst is increased with increasing the chain length of olefin (Fig. S3). An increase in the olefin chain length resulted in better activity which can be attributed to the increased steric hindrance at the catalytic center and facilitating the oxygen transfer in the active intermediate $[Mn-O-CH_2-\dot{C}HR]^{\dagger}$ (such as Scheme 4). It

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needs additional studies to explore how the steric hindrance of the long chain olefin does not hinder its interaction with the Mn in formation of the intermediate.

Main product in the oxidation of styrene and β methylstyrene was the corresponding epoxides with about 68% ee; benzaldehyde was also formed with 33% and 37% selectivity, respectively (entries 3, 4). Similarly, in addition to the epoxide, acetophenone (53%) was resulted in the oxidation of α -methyl styrene; enantioselectivity (ee 40%) was lower than those of styrene and β -methylstyrene (entry 5). Probably, the stability of the plausible intermediate benzyl radical favors breaking of the olefin double bond in the oxidation of styrene, α - and β -methyl styrene. In the case of α methyl styrene the product results from the breaking of the olefin double bond (acetophenone) is high because the double bond is rich in electron and stable (compare entries 3-5).

cis-Stilbene is a frequently used substrate for the study of olefin epoxidation mechanism⁷¹ because of mechanistic information associated with the ratio of cis- and trans-isomers in the stilbene oxide product. The oxidation of cis-stilbene proceeded to cis- and trans-stilbene oxide with molar ratio of 39/61 and mainly S-enantiomer trans-stilbene oxide with 84% ee (entry 6). This finding shows the important role of steric effect in determining the product selectivity by this catalyst. The oxidation reaction probably proceeds through a benzyl radical intermediate, which is sufficiently stable and allows free rotation about the C-C bond axis. The formation of transstilbene oxide from cis- and trans-stilbenes as the main product via a radical intermediate is expected due to the higher thermodynamic stability of the trans in comparison to the cis stereoisomer, in which the phenyl groups are located in anti-position with respect to each other. Our finding is similar to the oxidation of *cis*-stilbene with the O₂/isobutyraldehyde catalyzed by iron(II) cyclam which gave trans-stilbene oxide as the predominant product⁷² and the system appeared to proceed by a mechanism different from that of the oxidation by peracids which gave predominantly *cis*-stilbene oxide.⁷³ The reaction with Mn(TPP)Cl and O₂/isobutyraldehyde give higher ratio of cis- to trans-stilbene oxide products, implying that the product ratios were seriously influenced by the types of ligands bound to manganese.⁷³ In the reaction of mCPBA (0.8 mmol) with cis-stilbene (1 mmol) and isobutyraldehyde (1 mL) in CH₃CN (5 mL) under Ar, only the cis-stilbene oxide and not trans-stilbene oxide has been detected in the products.73 trans-Stilbene was oxidized quantitatively by Fe₃O₄/tart/Mn(TCPP)Cl to the corresponding epoxide with 100% selectivity (entry 7).

Indene was oxidized successfully to indene oxide with conversion 82% and selectivity to epoxide was 100%, but ee 20% was low (entry 8). This result again elucidates importance of the steric effect of the substrate during the chirality induction step of the reaction. Indene is not oxidized by Fe₃O₄/tart-NPs even after 24 h.³⁰ Epoxide selectivity and enantioselectivity (ee) of catalyst Fe₃O₄/tart/Mn(TCPP)Cl are much better than the support (Fe₃O₄/tart-NPs) activity as catalyst.³⁰

Furthermore, to probe the activity and selectivity of the catalyst, we chose the oxidation of cyclohexene because it can lead to several distinct products, where their identities depend on the combination of catalyst and oxidant used. For example, radical-mediated oxidation pathways can lead to the allylicoxidation products 2-cyclohexen-1-ol and 2-cyclohexen-1-one. Alternatively, the peroxide oxidant can be activated, through binding to the metal center, to undergo reactions with the cyclohexene double bond, affording cyclohexene oxide. High yields of cyclohexene oxide was obtained as the predominant product, with small amount of the allylic oxidation product 2cyclohexen-1-ol (conversion 98%, epoxide selectivity 88%; Table 2, entry 9). This result is similar to those obtained by previous investigators using other metal complexes of porphyrin and non-porphyrin, as catalysts.⁷⁴ In the oxidation of cyclohexene with $O_2/^i$ PrCHO, the activity and selectivity of Fe₃O₄/tart/Mn(TCPP)Cl is very different from that of Fe₃O₄/tart-NPs (conversion 58%, epoxide selectivity 61%) as catalyst³⁰ and favoring the epoxide product over the allylic oxidation (conversion 98%, epoxide selectivity 88%; Table 2, entry 9).

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Scientists frequently employ *cis*-cyclooctene substrate as a diagnostic compound in catalytic systems involving metalloporphyrins. Cyclooctene was converted to its epoxide by 90% after 2 h and 98% after 4 h and the selectivity was 98% (entry 10). It is easy to oxidize *cis*-cyclooctene in the presence of metalloporphyrins. The low stability of the allyl species formed from this substrate as compared with the allyl species generated from cyclohexene, favors epoxide production.⁷⁵

The catalytic activity and enantioselectivity of the present catalyst are higher than those of complicated and difficult to synthesis chiral Mn-porphyrins which have been used for the epoxidation of olefins with NaOCl, PhIO or H₂O₂ as oxidant, such as, for example, chiral Mn(III)-meso-tetrakis-[2.2]-pcyclophanyl-porphyrin and dinorbornabenzene-derived Mnporphyrins,⁷⁶ chiral Mn-meso-tetrakis[(aS)-2'-methoxy-1,1'binaphth-2-yl]porphyrin⁷⁷ and Mn-tetrakis[(R)-1,1'-binaphth-2yl]porphyrin.78 Some comparisons in the epoxidation of styrene are summarized in Table S1 (in Supplementary Information). In addition to the simplicity of the synthesis of Fe_3O_4 /tart/Mn(TCPP)Cl, its potential in using molecular oxygen enantioselective oxidation is highly remarkable. for Enantioselectivity of Fe₃O₄/tart/Mn(TCPP)Cl in the epoxidation of olefins with O2/isobutyraldehyde is comparable to the enantioselctivity of homogeneous threitol-strapped manganese-porphyrin/1,5-dicyclohexylimidazole in the oxidation of olefins which oxidize styrene with iodosylbenzene to styrene oxide in 86% yield and ee 69%.⁷⁹

Recycling of the catalyst

The recyclability of Fe_3O_4 /tart/Mn(TCPP)Cl was examined using the oxidation of tetralin. The only product was 1-tetralol with S-configuration and ee about 83%. After each run, the solution was simply decanted with the assistance of a small magnet. The catalyst was quickly concentrated to the side wall of the reaction flask once a magnet is placed nearby. After a simple wash by CH₃CN and subsequent removal of residual solvent by

drying at 60 °C for 6 h, the catalyst was reused for the next run. Washing the catalyst and, specially, drying at 60 °C for 6 h is essential for achieving high efficiency. When the separated catalyst was washed and reused without drying, the activity decreased significantly. To our delight, the obtained catalyst by the adsorption of Mn(TCPP)Cl on magnetic chiral support (Fe₃O₄/tart-NPs) showed excellent activity and reusability for 4 recycles. The yield and enantioselectivity was maintained at similar level after 4 cycles (Fig. 7), however, activity of the catalyst decreased somewhat in the fifth run from 72% to 62% without any reduction in its enantioselectivity. The spectra of the filtrates after each recycle are shown in Fig. S10. It is obviously seen that there is no Mn-porphyrin leaching up to four cycle, but porphyrin is leached during the fifth run. These data are consistent with results of the catalyst activity shown in the recycle experiments (Fig. 7). Probably, the carboxylate groups of the immobilized Mn(TCPP)Cl is gradually protonated during each recycle by the produced isobutyric acid and in the fifth run the protonation is enough to begin the Mn(TCPP)Cl separation. UV-Vis spectrum of the filtrate after 5th run shows the spectrum of H₂TCPP instead of Mn(TCPP)Cl. This finding also confirms our prediction concerning the protonation of the immobilized Mn(TCPP)Cl.

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Table 2 Aerobic asymmetric oxidation olefins catalyzed by Fe ₃ O ₄ /	'tart/Mn(TCPP)Cl ^a
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Entry	Substrate	Conv.	Product(s)/Yield (%) ^b	Epoxide	ee (%)
		(%) ^b	(configuration)	Select. (%)	(config.) ^c
1	\downarrow	95	4 P>	100	100 (S)
	7		7		
			н		
			100 (S)		
2	4	68	ω	100	100 (S)
	5				
			Ĥ		
			68 (S)		
3		100		67	67 (S)
	\sim				
			56 (S) 11 (P) 33		
1		100		62	69 5)
4		100		03	08 3)
			CHO		
			I L I O H L I O H L I		
			53 (S.S) 10 (R.R) 37		
5		100		47	40 (R)
	$\land \land$. ,
		(53 33 (R) 14 (S)		(-)
6	Ph 	100°	Ph	100	84 (S)
	Ph		Ph Ph Ph Ph		
			of anovida (P) trans anovida (S) trans anovida		
			(39) (5) (56)		
7	/Ph	100 ^d	0,Dh	100	ND
	Ph//		Phuu		
			<i>trans</i> -epoxide		
			(100)		
				100	a a (a a)
8		82		100	20 (S,S)
	~		49 (S,S) 33 (R,R)		
9	\frown	98	ОН ОН	88	50 (S)
			86 3 (R) 9 (S)		
10		98 ^e		98	
			96		

^a Reaction conditions: catalyst Fe₃O₄/tart/Mn(TCPP)Cl 1.0 mg (0.17 μ mol Mn-porphyrin), substrate 2 mmol, chlorobenzene 0.1 g, isobutyraldehyde 5 mmol, CH₃CN 5 mL, O₂ balloon, reaction temperature 25 °C, reaction time 8 h. ^b Conversions and yields calculated on the basis of the substrate. ^c *cis*-stilbene 1 mmol. ^d *trans*-stilbene 0.5 mmol. ^e After 4 h; after 2 h the conversion was 90%. All data were reproduced at least twice and reported as an average.



Fig. 7 Recycling experiments. Reaction conditions: Fe₃O₄/tart/Mn(TCPP)Cl 3.0 mg (0.51 μ mol), tetralin (2 mmol), CH₃CN 5 mL, isobutyraldehyde 5 mmol, 25 °C and time 8 h. ee (%) Determined by chiral GC. Averages of duplicate experiments and error bars represent the standard deviations.

UV-Vis spectrum of the recycled catalyst (Fig. 8) shows the presence of the Mn(TCPP)Cl on the recycled catalyst. The FE-SEM image of the catalyst after recycle indicated that the catalyst is quite robust and no significant aggregation was found (Fig. 8).



Average particles size 55.9 ± 13.6 nm after 4 times recycle.

Fig. 8 UV-Vis spectra of fresh and used Fe_3O_4 /tart/Mn(TCPP)Cl (above) and FE-SEM of the recovered Fe_3O_4 /tart/Mn(TCPP)Cl (bottom).

The oxidation mechanism

The key role of Fe₃O₄/tart/Mn(TCPP)Cl catalysis is evident in the oxidation of hydrocarbons. In the absence of the catalyst no reaction occurred under our mild operating conditions with O₂/isobutyraldehyde, while an increase in Fe₃O₄/tart/Mn(TCPP)Cl concentration led to higher conversion in the oxidation of tetralin (Table 1, entry 5). In addition, producing the epoxide (80%) as main product (Table 2, entry 9) suggests that a normal free radical is not the predominant pathway in the oxidation of cyclohexene bv Fe₃O₄/tart/Mn(TCPP)Cl and O₂/aldehyde. It has often been assumed that high-valent metal oxo species are the most likely active intermediates when olefins are selectively oxidized to the corresponding epoxides in metal complex-catalyzed oxygen atom transfer reactions.^{80,81,74} It has been also reported that species such as metal-OOR complexes (R = H, CR', C(O)R'),⁸² which are the precursors to the high-valent metal oxo complexes, are sometimes themselves competent as epoxidizing agents that can react directly with olefins. We suppose that the oxygenation of substrates with Fe₃O₄/tart/Mn(TCPP)Cl and O₂/isobutyraldehyde occurs by a mechanism proposed to the oxidation with O₂/aldehydes catalyzed by metal complexes as is given in Scheme 2.83 In this mechanism, the supported Mn-porphyrin complex ($[Mn^{III}]$) is assumed to play two roles. First, the Mn complex reacts with the aldehyde to generate an acyl radical (RC(O)[•]). The acyl radical then reacts with dioxygen to give an acylperoxy radical (RC(O)OO[•]). The acylperoxy radical acts as a carrier in a chain mechanism by reacting with another aldehyde molecule to give the peroxyacid, thereby generating another acyl radical. Oxygenation of substrate is assumed by this mechanism to occur via a reactive high-valent Mn-oxo intermediate, which is produced by the reaction of the peroxyacid with the Mnporphyrin of Fe₃O₄/tart/Mn(TCPP)Cl and which then reacts with the substrate (olefin) to give the oxygenated product.

[Mn ^{III}] + RCHO		[Mn ^{II}] + RĊO + H ⁺
$\dot{RCO} + O_2$	\longrightarrow	RCO ₃
RCO ₃ + RCHO		RCO₃H + RĊO
[Mn ^{III}] + RCO ₃ H	\longrightarrow	[Mn [∨] =O] + RCO ₂ H
Mn ^V =O] + Substrate	>	[Mn ^{III}] + Product(O)

 $\label{eq:scheme} Scheme \ 2 \ \ The \ suggested \ \ mechanism \ \ for \ \ the \ \ oxidation \ \ of \ \ olefins \ \ by \ Fe_3O_4/tart/Mn(TCPP)Cl \ and \ O_2/isobtyraldehyde.$

It has been shown that the acylperoxy radical generated in the radical reaction of dioxygen and aldehyde is a competent oxidizing agent for olefin epoxidations.⁸⁴ The acylperoxy radical has a greater tendency to yield epoxides by addition to the double bond of olefins rather than to abstract an allylic hydrogen atom of the olefins to give allylic oxidation products, whereas hydroxyl and alkylperoxy radicals tend to abstract an allylic hydrogen.⁸⁵ However, the high enantioselectivity of Fe₃O₄/tart/Mn(TCPP)CI catalyst shows that direct involvement of acylperoxy radical in the epoxidation is probably not

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favorable in this system. Another possible epoxidizing agent in this system is percarboxylic acids, which is a potential epoxidizing intermediate since such peracids can be formed from reaction of acylperoxy radicals with aldehydes (see Scheme 2). Peroxy acids are known to epoxidize *cis*-stilbene stereoselectively to give only the *cis*-oxide as product. The oxidation of *cis*-stilbene by $[Mn^{III}]/O_2$ /isobutyraldehyde gave *trans*-stilbene oxide as the predominant product (Table 2, entry 6). Therefore, we can conclude that the epoxidizing intermediate is not the peroxyacid, presumably because the rate of the reaction of the acylperoxy radical with $[Mn^{III}]$ is faster than that of its reaction with aldehyde under our reaction conditions.

Additional evidence for this was obtained from stereochemical investigations of the epoxidation of *cis/trans* stilbene (Table 2). The epoxidation of *trans*-stilbene proceeded stereospecifically with retention of configuration at the double bonds (Table 2, entry 7). In oxidation of *cis*-stilbene a mixture of *cis*- and *trans*-stilbene oxide with 1:1.56, molar ratio was obtained (Table 2, entry 6). This result showed that oxygen transfer to olefin is not concerted and that it goes through a radical intermediate. The radical intermediate can be transferred to *cis*-epoxide via direct collapse or there is a rotation of the radical intermediate which then collapses to *trans*-epoxide as shown in Scheme 3.⁸⁶



Although detailed considerations on the transition state which results in enantioselectivity are not yet clear, the stereochemistry of all the products indicates that Fe₃O₄/tart/Mn(TCPP)Cl approaches the carbon-carbon double bond preferentially from the pro-S face of the olefin plane consisting of RCH=CHR' group. Chirality is induced by the chiral L-tartaric acid when the olefin is closing the nanocatalyst surface. Product analyses of the various olefin epoxidation (Table 2) proves that the S-face of the prochiral olefin is mainly preferred for oxygenation, thereby the approching of olefin is through pro-S face, as shown in Fig. 9. Facial selectivity in addition of the olefin to Fe₃O₄/tart/Mn(TCPP)Cl would be established by hydrogen bond interaction between the hydrogen atom on the olefin double bond and the hydroxyl group of the tartrate (suggested transition state in Fig. 9). Similar intermediate has been proposed for the asymmetry achieved in the osmium tetroxide oxidation of olefins by employing chiral amines.87,88



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Fig. 9 The proposed intermediate for the olefin epoxidation by Fe₃O₄/tart/Mn(TCPP)Cl

Conclusion

In summary, we have successfully developed, for the first time, a novel magnetically separable catalytic system bv immobilization of Mn-porphyrin on chiral Fe₃O₄/tart nanoparticles stabilized by a chiral stabilizer. The immobilized Mn-porphyrin catalyst showed excellent catalytic activities and enantioselectivities for the asymmetric epoxidation of various terminal, cyclic and aromatic olefins by O₂/aldehyde and could be reused for at least 5 times. Asymmetric induction is done through the supported L-(+)-tartaric acid and anchoring Mn(TCPP)Cl on magnetite helps easy separation of the catalyst by magnetic decantation. This strategy work shows that valuable chiral epoxide can be synthesized without using any complicated and expensive metal catalysts which have been proved difficult to prepare. The generality of this catalystchiral inducer immobilization strategy should allow the design of many highly active and enantioselective heterogeneous asymmetric catalysts which are one of the most promising solutions to the problems presented by homogeneous catalysts.

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For Table of Contents Graphic and Synopsis

A highly efficient green process for the asymmetric epoxidation of olefins by an easy to synthesis Mnporphyrin and O_2 /aldehyde is reported.