ORIGINAL PAPER



Cis-dioxo-Mo(VI) salophen complex supported on $Fe_3O_4@SiO_2$ nanoparticles as an efficient magnetically separable and reusable nanocatalyst for selective epoxidation of olefins

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Abstract In this work, paramagnetic Fe_3O_4/SiO_2 nanoparticles were synthesized, characterized and functionalized with dioxo-Mo(VI) tetradentate Schiff base complex and characterized using IR spectroscopy, X-ray powder diffraction spectroscopy, scanning electron microscopy, transmission electron microscopy, vibrating sample magnetometry, diffuse reflectance spectroscopy and atomic absorption spectroscopy. Catalyst was used for the selective epoxidation of cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-hepten, 1-octene, 1-dodecen and trans-stilbene using *tert*-butyl hydroperoxide as oxidant in 1,2-dichloroethane. This catalyst is efficient for oxidation of cyclooctene with a 100% selectivity for epoxidation with 100% conversion in 1 h. After the reaction, the magnetic nanocatalyst was easily separated by simply applying an external magnetic field and was used at least five successive times without significant decrease in conversion.

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Introduction

Epoxidation of olefins is one of the fundamental reactions in industrial organic synthesis [1, 2]. Recently, Schiff base transition metal complexes have been extensively studied as catalysts in a wide range of reactions [3-7]. There are many reports in synthesis and catalytic activity of molybdenum(VI) Schiff base complexes to be very effective catalysts for the various oxidations of organic compounds including sulfides, alcohols and alkenes with *tert*-butyl hydroperoxide (TBHP) as the oxidant [8-10]. It is noteworthy that *tert*-butyl hydroperoxide is environment-friendly organic peroxide widely used in a variety of epoxidation processes with good thermal stability [11– 13]. Homogenous catalysts of transition metal complexes are deactivated in the reaction matrix through the formation of oxo and peroxo dimeric species [14, 15]. Furthermore, separation, insufficient chemical and thermal stability, decomposition and recycling of catalyst remain a scientific challenge. This problem may be solved by immobilization of the homogeneous metal complex onto solid supports. Therefore, supporting of metal complexes has been the subject of a lot of research in catalytic fields [3, 4, 7, 16, 17].

A main idea for supporting of metal complexes is to anchor the metal complex onto large surface area of inorganic materials such as zeolite and metal oxide [18–22].

Nowadays, core-shell paramagnetic Fe_3O_4 nanoparticles have been used strongly as supporting surface because of their unique properties including the high surface area, low toxicity, separate-ability and biocompatibility [6, 23–25]. Magnetic separation renders the recycling of catalysts from the solution by external magnetic fields much easier than filtration and centrifugation. Meanwhile, using silica layer can prevent the occurrence of aggregation of magnetic Fe_3O_4 nanoparticles [26].

Following of our previous research in catalytic activity of Schiff base complexes, herein we report the immobilization of N,N-bis(5-chloromethyl salicylidene)-1,2-phenylenediamine dioxomolybdenum(VI) (CM–SalophMoO₂) onto the surface of amino-modified core–shell paramagnetic nano-

particles (Fe₃O₄@APTMS/CM–SalophMoO₂) (Scheme 1). The resulted catalyst has been characterized by using different techniques and examined for the selective epoxidation of cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-hepten, 1-octene, 1-dodecen and trans-stilbene with *tert*-butyl hydroperoxide (70% aqueous) as oxidant. The catalytic performances of supported catalyst have been compared to homogeneous analogues. The reusability of Fe₃O₄@APTMS/CM–SalophMoO₂ was also studied in the epoxidation of cyclooctene with TBHP (70% in water) in 1,2-dichloroethane.

Experimental

Materials and physical measurements

5-chloromethyl salicylaldehyde [27] was prepared according to literature procedures. Cyclooctene, 3-aminopropyltrimethoxysilane (APTMS), o-phenylenediamine, cyclohexene, styrene, indene, α -pinene, 1-hepten, 1-octene, 1-dodecen, trans-stilbene, iron(II) chloride (FeCl₂·4H₂O),

Scheme 1 Preparation of heterogeneous nanocatalyst iron(III) chloride(FeCl₃·6H₂O) and ammonium hydroxide (25%[w/w]) were purchased from Merck Chemical Company. ¹HNMR spectra were recorded using a Bruker FT NMR 500 (500 MHZ) spectrometer (CD₃)₂SO. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. The purity of the solvents, cyclooctene, cyclohexene, styrene, indene, α-pinene, 1-hepten, 1-octene, 1-dodecen, trans-stilbene and analysis of the oxidation products was determined by gas chromatography using Agilent 7890 with a capillary column and FID detector. Column temperature was programmed between 180 and 200 °C (2 °C/min). Nitrogen was used as carrier gas (25 ml/min) at injection temperature. FT-IR spectra were obtained by Shimadzu 8400S spectrophotometer in KBr pellets. Diffuse reflectance spectra (DRS) were taken on a Scinco 4100 in the range 200–1100 nm using BaSO₄ as reference. VSM was recorded with MDKF-FORC/VSM) MEGNATIS-DAGHIGH-KASHAN Co.). DRS data were recorded by Scinco 4100 in the range 200-900 nm using



barium sulfate as reference. The powder small angle X-ray diffraction patterns were recorded on ITALSTRUCTURE X-ray diffractometer with CuK α ($\lambda = 1.54$ Å) radiation. The voltage and current applied to the X-ray tube were 40 kV and 30 mA, respectively, with scanning speed as 0.001 min⁻¹. Surface morphology and distribution of particles were studied via VEGA-TESCAN scanning electron microscopy.

Preparation of Fe₃O₄@ APTMS

Nanoparticle of Fe_3O_4 and $Fe_3O_4@SiO_2$ was synthesized and characterized as described in the literature [28, 29]. $Fe_3O_4@SiO_2$ (0.5 g) was suspended in ethanol (50 ml), and 3-aminopropyltrimethoxysilane (APTMS) (2.5 ml) dissolved in 50 ml ethanol was added dropwise to the suspension. The mixture was stirred at 70 °C for 5 h. Finally, the brown MNPs was separated magnetically and washed with distilled water for several times to remove any unbound APTMS. FT-IR (KBr, cm⁻¹): 3406 [ν (O– H)], 1033 [ν (Si–O–Si)], 575 [ν (Fe–O)].

Preparation of *N*,*N*′-bis(5-chloromethyl salicylidene)-1,2-phenylenediamine (5-CM-saloph)

o-phenylenediamine (2.5 mmol, 0.27 g) was dissolved in 20 ml dichloromethane and added dropwise to the solution of 5-chloromethylsalicyaldehyde (5 mmol, 0.85 g) in 20 ml dichloromethane. The mixture was refluxed for 2 h. The orange-colored precipitates were collected, washed with dichloromethane and then dried in vacuum (yield 1 g, 96%). Anal. Calcd for $C_{22}H_{18}N_2O_2Cl_2$.: C, 63.61; H, 4.81; N, 6.71. Found: C, 63.81; H, 4.51; N, 6.49. IR (KBr, cm⁻¹): 1654 [ν (C=N)], 3401 [ν (O–H)]. ¹HNMR (500 MHz, DMSO-d₆) δ_{ppm} : 11.2 (s, 2H, OH), 8.1 (s, 2H, Ar–CH=N), 6.8–7.5 (m, 10H, Ar), 4.22 (s, 4H, alkane) (supporting information, Fig. S1). ¹³CNMR (500 MHz, CDCl₃): 55.9, 115.2, 118.3, 118.8, 119.6, 120.8, 127.7, 142.5, 152.2, 155.6, 163.3 (supporting information, Fig. S2).

Preparation of 5-CM-salophen complex of dioxomolybdenum(VI)

An ethanol solution (25 ml) of $[MoO_2(acac)_2]$ (2 mmol) was added dropwise to the ligand 5-CM-saloph (2 mmol) that was dissolved in absolute ethanol (25 ml), and the mixture was refluxed for 3 h. Then, the desired orange MoO_2 complex was filtered and washed with cooled absolute ethanol and dried at vacuum conditions (yield 0.6 g, 44%). Anal. Calcd for $C_{22}H_{16}N_2O_4Cl_2Mo.$: C, 49.1;



Fig. 1 FT-IR spectrum of (a) Schiff base ligand, (b) MoO_2 -Schiff base complex, (c) Fe₃O₄@APTMS/CM–SalophMoO₂

H, 2.97; N, 5.21. Found: C, 48.6; H, 3.20; N, 4.9. IR (KBr, cm⁻¹): 1620 [ν (C=N)], 944 and 912 [ν (Mo=O)]. ¹HNMR (500 MHz, DMSO-d₆, 25 °C) δ_{ppm} : 8.5, 8.6 (s, 2H, Ar–CH=N), 6.4–7.8 (m, 10H, Ar), 4.4, 4.6 (s, 4H, alkane) (supporting information, Fig. S3). ¹³CNMR (500 MHz, DMSO-d₆): 56.2, 57.2, 111.3, 111.6, 112.6, 114.8, 116.2, 117.6, 118.5, 119.5, 121.3, 123.1, 124.5 143.3, 144.2, 155.5, 156.3, 161.3, 162.6, 166.4, 167.3, 169.6 (supporting information, Fig. S4). DRS (solid phase, nm): 362 and 430 nm.

Preparation of Fe₃O₄@APTMS/CM-SalophMoO₂

the 5-CM-salophen А solution containing dioxomolybdenum(VI) complex (5 mmol, in 50 ml toluene) was added to a suspension of amine-functionalized Fe_3O_4 @APTMS (1.0 g in 50 ml toluene). The resulting mixture was stirred at 70 °C for 24 h. After cooling, the brown Fe₃O₄@APTMS/CM–SalophMoO₂ nanocatalyst was separated using an external magnet and washed several times with water and ethanol. 3.5% of Mo on Fe₃O₄@APTMS was detected by atomic absorption and EDAX.



Fig. 2 DRS spectrum of (a) $Fe_3O_4@APTMS/CM-SalophMoO_2$ as heterogeneous catalyst, (b) MoO_2 -Schiff base complex as homogenous catalyst



Fig. 3 Small angle X-ray diffraction pattern of: **a** Fe₃O₄@APTMS/ CM–SalophMoO₂, **b** Fe₃O₄ nanoparticles

Catalytic activity of heterogeneous and homogeneous complex in olefins epoxidation

Catalyst was used for the selective epoxidation of cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-hepten, 1-octene, 1-dodecen and trans-stilbene using *tert*-butyl hydroperoxide as oxidant in 1,2-dichloroethane. The system was purged with argon gas. In a typical experiment, a mixture of 0.2 g of Fe₃O₄@APTMS/CM–SalophMoO₂ (2.3 × 10⁻⁵ mol for unsupported complex), and 1, 2-dichloroethane (DCE) (5 ml), 5 mmol freshly distilled olefins and 12.5 mmol of *tert*-butyl hydroperoxide was refluxed for 1 h. The reaction was followed by a magnetic separation of Fe₃O₄@APTMS/CM–SalophMoO₂ using an external magnetic field. The separated catalyst washed with absolute ethanol could be reused after drying at 80 °C under vacuum. 1, 2-dichlorobenzene was used as an internal standard. The solution was injected to GC analysis, finally.

Result and discussion

Synthesis and characterization

Dioxomolybdenum(VI) complex Schiff base (derived from 5-chloromethylsalicyaldehyde and o-phenylenediamine) was prepared, characterized and immobilized on Fe₃O₄/ SiO₂ core-shell nanoparticles as a heterogeneous recyclable nanocatalyst. Figure 1 compares the FT-IR spectra of the Schiff base ligand in Mo complex and Fe₃O₄@ APTMS/CM-SalophMoO2. The FT-IR spectrum of free ligand exhibits the C=N stretching vibration intense band at 1654 cm^{-1} , which shifts to 1620 and 1622 cm^{-1} in the corresponding complex and Fe₃O₄@APTMS/CM-SalophMoO₂, respectively, indicating coordination of azomethine nitrogen. The appearance of two adjacent bands of molybdenum complex and Fe₃O₄@APTMS/CM-SalophMoO₂ at 944 and 912 cm⁻¹ was characteristic of the presence of asymmetric and symmetric stretches of cis-[O=Mo=O] group [30, 31]. Two bands in Fig. 1c at 1100 and 592 cm⁻¹ can be assigned to Si–O–Si and Fe–O stretching, respectively. Comparison of the FT-IR spectra suggests that the MoO₂ is bonded to the Schiff base ligand and it is supported successfully on Fe₃O₄@ APTMS.

¹H NMR and ¹³CNMR of Schiff base ligand and Mo complex confirm the proposed structure of compounds. In the ¹H NMR spectra of the CM–Saloph, the signal at 11.2, 8.1 and 4.22 was assigned for H-phenol, H-imine and H-methylene, respectively. By considering the ¹H NMR and ¹³CNMR spectra of Mo(VI) complex, it seems that the more splitting is shown because of the non-equivalence chelate ring (supporting information, Fig. S1-S4).

As shown in Fig. 2, the diffuse reflectance spectra (DRS) of the net complex and Fe₃O₄@APTMS/CM–SalophMoO₂ show two bands at 362 and 430 nm assigned to $n-\pi^*$ of Schiff base ligand and ligand-to-metal charge transfer (LMCT) transitions, respectively [8, 32]. The comparison of diffuse reflectance spectra (DRS) of the Fe₃O₄@APTMS/CM–SalophMoO₂ and MoO₂(VI) Schiff base complex shows that there is no geometrical change



Fig. 4 EDS spectrum of synthesized $Fe_3O_4@APTMS/CM-SalophMoO_2$ heterogeneous nanocatalyst for epoxidation of olefins with TBHP in 1,2-dichloroethane



Fig. 5 Magnetization curves at 298 K for Fe_3O_4 (*solid*) and Fe_3O_4 @ APTMS/CM–SalophMoO₂ (*dot*)

in dioxomolybdenum(VI) complex after supporting on $Fe_3O_4@APTMS NPs$.

The X-ray diffraction pattern of crystalline structures of Fe_3O_4 NPs and core–shell magnetic $Fe_3O_4@APTMS/CM$ –SalophMoO₂ (See Fig. 3) shows characteristic diffraction peaks corresponding to (220), (311), (400), (422), (511) and (440) reflections of inverse spinel Fe_3O_4 NPs, respectively. It showed the characteristic peaks, and the relative intensities matched well with those of standard Fe_3O_4 nanoparticles (reference JCPDS card no. 87-2334). A weak

broad peak that appeared in the range from $2\theta = 19^{\circ}$ to 27° indicates the existence of amorphous silica. The crystal size of Fe₃O₄ NPs and core-shell magnetic Fe₃O₄@ APTMS/CM-SalophMoO₂ was estimated by using the Debye–Scherrer equation $(d_{\text{hkl}} = 0.94 \ \lambda/\beta \cos\theta)$ where β is the half-width of the highest intensity X-ray diffraction lines, d is the average crystalline diameter, 0.94 is the Scherrer constant, θ is the Bragg angle in degree, and λ is the X-ray wavelength. Here, the (311) peak of the highest intensity was selected and d_{311} obtained 23 nm for Fe₃O₄ NPs. Comparing between X-ray diffraction patterns of Fe₃O₄ NPs and Fe₃O₄@APTMS/CM-SalophMoO₂ shows that the coating of silica and dioxomolybdenum Schiff base complex on Fe₃O₄ NPs did not significantly affect the structure of NPs. As shown in Fig. 4, the EDX spectra of catalyst provide existence of Mo, Si, C and the other elements on catalyst surface. The plots of magnetization versus magnetic field show the absence of hysteresis phenomenon and indicate that product appeared paramagnetic at room temperature. The magnetic saturations of Fe₃O₄ and Fe₃O₄@APTMS/CM-SalophMoO₂ are 57.8 and 37.02 emu/g, respectively. These results indicated that the magnetization of Fe₃O₄ decreased considerably with the formation of SiO₂ shell and Mo(O)₂ Schiff base complex anchoring. However, we were able to separate the $Fe_3O_4@$ APTMS/CM-SalophMoO₂ from the solution by using an external magnetic field (Fig. 5).

SEM (Fig. 6a, b) and TEM (Fig. 6c, d) images of Fe_3O_4 and Fe_3O_4 @APTMS/CM–SalophMoO₂ were utilized for morphological studies. TEM images show that the



Fig. 6 SEM images of a Fe_3O_4 NPs, b $Fe_3O_4@APTMS/CM$ -SalophMoO₂ and TEM images of c Fe_3O_4 NPs, d $Fe_3O_4@APTMS/CM$ -SalophMoO₂

Entry	Catalyst	Solvent	Ultrasonication time (min)	Oxidant	Conversion (%)/selectivity (%)
1	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	ClCH ₂ CH ₂ Cl	_	TBHP	32/100
2	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	ClCH ₂ CH ₂ Cl	10 ^a	TBHP	61/100
3	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	ClCH ₂ CH ₂ Cl	22 ^a	TBHP	100/100
4	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	CH ₃ CN	22 ^a	TBHP	80/100
5	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	CH ₃ OH	22 ^a	TBHP	63/100
6	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	CH_2Cl_2	22 ^a	TBHP	60/100
7	Blank run/without cat.	ClCH ₂ CH ₂ Cl	_	TBHP	16/100
8	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	ClCH ₂ CH ₂ Cl	22 ^a	UHP	52/100
9	Fe ₃ O ₄ @APTMS/CM-SalophMoO ₂	ClCH ₂ CH ₂ Cl	22 ^a	NaIO ₄	32/100

Table 1 Results of catalytic epoxidation of cyclooctene solvent = 5 ml; catalyst = 2.3×10^{-5} mol; duration = 1 at reflux; with the molar ratio of cyclooctene: TBHP are 1:2.5

^a The catalyst ultrasonicated in DCE before adding the substrate and TBHP



Fig. 7 Effect of reaction temperature on conversion catalytic epoxidation of cyclooctene by $Fe_3O_4@APTMS/CM-SalophMoO_2$ catalyst with TBHP as oxidant and 1,2-dichloroethane as solvent in 2:1 ratio of [TBHP]/[cyclooctene]



Fig. 8 Effect of [TBHP]/[cyclooctene] ratio on conversion catalytic epoxidation of cyclooctene by $Fe_3O_4@APTMS/CM-SalophMoO_2$ catalyst with TBHP as oxidant 1,2-dichloroethane as solvent at 80 °C

particle size has changed after immobilization of complex on modified MNPs. The synthesized catalysts are well dispersed, and the nanoparticles are almost spherical in shape. The average particle size was estimated about 30 and 40 nm for Fe_3O_4 and Fe_3O_4 @APTMS/CM–SalophMoO₂, respectively.

Catalytic activity

Selective epoxidation of cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-hepten, 1-octene, 1-dodecen and trans-stilbene by using heterogeneous (Fe₃O₄@APTMS/ CM–SalophMoO₂) and homogeneous (CM–SalophMoO₂) catalysts was tested with *tert*-butyl hydroperoxide (70% aqueous) as oxidant. The catalytic testing of heterogeneous

catalyst was optimized for epoxidation of cyclooctene. The time of catalytic reaction, kind of solvent, the reaction temperature and the molar ratio of [TBHP]/[cyclooctene] were investigated. To choose the suitable solvent, dichloromethane, methanol, acetonitrile, 1,2-dichloroethane were examined and 1,2-dichloromethane has been selected, finally. The optimizing results are summarized in Table 1, which shows dichloroethane to be the best solvent. Apparently, highly coordinating solvents, such as methanol, cause a significant decrease in the catalytic activity since they compete with tert-butyl hydroperoxide for binding to the metal center [33]. It seems the limitation of lower reflux reaction temperature is an important factor of least conversion in dichloromethane (60%). The conversion increased with increasing the reaction temperature from 25 to 80 °C (Fig. 7). The percent of conversion increased with increasing the molar ratio of [TBHP]/[cyclooctene] from 0.5 to 2.5, and the conversion of cyclooctene was maximum at 2.5:1 molar ratio of [TBHP]/[cyclooctene] (Fig. 8). In the presented work, different oxidants such as NaIO₄, UHP $(urea-H_2O_2)$ and TBHP (*tert*-butylhydroperoxide) were examined in epoxidation of cyclooctene in 1, 2-dichloroethane (DCE). Results in Table 1 show that TBHP is the best oxidant for epoxidation of cyclooctene in DCE. It has several advantageous such as high percent of conversion, environment friendly and good thermal stability. The effect of nanoparticles dispersion before reaction was investigated on catalytic activity using ultrasonicating. It appears that the dispersion of nanoparticles in solvent increased the catalytic activity from 32 to 100% (See Table 1).

Hence, typical catalytic reaction conditions involve DCE (5 ml) solutions at 80 \pm 2 °C, alkene (5 mmol), TBHP (12.5 mmol) with the 1:2.5 molar ratio of cyclooctene: TBHP and catalyst $(2.3 \times 10^{-5} \text{ mol}, 0.2 \text{ g for Fe}_{3}\text{O}_{4}\text{@}$ APTMS/CM-SalophMoO₂, complex loading on Fe₃O₄@ APTMS detected by atomic absorption and EDAX) stirred for 1 and 2 h. The final solution exhibited no color. So, no presence of metal was detected in the solution after using heterogeneous catalyst (it was confirmed by atomic absorption spectroscopy). The product distributions in the epoxidation of various alkenes using homogeneous and heterogeneous catalysts are shown in Table 2. Generally, one of the main problems of homogeneous transition metal complexes as catalysts is the formation of oxo and peroxo dimeric and other polymeric species. The formation of these compounds can deactivate catalysts irreversibly. As summarized in Table 2, Fe₃O₄@APTMS/CM-SalophMoO₂ gives higher percent of conversion of alkenes than the net complex.

The cyclooctene oxidation proceeds with a significant selectivity (100%) of epoxidation with 100% conversion in 1 h using $Fe_3O_4@APTMS/CM-SalophMoO_2$, while the

Alkene	% Conversion				% Epoxy		TON ^b Fe ₃ O ₄ @SiO ₂ -complex (net complex)	
	Fe ₃ O ₄ @SiO ₂ - complex		Net complex		Fe ₃ O ₄ @SiO ₂ -complex	Net complex		
	1 h	2 h	1 h	2 h				
\bigcirc	100	100	60	70	100	100	218 (152)	
¢-	76	82	50	62	56 ^c	44 ^d	100 (59)	
	66	70	47	58	100	100	152 (126)	
	44	78	26	35	>99	>97	168 (74)	
\bigcirc	48	62	44	54	98	98	132 (115)	
	68	76	52	63	100	100	165 (137)	
$\sim\sim\sim$	58	64	32	48	100	100	139 (104)	
$\sim\sim\sim$	50	65	42	46	100	100	142 (100)	
~~~~~	/ 35	40	32	36	100	100	87 (79)	

**Table 2** Results of catalytic epoxidation of various alkenes with TBHP catalyzed by  $Fe_3O_4@APTMS/CM-SalophMoO_2$  and net complex, 1, 2-dichloroethane = 5 ml; catalyst =  $2.3 \times 10^{-5}$  mol^a; duration = 1 and 2 h at reflux; the molar ratio of cyclooctene/TBHP is 1:2.5

 $^{\rm a}\,$  The mole of catalyst in 0.2 g heterogeneous catalyst calculated by % Mo

^b TON: The mole of epoxide/mole of catalyst during 2 h

^{c,d} The by-products are verbenone and verbenol for heterogeneous system and homogeneous system

unsupported complex shows 60% conversion in the same condition. This trend was illustrated for all alkenes in Table 2. Catalytic reactions were not affected by the presence or absence of light. The catalytic oxidation of substrate with TBHP in the absence of catalysts (blank run) occurs with low conversion (~16%). We were able to separate magnetically nanocatalyst by using external magnetic field and use the catalyst at least five successive times without significant decrease in conversion (Table 3).

As shown in Scheme 2, the observed results support a proposed mechanism via a seven-coordinate intermediate similar to the literature [34]. In the first step, the mechanism involves the transfer of TBHP's proton to the terminal of oxo atom of the  $MoO_2$  group and coordination of t-BuOO⁻ to molybdenum(VI) as a Lewis acidic metal center and formation of the oxoperoxomolybdenum(VI) intermediate. In the sequence, the next step proceeds by approach of olefin to coordinated oxygen. Then, the forming of hydrogen bond between the (O) and coordinated OH releases epoxide and alcohol from the intermediate.

Table 4 illustrates the comparison of the most relevant catalytic systems. Comparison and review of these results indicate the efficiency of the presented magnetic nanocatalyst in catalytic activity, selectivity, catalytic reaction time and reusability and easy separation. The presented nanocatalyst showed higher catalytic

 Table 3 Results obtained from catalyst reuse in the epoxidation of cyclooctene

Run	% Conversion ^a	% Epoxy ^a	% Mo leached ^b		
1	100	100	0		
2	100	100	0		
3	99	100	0		
4	99	100	0		
5	98	100	0		

^a GC conversion based on starting alkene

^b Determined by atomic absorption spectroscopy

activity than the [MoOCl(L)] [35], [Mo(CO)₆@PS] [36], [MoO₂(py)₂]-MCM41 [37], MoO₂acpyAmpMCM-41 [38], MoO₂-thio-SCMNPs [10], Mag-Mo-nanocatalyst [39] and MoO₂(L)(EtOH)ZBS-PVPA [40]. The epoxidation reaction time of our catalyst (1 h) is considerable in comparison with the other reports (24 h) [10, 35], (8 h) [40], (7 h) [37] and (5 h) [39]. However, there is some homogenous [MoO₂(L)(CH₃OH)] [41] and [MoO₂L¹(CH₃OH)] [42] catalysts with epoxidation reaction time, 0.5 and 1 h, respectively, but our novel heterogeneous catalyst has more important advantages such as easy magnetic separation for several times with suitable reusability and stability of catalyst.





Table 4 Comparison of literature reports on the epoxidation of cyclooctene under various conditions

Catalyst	Substrate	Reaction conditions	Recoverability	% Epoxy	References
[MoOCl(L)]	Cyclooctene	TBHP/CDCl ₃ /24 h	Non-recoverable	100	[35]
[Mo(CO) ₆ @PS]	Cyclooctene	H ₂ O ₂ /CCl ₄ /2.5 h	Filtration	96	[36]
[MoO ₂ (L)(CH ₃ OH)]	Cyclooctene	TBHP//DCE/0.5 h	Non-recoverable	99	[41]
$[MoO_2(py)_2]$ -MCM41	Cyclooctene	TBHP/CHCl ₃ /7 h	Filtration	89	[37]
MoO ₂ acpyAmpMCM-41	Cyclooctene	TBHP/CHCl ₃ /4 h	Filtration	99	[38]
$[MoO_2L^1(CH_3OH)]$	Cyclohexene	CH ₃ OH/CH ₂ Cl ₂ /1 h	Non-recoverable	100	[42]
MoO ₂ -thio-SCMNPs	Cyclooctene	TBHP/CHCl ₃ /24 h	Magnetically	100	[10]
Mag-Mo-Nanocatalyst	Cyclooctene	TBHP/CCl ₄ /5 h	Magnetically	99	[39]
MoO2(L)(EtOH)ZBS-PVPA	Cyclooctene	TBHP/DCE/8 h	Filtration	100	[40]
Fe ₃ O ₄ @APTMS/CM-salophMoO ₂	Cyclooctene	TBHP/DCE/1 h	Magnetically	100	This work

# Conclusion

In this research work, we successfully synthesized the magnetically separable  $Fe_3O_4@APTMS/CM-Sal-$ ophMoO₂ nanocatalyst characterized by physicochemical methods. The homogeneous dioxomolybdenum(VI) Schiff base complex and solids containing immobilized Mo(VI) tetradentate Schiff base complex have been studied as catalyst for selective epoxidation of alkenes. Our results showed that the conversion of heterogamous catalyst was higher than that of unsupported Mo(VI) complex. So novel heterogeneous catalyst has more important advantages such as easy magnetic separation for several times with suitable reusability, stability of catalyst and short catalytic reaction time than the other Mo(VI) complexes reported in the literature [10, 35-42]. The catalyst can be separated by using a small external magnetic field from the reaction system and reused for at least five times without significant decrease in conversion. The catalyst shows excellent conversion (100%) in 1 h.

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