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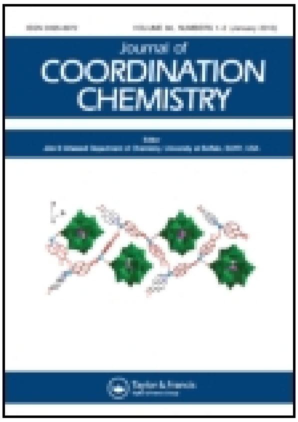

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Synthesis, characterization, and catalysis of recyclable new piperazine-bridged Mo(VI) polymers $[MoO_2(Salen)(piperazine)]_n$ in highly selective oxygenation of alkenes and sulfides

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Synthesis, characterization, and catalysis of recyclable new piperazine-bridged Mo(VI) polymers [MoO_2(Salen)(piperazine)]$_n$ in highly selective oxygenation of alkenes and sulfides

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This study reports synthesis and characterization of polymeric [MoO_2(Salen)] complexes that combine $MoO_2(acac)_2$ and polymeric ligands bearing N_2O_2 coordination sites, abbreviated herein as [piperazinCH$_2${MoO_2(Salen)}]$_n$ (**6**), [piperazinCH$_2${MoO_2(Salophen)}]$_n$ (**7**), and [piperazin CH$_2${MoO_2(Salpn)}]$_n$ (**8**). The epoxidation of alkenes using tert-butyl hydroperoxide and oxidation of sulfides to sulfoxides by urea hydrogen peroxide were enhanced with excellent selectivity under the catalytic influence of these coordination polymers. No relevant difference in activity was found due to change in the diamine in the Schiff's base ligands. The stability of polymeric catalysts was assessed by recycling a sample five times in small batch reactions in both epoxidation and sulfoxidation. In the case of cyclooctene epoxidation, catalytic activity of [piperazinCH$_2${MoO_2(Salen)}]$_n$ increased without losing the selectivity, whereas the catalytic activity and selectivity of the spent catalyst decreased in sulfoxidation of methyl phenyl sulfide in consecutive runs. Loss of Mo from the coordination polymer has been investigated using the filtrates as potential catalysts in sulfoxidation reactions. Molybdenum leaching degree decreases through five cycles. Moreover, the catalyst can be recovered from the reaction mixture unchanged as determined by IR and UV–Vis spectra.

Keywords: Oxidation; Heterogeneous catalysis; Molybdenum; Polymeric complexes

1. Introduction

Coordination chemistry of molybdenum(VI) has attracted interest due to a large number of stable and variable oxidation states as well as coordination numbers that can vary from four to eight. Dioxomolybdenum(VI) complexes are model systems for active sites of molybdoenzymes such as nitrogenase, aldehyde oxidase, xanthine oxidase, sulfite oxidase, nitrate reductase, and xanthine dehydrogenase [1–3]. Molybdenum Schiff's base complexes were efficient homogeneous catalysts for olefin epoxidation [4, 5], oxidation of saturated hydrocarbons [6], and oxidations of sulfides [7, 8], but there are serious problems including the difficulty in separation and recycling of expensive catalysts, as well as leaching of the active metal into the solvent and insufficient stability of the catalysts. An approach to solve these problems involves incorporation of metals into polymers. Polymers containing transition metals in the backbone offer properties of solid heterogeneous catalysts while retaining most of their original character. The relatively easy preparation, the local C_2

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*Corresponding author. Email: bagherzadeh@sharif.edu symmetry in the individual Salen units and wide variety of Salen-type ligands have provided opportunities to prepare Schiff base polymers and to develop catalytic processes for various reactions. There have been extensive studies on metal-containing polymers. Reaction conditions such as condensation strategies, linker units, use of endcaps, reaction solvent, and temperature have been studied in polymerization of Salen units [9–11]. Kureshy *et al*. incorporated a whole range of Salen complexes {e.g. [Mn(Salen)], [Cu(Salen)], and [V(Salen)]} into polymers and studied their catalytic activities for various reactions [12–14]. Jacobsen *et al*. synthesized the polymeric Co(Salen) catalysts for asymmetric epoxide ring – opening reactions [15].

In continuation of our research on transition metal complexes with Schiff bases, we report the synthesis and characterization of polymeric [MoO_2(Salen)] complexes and test their catalytic activity for the oxidation of a range of olefins and sulfides. The reusability of cyclic polymeric [MoO_2(Salen)] complex was also investigated in the reaction of cyclooctene with tert-butylhydroperoxide (TBHP) in 1,2-dichloroethane and reaction of methyl phenyl sulfide (MPS) with urea-hydrogen peroxide (UHP) in mixture of methanol/dichloromethane. IR and UV–vis spectral data of freshly prepared and recovered catalysts are identical, which indicate the metal complex is intact during the catalytic reaction.

2. Experimental

2.1. *Materials and methods*

All reagents were used as received from Aldrich unless otherwise noted. $MoO_2(acac)_2$ has been synthesized according to published procedure [16]. FT-IR spectra were recorded on a Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. ^{1}H spectra of the monomer and polymeric ligand were recorded on a Bruker FT-NMR 500 MHz spectrometer. Electronic spectra of polymers in the UV–vis region were recorded in DMSO using a Shimadzu UV–Vis scanning spectrophotometer. The loading and leaching of molybdenum was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) which was recorded on a Perkin-Elmer AA-300 spectrophotometer. Gas chromatography (GC) analyses were performed on an Agilent Technologies 6890N, 19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary 60.0 m × 250 μm × 1.00 μm.

2.2. *Sample preparation*

2.2.1. Preparation of 5-(chloromethyl)salicylaldehyde (1). **1** was prepared by synthetic methodology previously reported in the literature with little modification [17]. To a mixture of salicylaldehyde (5.8 g, 53 mM) and paraformaldehyde (1.6 g, 53 mM), concentrated HCI(100 mL) was added dropwise at 0°C. The mixture was stirred at 20°C for 5 h and extracted with CH_2Cl_2 (20 mL), and the organic phase was separated and washed with saturated sodium hydrogen carbonate solution and deionized water and was dried over anhydrous Na_2SO_4. The CH_2Cl_2 was then removed under reduced pressure to afford the product as a white solid. Yield: 94%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 11.10 (s; 1H; OH); 9.93 (s; 1H; CHO); 7.03–7.63 (3H; aromatic ring); 4.63 (s; 2H; CH_2).

2.2.2. Preparation of piperazinCH$_2$(sal)$_2$ (2). A solution of **1** (1.50 g, 5.54 mM) in dry CH_2Cl_2 (30 mL) was added dropwise to a stirred solution of Et_3N (1.11 g, 11.0 mM), and piperazine (0.24 g, 2.77 mM) in dry CH_2Cl_2 (15 mL). The yellow solution was stirred for 24 h at room temperature. The solution was washed with water and the organic phase dried over anhydrous Na_2SO_4. Removal of the organic solvent afforded a cream solid. Yield: 68%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 10.94 (s, 2H, OH); 9.93 (s, 2H, CHO); 6.93–7.54 (6H; aromatic ring); 3.53 (s, 4H, CH_2), 2.52 (br s, 8H, CH_2 in piperazine). IR (KBr, cm^{-1}): 3113 (br, ν(OH + H-bonding)); 2939, 2810, 2771(m, νC–H); 1651(s, νC = O); 1592, 1483 (s, νC = C vibration band of the aromatic ring), UV–vis (DMSO), λ_{max} (ε): (nm (10^5 dm^3 M^{-1} cm^{-1}) 260 (0.214), 328 (0.137). Anal. Calcd (found) for $C_{20}H_{22}O_4N_2 \cdot \frac{1}{4} H_2O$: C, 67.00 (67.20); H, 6.30 (6.25); N, 7.80 (7.77).

2.2.3. Preparation of [piperazinCH$_2$(Salen)]$_n$ (3). A solution of ethylenediamine (0.06 g, 1 mM) was added dropwise to a stirred solution of **2** (0.354 g, 1 mM) in CH_2Cl_2 (40 mL) and the mixture was refluxed for 6 h. The solvent was removed under vacuum to produce the yellow solid, which was washed with 5 mL of cooled methanol and then dried in air. Yield: 90%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 13.13 (s, 2H, OH); 8.37 (s, 2H, C=N); 6.9–7.3 (6H; aromatic ring); 3.94 (s, 4H, CH_2–N), 3.50 (s, 4H, CH_2 attached with benzene ring), 2.52 (br s, 8H, CH_2 in piperazine). IR (KBr, cm^{-1}): 3415 (br, ν(OH + H-bonding)); 2928, 2804, 2775 (w, νC–H); 1634 (s, νC=N); 1583, 1490 (s, νC=C vibration band of the aromatic ring). UV–vis (DMSO), λ_{max} (ε): (nm (10^5 dm^3 M^{-1} cm^{-1}) 260 (0.183), 320 (0.084), 405 (0.007). Anal. Calcd (found) for $C_{22}H_{26}N_4O_2 \cdot CH_3OH$: C, 67.29 (67.63); H, 7.37 (7.31); N, 13.65 (13.56).

2.2.4. Preparation of [piperazinCH$_2$(Salophen)]$_n$ (4). A solution of orthophenylenediamine (1 mM) was added dropwise to a stirred solution of **2** (0.108 g, 1 mM) in CH_2Cl_2 (10 mL) and the mixture was refluxed for 6 h. The solvent was removed under vacuum to produce the yellow-orange solid, which was washed with 5 mL of cooled methanol and then dried in air. Yield: 88%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 12.98ν (s, 2H, OH); 8.64 (s, 2H, C=N); 6.96–7.35 (10H; aromatic ring); 3.48 (s, 4H, CH_2 attached with benzene ring), 2.36 (br s, 8H, CH_2 in piperazine). IR (KBr, cm^{-1}): 3415 (br, ν(OH + H-bonding)); 2926, 2800, 2762 (w, νC–H); 1619 (s, νC = N); 1577, 1483 (s, C = C vibration band of the aromatic ring). UV–vis (DMSO), λ_{max} (ε) (nm (10^5 dm^3 M^{-1} cm^{-1}): 276 (0.121), 297 (0.112), 325 (0.118), 337 (0.122). Anal. Calcd (found) for $C_{26}H_{26}N_4O_2 \cdot CH_2Cl_2$: C, 63.39 (63.75); H, 5.52 (5.54); N, 10.93 (11.01).

2.2.5. Preparation of [piperazinCH$_2$(Salpn)]$_n$ (5). A solution of 1,2-propanediamine (1 mM) was added dropwise to a stirred solution of **2** (0.074 g, 1 mM) in CH_2Cl_2 (10 mL), and the mixture was refluxed for 6 h. The solvent was removed under vacuum to produce the yellow solid, which was washed with 5 mL of cooled methanol and then dried in air. Yield: 94%. ^{1}HNMR [$CDCl_3$, 500 MHz; δ (ppm)]: 13.19 (br s, 2H, OH); 8.37 (s, 1H, C=N); 8.33 (s, 1H, C=N); 6.9–7.3 (6H; aromatic ring); 3.72–3.85 (m, 3H, CH–N), 3.5 (br s, 4H, CH_2 attached with benzene ring), 2.46 (br s, 8H, CH_2 in piperazine), 1.42 (s, 3H, CH_3). IR (KBr, cm^{-1}): 3445 (br, ν(OH + H-bonding)); 3009, 2803, 2768 (w, νC–H); 1635 (s, νC=N); 1586, 1493 (s, νC=C vibration band of the aromatic ring). UV–vis (DMSO), λ_{max} (ε) (nm (10^5 dm^3 M^{-1} cm^{-1}): 260 (0.191), 320 (0.080), 400 (0.0049). Anal. Calcd (found) for $C_{23}H_{28}N_4O_2 \cdot CH_3OH$: C, 67.90 (67.83); H, 7.60 (7.51); N, 13.20 (13.26).

2.2.6. Preparation of [piperazinCH$_2${MoO$_2$(Salen)}]$_n$ (6). Dichloromethane solution of **3** (0.378 g, 1 mM) was refluxed with MoO$_2$(acac)$_2$ (0.326 g, 1 mM) in 10 mL of methanol under air for 12 h. The desired MoO$_2$ complex was filtered off, washed with dichloromethane and methanol, and dried in vacuum. Yield: 83%. IR (KBr, cm^{-1}): 3415 (br, ν(OH + H-bonding)); 2929, 2810, 2765 (w, νC–H); 1631 (s, m, νC=N); 1487, 1457 (s, νC=C vibration band of the aromatic ring), 948 (w, νMo=O), 900 (m, νMo=O). UV–vis (DMSO), λ_{max} (ε) (nm (10^5 dm^3 M^{-1} cm^{-1}): 260 (0.178), 327 (0.088). Anal. Calcd (found) for $C_{22}H_{24}N_4O_4$-Mo·(3H$_2$O·1/3 CH$_3$OH): C, 47.12 (46.75); H, 5.54 (5.49); N, 9.84 (9.84).

2.2.7. Preparation of [piperazinCH$_2${MoO$_2$(Salophen)}]$_n$ (7). The procedure was similar to the one used for synthesis of **6**. Dichloromethane solution of **4** (0.424 g, 1 mM) was refluxed with MoO$_2$(acac)$_2$ (0.326 g, 1 mM) in methanol (10 mL) under air for 12 h. The desired MoO$_2$ complex was filtered off, washed with dichloromethane and methanol, and dried in vacuum. Yield: 79%. IR (KBr, cm^{-1}): 3435 (br, ν(OH + H-bonding)), 2926, 2813, 2790 (w, νC–H); 1621 (s, νC=N), 1485 (s, νC=C vibration band of the aromatic ring), 933 (w, νMo=O), 897 (m, νMo=O). UV–vis (DMSO), λ_{max} (ε) (nm (10^5 dm^3 M^{-1} cm^{-1}): 260 (0.310), 323 (0.210), 370 (0.106), 500 (0.021). Anal. Calcd (found) for $C_{26}H_{24}N_4O_4$-Mo·(3H$_2$O·1/3 CH$_3$OH): C, 51.24 (51.01); H, 5.12 (5.18); N, 9.08 (9.12).

2.2.8. Preparation of [piperazinCH$_2${MoO$_2$(Salpn)}]$_n$ (8). The procedure was similar to the one used for synthesis of **6**. Dichloromethane solution of **5** (0.392 g, 1 mM) was refluxed with MoO$_2$(acac)$_2$ (0.326 g, 1 mM) in methanol (10 mL) under air for 12 h. The desired MoO$_2$ complex was filtered off, washed with dichloromethane and methanol, and dried in vacuum. Yield: 82%. IR (KBr, cm^{-1}): 3432 (br, ν(OH + H-bonding)); 2929, 2964, 2819, 2772 (s, νC–H); 1631 (s, νC = N); 1492, 1454 (s, νC = C vibration band of the aromatic ring); 948.7 (w, νMo = O); 899 (m, νMo = O). UV–vis (DMSO), λ_{max} (ε) (nm (10^5 dm^3 M^{-1} cm^{-1}): 260 (0.185), 327 (0.088). Anal. Calcd (found) for $C_{23}H_{26}N_4O_4$Mo·(3H$_2$O·1/3 CH$_3$OH): C, 48.00 (47.82); H, 5.76 (5.71); N, 9.61 (9.62).

2.3. *Catalytic reactions*

2.3.1. General procedure for oxidation of olefins. A mixture of the substrate (1 mM), polymeric MoO$_2$Salen complexes (0.005 mM) and $C_2H_4Cl_2$ (2 mL) was stirred in a 5-mL tube for 10 min at 75°C. The oxidant TBHP (80% in di-tert-butyl peroxide/water 3:2) (1 mM) was then added, and the system was stirred for 4–12 h at 75°C, and the reaction progress was monitored by GC. Assignments of products were made by comparison with authentic samples. All reactions were run at least in duplicate.

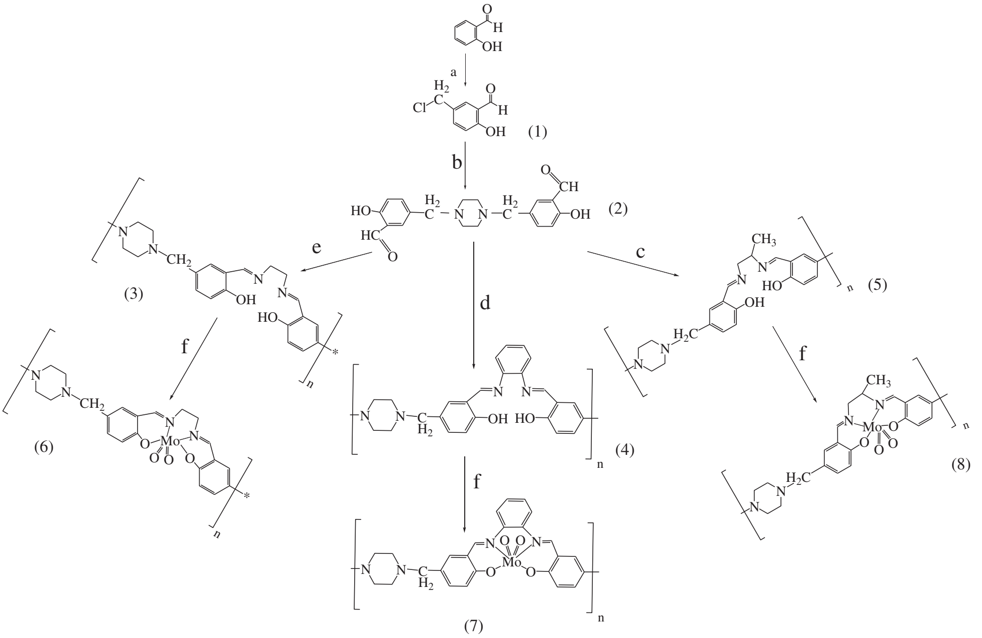
2.3.2. General procedure for oxidation of sulfides. A mixture of MPS (3mM), polymeric MoO$_2$Salen complexes (0.005 mM) and (1 : 1) mixture of CH$_3$OH/CH$_2$Cl$_2$ (2 mL) was stirred in a 5-mL tube for 10 min at room temperature. The oxidant UHP (3.75 mM) was then added, and the system was stirred at room temperature for approximately 2 h, and the reaction progress, was monitored by GC. Assignments of products were made by comparison with authentic samples. All reactions were run at least in duplicate.

3. Results and discussion

3.1. *Synthesis and characterization*

Scheme 1 shows the synthesis of polymeric $[MoO_2(Salen)]$ complexes with ethylenediamine, orthophenylenediamine and 1,2-propanediamine. Compound **1**, a starting compound in this approach, was synthesized by reacting salicaldehyde with paraformaldehyde $(CH_2O)_n$ in the presence of HCl. The reaction of 5-(chloromethyl)salicylaldehyde with piperazine yielded 5,5′-(N,N-piperazine bis(methylene))-bis-(salicylaldehyde). The polymeric ligands (**3**, **4**, and **5**) were easily prepared by condensation of dialdehyde with a diamine in excellent yield. Mo (VI) complexes (**6**, **7**, and **8**) were synthesized by reaction of corresponding polymeric ligands with $MoO_2(acac)_2$ under reflux in air in mixture of MeOH and dichloromethane for 12 h. The compounds were characterized by various spectroscopic and analytical techniques (data are given in the experimental section).

Polymeric ligands **3**, **4**, and **5** are very slightly soluble in THF, methanol, and ethanol but soluble in chloroform, dichloromethane, DMF and DMSO. Polymers **6**, **7**, and **8** are insoluble in common solvents but very slightly soluble in DMF, and DMSO. All compounds are air-stable solids. These compounds are formulated on the basis of elemental analysis and a variety of physical measurements. In ^1H NMR spectrum of **1**, the resonance



Scheme 1. Procedure for the synthesis of molybdenum-containing polymers. The process starts with chloromethylation of salicylaldehyde to form 5-(chloromethyl)salicylaldehyde (**1**) and then reaction with piperazine for formation of dialdehyde. This was followed by addition of ethylenediamine, orthophenylenediamine or 1,2-propanediamine to dialdehyde for formation of polymeric ligands (**3**, **4** and **5**), and finally the binding of MoO_2 to the polymeric ligands (**6**, **7** and **8**). Reagents and conditions: (a) CH_2O,HCl, stirring at 20 °C, 5 h, (b) piperazine, triethylamine, CH_2Cl_2, stirring at room temparature, 24 h, (c) 1,2-propanediamine, CH_2Cl_2, reflux, 6 h, (d) orthophenylenediamine, CH_2Cl_2, reflux, 6 h, (e) ethylenediamine, CH_2Cl_2, reflux, 6 h, (f) $MoO_2(acac)_2$, CH_3OH,CH_2Cl_2, reflux, 12 h.

of CH_2 attached to benzene appears at 4.63 ppm. The ^1H NMR spectrum of **2** shows a singlet at 2.5 ppm for CH_2 protons of piperazine as linker. The signal at δ 9.92 ppm (proton of aldehyde) in the spectrum of **2** disappears because of formation of ligand. A peak for HC=N is at 8.37 and 8.64 ppm in the case of **3** and **4**, respectively, whereas for **5** two peaks are at 8.33 and 8.37 ppm. The splitting of the signals in the ^1H NMR spectrum of **5** confirms the nonequivalence of C=N bands [18–20]. IR spectra of ligands show intense bands at 1634, 1619, and 1634 cm^{-1} for **3**, **4,** and **5** associated with the C=N stretch of the free ligands, which shift to 1631, 1621, and 1631 cm^{-1}, respectively, in the corresponding complexes (**6**, **7,** and **8**, respectively), indicating coordination of azomethine nitrogen [21]. Molybdenum complexes exhibit two (O=Mo=O) vibrations at 930–950 and 890–900 cm^{-1}, confirming the presence of a *cis*-MoO_2 structure [20, 22]. UV–vis spectra of **3** and **5** in DMSO exhibit two bands at 260 and 320 nm due to π–π^* and n–π^* transitions, respectively. The π–π^* band has no definite trend in metal complexes while n–π^* transition shifts to higher wavelengths, indicating coordination of the azomethine nitrogen to Mo(VI). The band due to ligand to metal charge transition in **6** and **8** is generally not observed. Complex **7** shows a band at 500 nm due to ligand to metal charge transfer [21], in addition to bands in the UV region, which correspond to the π–π^* and n–π^* transitions of the ligand.

The ICPAES data confirm complete metalation of the ligands to give the polymeric complexes.

3.2. *Catalytic activities*

3.2.1. Oxidation of olefins. To test the catalytic potential of the complexes prepared, cyclooctene was chosen as a model substrate. Thus, the oxidation of cyclooctene catalyzed by **6** was carried out using TBHP as an oxidant. The effect of various reaction media have been studied on catalytic epoxidation of cyclooctene catalyzed by **6** (table 1). It is apparent that the efficiency of the catalysts in different solvents decreases in the order dichloroethane > acetonitrile > dichloromethane > toluene > methanol > DMF. No clear relationship exists between the dielectric properties of these solvents and the catalytic activity, which may be at least partly because of the major differences in polarity between the olefin and the oxidant. The detrimental effect of methanol on the reaction rate may be related with its polar protic nature inhibiting the reaction by competing with the oxidant for coordination to the metal center similar to tert-butyl alcohol, a by-product of the decomposition of TBHP [23]. Use of acetonitrile, an aprotic coordinating solvent, led to a

Table 1. Effect of solvent on conversion in oxidation of cyclooctene with TBHP[a].

Entry	Solvent	Con %[b]	Selectivity to epoxide %[b]
1	DMF	0	–
2	CH_3OH	28	>99
3	CH_3CN	86	98
4	CH_2Cl_2	12	>99
5	$C_2H_4Cl_2$	95	98
6	Toluene	39	>99

[a] