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Research Paper

Schiff base functionalized Fe_3O_4@Boehmite Core-Shell Nano-Particles to Support $MoO_2(acac)_2$ for Catalytic Epoxidation of Alkenes

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ABSTRACT

Fe_3O_4 nanoparticles were prepared solvothermally and then covered with a boehmite shell via hydrothermal assisted sol-gel processing of aluminum 2-propoxide. Then the hydroxyl covered the outer surface of the boehmite shell was covalently functionalized with 3-(tri-methoxysilyl) propylamine, and the terminal amine groups converted to imine by refluxing with 2-hydroxybenzaldehyde. Then it was used to support bis-acetylacetonato-di-oxo-molybdenum (VI). The supported catalyst was characterized by Fourier transform Infrared spectroscopy, elemental analysis, inductively coupled plasma, and transmission electron microscopy analysis, and it was applied in the epoxidation of cis-cyclooctene. The catalytic procedure was optimized for different parameters such as solvent, oxidant, and temperature. The reaction progress was investigated by gas-liquid chromatography analysis. The used catalyst was simply recovered from the solution by applying a magnet, and recycling experiments revealed that this heterogeneous nano-catalyst could be repeatedly applied for the epoxidation of cis-cyclooctene. The optimized conditions were also used for the epoxidation of some other alkenes successfully.

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1. Introduction

Separation of catalyst is one of the most important steps in the catalytic production of materials, and it became critical when the produced materials have potential use in pharmaceuticals, sweeteners, cosmetics, perfumes, and so on [1, 2]. One of the early enhancements to achieve this point was the physical adsorption of homogenous catalysts onto the surface of solid beds [2]. Although this successfully solved the problem in gas phase reactions but in the liquid phase, it may suffer from solvent elution. Therefore, the scientists tried to chemically graft the catalysts onto the surface of solid beds. This second enhancement solved the problem in liquid-phase reactions, too. Additionally, it explored another factor that affects the yield of heterogeneous catalytic reactions. This factor was the surface area of the solid beds, which improved with the development of nanoparticle production successfully [1]. In continuation, the use of magnetic core inside the shell of different heterogeneous nano-catalysts eased their separation process to use a simple magnet. Currently, this new separation process was used for many different catalytic reactions such as epoxide hydrogenolysis [3], oxidation of alcohols and thio-ethers, multicomponent reactions, and epoxidation of alkenes [2].

Our studies on catalytic epoxidation of alkenes using chemical grafted molybdenum-containing catalysts onto the surface of boehmite nano-particles [4-7] motivated us to prepare magnetite core-boehmite shell as catalytic support, which could easily separate from the reaction media by the above-described strategy. This magnetite core-boehmite shell nano-particles were used to covalently graft 3-(tri-methoxysilyl)-propylamine (MSPA), which then changed to imine and used to support bis-acetylacetonato-di-oxo molybdenum (VI). Finally, it was employed in the epoxidation of *cis*-cyclo-octene substrate, and the reaction progresses were optimized for different parameters involved. Epoxides are precursors for the industrial production of chiral pharmaceuticals, pesticides, detergents, epoxy paints, agrochemicals, polymers, surfactants, textiles, sweeteners, cosmetics perfumes, and so on [8]. Therefore, the prepared catalysts were also used for the epoxidation of different alkene substrates.

2. Materials and Methods

Solvents and reagents were purchased from Merck and used without any further purification. IR spectra were recorded on a Rayleigh WQF-500 FTIR instrument at the 4 cm^{-1} resolution, using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected on a STOE diffractometer with Cu Kα radiation. Elemental analyses were carried out on a Leco TruSpec CHN Analyzer. Electron microscopy was performed on a JEOL JSM-6360LV transmission electron microscope. Gas-liquid chromatography (GLC) was carried out on a Shimadzu GC-16A instrument using a 2 m column, peaked with silicon DC-200.

3. Experimental

3.1. Preparation of Fe_3O_4@Boehmite Core-Shell Nano-Particles (Fe@B)

According to the literature report [9], the magnetite core was prepared by dissolving 0.35 g (1.7 mmol) $FeCl_3.6H_2O$, 0.972 g polyvinylpyrrolidone and 0.972 g (12 mmol) sodium acetate in 13 ml ethylene glycol. The solution was stirred for 30 minutes at room temperature and then placed in a Teflon-lined autoclave and heated at 200 ºC for 12 hours. The produced magnetite powder was recovered by a magnet (figure 1), washed several times with isopropanol and water, and then dried in a vacuum for 12 hours.

Aluminium 2-propoxide was synthesized from aluminum and 2-propanol according to the general preparation procedure of aluminum alkoxides [10]. The product was vacuum distilled and diluted with 2-propanol to prepare a 0.015 M solution. Then, 0.1 g magnetite powder was added to 75 ml of this solution under N_2 inert atmosphere and homogenized in an ultrasonic bath for 30 minutes. The suspension was heated at 45 ºC for another 12 hours. Then, the adsorbed molecules of aluminum 2-propoxide were hydrolysed by hydrothermal assisted sol-gel process. In this process, the container of the suspension was placed in an autoclave which was charged with 50 ml of water, and then the autoclave was sealed and heated at 100 ºC for 5 hours. The produced powder was recovered by a magnet (figure 1), washed several times with isopropanol and water, and then dried in a vacuum for 12 hours. This process was repeated twice to achieve acceptable layer thickness of the boehmite shell over the magnetite core.

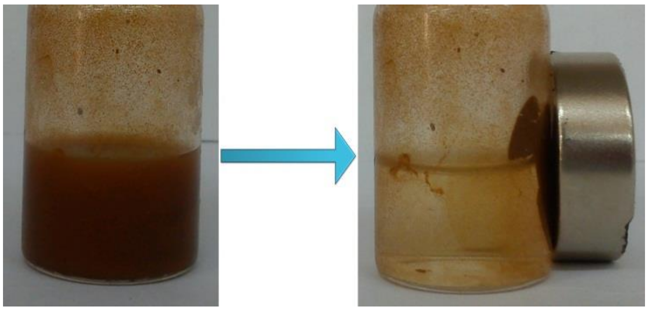


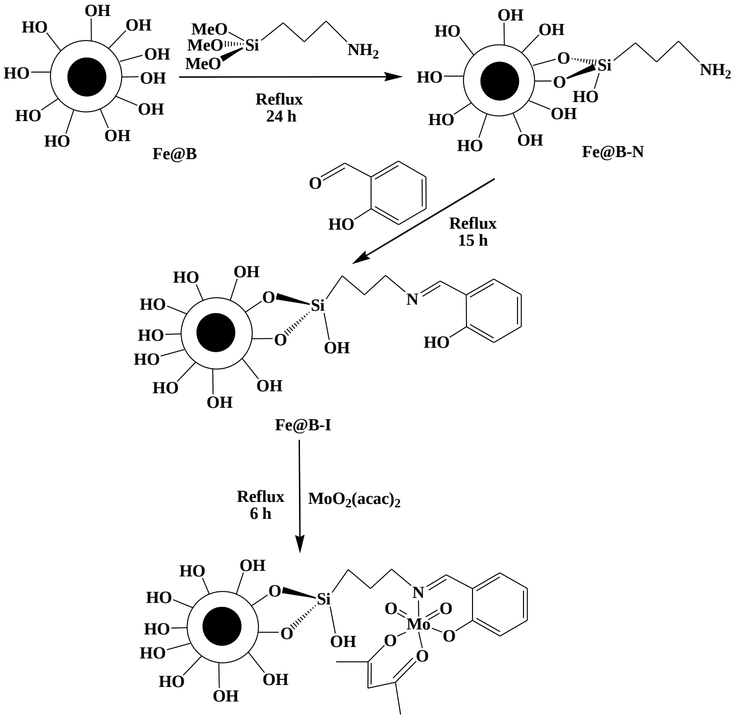
Fig. 1. The process of recovering Fe_3O_4, Fe@B, Fe@B-N, Fe@B-I and Fe@B-I-Mo by using a magnet.

3.2. Functionalization of Fe_3O_4@Boehmite Core-Shell Nano-Particles with MSPA (Fe@B-N) and changing the amine groups to imine (Fe@B-I)

For the preparation of Fe@B-N, 1.00 g Fe@B was refluxed with MSPA (120 µl, 0.35 mmol) in dry toluene (50.0 ml) for 24 hours (Scheme 1). The Fe@B-N was recovered by a magnet, washed several times with toluene and then dried in vacuum for 12 hours. Then 1.00 g Fe@B-N was refluxed with 2-hydroxybenzaldehyde (370.0 µl, 0.35 mmol) in ethanol (20.0 ml) for 15 hours (Scheme 1). The Fe@B-I was recovered by a magnet (figure 1), washed several times with ethanol, and then dried in a vacuum for 12 hours.

3.3. Supporting of $MoO_2(acac)_2$ on Fe_3O_4@Boehmite Core-Shell Nano-Particles (Fe@B-I-Mo)

For this purpose, 30 ml ethanol was added to $MoO_2(acac)_2$ (0.59 g, 1.82 mmol) and Fe@B-I (1.00 g) and the mixture was refluxed for 6 hours. Then the mixture was cooled down, recovered by a magnet (figure 1), washed several times with ethanol, and then dried in a vacuum for 12 hours to prepare Fe@B-I-Mo.



Scheme 1. Preparation of Fe@B-N, Fe@B-I, and Fe@B-I-Mo.

3.6. Catalytic Epoxidation of Alkenes

In a typical procedure, a 25 ml round bottom flask, equipped with a magnetic stirrer bar and a condenser, was charged with an alkene (0.5 mmol), an oxidant, the catalyst (Fe@B-I-Mo), and solvent, and the mixture was refluxed. All the reactions were performed at least two times, and the reaction progress was monitored by GLC. Since different alkenes have different reactivity toward oxidation, these reactions were continued until no further progress was observed. The characterization of the main and by-products was performed by comparison of their retention times with standard samples. The alkenes conversion and products selectivity were calculated from peak area by standard addition method.

3.7. Catalysts Recycling

In a typical experiment, after recovering the catalyst from the reaction mixture at optimum conditions, it was washed several times with $C_2H_4Cl_2$ and then used in the same procedure under the same conditions.

4. Results and Discussion

Magnetite core was prepared via solvothermal process, and then it was covered with boehmite shell in a hydrothermal-assisted sol-gel process. Then Fe@B particles were grafted with MSPA, and the terminal amine groups were changed to imine by refluxing with 2-hydroxybenzaldehyde. Then these functionalized Fe@B samples were used to support $MoO_2(acac)_2$ in order to investigate the epoxidation of cis-cyclooctene. The catalytic procedures for these catalysts were optimized for different parameters such as catalyst, solvent, and oxidant. Then it was used for the catalytic epoxidation of different olefins in optimum conditions. In addition, recycling experiments were done to reveal the reusability of these catalysts.

4.1. Preparation and characterization of supported $MoO_2(acac)_2$ on functionalized Fe@B

Magnetite (Fe_3O_4) was prepared by solvothermal process on $FeCl_3$, polyvinylpyrrolidone and sodium acetate in ethylene glycol, according to the literature reports [9]. The IR spectrum of it (figure 2a) shows a band at 580 cm^{-1} which assigned to the Fe-O stretching vibration of magnetite [11]. Then it was covered with boehmite shell by hydrothermal assisted sol-gel processing of aluminum 2-propoxide solution in 2-propanol. The IR spectrum of the product (Fe@B, figure 2b), shows only the characteristic bands of boehmite which completely covered the bands of magnetite and confirmed the full coverage of magnetite surface by boehmite. These bands are 480, 883, 1070, 1142, 3075 and 3415 cm^{-1} which all of them related to the Al-O-H vibrations in boehmite [12]. XRD pattern of Fe@B (figure 3) also shows the characteristic diffractions of both Fe_3O_4 (JCPDS No: 88-0866) and boehmite (JCPDS No: 21-1307). The transmission electron microscopy (TEM) image of Fe@B (figure 4a) shows a needle-shaped Boehmite shell which covered the magnetite core.

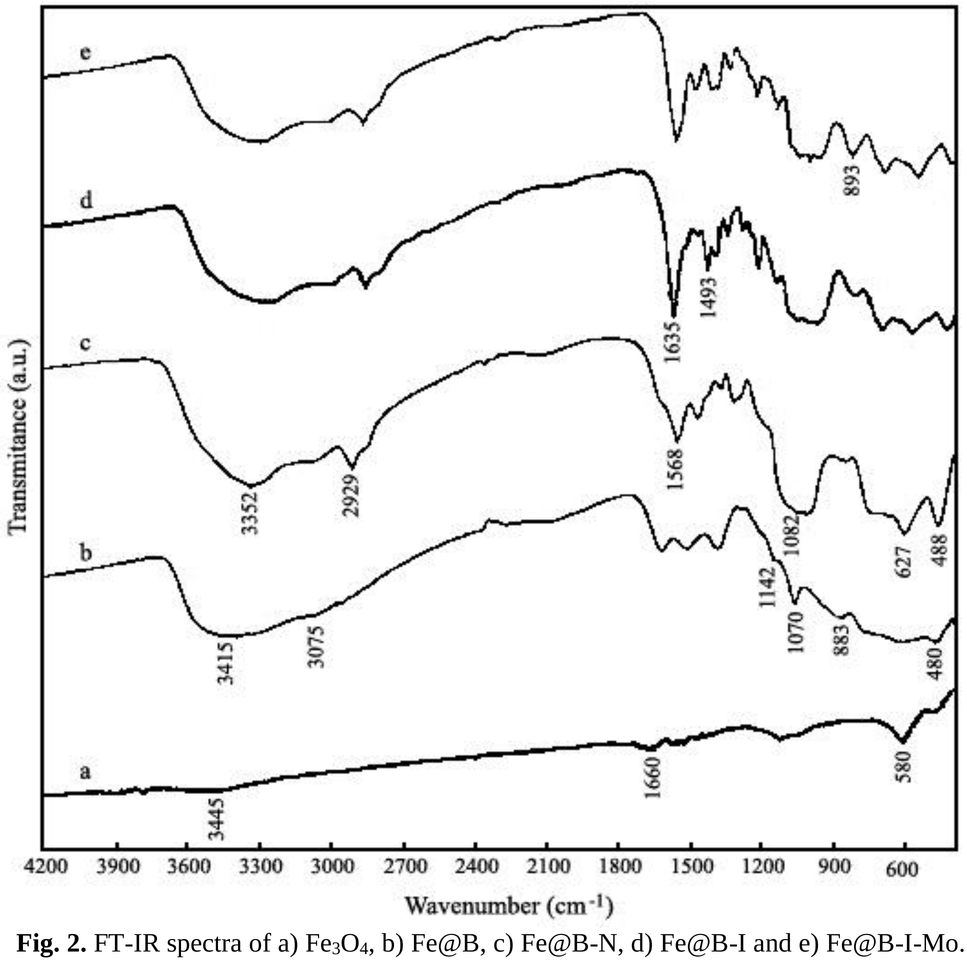


Fig. 2. FT-IR spectra of a) Fe_3O_4, b) Fe@B, c) Fe@B-N, d) Fe@B-I and e) Fe@B-I-Mo.

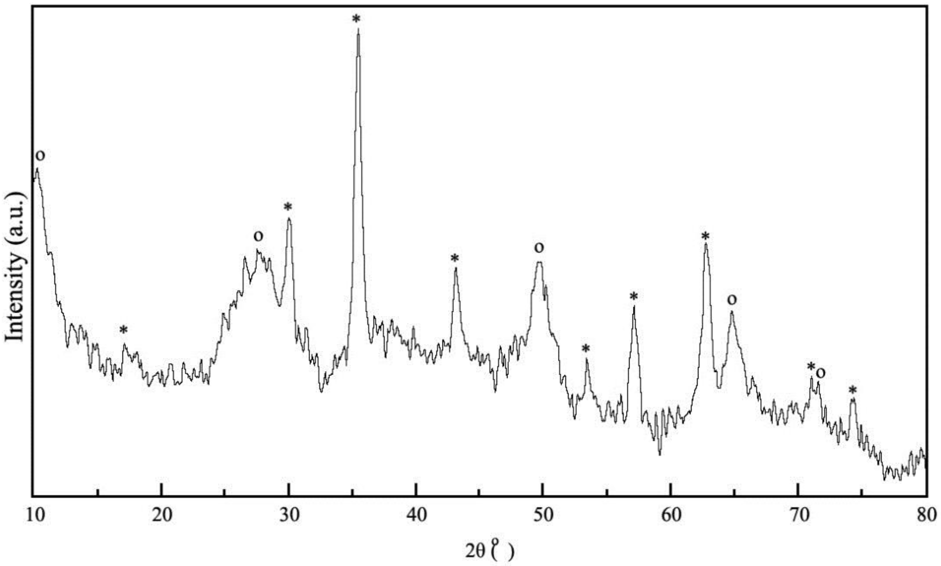


Fig. 3. XRD pattern of a) Fe@B (Fe_3O_4: * and boehmite: o).

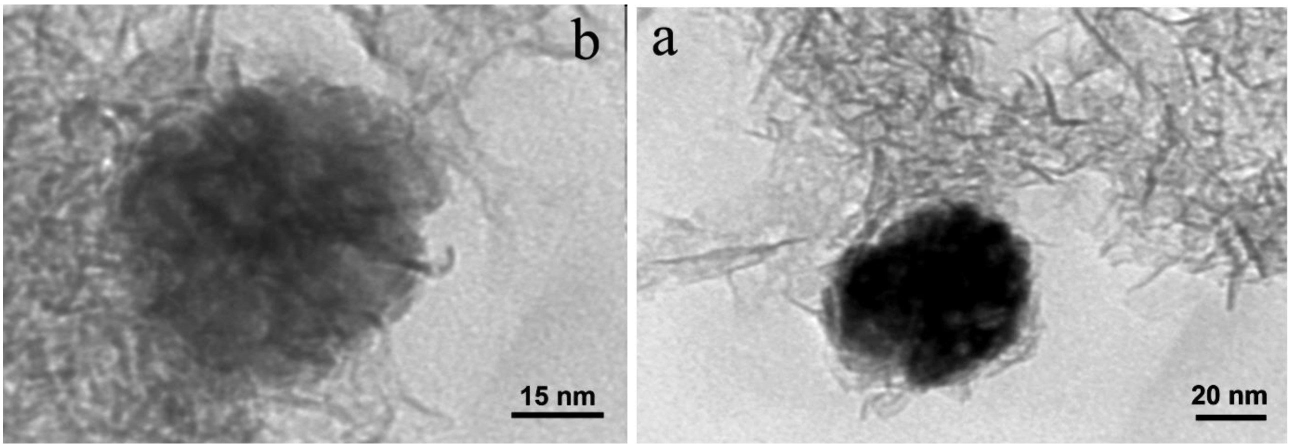


Fig. 4. TEM images of a) Fe@B and b)Fe@B-I-Mo.

As reported earlier, boehmite has low efficiency in the epoxidation of alkenes [6]. However, its surface is covered with hydroxyl groups which are ready for further functionalization and supporting of metal complexes [4-7]. The presence of metal complexes is vital for catalytic epoxidation of alkenes because the oxidant could coordinate to these sites and be activated for the epoxidation process. Here, functionalization of the boehmite shell surface was done by refluxing the mixture of Fe@B and MSPA in dry toluene for 24 hours (Fe@B-N, scheme 1). IR spectrum of Fe@B-N (figure 2c) shows new bands for C-H stretching and N-H bending vibrations of grafted silyl propyl amine groups at 2929 and 1568 cm^{-1}, respectively [4], in addition to the boehmite characteristic bands. N-H stretching vibration of the amine group should be shown at 3300-3400 cm^{-1}, but it is probably covered by the broad O-H stretching vibration of boehmite in this region [4-5, 7]. Then the amine groups were changed to imine by refluxing with 2-hydroxybenzaldehyde in ethanol for 15 hours (Fe@B-I, scheme 1).

IR spectrum of Fe@B-I (figure 2d) shows new bands for C=C and C=N stretching vibrations of the aromatic ring and imine groups at 1493 and 1635 cm^{-1}, in addition to deletion of N-H bending vibrations of propylamine groups at 1568 cm^{-1}[4]. Then Fe@B-I was used to anchor $MoO_2(acac)_2$ by refluxing them in ethanol for 6 hours (Fe@B-I-Mo, scheme 1). The IR spectrum of Fe@B-I-Mo (figure 2e) shows new band at 893 cm^{-1} which assigned to the Mo=O stretching vibrations of oxo ligands, in addition to the Fe@B-I characteristic bands [6]. Elemental analysis shows that the nitrogen content of Fe@B-I was 1.6% which means that 1.14 mmol of pending Schiff base groups were covalently bond to the surface of 1.00 g Fe@B-I. ICP analysis shows no molybdenum contaminant in Fe@B-N and Fe@B-I and they show no reactivity in the catalytic epoxidation of olefins as predictable according to the above discussion. This analysis also showed that there is 0.67 mmol molybdenum in 1.00 g Fe@B-I-Mo which means 66% of imine groups on the surface of Fe@B-I were used to anchor the molybdenum complex. TEM image of Fe@B-I-Mo (figure 4b) did not show any sensible changes in comparison with Fe@B (figure 4a). This could confirm that functionalization and support of metal complexes did not disturb Fe@B morphology at all. BET analysis showed that the surface area of the Fe@B-I-Mo is 283 m^2/g which is lower than pure boehmite (326 m^2/g) prepared at the same conditions [13].

TG/DTA thermogram of the Fe@B-I-Mo in the temperature range of 25 to 500 °C was shown in figure 5. It showed three weight losses in the DTG curve. The first one is below 100 °C with about 5% weight loss in the TG curve, which is accompanied by an endothermic peak at the DTA curve, which may be related to the desorption of physically adsorbed water. The next one at about 150-300 °C with about another 5% weight loss in the TG curve, which is accompanied by an exothermic peak at the DTA curve, may be related to the combustion of the pending organic groups grafted onto the surface of the catalyst. The last 12% weight loss in the TG curve at about 350-500 °C, which is accompanied by an endothermic peak at the DTA curve should be related to the dehydroxylation of boehmite that caused crystallization of γ-alumina [13].

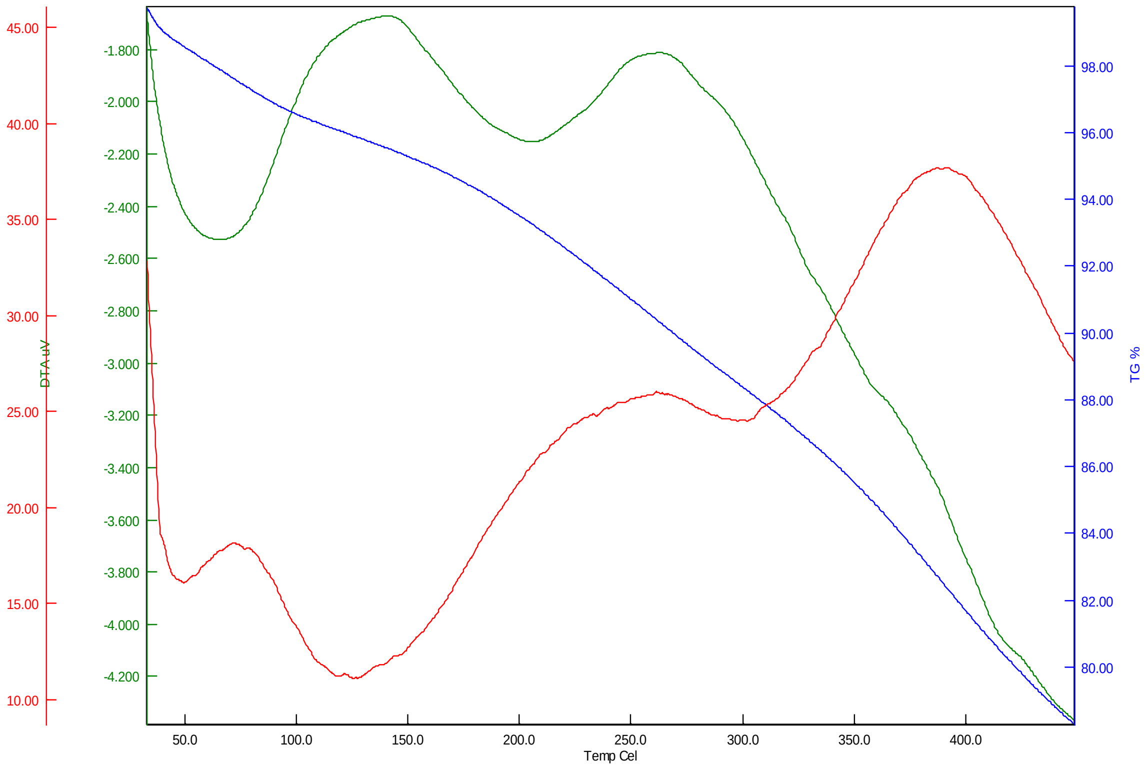


Fig. 5. TG/DTG/DTA thermogram of Fe@B-I-Mo.

4.2. Alkene epoxidation with TBHP catalyzed by Fe@B-I-Mo

In order to find optimum conditions for the title reaction and also the comparison of the results with the previous reports, epoxidation of cyclooctene was investigated by changing different parameters, including the solvents, oxidant, catalyst, and time. The experiments show that with these catalysts, *tert*-butylhydroperoxide (TBHP) is the only oxidizing system which can precede the epoxidation of cyclooctene in $C_2H_4Cl_2$. Other oxygen sources such as hydrogen peroxide and urea-hydrogen peroxide in $C_2H_4Cl_2$, CCl_4 or CH_3CN show very low activity. We have also used sodium periodate as oxidant, but even in the presence of 0.01 g of tetrabutylamonium bromide as the phase-transfer reagent, it does not show any reactivity. In addition, under the mild conditions, the epoxidation of cyclooctene by TBHP did not proceed in the absence of a catalyst. The detailed procedure of the reaction conditions are summarized in Table 1.

Table 1. Epoxidation of cis-cylooctene with Fe@B-I-Mo usingTBHP under reflux conditions [a,b].

Entry	Catalyst (mg)	Solvent [c]	Catalyst loading [d] (mol%)	Oxidant/Substrate molar ratio	Epoxide Yield (%) [e]
1	20	CH_3CN	3.04	2	No reaction
2	20	CH_3OH	3.04	2	No reaction
3	20	$(CH_3)_2CO$	3.04	2	No reaction
4	20	CH_2Cl_2	3.04	2	42
5	20	$CHCl_3$	3.04	2	73
6	20	CCl_4	3.04	2	95
7	20	$C_2H_4Cl_2$	3.04	2	98
8	5	$C_2H_4Cl_2$	0.76	2	21
9	10	$C_2H_4Cl_2$	1.52	2	38
10	15	$C_2H_4Cl_2$	2.28	2	82
11	25	$C_2H_4Cl_2$	3.80	2	98
12	20	$C_2H_4Cl_2$	3.04	0.5	32
13	20	$C_2H_4Cl_2$	3.04	1.0	61
14	20	$C_2H_4Cl_2$	3.04	1.5	88
15	20	$C_2H_4Cl_2$	3.04	2.5	98
16	20[f]	$C_2H_4Cl_2$	3.04	2	No reaction
17	20[g]	$C_2H_4Cl_2$	3.04	2	28

[a] The amount of metal loadings is 0.76 (mmol)/g Fe@B-I-Mo.
[b] The time of reactions are 30 minutes.
[c] The amount of solvent are 1 ml.
[d] Calculated for 0.5 mmol cyclooctene.
[e] GLC yields are based on the starting cyclooctene.
[f] The reaction was performed at room temprature.
[g] The reaction temprature was 40 °C.

The effect of solvent is the first parameter which was investigated, and some solvents with different coordinating abilities were used in the epoxidation of cyclooctene with TBHP. The observed trend in Table 1, entries 1-7 is the same as literature reports on homogeneous alkene epoxidation by Mo-containing catalyst [14]. Coordinating solvents such as CH3CN and CH3OH compete with TBHP to occupy the coordination sites on transition metal catalysts. Therefore in the presence of these solvents, the observed yields are too low. Among other solvents, CCl4 and 1,2-dichloroethane have the highest yield of epoxide products. This could be attributed to their higher boiling points in comparison to others. But because of economic and environmental concerns, 1,2-dichloroethane was chosen as the optimum solvent for the epoxidation of cyclooctene with TBHP.

As another parameter, the amount of catalysts was changed in the title reaction. The results in Table 1 (entries 7-11) show that increasing the amount of catalyst up to 20 mg increased the yield of cyclooctene epoxide and then became constant. The ratio of oxidant to the substrate is one of the most crucial parameters in catalytic epoxidation processes. The results in Table 1 show that the optimum ratio of oxidant to the substrate is 2 (entries 7 and 12-15). Decreasing the ratio from 2 decreased the yield considerably, but its increase did not change the yield. Figure 5 shows the effect of reaction time on epoxidation of cyclooctene with TBHP by Fe@B-I-Mo in $C_2H_4Cl_2$, which shows that it takes only 30 minutes for complete reaction. This high activity for Mo-containing catalysts was also reported in previous reports [4, 6].

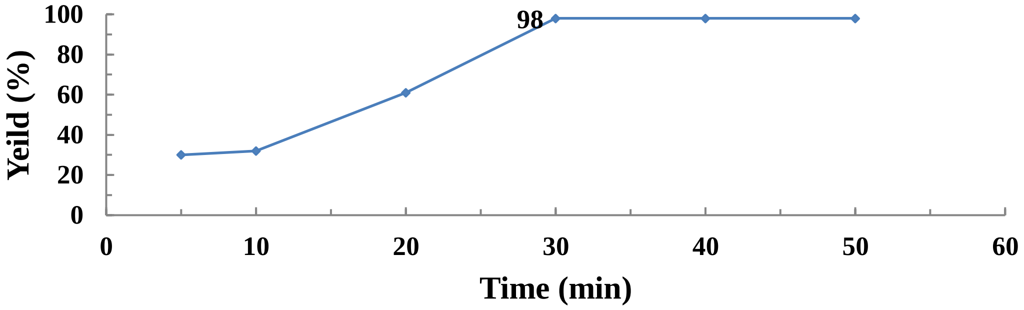


Fig. 6. Epoxidation of 0.5 mmol cis-cyclooctene with 1.0 mmol TBHP catalyzed by 20 mg Fe@B-I-Mo in 1 mL $C_2H_4Cl_2$ under reflux conditions.

Moreover, the heterogenic character of this catalyst was checked by the hot filtration test. For this purpose, the catalyst was removed by using a magnet after 15 minutes, and the procedure was continued up to 30 minutes. The results obtained showed that when the catalyst was removed from the reaction medium, the catalytic procedure stopped and did not continue anymore. This test proves that the catalytic reaction is held on heterogeneous conditions, and the catalyst is not leached to the reaction medium. We also investigate the reaction progress of the related homogenous catalysts. The results showed that by the use of $MoO_2(acac)_2$ as a catalyst at the same conditions of heterogeneous Fe@B-I-Mo counterpart, the yields reduced to 82%. The greater reactivity of the heterogeneous catalysts may be related to the homogenous dispersion of active catalytic sites onto the surface of Fe@B. This efficiently increased the effective collision of regents to the metal sites in comparison to the homogeneous counterpart and consequently improved the catalytic properties of the cyclooctene epoxidation process..

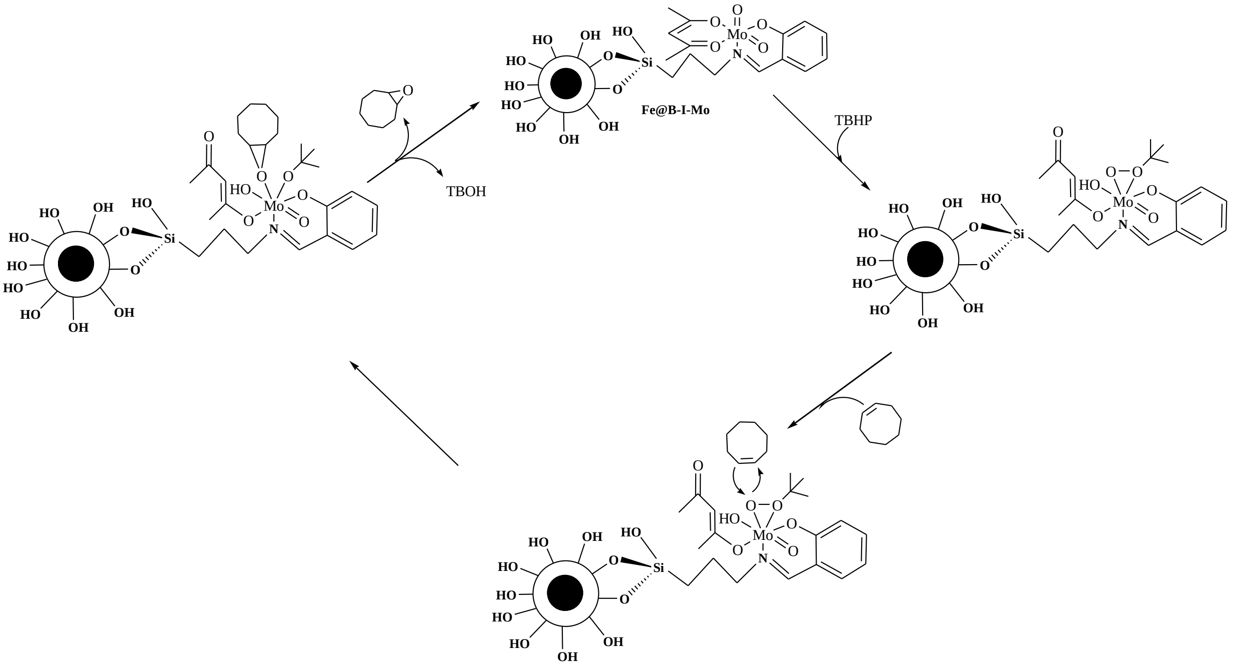
Many molybdenum complexes have been reported for the catalytic epoxidation of alkenes with TBHP. However, the catalytic system which has been prepared in this research is superior to most of the reported catalytic protocols in terms of easy recovering and TOF. Recently, Mohammadikish *et al.* have been supported the molybdenum complex onto the surface of nano-magnetite, and they have been reported a TOF of 19 [15], which is very lower than this research catalysts. In addition, the TOF values for Fe@B-I-Mo (64 hr^{-1}) in the present report is some lower than its not magnetic counterparts, Mo-AFBNPs (75 hr^{-1}) in our previous report [4]. This new catalyst, Fe@B-I-Mo, can also be used for the epoxidation of a wide range of substituted alkenes (Table 2). Blank experiments, performed without catalysts or with Fe3O4, boehmite, Fe@B, Fe@B-N, or Fe@B-I, show a very low conversion even after five hours of reflux, but in the presence of this catalyst, a wide range of both cyclic and linear alkenes could efficiently and selectively convert to epoxides. Based on the epoxidation mechanism suggested earlier [4-7], the higher electron-donating ability of the olefin double bond is expected to show more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with inner double bonds should exhibit more activities in comparison to 1-octene and 1-hexene, which contain terminal double bonds.

Table 2. Epoxidation of some alkenes with TBHP catalyzed by Fe@B-I-Mo under refluxing condition [a,b].

Entry	Alkene	Conversion (Epoxide) (%)	Time (min)
1	cyclooctene	98(98)	30
2	cyclohexene	93(85)[c]	30
3	1-octene	58(58)	120
4	1-hexene	62(62)	120
5	styrene	82(76)[d]	120
6	α-methyl styrene	92(85)[e]	90

[a] Reaction conditions: Alkene (0.5 mmol), TBHP (1.0 mmol), catalyst (20mg), $C_2H_4Cl_2$ (1 mL).
[b] GLC yield based on the starting alkenes.
[c] The by-product (cyclohexanone) is 8%.
[d] The by-product (benzaldehyde) is 6%.
[e] The by-product (acetophenone) is 7%.

On the basis of experimental results, probable mechanisms are also proposed for the epoxidation of cyclooctene with TBHP by Fe@B-I-Mo catalyst (Scheme 2). There are some crucial stages in this process. The first step involves transferring TBHP proton to an oxo ligand which was resulted in the coordination of *the tert*-butylperoxide anion to the Lewis acidic metal center. Then, olefin substrate coordinated to the metal center and, as a nucleophile, inserted to the metal-oxygen bond of coordinated peroxide electrophile anion. This mechanism easily explains the faster reaction of electron-rich olefins in comparison to electron-poor olefins. In the next step, an epoxide product was formed, and *the tert*-butylperoxide anion was converted into the *tert*-butoxide anion. Then the peroxide product is released and the catalytic cycle continued by substitution of a new *tert*-butylperoxide instead of *tert*-butoxide anion.



Scheme 2. Proposed mechanism for the epoxidation of olefin with TBHP by Fe@B-I-Mo.

4.3. Catalyst recovery and reuse

As discussed earlier, the reusability of solid-supported catalysts is one of their most important benefits. Therefore, the reusability of the Fe@B-I-Mo catalyst was monitored by means of multiple sequential epoxidations of cyclooctene with TBHP (Table 3). After each cycle, the reaction mixture was separated by the use of a magnet (figure 1), and the supernatant solution and recovered catalyst were analyzed with ICP. This analysis shows that there is no metal contaminant in the supernatant solution and no decrease in metal loading of the recovered catalyst. This also confirmed that metal ions did not leach from the heterogeneous catalysts, and the reaction was done entirely in heterogeneous conditions. But after five cycles of recovering this catalyst, it loses 13% of its activity in the epoxidation of olefins. The reason for the gradual decrease in the yield with this heterogeneous catalyst was attributed to the poisoning effect of water vapor which may be adsorbed during recovering process and blocked the catalytic sites on the metal center.

Table 3. Epoxidation of cis-cylooctene with TBHP in reflux conditions using recycled Fe@B-I-Mo catalyst [a].

Number of cycle	Epoxide Yield [b] (%)	TOF [c] (hr^{-1})	Mo Leached [d] (%)
1	98	64	ND
2	93	61	ND
3	91	60	ND
4	88	58	ND
5	85	56	ND

[a] Reaction conditions: Alkene (0.5 mmol), TBHP (1.0 mmol), catalyst (20mg), $C_2H_4Cl_2$ (1 mL) during 30 min for Fe@B-I-Mo.

[b] GLC yields are based on the starting cyclooctene.

[c] TOF= (mole of reactant)(yield)/(mole of catalyst)(time)

[d] Determined by ICP analysis. ND: not detected

5. Conclusion

We have successfully prepared new hybrid heterogeneous catalysts by anchoring bis-acetylacetonato-di-oxo molybdenum complex onto the Fe@B core-shell bed, which was functionalized with a Schiff base. It is an active catalyst for the epoxidation of various substituted alkenes under entirely heterogeneous conditions. The highlighted benefit of this new heterogeneous catalyst over our and other previous reports is their ease of recovering by a simple magnet. There are also some crucial factors that considerably change the yields. Among them, type of solvent is the most predominant, and

$C_2H_4Cl_2$ as an aprotic, non-polar, and hydrophobic solvent gave the best results.

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