

Magnetic Nanoparticles Functionalized with Dendritic Polymer as a Host for Immobilization of $\text{MoO}_2(\text{acac})_2$ and Investigation of its Catalytic Activity in the Epoxidation of Alkenes

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The new heterogeneous catalyst based on $\text{MoO}_2(\text{acac})_2$ immobilized on superparamagnetic nanoparticle functionalized with dendrimer was synthesized. The dendrimer with amine and sulfur functional groups offer proper positions for a strong connection between $\text{MoO}_2(\text{acac})_2$ and support. The synthesized catalyst was characterized by FT-IR spectroscopy, ICP, TGA, SEM, TEM and XRD. This catalyst showed high activity in the epoxidation of alkene with *tert*-BuOOH. These reactions displayed the best performance in the presence of 1,2-dichloroethane as a solvent and 0.0108 mmol of the catalyst. The use of magnetic nanoparticles (MNPs) as support facilitates the separation of the catalyst from the reaction media by simple magnetic decantation. Eventually, the catalyst can be recovered and reused without a decrease in its catalytic activity and significant Mo leaching for five times.

Keywords: Molybdenum catalyst, Superparamagnetic nanoparticle, Dendrimer, Epoxidation of alkene, Reusable catalyst

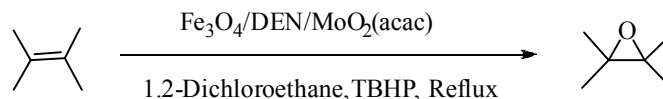
INTRODUCTION

One of the disadvantages of homogeneous catalyst is its separation from the reaction media. In recent years, many attempts have been made to solve this problem. Immobilization of homogeneous catalysts on solid supports is one of the best ways to conquer this defect in homogeneous catalysts [1-2]. Different organic and inorganic supports such as modified MCM-41 [3], multi-wall carbon nanotube [4], polymers [5] and amorphous silica [6] have been used. There are several methods for the immobilization of homogeneous catalyst on support. Impregnation [7] encapsulation [8] diffusion [9], surface adsorption and electrostatic interactions [10] and forming covalent bonds [11] have been used widely for heterogenization of catalysts. Enhancing the catalytic activity, facilitation of their separation of the reaction

media, and minimization of catalyst leaching are the factors for selecting an efficient support and useful method. In this area, Fe_3O_4 magnetic nanoparticle can be used because of their unique properties at the nanoscale such as superparamagnetism, mesoscopic, low toxicity and, the most important one, very easy separation of catalyst with an external magnetic field [12-14]. Another challenge in heterogenization of homogeneous catalysts is the leaching of the catalyst from the surface and the lack of stability in the heterogenized catalyst. Modifying of the surface of magnetic nanoparticles with tunable structures which have proper functional group for making covalent bond and does not decrease the paramagnetic properties is the key for solving the problem. One of the best candidates for improving the performance of Fe_3O_4 nanoparticle is dendrimer which can make a core/shell system as Fe_3O_4 @dendrimer.

Dendrimers are a class of polymers with a highly branched three-dimensional structure. They have three major parts: core, branches, and end groups. Their physical

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Scheme 1. Alkene epoxidation with *tert*-BuOOH catalyzed by APMNP/DEN/MoO₂(acac)

and chemical properties determined by the functional groups on their surface [1,15]. Due to their large number of functional groups, perfect symmetry, and internal cavities, they are suitable for a wide range of biomedical and industrial applications [16-17]. Furthermore, they can be used in the preparation of homogeneous and heterogeneous catalysts with trapping of metal ions by space agents, or by complex formation of them by terminal groups of dendrimer [18-20]. The metal-dendrimer complexes have been investigated to catalyze different organic reactions such as oxidation reaction, allylic alkylation, hydrogenation of olefin, hydroformylation, Diels-Alder reaction [21-22].

Epoxides are useful intermediate and broadly have been used for the synthesis of many organic compounds [23-24]. Epoxidation of alkenes is a common method for the preparation of epoxides [25]. However, this reaction can occur without a catalyst, achievement of high selectivity, and good conversion are obtained in the presence of an efficient catalyst. Epoxidation of unsaturated hydrocarbon usually catalyzed by transition metal such as Ti [26], V [27], Mn [28], Mo [29], Co [30] and Cu [31]. Molybdenum-containing catalysts with high oxidation state have attracted the attention of scientists because of their high catalytic activity for selective oxidation [29,32]. Solubility and homogeneity of most of these catalysts can be considered as the most important problem in point of economic view. To overcome this disadvantage, many strategies have been reported for immobilization of Mo(IV) catalysts on suitable supports without loss of their activity and selectivity in the epoxidation of alkene [33-34].

Regarding the easy reusability of magnetic nanoparticle and tunability of dendrimer, the core/shell structure of Fe₃O₄/dendrimer was selected for anchoring of MoO₂(acac)₂ on the surface. For the achievement of the high efficiency and minimum leaching of catalyst, the thiol and amine decorated dendrimer was synthesized and utilized for trapping Mo-complex. The new synthesized heterogeneous

system was investigated in the epoxidation of alkenes with *tert*-BuOOH as oxidant (Scheme 1).

The use of magnetic nanoparticle in the core of heterogeneous catalyst leads to easy separation just with an external magnetic field that it is an excellent advantage ratio than other heterogeneous catalysts. Furthermore, highly branched dendrimer with very useful and diverse functional groups presents an appropriate platform for immobilization of molybdenum. The strong interaction between Mo and support makes it very stable in reaction media without significant leaching of the catalyst after reuse.

EXPERIMENTAL

All materials used in this work, were purchased from Fluka, Merck, and Aldrich companies. Elemental analysis was performed on a LECO, CHNS-932 analyzer. The powder XRD data were obtained on a D8 Advanced Bruker using Cu K α radiation. The FT-IR spectra were obtained as potassium bromide pellets in the range 400-4000 cm⁻¹ with a Nicolet-Impact 400D spectrophotometer. The thermogravimetric analysis (TGA) was carried out from on a TGA-601 instrument under airflow at a uniform heating rate of 20 °C min⁻¹ in the range 25-800 °C. Gas chromatography (GC) analysis was performed from Shimadzu GC-16A instrument using a 2 m column peaked with silicon DC-200 or Carbowax 20m. In GC experiments, n-decane was used as an internal standard. The transmission electron microscopy (TEM) was carried out on a Philips CM120. The scanning electron microscopy (SEM) was obtained from VEGA-II TESCAN. The ICP analyses were performed from a Jarrell-Ash 1100.

Synthesis of Magnetic Nanoparticle (MNP) Modified Silica (Fe₃O₄/SiO₂)

A mixture of FeCl₂.4H₂O (3.0 g, 1 mmol) and FeCl₃.6H₂O (8.5 g, 2 mmol) was added to a solution of HCl

(0.4 M, 38 ml) under N₂ atmosphere. After the dispersion of this solution in ammonium hydroxide (0.7 M, 375 ml), the mixture was sonicated for 30 min at room temperature. The obtained black solid of Fe₃O₄ nanoparticles was filtered easily by the magnetic field and add to deionized water (150 ml).

The superparamagnetic Fe₃O₄ coated with silica was obtained by sol-gel method. 50 ml of Fe₃O₄ dispersed in deionized water were added to 250 ml of 2-propanol and 50 ml of deionized water and sonicated for 15 min. Then 12 ml polyethylene glycol, 25 ml of ammonium hydroxide and 3 ml of TEOS were consecutively added to the mixture and obtained suspension was kept at room temperature for 24 h under continuous mechanical stirring. The Synthesized magnetic nanoparticles coated with SiO₂, were washed by ethanol (3 × 20 ml) and water (3 × 20 ml) and dried under vacuum oven at 50 °C overnight [35].

Synthesis of Aminopropyl Functionalized Magnetic Nanoparticles (APMNP)

A mixture of Fe₃O₄/SiO₂ (3.0 g) and 3-aminopropyltrimethoxysilane (8 ml) was added to anhydrous toluene (30 ml) and stirred vigorously under reflux condition for 24 h. The mixture washed with deionized water, ethanol, and acetone, separated by magnetic decantation and dried under vacuum oven at 60 °C for overnight [36]

Synthesis of Magnetic Nanoparticle Functionalized Triazine Based on Dendrimer

Magnetic nanoparticle functionalized with dendrimer was prepared according to literature (Scheme 2) [36].

Synthesis of APMNP-CC1. A solution containing the APMNP (2.0 g), cyanuric chloride (1.85 g), and diisopropylethylamine (1.7 ml) in THF (10 ml) was stirred for 12 h at 0 °C. The solid was washed with THF and ethanol, separated by magnetic decantation and dried in a vacuum oven at 50 °C overnight.

Synthesis of G1 of dendrimer. APMNP-CC1 (1.0 g), diisopropylethylamine (1 ml) and bis(3-aminopropyl)amine (1.4 ml) were added to THF (12 ml) and the mixture was stirred for 24 h at 75 °C. The obtained solid was washed with THF and ethanol, separated by magnetic decantation and dried in a vacuum oven at 50 °C overnight.

Synthesis of APMNP-CC2. Magnetic nanoparticles

supported triazine dendritic polymer, G1, (1.0 g) was added to a solution of cyanuric chloride (1.7 g) and diisopropylethylamine (1.6 ml) in THF (20 ml) under continuous stirring for 16 h at 0 °C. The mixture was washed with THF and ethanol and dried in a vacuum oven at 50 °C overnight after separation by magnetic decantation.

Synthesis of G2 of dendrimer. APMNP-CC2 (1 g), diisopropylethylamine (1.14 ml) and cysteamine (0.76 g) were mixed in THF (20 ml) under continuous stirring for 24 h at 75 °C. The solid was washed with THF and ethanol, separated by magnetic decantation and dried in a vacuum oven at 50 °C overnight.

Preparation of APMNP/DEN Supported MoO₂(acac)₂ (APMNP/DEN/MoO₂(acac))

MoO₂(acac)₂ was synthesized according to the literature procedure [37]. The APMNP/DEN (1.0 g) was added to a solution of MoO₂(acac)₂ (0.65 g) in methanol (20 ml) and stirred under reflux conditions for 24 h. The obtained solid was washed with diethylether and methanol and activated in a vacuum oven at 50 °C overnight after separation using a magnetic field (Scheme 3).

General Procedure for Epoxidation of Alkenes with *tert*-BuOOH Catalyzed by APMNP/DEN/MoO₂(acac)₂

A mixture of alkene (0.5 mmol), *tert*-BuOOH (1.0 mmol), catalyst (0.04 g, 0.0108 mmol Mo) in 1,2-dichloroethane was stirred under reflux conditions for desired time. The reaction progress was monitored by GC.

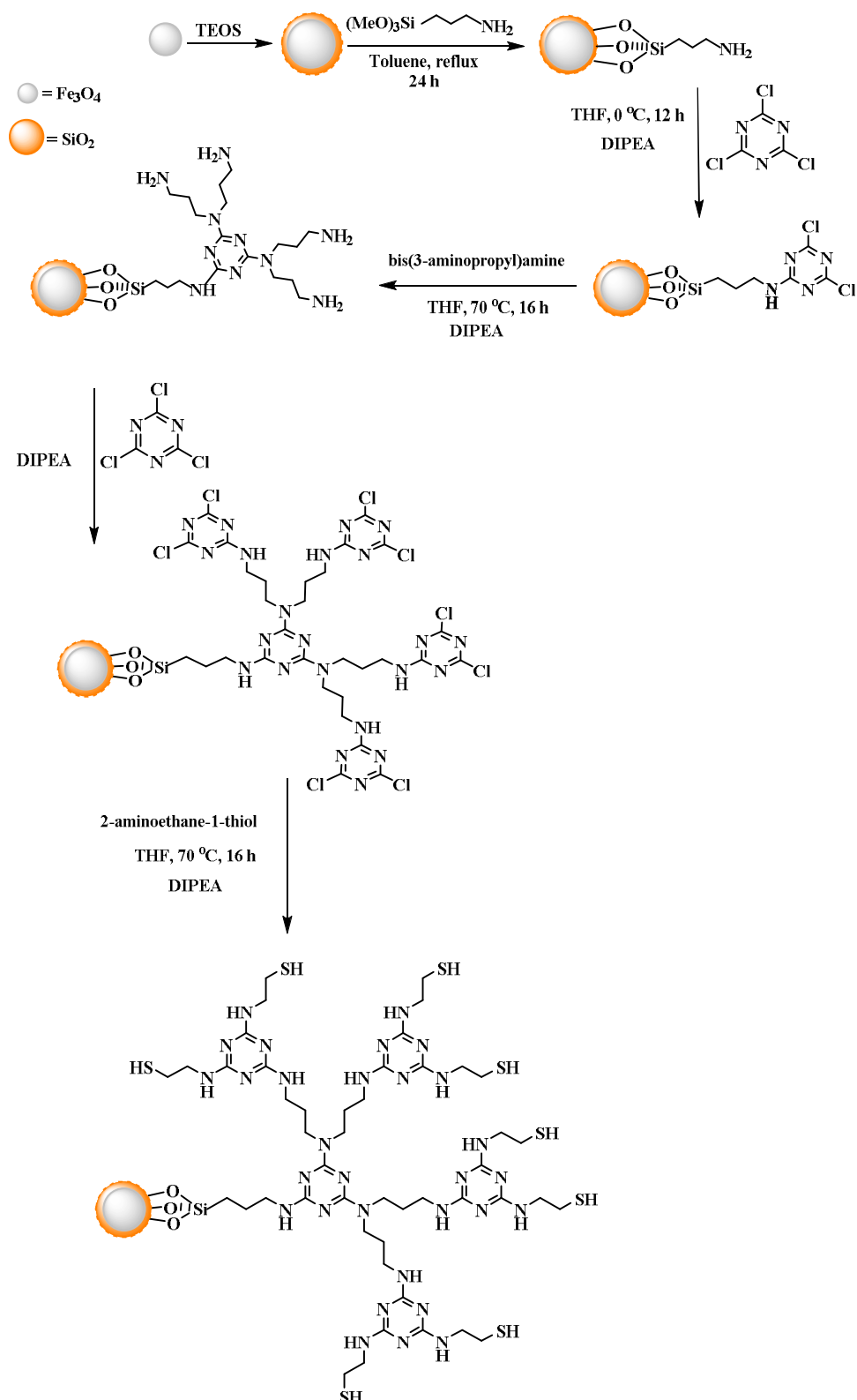
Catalyst Reuse and Stability

The reusability of the catalyst was investigated in the repeated epoxidation reaction of *cis*-cyclooctene as a model reaction under optimized conditions. At the end of each cycle, the catalyst was separated by a magnet, washed with methanol and diethylether and dried in an oven at 50 °C and reused in the next cycle.

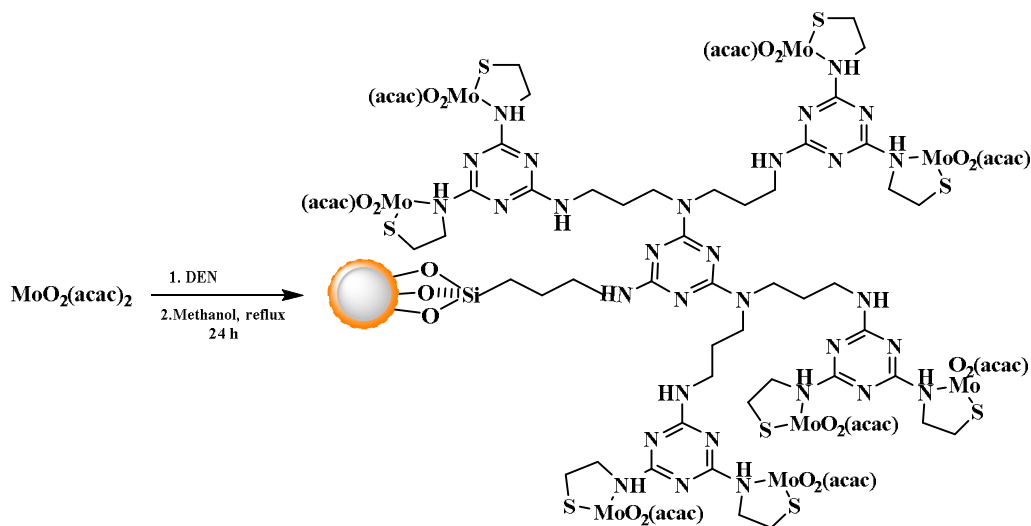
RESULTS AND DISCUSSION

Synthesis and Characterization of MoO₂(acac)₂ Supported on APMNP/DEN/MoO₂(acac)

Magnetic nanoparticles, Fe₃O₄ (magnetite), were



Scheme 2. The synthetic route of aminopropyl magnetic nanoparticle/dendrimer (APMNP/DEN)



Scheme 3. Synthesis of the APMNP/DEN/MoO₂(acac) catalyst

synthesized by co-precipitation mixture of ferric chloride and ferrous chloride in alkaline medium. In this route, some experimental conditions such as the molar ratio of ferric and ferrous, pH of the medium, and temperature are very important to control the particle size distribution and the synthesis efficiency. In the presence of the air, magnetite will be oxidized to maghemite (Fe₂O₃), therefore N₂ was used to prevent this problem [38].

