

RESEARCH PAPER

Immobilization of a new (salen) molybdenum(VI) complex onto the ion-exchangeable polysiloxane as a heterogeneous epoxidation catalyst

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ABSTRACT

In this study, a new recoverable catalyst for the epoxidation of olefins was developed using a layered polysiloxane as a support for immobilizing (salen) molybdenum(VI) complex by electrostatic interaction between the surface of the solid support and the electrically charged molybdenum complex. Characterization of the heterogeneous catalyst by Fourier transform infrared, XRD, ¹H NMR, and atomic absorption spectroscopies as well as thermogravimetric and CHN elemental analyses confirmed successful immobilization of the (salen) molybdenum(VI) complex to the support. The prepared catalyst catalyzed the epoxidation of olefins efficiently. The effect of different factors on the epoxidation of cyclooctene was investigated. Reaction conditions including reaction temperature, solvent type, substrate amount, catalyst amount and oxidant amount were systematically optimized in order to achieve the highest conversion of cyclooctene. Various other olefins showed high catalytic activity and selectivity under the optimal reaction conditions. Regenerability test demonstrated that the catalyst can be recycled for at least five times without leaching of molybdenum. Moreover, the catalyst showed good stability under the reaction conditions as determined by FT-IR and ICP-OES analyses.

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INTRODUCTION

In the last decade, considerable efforts have been devoted to develop salen ligands [salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] and their derivatives due to the extensive applications in the fields of synthesis and catalysis [1-3]. In this respect, metallosalen complexes have been proved to be effective catalysts for many asymmetric conversions comprising (ep)oxidations, ring opening reactions of epoxides and polymerizations [4-6]. Great attempts have been made to synthesize

the metallosalen complexes for catalysis because of the structural rigidity combined with the ease of preparation and derivatization of salen ligands [7-8]. However, one of the most important challenges in catalysis is developing of an ideal heterogeneous catalyst with high activity and stability [9-11].

In recent years, significant efforts have been devoted to develop metallosalen complexes as heterogeneous catalysts for the epoxidation of olefins since epoxides are valuable intermediates providing an access to various fine chemicals [12-13]. Since

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Jacobsen and Katsuki developed manganese(III) salen complexes [14-15], heterogenization of these complexes on various supports has received considerable attention in order to prepare recyclable and economical catalyst. In this regard, many attempts have been made to immobilize manganese(III) salen complexes into zeolites, silica materials, carbon materials, polymers, organosilica materials and metal organic frameworks [16-20]. Furthermore, heterogenization of other metallosalen complexes such as Cr(III), Ni(II), Cu(II), Co(II), V(IV) and Fe(III) has been proved to be effective catalysts in the epoxidation reactions [21-24].

Among the heterogeneous catalysts, molybdenum types have attracted considerable academic and industrial interests because a variety of industrial chemical reactions especially oxygen transfer reactions such as epoxidation of olefins are catalyzed with these complexes [25]. It is well known that catalysis is most effective when the molybdenum is in its highest oxidation state [26]. During the last few decades, numerous molybdenum (VI) complexes have proved to be successful catalysts for many reactions ranging from Lewis acid catalyzed transformations to oxidation and reduction reactions [27-28].

In spite of many attempts to attach different molybdenum complexes on solid supports [29-31], there are little reports in the literature regarding immobilization of effective molybdenum complexes derived from salen ligands [32].

Herein, for the first time, we report the utilization of a layered ion-exchangeable polysiloxane, prepared by Kaneko and coworkers, [33-34] as support to immobilize a new and efficient (salen)Mo(VI)-based epoxidation catalyst. For this purpose, the Mo(VI) tetradentate complex was supported onto polysiloxane by electrostatic interaction between the surface of the solid support and an electrically charged molybdenum complex. To the best of our knowledge, there is no report about the preparation and characterization of such electrostatically attached molybdenum complex on the surface of polysiloxane. The advantages of the prepared material are the easy recovery of the catalyst as well as good activity, selectivity and high stability in the epoxidation reaction of different olefins.

EXPERIMENTAL

Catalyst characterization

All reagents were purchased from Merck and Aldrich.

Fourier transform infrared (FT-IR) spectra of the materials were recorded on a Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a PW1800 diffractometer using Cu K α radiation in the 2θ range of 5-50° ($\lambda=1.5406 \text{ \AA}$).

^1H spectra of the synthesized materials were recorded on a Bruker FT-NMR 250 MHz spectrometer. Elemental analyses were performed with ICP-OES Optima 8000 (inductive coupled plasma optical emission spectroscopy) atomic emission spectrometer. Nitrogen content of the modified materials was determined with a Thermo Finnigan (Flash 1112 Series EA) CHN analyzer. Thermogravimetric analysis (TGA) measurement was performed using a Mettler Toledo TGA/DSC1 Instrument. The samples were heated in air with a heating rate of 5 °C min $^{-1}$. The oxidation products were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a flame ionization detector (FID). Gas chromatography-mass spectrometry (GC-MS) was recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

Catalyst preparation

Synthesis of N-phenyl-salicylaldimine

A solution of salicylaldehyde (4.27 g, 35 mmol) in methanol (40 ml) was added to aniline (3.26 ml, 35 mmol) and refluxed for 1 h. The mixture was cooled in an ice-bath to yield yellow crystalline product. The obtained yellow solid was filtered and dried at room temperature [35] (6.3 g, 91 %).

Synthesis of N-phenyl-5-sulfonato-salicylaldimine

N-phenyl-salicylaldimine (2 g, 10 mmol) was added slowly to the concentrated sulfuric acid (5.4 ml). The mixture was stirred and heated at 100 °C for 2.5 h. The hot solution was added to 57 ml ice water and a yellow product was obtained. The suspension was then reheated. After dissolving the product a bright orange solution was formed. The yellow product was filtered and washed with cold water [35] (2.29 g, 81 %).

Synthesis of 5-sulfonato-salicylaldehyde sodium salt

N-phenyl-5-sulfonato-salicylaldimine (1 g, 3.6 mmol) was dissolved in aqueous solution of Na $_2$ CO $_3$ (0.55 g, 5 ml). The solution was boiled vigorously and stirred in an open flask for 2.5 h. Glacial acetic acid was then added to the cooled solution till the pH reached 5. The same amount of ethanol

was added and the solution cooled to 0 °C. The solid product filtered and washed with ethanol [36] (0.6 g, 75 %).

Synthesis of N-N'-bis(salicylidene-5-sulfonato)-diaminoethane disodium salt (Na₂(salen/SO₃))

5-sulfonato-salicylaldehyde sodium salt (0.94 g, 4.19 mmol) was dissolved in a mixture of ethanol-water and ethylenediamine (2.1 mmol) was added. The mixture was refluxed at 90 °C for 1 h. The prepared yellow solid was filtered and washed with ethanol [37] (0.61 g, 61.5 %).

Synthesis of Disodium [N-N'-bis(salicylidene-5-sulfonato)-iminato] dioxomolybdenum(VI) complex (Na₂[MoO₂(salen/SO₃)])

Bis(acetylacetonato)dioxomolybdenum(VI), MoO₂(acac)₂, was prepared according to the literature method [38]. A solution of MoO₂(acac)₂ (0.21 g, 0.65 mmol) in methanol was added to a solution of 5-sulfonato-salicylaldehyde sodium salt (0.29 g, 1.29 mmol) in methanol. The mixture was refluxed for 1 h and then ethylenediamine (0.043 ml, 0.65 mmol) was added dropwise. The resultant mixture was refluxed for 24 h. The yellow precipitate was collected and washed with methanol and diethyl ether (0.17 g, 44%).

Synthesis of poly-(3-aminopropyl)siloxane hydrochloride (PAPS-Cl)

A mixture of 3-aminopropyltrimethoxysilane (APTMOs) (6.3 ml, 36 mmol) was added to hydrochloric acid aqueous solution (90 ml, 0.5 M) and the reaction solution was stirred for 2.5 h at room temperature, followed by heating to 60°-70 °C in the open system until the solvent was completely

distilled away. The product was left overnight at 100 °C and then dissolved in distilled water (300 ml). The product solution was lyophilized to yield PAPS-Cl [33].

Synthesis of polysiloxane-supported (salen) Mo(VI) catalyst (Na₂[MoO₂(salen/SO₃)]/PAPS-Cl)

A solution of Na₂[MoO₂(salen/SO₃)] (0.17mmol) in 2 ml distilled water was added to PAPS-Cl (45 mg).The solution was then stirred for 3 days at room temperature. The resultant precipitate was centrifuged, collected and washed with distilled water and dichloromethane. The obtained molybdenum catalyst was dried at 60°C for 24 h.

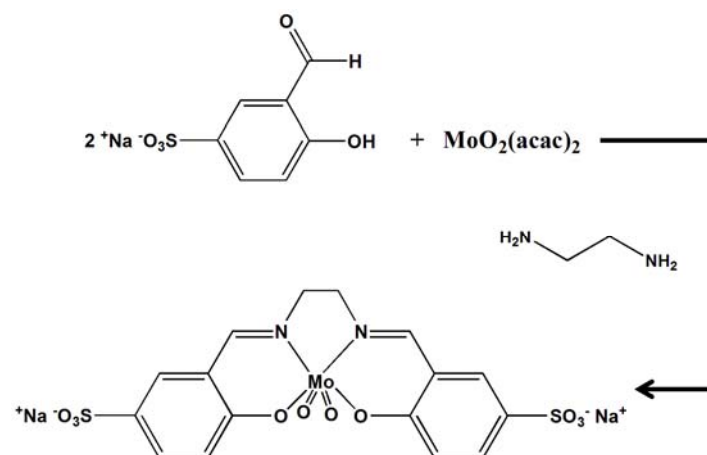
General procedure for epoxidation of alkenes catalysed by Na₂[MoO₂(salen/SO₃)]/PAPS-Cl catalyst

As a typical procedure, the epoxidation reaction was carried out as follows: 3mmol Tert-butyl hydroperoxide (TBHP, 80% in di-tertiary butyl peroxide), as oxidant, was added to a mixture of Na₂[MoO₂(salen/SO₃)] complex (0.0025 mmol) and olefin (2mmol) in solvent (1 ml). The mixture was refluxed for an appropriate time and the final products were quantified with isooctane as internal standard.

RESULTS AND DISCUSSION

Preparation and characterization of polysiloxane-supported (salen)Mo(VI) complex (Na₂[MoO₂(salen/SO₃)]/PAPS-Cl)

The synthetic route used to prepare the Na₂[MoO₂(salen/SO₃)] complex is illustrated in Scheme 1. It can be seen that the complex is synthesized by the reaction of 5-sulfonato-salicylaldehyde sodium salt and MoO₂(acac)₂,



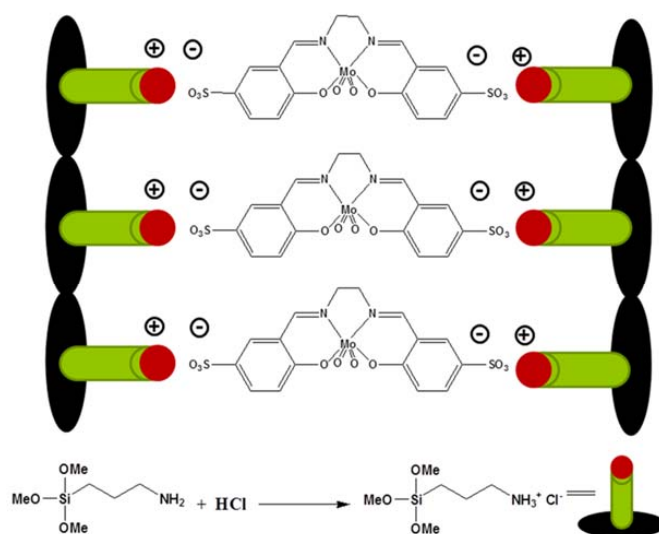
Scheme 1. Schematic illustration for preparation of Na₂[MoO₂(salen/SO₃)]complex.

followed by the addition of ethylenediamine.

The tethering approach for immobilization of $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex to the PAPS-Cl support and proposed structure of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst is schematically shown in Scheme 2. Since PAPS-Cl has ammonium groups around the polysiloxane core portion and Cl^- anions as counterions, an anion-exchange property is expected between PAPS-Cl and the catalyst in aqueous solution which

both are miscible in water.

The FT-IR spectra of the samples were employed to prove the successful preparation of the synthesized materials. In the FT-IR spectrum of the 5-sulfonato-salicylaldehyde sodium salt (Fig. S1), the bands at $1035\text{-}1293\text{ cm}^{-1}$ are assigned to the SO_3^- symmetric and asymmetric vibrations [39]. The characteristic peak of the aldehyde fragment is appeared at $1500\text{-}1600\text{ cm}^{-1}$ due to the stretching vibration of the $\text{C}=\text{O}$ group. The band at 3000 cm^{-1}



Scheme 2. Schematic illustration for preparation of $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$.

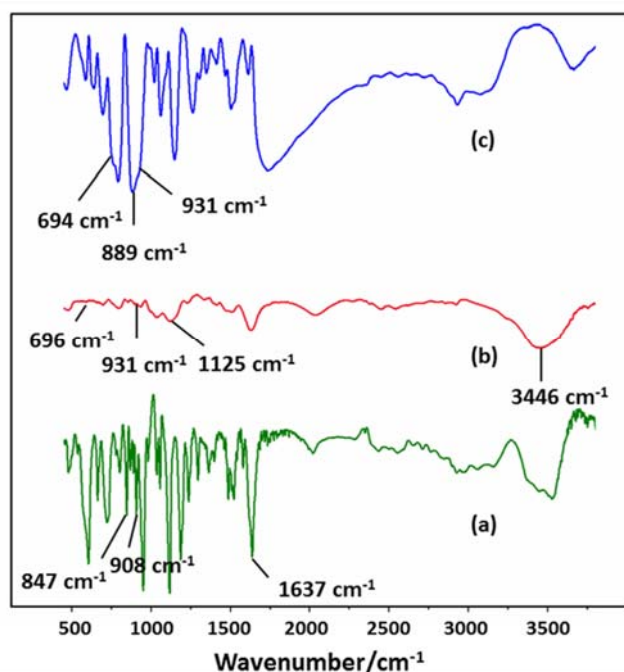


Fig. 1. FT-IR spectra of (a) $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$, (b) PAPS-Cl, (c) $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst.

can be ascribed to the O-H stretching vibration. The FT-IR spectrum of the $\text{Na}_2(\text{salen}/\text{SO}_3)$ sample is shown in Fig. S2. The absorption band appearing at 1631 cm^{-1} is due to the presence of C=N groups in the imine fragment of the $\text{Na}_2(\text{salen}/\text{SO}_3)$ sample. Furthermore, the absorption band of O-H group is appeared at 3400 cm^{-1} . Although $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex cannot be synthesized from the direct reaction between $\text{Na}_2(\text{salen}/\text{SO}_3)$ and $\text{MoO}_2(\text{acac})_2$, $\text{Na}_2(\text{salen}/\text{SO}_3)$ synthesis and characterization was performed to obtain insight into the structural features of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ sample. As shown in Fig. 1a, the characteristic bands at around 847 , 908 and 1637 cm^{-1} appeared distinctively in the FT-IR spectrum of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex which are assignable to the vibrations of *cis*- MoO_2 and C=N groups in the molybdenum complex, respectively[29]. These IR results demonstrate that $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex has been successfully synthesized. The FT-IR spectrum of PAPS-Cl (Fig. 1b) shows the characteristic bands of the N-H and Si-C bonds at 3446 and 1125 cm^{-1} as well as two bands at 931 and 696 cm^{-1} assigned to two different Si-O bonds [39]. In comparison of PAPS-Cl (Fig. 1b) with $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst (Fig. 1c), IR bands of two Si-O bonds (931 and 694 cm^{-1}) retained in the catalyst, indicating an electrostatic linkage of catalyst with PAPS-Cl. Furthermore, the presence of the adjacent band at 889 cm^{-1} is attributed to Mo=O vibration in the heterogeneous catalyst.

Fig. 2 shows the XRD measurement of the powdered PAPS-Cl and $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst. The patterns of PAPS-Cl (Fig. 2a) exhibits two characteristic peaks at $2\theta=7$ and 12 which can be attributed to the hexagonal phase of PAPS-Cl [33]. The broad peak centered at $2\theta=22-24$ is attributed to the aminopropyl chains packing within the layer. Generally, polysiloxanes with alkyl side chains have been proved to show broad peaks at $2\theta=20-30$ [33].

In the XRD patterns of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst (Fig. 2b), the broad peak centered at $2\theta=22-24$ is shifted to lower diffraction angles and confirms the successful immobilization of the molybdenum complex to PAPS-Cl.

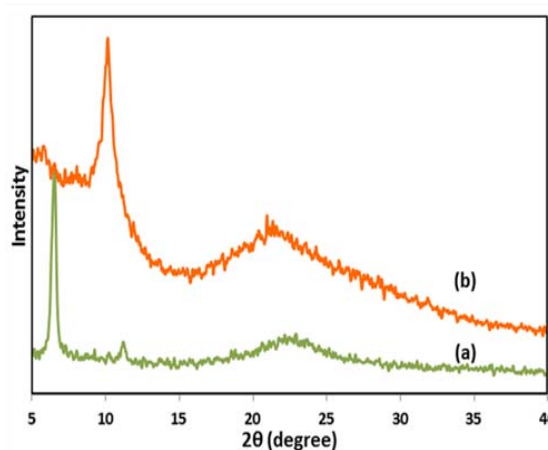


Fig. 2 XRD patterns of (a) PAPS-Cl, (b) $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$.

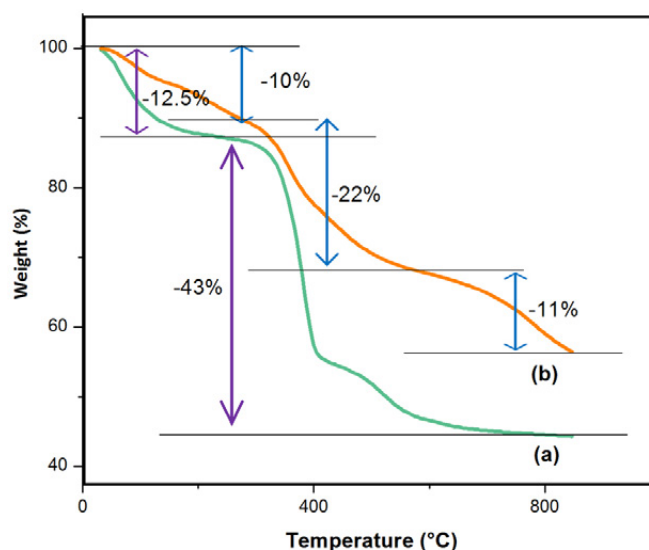


Fig. 3 TGA curves of (a) PAPS-Cl, (b) $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$.

To assure the successful synthesis of the molybdenum complex, ^1H NMR analysis was performed. In the ^1H NMR spectrum of 5-sulfonato-salicylaldehyde sodium salt (Fig. S3) the signal at 10.2 ppm is attributed to proton group in the aldehyde fragment. Moreover, the signals at 6.9, 7.7 and 7.8 ppm are due to the presence of aromatic ring. In the ^1H NMR spectrum of $\text{Na}_2(\text{salen}/\text{SO}_3)$ (Fig. S4), the signal at about 8.7 ppm confirms the formation of $\text{HN}=\text{C}$ groups in the Schiff base. The signals at 6.8, 7.5, 7.6 and 3.9 ppm are ascribed to the aromatic rings and CH_2 protons. The ^1H NMR spectrum of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex exhibits a signal at 8.67 ppm assignable to the azomethin groups. Furthermore, the signals for the aromatic ring are appeared in the region 5.6-7.7 ppm (Fig. S5).

The CHN elemental analysis of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]$ complex showed a good agreement between theoretical and measured values (calc., C, 32.12; H, 2.02; N, 4.68%, found, C, 32.45; H, 2.10; N, 4.79%). The metal content was determined by ICP-OES which revealed the existence of 1.82 mmol g^{-1} molybdenum in the prepared complex.

The immobilization of the complex was investigated by the thermal analysis. The decomposition behaviour of the PAPS-Cl and $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst has been compared in order to understand the effect of immobilization. The obtained results are depicted in Fig. 3. In the TGA curve of PAPS-Cl, the main weight loss due to the decomposition of the material (~43%) is resulted from the combustion of the organic components in the range of 300-600 °C. As seen in Fig. 3b, the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst shows a first weight loss of about 10% corresponding to the loss of absorbed solvent molecules, occurred in the range of 30-200 °C. In the second step (between 300-600 °C), the main weight loss of about 22% is resulted from the PAPS-Cl decomposition. Upon further heating, there is about 11% weight loss at 600-800 °C, which is owing to the combustion of the organic

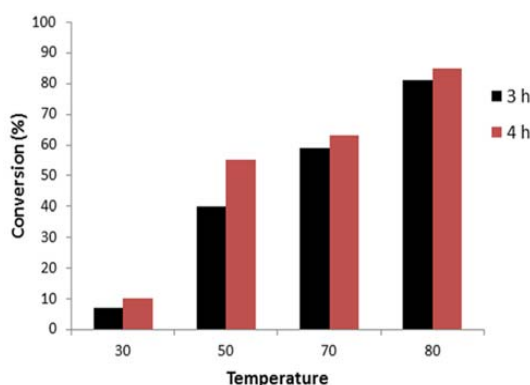


Fig. 4 Effect of temperature on the cyclooctene conversion in the presence of $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$.

Reaction conditions: Catalyst (0.01 mmol), cyclooctene (0.5 mmol), TBHP (2mmol), dichloroethane (1ml).

components attached to the molybdenum complex.

Catalytic activity studies of polysiloxane-supported (salen)Mo(VI) complex ($\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$)

The catalytic activity of the prepared $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst was evaluated in the selective epoxidation of different olefins. Initially, the effect of different parameters on the epoxidation of cyclooctene over the catalyst was tested to assess the optimal reaction condition. In all cases, the obtained conversion is GC yield based on starting substrate, and selectivity is determined toward the formation of epoxide by GC-Mass or injection of reference.

The study of the effect of temperature is essential as it can have a great influence on the reaction rate. As depicted in Fig. 4, substrate conversion increases with increasing the temperature up to 80 °C.

The optimal reaction condition was also investigated using TBHP as oxidant in the presence of different solvents (Table 1). The $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst is more active in 1,2-dichloroethane, tetrachlorocarbon and toluene rather than acetonitrile and ethanol. This observation can be explained with the coordination ability of the acetonitrile and ethanol

Table 1. The screening solvent nature for the epoxidation of cyclooctene using $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ as catalyst.

Solvent	Conversion (%)	Selectivity (%)	TON ^a
1,2-dichloroethane	85	100	42.5
tetrachlorocarbon	51	100	25.5
Toluene	>99	100	50
Acetonitrile	48	100	24
Ethanol	85	100	42.5

Reaction conditions: Catalyst (0.01 mmol), cyclooctene (0.5mmol), TBHP (2mmol), Solvent (1 ml), temperature (80 °C), time (4h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

solvents and their competition with the oxygen molecule of TBHP to occupy the coordination sites of the catalyst. In the case of toluene, as solvent, higher reactivity of the substrate was obtained. Furthermore, the ionic nature of $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ made it insoluble in toluene as nonpolar solvent and resulted in easier separation of the heterogeneous catalyst.

Reaction conditions: Catalyst (0.01 mmol), cyclooctene (0.5mmol), TBHP (2mmol), Solvent (1 ml), temperature (80 °C), time (4h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

The effect of catalyst amount on the epoxidation of cyclooctene has been summarized in Table 2. It is clear that substrate conversion increases with increasing the amount of catalyst up to 0.0025 mmol, and then remains constant with larger amount of the catalyst.

To measure the catalytic activity of the prepared catalyst, the TON was evaluated using various ratios of the substrate to catalyst and the results are shown in Table 3. According to these results, the reaction proceeds at substrate to catalyst ratio from 200 to 800 with increasing TON. The highest amount of TON is obtained using 0.0025 mmol catalyst.

Further tests were carried out to assess the influence of the oxidant amount on the catalytic properties of the catalyst for the epoxidation of cyclooctene (Table 4). The conversion of substrate improves from 73% to 97% as the molar ratio increases from 2 to 4.

To clarify the general applicability of the supported molybdenum catalyst, various substrates were subjected to the epoxidation reaction and the results are summarized in Table 5. The epoxidation reactions were conducted using the optimal

Table 2. The screening catalyst amount for the epoxidation of cyclooctene using $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ as catalyst.

Catalyst amount (mmol)	Conversion (%)	Selectivity (%)	TON ^a
0	11	100	0
0.0025	98	100	196
0.005	>99	100	100
0.01	>99	100	50

Reaction conditions: cyclooctene (0.5mmol), TBHP (2mmol), toluene (1 ml), temperature (80 °C), time (4 h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

Table 3. The screening substrate amount for the epoxidation of cyclooctene using $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ as catalyst.

Substrate/Catalyst	TBHP amount (mmol)	Conversion (%)	Selectivity (%)	TON ^a
200	2	98	100	196
400	2	99	100	396
600	3	97	100	582
800	4	96	100	768

Reaction conditions: Catalyst (0.0025), cyclooctene (0.5, 1, 1.5, 2 mmol), toluene (1 ml), temperature (80 °C), time (4 h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

Table 4. The screening oxidant amount for the epoxidation of cyclooctene using $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ as catalyst.

TBHP (mmol)	Oxidant/Olefin	Conversion (%)	Selectivity (%)	TON ^a
2	1	73	100	584
3	1.5	92	100	736
4	2	97	100	776

Reaction conditions: Catalyst (0.0025mmol), cyclooctene (2mmol), toluene (1 ml), temperature (80 °C), time (4 h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

Table 5. Catalytic epoxidation of different olefins using $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ as catalyst.

Substrate	Conversion (%)	Selectivity (%)	TON ^a
Cyclooctene	>99	100	800
Cyclohexene	85	100	680
Styrene	71	89	568
α -methylstyrene	69	80	552
Indene	60	85	480
1-octene	74	100	592

Reaction conditions: catalyst (0.0025mmol), substrate (2mmol), TBHP (3 mmol), toluene (1 ml), temperature (110 °C), time (4 h). ^aCalculated as mmol of product per mmol of molybdenum in the catalyst

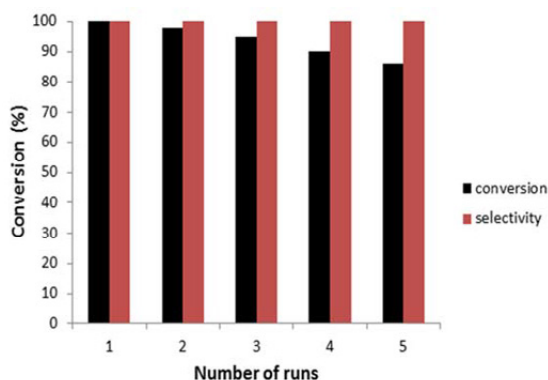


Fig. 5. Recyclability of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst.

Reaction conditions: catalyst (0.0025 mmol), cyclooctene (2 mmol), TBHP (3 mmol), toluene (1 ml), time (1 h).

reaction conditions. Since toluene was selected as the solvent, epoxidation reaction was performed at 110 °C. The resultant conversions revealed the high catalytic activity of the synthesized material. Furthermore, the higher selectivity toward the formation of epoxides was obtained in the presence of allylic substrates compared to cyclic ones.

The reusability of the $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst was tested in the epoxidation of cyclooctene after 1 h of reaction for five times and the results are shown in Fig. 5. It can be concluded that the catalytic system shows good stability over several cycles, as the ICP analysis showed no significant loss of the molybdenum after five cycles of the epoxidation reaction. In addition, the similarity of the FT-IR spectrum of the recycled catalyst to the fresh one (Fig. S6) clearly indicates the catalyst stability under the reaction conditions.

CONCLUSIONS

In summary, a new(salen) molybdenum(VI) complex was synthesized followed by attachment to the layered polysiloxane. The resulting catalyst demonstrated high catalytic activity and selectivity in the epoxidation reaction. The ionic nature of $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ made it insoluble in toluene, as nonpolar solvent, and resulted in easier separation of the heterogeneous catalyst. The $\text{Na}_2[\text{MoO}_2(\text{salen}/\text{SO}_3)]/\text{PAPS-Cl}$ catalyst was found to be catalytically active in the epoxidation reaction over five successive cycles without loss of its activity or stability.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <http://nanochemres.org/>

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