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Molybdenum complex tethered to the surface of activated carbon as a new recoverable catalyst for the epoxidation of olefins

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ABSTRACT

A new recoverable catalyst for the epoxidation of olefins was developed by covalent attachment of aminopropyl groups on the surface of oxidized activated carbon (AC) and next reaction with bis(acetylacetonato)dioxomolybdenum(VI). Characterization of the prepared catalyst was performed with different physicochemical methods such as Fourier transform infrared and atomic absorption spectroscopies, scanning electron microscopy, energy-dispersive X-ray and nitrogen sorption analyses. Nitrogen adsorption–desorption analysis revealed that the textural characteristics of the support were changed during the grafting experiments but the channels remained relatively accessible despite sequential reduction in surface area, pore volume and pore size. Elemental analysis showed the presence of 0.06 mmol g^{-1} molybdenum in the catalyst. The prepared catalyst catalyzed the epoxidation of olefins and allyl alcohols with *tert*-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) quantitatively with excellent selectivity toward the corresponding epoxides under mild reaction conditions. The results indicated that the hydrophobicity of the AC support promoted the catalytic efficiency of the catalyst in the epoxidation of olefins.

1. Introduction

Recently, waste minimization by using supported reagents and catalysts has increased trends to develop environmentally friendly processes in industrial chemistry [1–9]. One of the most important contributions to waste production in chemical processes is the separation of products or catalysts from the reaction mixture. Thus, preparation of supported catalysts through immobilization of soluble transition metal complexes on solid supports has attracted great interest due to combining the advantages of both homogeneous and heterogeneous catalysts especially easier work-up, recyclability and stability of the heterogeneous systems. Among the various approaches used for immobilizing metal complexes, the covalent tethering has been the most efficient strategy as the resulting heterogeneous catalysts have enough stability during the course of catalytic reactions. The stable covalent bonds experience no leaching from the support and thus provide an efficient method to prepare truly heterogenized catalysts.

In this regard, heterogenization of molybdenum complexes has been the subject of great interests and many attempts have been made, including grafting of Mo compounds to functionalized polymer supports [10,11], preparation of amorphous Mo silicates with the sol-gel method [12], incorporation of Mo in the framework of silicalite [13] and especially immobilization of homogeneous molybdenum catalysts on the surface of silica coated magnetite nanoparticles [14–16] and mesoporous materials (for example MCM-41, MCM-48, etc) [17–23].

Due to its high surface area and porosity, activated carbon (AC) is a good candidate as catalyst support in place of inorganic oxide materials especially for liquid phase reactions, since it has the advantages of higher stability in acid and base conditions and the benefit of modification of its porous texture and surface properties by appropriate methods. It possesses several types of oxygenated surface groups which can be increased by thermal and chemical processes and can be used for covalent tethering of homogeneous catalysts. On the other hand, AC is a readily available and inexpensive material. Thus, immobilization of metal complexes on the surface of AC has attracted much interest in recent years. Some examples include chiral manganese(III) Schiff base complexes anchored onto AC as enantioselective heterogeneous catalysts for alkene epoxidation [24–29], amine-functionalized nickel(II) Schiff base complexes immobilized onto AC treated with thionyl chloride [30], rhodium complexes bound to AC [31–36], reusable cobalt(III)-salen complex supported on AC as an efficient heterogeneous catalyst for synthesis of 2-arylbenzimidazole derivatives [37], and

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Table 1
Elemental analysis and texture parameters of the samples taken from nitrogen sorption studies.

Sample	N content (mmol g^{-1})	Mo content (mmol g^{-1})	S_{BET} ($m^2 g^{-1}$)	S_{micro}[a] ($m^2 g^{-1}$)	V_T[b] (ml g^{-1})	V_{micro}[a] (ml g^{-1})	V_{meso}[c] (ml g^{-1})
AC	0.25	–	865	720	0.597	0.353	0.244
APTS-AC	0.52	–	406	256	0.290	0.120	0.170
Mo-APTS-AC	0.48	0.06	12	0	0.0264	0	0.0264

[a] Calculated by the *t*-method.
[b] Total pore volume at $p/p_0 = 0.98$.
[c] Obtained by subtracting the micropore volume from the total pore volume at $p/p_0 = 0.98$.

copper(II) acetylacetonate anchored onto AC as a heterogeneous catalyst for the aziridination of styrene [38].

The effect of hydrophobicity of the supports on the activity of heterogeneous catalysts has been of less concern in the literature [39]. Hydrophobic properties affect the adsorption and desorption of molecules on the surface of the catalysts. But, the study of the correlation between the hydrophobicity of the supports and catalytic activity is still lacking.

In continuation of our research program devoted to the development of immobilized homogeneous molybdenum catalysts [13–15,19–23], our objective in this work is to functionalize AC with aminoropropyl groups and then incorporate a molybdenum complex with tethering method to obtain a heterogenized molybdenum catalyst for the epoxidation of olefins. To the best of our knowledge, there is no any report about the preparation and characterization of such covalently attached molybdenum complex on the surface of AC. The advantages of this system are the easy recovery of the solid catalyst at the end of reaction as well as good activity, selectivity and high stability in the epoxidation of olefins. Moreover, our proposed method of preparation does not involve the requirement of using thionyl chloride which is a toxic and hazardous reagent and thus is environmentally friendly. Also, we aim to correlate the hydrophobic effect of the AC support with the activity of the prepared catalyst in the epoxidation of olefins. Our results indicate that the more hydrophobicity of the AC support promotes the catalytic efficiency of the catalyst in the epoxidation of olefins.

2. Experimental

2.1. Materials and instrumentation

Bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(acac)_2$, was prepared according to the literature method [40]. All other chemicals as well as AC (charcoal activated GR for analysis Art No. 102186) were purchased from Merck chemical company. The details of the surface area, pore volume and other surface properties of the AC are given in Table 1.

Fourier transform infrared (FT-IR) spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer, using pellets of the materials diluted with KBr. Scanning electron microscopy (SEM) images of the samples were taken with ZEISS-DSM 960A microscope with attached camera. Elemental analyses were performed by a scanning electron microscope with EDX (energy dispersive X-ray) detector INCA Penta FETx3 and VARIAN VISTA-MPX ICP-AES (inductively coupled plasma atomic emission spectroscopy) atomic absorption spectrometer. Nitrogen content of the samples was analyzed on Thermo Finnigan (Flash 1112 Series EA) CHN Analyzer. Nitrogen sorption studies were performed at liquid nitrogen temperature (77 K) using Quantachrome Nova 2200e, Version 7.11 Analyzer. Before the adsorption experiments the samples were outgassed under high vacuum at 393 K. All calculations were performed using the program of Quantachrome Nova 2200e surface area analyzer.

2.1.1. Preparation of aminopropyl modified AC

First, the AC was washed with dichloromethane and toluene to remove the organic species and then refluxed with a 5 M nitric acid solution as oxidizing agent for 24 h to increase the surface oxygen groups [35]. The oxidized AC was washed with deionized water until pH 6–7 and then dried in vacuum oven at 383 K overnight. The resulted material (1 g) was further treated with sodium borohydride (5 g) in methanol (100 ml) at 277 K for 24 h to reduce the carbonyl groups and increase the surface hydroxyl groups. After washing with methanol and drying, the hydroxylated AC (1 g) was refluxed with 3-aminopropyltrimethoxysilane (APTS) (2 mmol) in dry toluene (100 ml) under nitrogen atmosphere for 24 h to give aminopropyl modified AC (APTS-AC). The prepared material was soxhlet extracted with dichloromethane to remove the unreacted residue of silylating reagent, and dried in vacuum oven at 383 K overnight.

2.1.2. Preparation of supported molybdenum catalyst

A solution of $MoO_2(acac)_2$ (2 mmol) in methanol (10 ml) and APTS-AC (1 g) was refluxed under nitrogen atmosphere for 24 h. The reaction mixture was filtered and the solid was soxhlet extracted with dichloromethane for 24 h to remove unreacted $MoO_2(acac)_2$. Finally, the resulting supported molybdenum catalyst (Mo-APTS-AC) was dried in vacuum oven at 383 K overnight.

2.2. Catalytic epoxidation of olefins in the presence of Mo-APTS-AC catalyst

Epoxidation of olefins was carried out in a 25 ml round bottom flask equipped with a condenser and a magnetic stirrer. *Tert*-butyl hydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) and cumene hydroperoxides (CHP, 80% in cumene) were used as oxidants. In a typical procedure, to a mixture of catalyst (100 mg) and olefin (8 mmol) in chloroform (10 ml) was added oxidant (14.4 mmol) under nitrogen atmosphere and the mixture was refluxed for a given time. Samples were withdrawn periodically and after cooling and dilution with solvent were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a flame ionization detector (FID). The products were quantified using isooctane (8.75 mmol) as internal standard. GC–MS (gas chromatography-mass spectrometry) of the products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

3. Results and discussion

3.1. Preparation and characterization of the supported molybdenum catalyst, Mo-APTS-AC

The tethering approach for functionalization of AC and proposed structure of the Mo-APTS-AC catalyst is schematically shown in Fig. 1. In the final step, according to literature [38], Schiff base condensation reaction of NH_2 group of APTS-AC and carbonyl group of

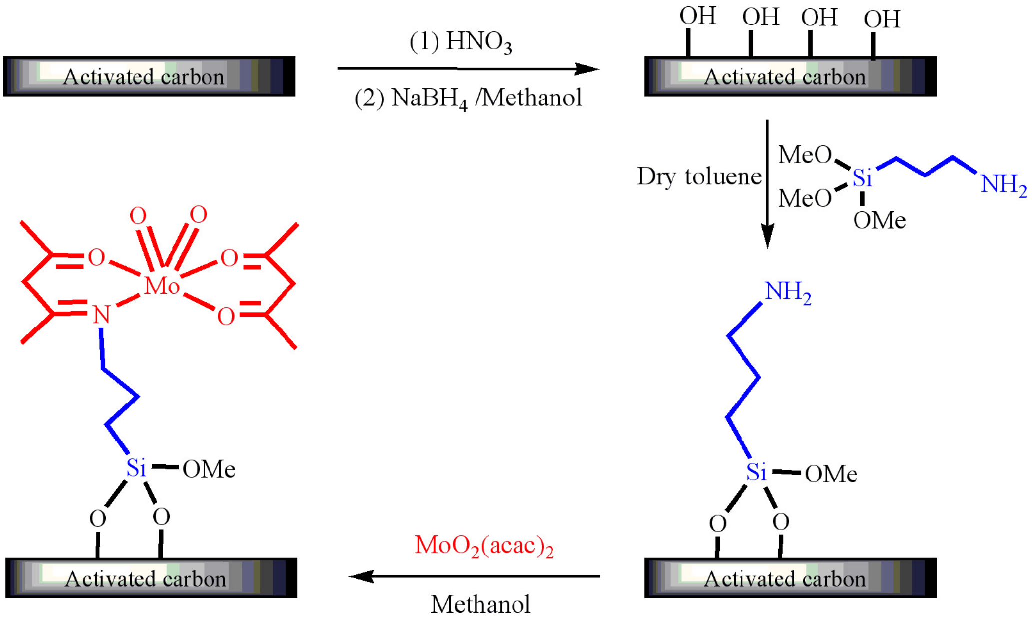

Fig. 1. The sequence of events in the preparation of Mo-APTS-AC.

acac ligand resulted in the formation of imine bond through which the molybdenum complex was covalently attached to the surface of AC.

In order to confirm the modification of the AC surface, the FT-IR spectra of the AC, APTS-AC, and Mo-APTS-AC materials were obtained and have been shown in Fig. 2. The aminopropyl silylation of hydroxylated AC was confirmed by the observation of a relatively broad band at about 1000–1100 cm^{-1} in the FT-IR spectrum of APTS-AC (Fig. 2b) which can be assigned to Si—O—C stretching vibrations. Furthermore, the presence of anchored propyl groups was confirmed by observation of C—H stretching vibrations at 2852 and 2924 cm^{-1} that was not present in the parent AC. In the FT-IR spectrum of Mo-APTS-AC (Fig. 2c), the appearance of two adjacent bands at 912 and 941 cm^{-1} was characteristic of the presence of *cis*-MoO_2 groups [41] in this material and clearly confirmed the formation of surface tethered molybdenum complex as depicted in Fig. 1.

Further evidences for the presence of molybdenum complex and surface chemical composition of the final product were provided by CHN, EDX analysis (Fig. 3a) and ICP-AES.

The results of the CHN analysis showed that reaction of APTS with AC resulted in 0.27 mmol g^{-1} increase of nitrogen content which indicated the extent of surface functionalization of the AC with APTS molecules.

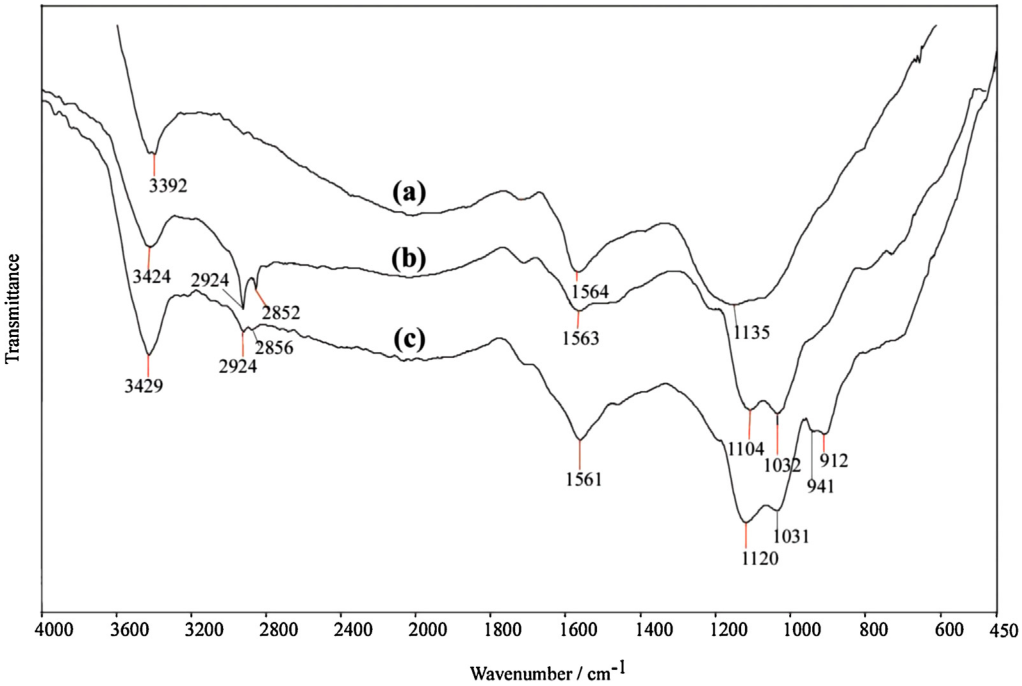

Fig. 2. FT-IR spectra of (a) AC, (b) APTS-AC, and (c) Mo-APTS-AC.

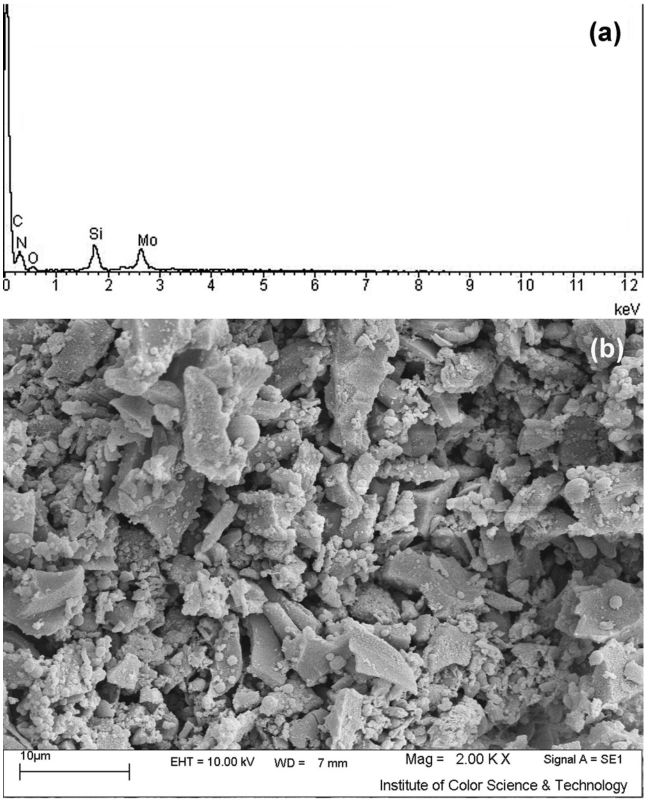

Fig. 3. (a) EDX spectrum, and (b) SEM image of Mo-APTS-AC.

ICP-AES analysis of the catalyst revealed the existence of 0.06 mmol g^{-1} molybdenum in the Mo-APTS-AC catalyst. It is worth noticing that despite the excess of molybdenum precursor used in the reaction, the amount anchored onto AC is lower than the amount of APTS that was anchored onto the surface of AC. This may be due to the poor accessibility of the amine groups of APTS-AC material which located in the micro- or mesopores.

The surface morphology of the obtained catalyst was observed by scanning electron microscopy (SEM). As can be seen in Fig. 3b, the SEM image of the Mo-APTS-AC catalyst shows disordered three-dimensional structure. The SEM image of the sample does not reflect the effects of the treatments conducted on the AC. After incorporation of molybdenum, there is no any significant difference in the micrographs of the commercial AC and Mo-APTS-AC.

Textural properties of the AC, APTS-AC, and Mo-APTS-AC catalyst were investigated with N_2 adsorption–desorption isotherms. Fig. 4a shows the adsorption isotherms of all materials at liquid nitrogen temperature. In the adsorption isotherm of the parent AC the uptake of N_2 increases at high relative pressure and shows a hysteresis loop which exhibits type IV isotherm according to the Brunauer–Deming–Deming–Teller (BDDT) classification [42]. The result suggests considerable amount of mesoporosity in parent AC. In the adsorption isotherm of APTS-AC which exhibits type IV isotherm with a hysteresis loop indicating the presence of some mesopores the inflection point shifts to lower relative pressures and the volume of nitrogen adsorbed decreases upon functionalization. As expected, this indicates the presence of aminopropyl groups tethered to the pore walls of the micro- and mesopores.

The adsorption isotherm of Mo-APTS-AC is mainly type II, as deduced from the shape of the isotherm at relative pressures below 0.2 and at higher relative pressures, which is characteristic of non-porous materials. This is mainly due to a pore blocking effect, especially micropores, which is also evident from the analysis of the uptake at low relative pressures in the adsorption–desorption isotherm. The pore blocking is probably resulted from the reaction of acac ligands of molybdenum precursor with aminopropyl groups located near the pore entrances [43]. The isotherm also presents a small hysteresis loop due to the presence of few mesopores in the Mo-APTS-AC catalyst.

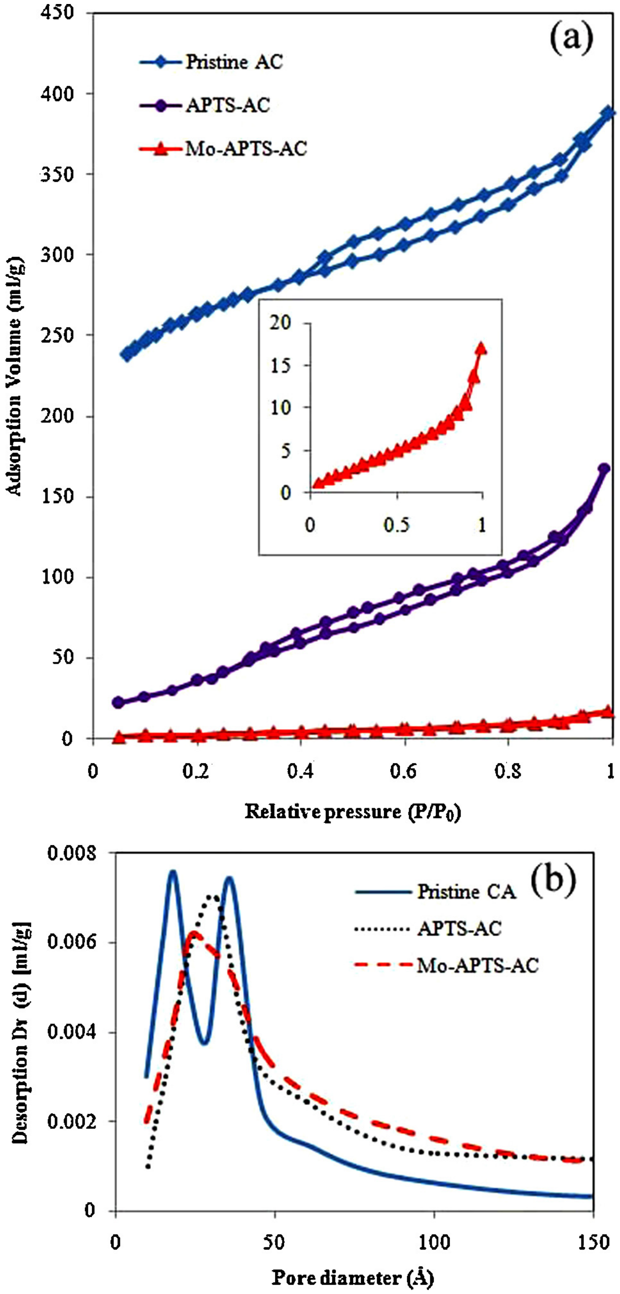

Fig. 4. (a) Nitrogen sorption isotherms (inset image shows magnified view of Mo-APTS-AC isotherm) and (b) BJH pore size distributions of AC, APTS, and Mo-APTS-AC materials.

Pore size distributions of AC, APTS-AC, and Mo-APTS-AC were obtained from the desorption branch of the isotherms using the Barrett, Joyner and Halenda (BJH) method [42] and are shown in Fig. 4b. AC shows a bimodal distribution with maxima located at 18 and 36 Å indicating the presence of micropores as well as mesopores. On the other hand, APTS-AC and Mo-APTS-AC present a broad monomodal distribution with the maximum radius centered at 31 and 23 Å, respectively. This reveals the blocking of the micropores during the immobilization of molybdenum complex and the presence of mesopores in both materials.

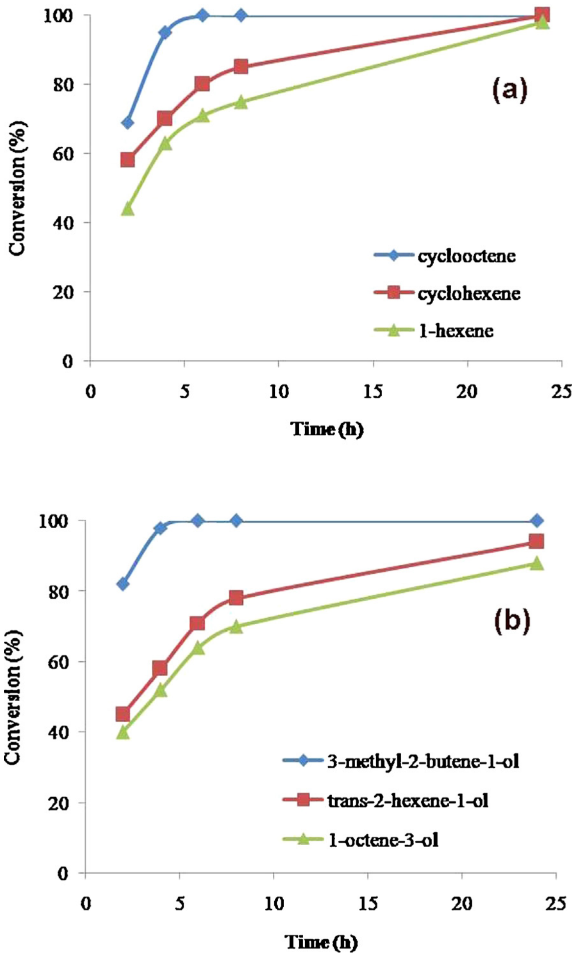

Fig. 5. Epoxidation of (a) olefins and (b) allyl alcohols with TBHP in the presence of Mo-APTS-AC. Reaction conditions: catalyst (100 mg), olefin or allyl alcohol (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml).

The textural parameters of AC, APTS-AC, and Mo-APTS-AC are collected in Table 1. Determination of total surface area is commonly based on the theory of multilayer adsorption developed by Brunauer, Emmett and Teller with the relative pressure (p/p_0) in range of 0.05–0.30. Micropore surface area and micropore volume were obtained from the *t*-plot method. The total pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure ($p/p_0 = 0.98$), using 0.8081 g cm^{-3} for the density of N_2 in its normal liquid state. The volume of mesopores (V_{meso}) was calculated by subtracting the micropore volume from the total pore volume.

As can be seen in Table 1, surface functionalization of AC with APTS resulted in approximately 53% decrease in the surface area. This is due to the anchoring of the APTS molecules onto the AC micropore and mesopore wall channels. Furthermore, upon tethering the molybdenum complex on the surface of AC there is a more significant decrease in the surface area and micropore volume which confirm the above-mentioned pore blocking effect.

3.2. *Catalytic epoxidation of olefins and allyl alcohols in the presence of supported Mo-APTS-AC*

Catalytic activity of the prepared catalyst was evaluated in the epoxidation of some olefins and allyl alcohols with TBHP and CHP as oxidants and the results are given in Figs. 5 and 6 and Table 2. The selectivities of the reactions toward the production of epoxides were found to be close to 100% in all of the entries of Figs. 5 and 6. In order to clear up the catalytic effect of the prepared Mo-APTS-AC, we have included the results of the epoxidation of cyclooctene in the presence of parent AC and blank (no catalyst) as well as different amounts of the catalyst in Table 2. As can be seen, no significant reaction occurred in the absence of the catalyst. Furthermore, with increasing the Mo-APTS-AC catalyst amount to 100 mg the conversion increases, and then remains constant with increasing the catalyst amount.

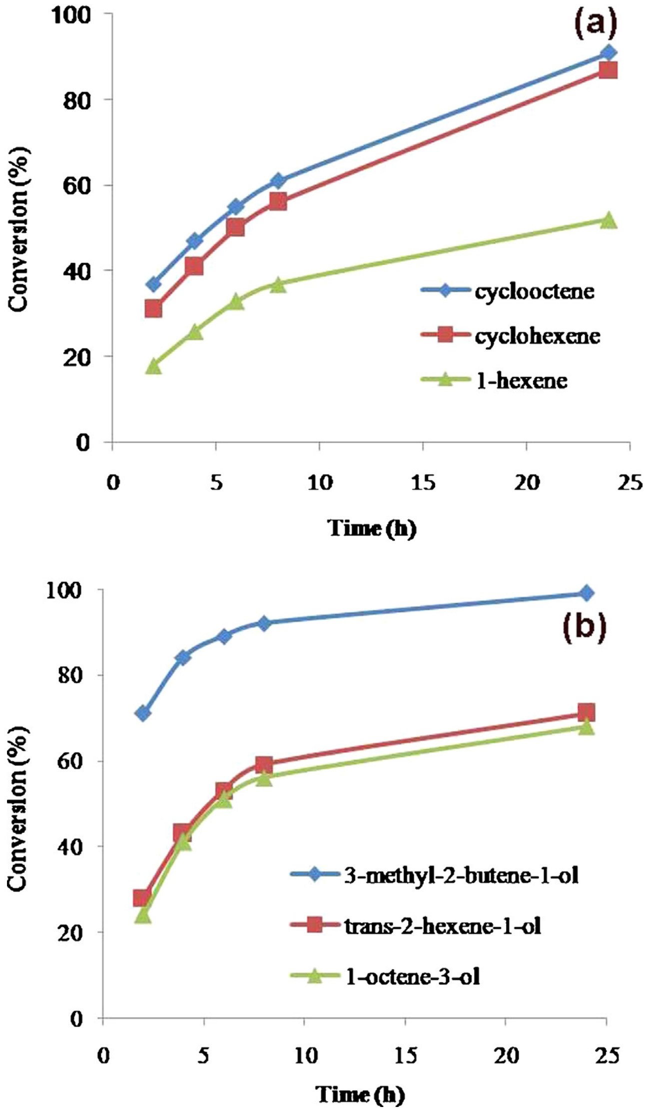

Fig. 6. Epoxidation of (a) olefins and (b) allyl alcohols with CHP in the presence of Mo-APTS-AC. Reaction conditions: catalyst (100 mg), olefin or allyl alcohol (8 mmol), CHP (14.4 mmol), refluxing chloroform (10 ml).

A clear point when comparing the results of Figs. 5 and 6 is the higher reactivity of TBHP in the epoxidation of olefins in comparison with CHP. This observation can be explained with more electrophilic character of the peroxidic oxygen in TBHP. On the basis of earlier experimental and theoretical investigations, it has been shown that the epoxidation of olefins in the presence of *cis*-dioxomolybdenum(VI) complexes involves the coordination of TBHP to the Lewis acidic molybdenum center in the first step [44]. The peroxidic oxygen would have electrophilic character and the catalytic epoxidation proceeds through electrophilic oxygen atom transfer from resulting molybdenum alkyl peroxide to the olefin (Fig. 7). On the other hand, the reaction rates for cyclic olefins with higher electron density are higher than that

Table 2
Investigation of the catalytic effect of the prepared Mo-APTS-AC on the epoxidation of cyclooctene with TBHP.

Run no.	Catalyst	Catalyst amount (mg)	Time (h)	Conversion (%)	Selectivity[a] (%)	TOF[b] (h^{-1})
1	AC	100	12	16	36	–
2	–	–	12	14	41	–
3	Mo-APTS-AC	25	8	71	>99	532
4	Mo-APTS-AC	50	8	80	>99	266
5	Mo-APTS-AC	100	8	99	>99	165
6	Mo-APTS-AC	150	8	99	>99	110

Reaction conditions: catalyst (100 mg), cyclooctene (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml).

[a] Selectivity toward epoxycyclooctane.

[b] Calculated as mmol of product formed per mmol of molybdenum in the catalyst per time.

Table 3
Investigation of the catalytic contribution of the possibly leached out molybdenum species.

Run no.		Time (h)	Conversion (%)	Selectivity[a] (%)
1	Before filtering the catalyst	2	70	>99
	After filtering the catalyst	24	73	98

Reaction conditions: catalyst (100 mg), cyclooctene (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml).

[a] Selectivity toward epoxycyclooctane.

Table 4
Results of the epoxidation of cyclooctene with TBHP in the presence of recycled catalysts.

Run no.	Time (h)	Conversion (%)	Selectivity[a] (%)	Mo content of the catalyst (mmol g^{-1})	TOF
1st	3	89	100	0.06	395
2nd	3	87	100	0.06	387
3rd	3	84	100	0.05	448
4th	3	82	100	0.05	437
5th	3	79	100	0.05	421
6th	3	78	100	0.05	416

Reaction conditions: catalyst (100 mg), cyclooctene (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml). A little fresh catalyst was added to the recovered catalysts to keep the same amount of catalysts in the reaction system in each run.

[a] Selectivity toward epoxycyclooctane.

of terminal olefins which further confirms the proposed mechanism. Furthermore, allyl alcohols are more reactive than simple olefins. This is probably due to the participation of hydroxyl group in approaching the double bond to the electrophilic oxygen center.

Comparison of the obtained results with our earlier work on the similar catalyst derived from mesoporous material (MCM-41), MoO_2acacAmp@MCM-41 [22], is interesting and instructive. Compared to MoO_2acacAmp@MCM-41 with higher surface area, the Mo-APTS-AC shows comparable (e.g. in the case of cyclooctene and cyclohexene) or even higher (e.g. in the case of 1-hexene) catalytic activities which can be interpreted by considering the fact that increasing the hydrophobic nature of the support increases the activity and selectivity of the catalyst toward the formation of epoxides. It seems that the hydrophobic properties of the AC support compensate the loss of porosity of the Mo-APTS-AC catalyst and as indicated in the catalytic results, the catalyst is active in the epoxidation of olefins. The more catalytic activity of the AC based catalyst in comparison with MCM-41 based catalyst indicates the effect of hydrophobic nature of the support on the catalytic activity of the catalyst. As a result of the presence of carbon atoms and nonpolar structure, AC has more hydrophobic character than MCM-41 which composed of hydrophilic silica material. It is evident that in comparison with more hydrophilic MCM-41 support, the hydrophobic reagents i.e. olefins and nonpolar solvents have more tendency to close to the catalytic active sites located on the surface of more hydrophobic AC support, and so the latter catalyst is more active than the former one.

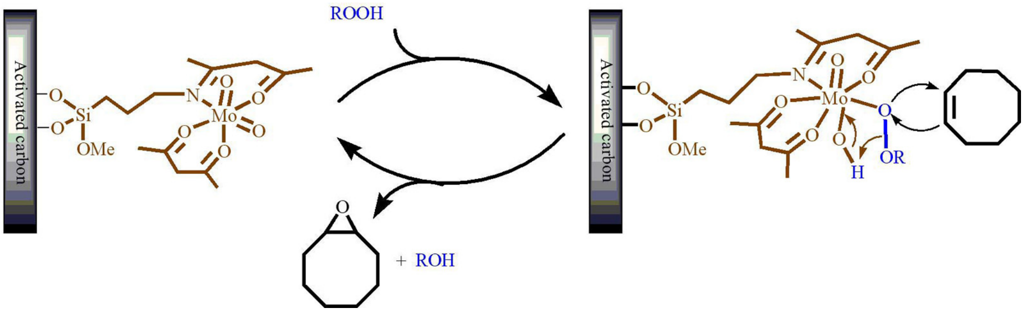

Fig. 7. Mechanism of the epoxidation of cyclooctene with TBHP in the presence of Mo-APTS-AC.

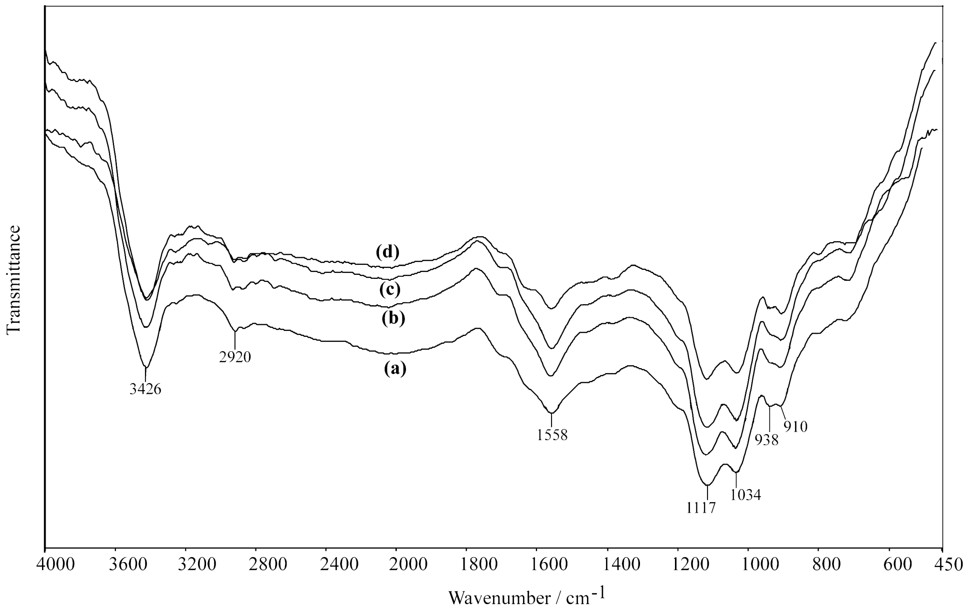

Fig. 8. FT-IR spectra of the (a) 1st, (b) 2nd, (c) 3rd, (d) 4th recycled Mo-APTS-AC catalysts.

In an attempt to assess the catalytic contribution of the solubilized molybdenum species, the solution was filtered off after 2 h reaction and then left to react for a further 24 h. As can be observed in Table 3, in this time interval the cyclooctene conversion rose only 3% suggesting that there is no any significant molybdenum species in the solution and the catalytic reaction is truly heterogeneous in nature.

The recyclability of the catalyst was investigated after separation of the catalyst from reaction mixture at the end of the reaction and washing with methanol. The recovered catalyst was reused at least six times for the epoxidation of cyclooctene and the obtained results are given in Table 4. As can be seen, the recovered Mo-APTS-AC maintains similar activity after 6 recycles. The ICP-AES molybdenum analyses of the recycled catalysts (Table 4) show no significant loss of the molybdenum content after 6 successive catalytic cycles. On the other hand, similar to MoO_2acacAmp@MCM-41 catalyst, very low molybdenum species was present in the filtrate as confirmed by ICP-AES analysis. Moreover, the FT-IR spectra of the recycled catalysts (Fig. 8) show no considerable change in catalyst structure after at least 4 recycles. Altogether, these results indicate the stability of the prepared catalyst under the reaction conditions.

4. Conclusion

Surface functionalization of AC with aminopropyltriethoxysilane and subsequent complexation with molybdenum complex affords a heterogeneous catalyst for epoxidation of olefins. Physicochemical characterization of the product confirms the formation of covalent bonds and successful tethering of molybdenum complex to the surface of AC. The prepared catalyst was found to be very efficient and stable heterogeneous catalyst in the selective epoxidation of olefins with TBHP and CHP as oxidants. Due to its increased hydrophobic nature, the activity and selectivity of the catalyst is comparable or even higher than other inorganic supports which besides its cheapness and availability makes it a good candidate for use in large scale catalytic production of epoxides.

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