MNPs tend to agglomerate due to their high surface energy and strong magnetic force, so the surface of MNPs was coated with silica for prevention of aggregation and also to facilitate the functionalization of MNPs surface. Then the silica-coated magnetic nanoparticles were modified with 3-aminopropyltriethoxysilane to obtain APMNPs. For the synthesis of dendrimer, cyanuric chloride is used. Cyanuric chloride (CC) as a triazine derivative is used for the synthesis of many organic compounds, because chlorine atoms possess high activity toward various nucleophiles. Replacement of chlorine atoms with different groups depends on different parameters such as the structure of nucleophiles, the nature of the solvent, and the most important one, temperature [39]. The investigations have illustrated that mono substitution is obtained at 0 °C and di and tri- substitution occurs at room temperature and above 60 °C, respectively. Different steps of the synthesis of triazine based dendrimer are shown in (Scheme 2).

At the first step, for mono substitution chlorine atom in cyanuric chloride, the APMNP was added to a solution of cyanuric chloride at 0 °C to obtain APMNP-CC1. In the next step, for di and tri substitution, bis(3-aminopropyl) amine was reacted with APMNP-CC1 to give G1 of the dendrimer, which will be converted to APMNP-CC2 in reaction with cyanuric chloride. Eventually, G2 of dendrimer was obtained by the reaction between APMNP-CC2 and cysteamine. As shown in Scheme 3, the prepared APMNP/DEN containing N- and S-donor ligands reacted with MoO₂(acac)₂ to give the heterogeneous catalyst, APMNP/DEN/MoO₂(acac). All these processes were characterized by FT-IR, TGA and CHNS analysis, XRD, SEM, TEM and ICP.

The FT-IR spectrum of APMNP/DENs (Fig. 1) showed a broad band at around 3430 cm⁻¹ due to O-H stretching vibration of the surface hydroxyls, the peak at 590 cm⁻¹ confirms the stretching mode of Fe-O bond and the presence of bands at 1098, 806 and 468 cm⁻¹ showed the asymmetric and symmetric stretching, and bending vibrations of Si-O-Si, respectively [40]. After modification of surface of Fe₃O₄/SiO₂ with dendrimer, the presence of bands at 1600 (C=N) and 2956 cm⁻¹ (C-H_{aliphatic}) confirmed that the dendrimer was successfully introduced onto the surface of Fe₃O₄/SiO₂. Also, the N-H band of amine was overlapped with the O-H band of silica at 3200-3400 cm⁻¹ [41].

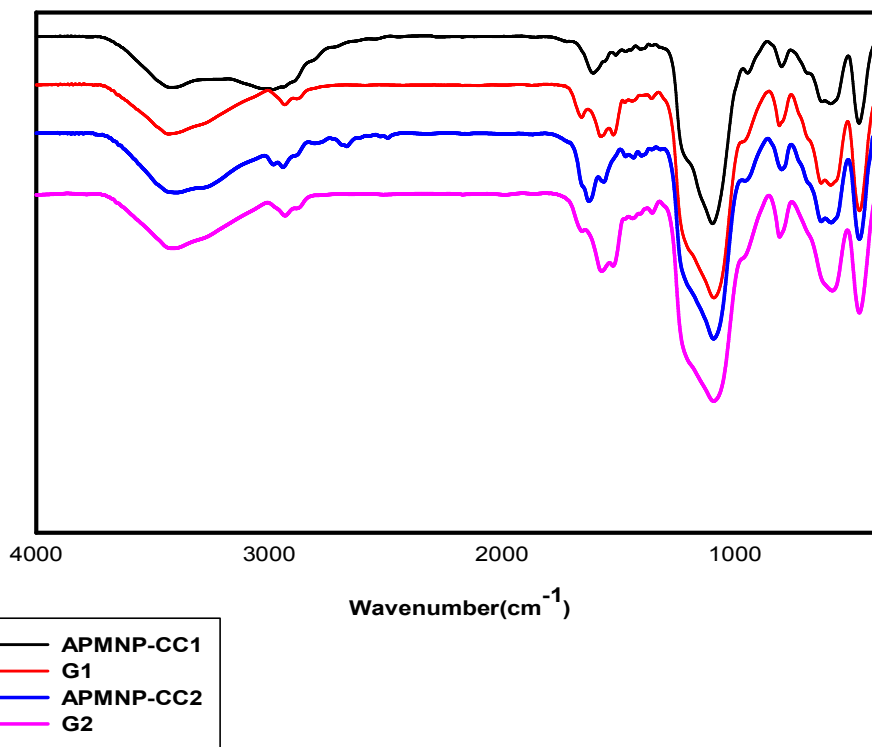
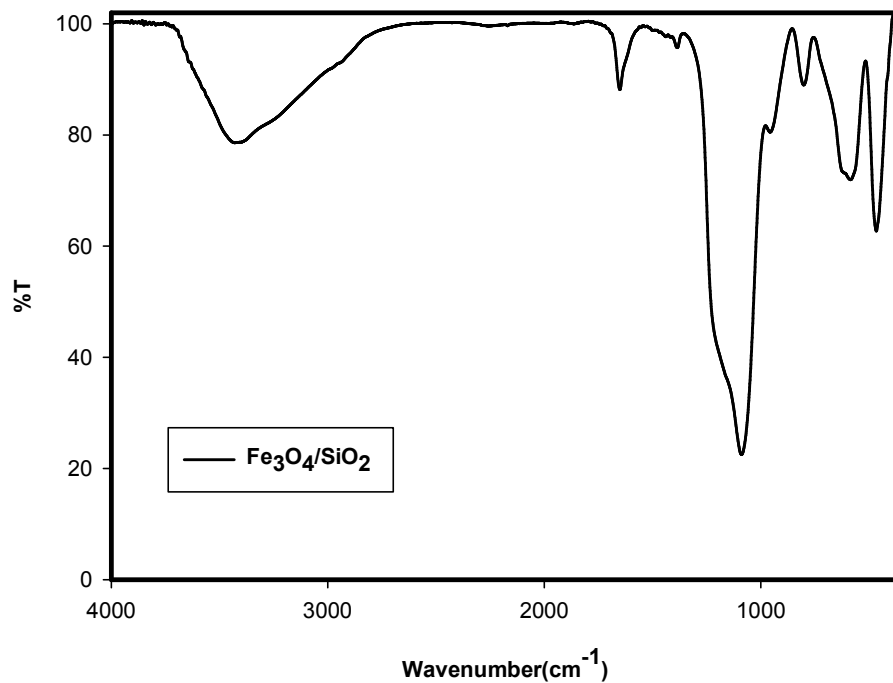


Fig. 1. The FT-IR spectra of: (A) Fe₃O₄/SiO₂; (B) Fe₃O₄/SiO₂/DEN (APMNP/DEN) and (C) Catalyst Fe₃O₄/SiO₂/DEN/Mo [APMNP/DEN/MoO₂(acac)].

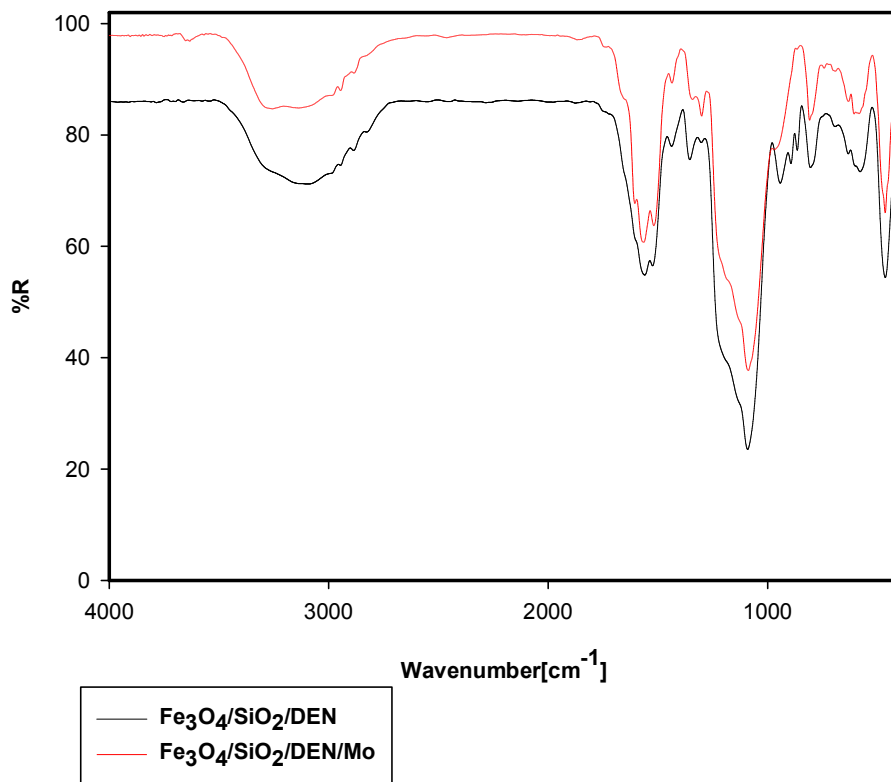


Fig. 1. Continued.

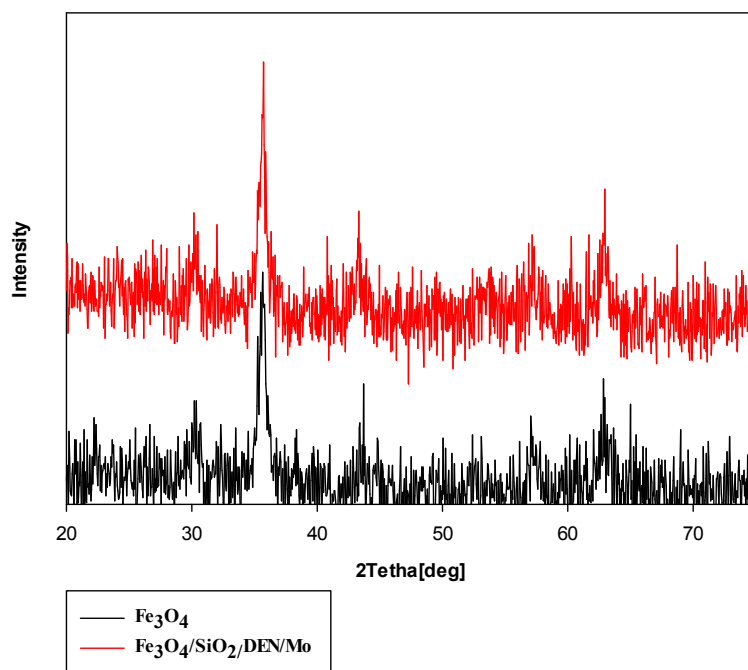


Fig. 2. The XRD pattern of MNPs before and after surface modification.

In the FT-IR spectrum of the [APMNP/DEN/MoO₂(acac)] catalyst, the presence of bands in the range of 850-1000 cm⁻¹ was assigned to Mo=O vibrations. In the FT-IR spectrum of homogeneous MoO₂(acac)₂, the MoO₂ species bands appear at 905 and 934 cm⁻¹. Considering to high dependence of wavenumber in IR spectrum on the nature of the coordinated ligand, this red shift in the catalyst can confirm the successful attachment of MoO₂(acac)₂ onto the dendrimer [42]. The coordinated acac ligand, showed bands at 1589, 1504 and 1360 cm⁻¹ (C=O). However, we could not observe these bands in the supported catalyst. The corresponding acac bands are masked with the dendrimer bands.

In order to investigate the effect of surface modification on structure of MNPs, X-ray diffraction pattern was used. The XRD patterns of MNPs before and after surface modification are shown in Fig. 2. The presence of characteristic peaks at 2θ = 30, 36, 44 and 63° at the functionalized and unfunctionalized MNPs verified the stability of magnetic nanoparticle structure during modification reaction. This result means that the Fe₃O₄/SiO₂/DEN/MoO₂(acac) have been synthesized successfully without damaging the crystal structure of Fe₃O₄.

To indicate the nitrogen content in aminopropyl functionalized magnetic nanoparticles, the elemental analysis was used. The nitrogen content of APMNP was 1.57%. Also, the metal loading of APMNP/DEN/MoO₂(acac), measured by ICP, was 0.272 mmol g⁻¹.

The TGA analysis was carried out between 25 to 800 °C at a rate of 20 °C min⁻¹ under air atmosphere (Fig. 3). The TGA curve of APMNP-CC1, G1, APMNP-CC2, G2 showed two-step thermal decomposition. The first region of weight loss corresponds to the removal of physically adsorbed water and solvent, whereas, in the second step, the weight loss is due to the removal of organic moieties on the surface of the dendrimer.

In order to study the surface morphology and the particle size of the catalyst, SEM was used (Fig. 4). According to SEM analysis, the diameter of particles is in the range of 50-70 nm. The TEM images of APMNP/DEN/MoO₂(acac) showed that most of the particles are almost spherical (Fig. 5).

Epoxidation of Alkenes Catalyzed by APMNP/DENs/MoO₂(acac)

For finding the optimized reaction conditions in the epoxidation of alkenes by APMNP/DENs/MoO₂(acac) catalyst, cyclooctene was chosen as a model reaction and effective factors including kind of solvent, kind and amount of oxidant and amount of catalyst were investigated in this reaction. Initially the model reaction was carried out in the presence of different solvents such as acetonitrile, acetone, methanol, dichloromethane, chloroform, carbon tetrachloride and 1,2-dichloroethane (Table 1). Based on the results, 1,2-dichloroethane was the best solvent for this reaction and presented the highest yield. The effect of different oxidants including sodium periodate (NaIO₄), hydrogen peroxide (H₂O₂), urea hydrogen peroxide (UHP), potassium peroxymonosulfate (KHSO₅) and *tert*-butyl hydroperoxide (*tert*-BuOOH) was studied and the results are illustrated in Table 2. As can be seen, *tert*-BuOOH was found as the best oxidant in the presence of APMNP/DENs/MoO₂(acac). The effects of the amount of catalyst and oxidant on epoxidation of cyclooctene were also investigated. The highest epoxide yield was detected in the presence of 0.01080 mmol of Mo and 1 mmol of *tert*-BuOOH (Tables 3 and 4).

On show the general applicability of this catalytic system, epoxidation of various alkenes was carried out under optimized conditions: alkene (0.5 mmol), *tert*-BuOOH (1.0 mmol), catalyst (0.04 g, 0.0108 mmol Mo) and 3 ml of 1,2-dichloroethane as solvent (Table 5). The results illustrated the excellent performance of the synthesized catalyst for epoxidation of both linear and cyclic alkenes and best results were obtained for cyclooctene and cyclohexene (Table 5, entries 1 and 2).

Investigation of APMNP/DEN/MoO₂(acac) Catalyst Recycling and Reusing for Epoxidation of Alkene

The recycling and reuse of a catalyst is a very important issue for economic and practical applications. The reusability of APMNP/DEN/MoO₂(acac) catalyst for epoxidation of cyclooctene with *tert*-BuOOH, was examined under optimized conditions.

After each cycle, the catalyst was removed by an external magnet and washed with diethylether (2 × 10 ml)

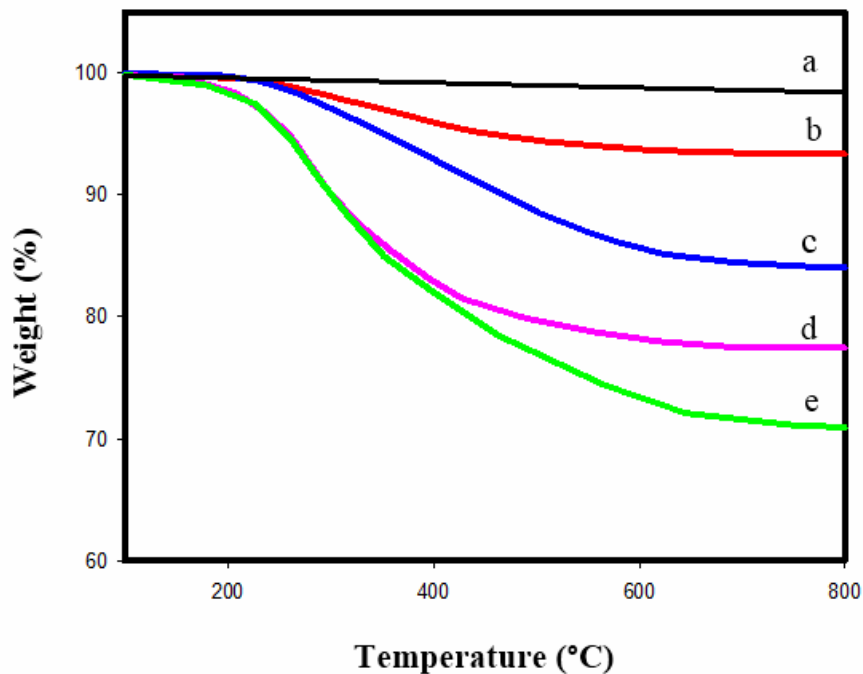


Fig. 3. TGA spectra of a) APMNP; b) APMNP-CCl₄; c) G1; d) APMNP-CCl₂ and e) G2.

Table 1. The Effect of Different Solvent on the Epoxidation of Cyclooctene with *tert*-BuOOH Catalyzed by APMNP/DEN/MoO₂(*acac*) under Reflux Conditions^a

Entry	Solvent	Yield (%) ^b	Time (min)
1	CH ₃ CN	5	120
2	(CH ₃) ₂ CO	7	120
3	CH ₃ OH	2	120
4	CH ₂ Cl ₂	13	120
5	1,2-DCE	95	45
6	CCl ₄	79	95
7	CHCl ₃	37	120

^aReaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1 mmol), catalyst (0.04 g, 0.0108 mmol Mo), solvent (3 ml).

^bGC based on starting cyclooctene.

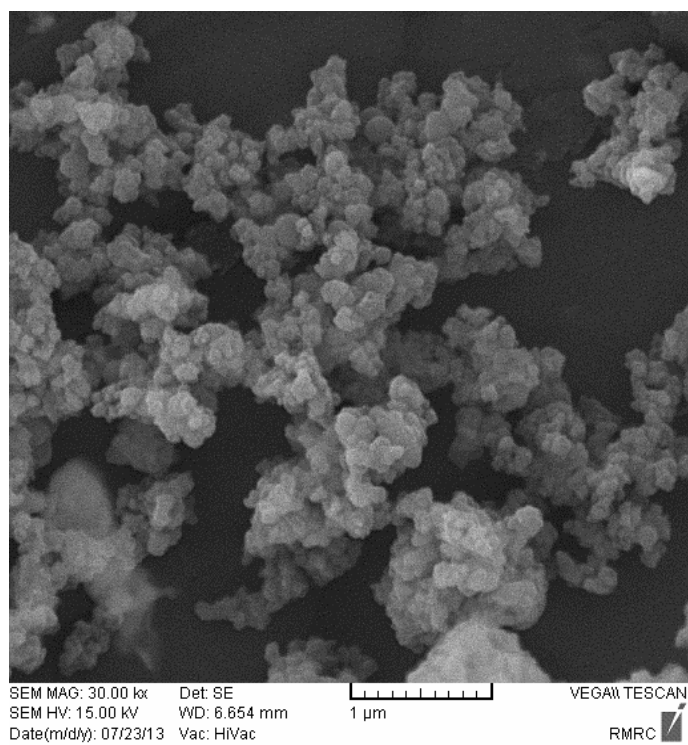
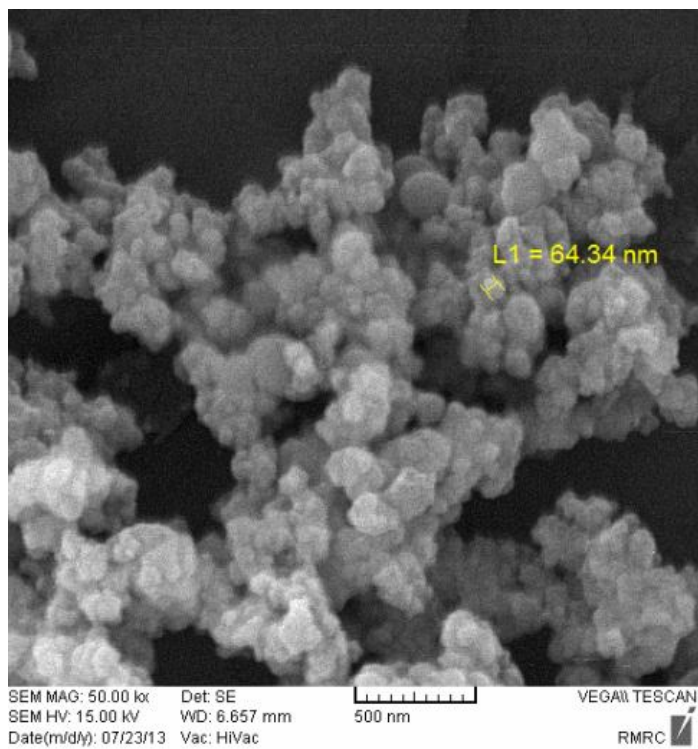


Fig. 4. SEM images of APMNP/DEN/MoO₂(acac)₂ catalyst.

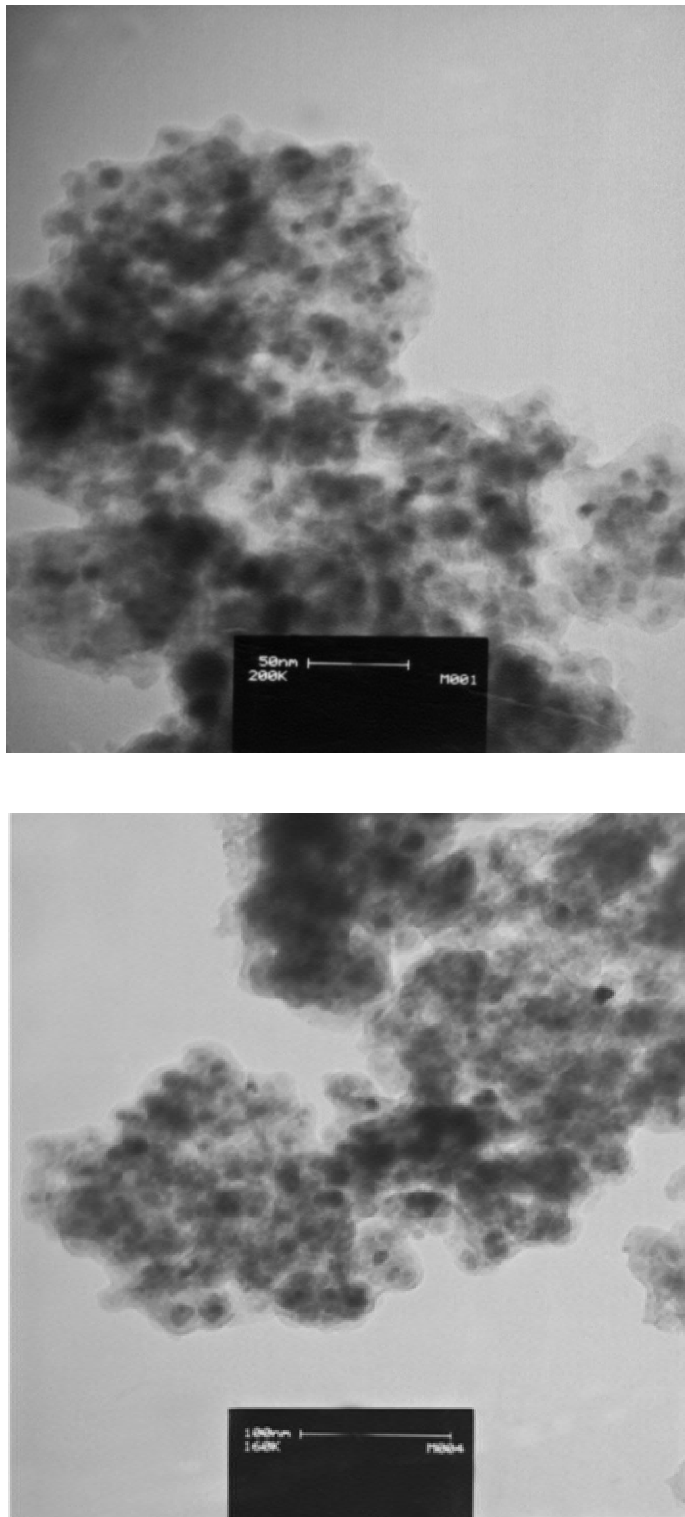


Fig. 5. TEM images of APMNP/DEN/MoO₂(acac) catalyst.

Table 2. The Effect of Different Oxidants on the Epoxidation of Cyclooctene Catalyzed by APMNP/DENs/MoO₂(acac) under Reflux Conditions^a

Solvent	Oxidant	Yield (%) ^b	Time (min)
1,2-DCE	NaIO ₄ ^c	14	120
1,2-DCE/H ₂ O (3:1)	H ₂ O ₂ ^c	24	120
	KHSO ₅ ^c	14	120
1,2-DCE	UHP	18	120
	<i>tert</i> -BuOOH	95	45

^aReaction conditions: cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst (0.04 g, 0.0108 mmol Mo), solvent (3 ml). ^bGC based on starting cyclooctene. ^cPhase transfer reagent: tetrabutylphosphonium bromide (0.01 g).

Table 3. The Effect of the Amount of Catalyst on the Epoxidation of Cyclooctene with *tert*-BuOOH under Reflux Conditions^a

Entry	Catalyst (mmol Mo)	Yield (%) ^b	Time (min)
1	0.0014	91	240
2	0.0027	87	190
3	0.0041	91	150
4	0.0054	95	120
5	0.0081	85	60
6	0.0108	95	45

^aReaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1 mmol), 1,2-dichloroethane (3 ml). ^bGC based on starting cyclooctene.

and methanol (2 × 10 ml), and dried for 2 h in an oven at 50 °C and used in the next cycle. The results showed that the catalyst could be reused five consecutive times without a significant decrease in its catalytic activity (Table 6). For the investigation of leaching of catalyst from the support, the ICP analysis was used which showed that only a trace

amount of Mo has been leached from the support in the first three runs.

CONCLUSIONS

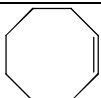

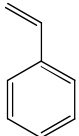
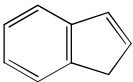

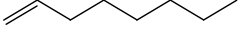

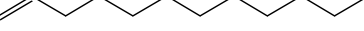
In summary, MoO₂(acac)₂ was successfully immobilized

Table 4. The Effect of the Amount of *tert*-BuOOH on the Epoxidation of Cyclooctene Catalyzed by APMNP/DEN/MoO₂(*acac*) under Reflux Conditions^a

Entry	<i>tert</i> -BuOOH (mmol)	Yield (%) ^b	Time (min)
1	0.25	53	120
2	0.5	76	120
3	0.75	84	120
4	1.0	95	45
5	1.5	95	40

^aReaction conditions: cyclooctene (0.5 mmol), catalyst (0.04 g, 0.0108 mmol Mo), 1,2-dichloroethane (3 ml). ^bGC based on starting cyclooctene.

Table 5. Epoxidation of Alkenes with *tert*-BuOOH Catalyzed by APMNP/DEN/MoO₂(*acac*) under Reflux Conditions^a

Entry	Alkene	Conversion (%)	Epoxide yield (%) ^b	Time (h)	TOF (h ⁻¹)
1		95	95	0.75	58.64
2		91	91	1.5	28.08
3		87	78	5.5	7.32
4		84	84	4	9.72
5		83	83	7	5.48
6		79	79	8.5	4.30
7		77	77	10	3.56
8		79	79	11.5	3.18

^aReaction conditions: alkene (0.5 mmol), *tert*-BuOOH (1.0 mmol), catalyst (0.04 g, 0.0108 mmol Mo), solvent (3 ml).

Table 6. Investigation of APMNP/DEN/MoO₂(acac) Catalyst Reuse in Epoxidation of Cyclooctene with *tert*-BuOOH under Reflux Conditions^a

Run	Yield of epoxide (%) ^b	Mo leached (%) ^c
1	95	2
2	91	1
3	89	1
4	90	0
5	87	0

^aReaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1.0 mmol), catalyst (0.04 g, 0.0108 mmol Mo), solvent (3 ml). ^bGC based on starting cyclooctene. ^cDetermined by ICP.

on the magnetic nanoparticles modified with dendrimer decorated by amine and sulfur for a firm bond to complex. The new synthesized catalyst illustrated excellent efficiency in the epoxidation of various alkenes including linear and cyclic ones, which means that the Mo catalyst retains its activity after immobilization. Also, the five-times recyclability of the catalyst without losing of its catalytic activity and no significant leaching confirmed the stability of MoO₂(acac)₂ on the APMNP/DEN. The use of dendrimer with proper functional groups for making strong bonds with the homogeneous catalyst and application of magnetic nanoparticles in the core of the catalyst make it stable and simplify its separation and reuse.

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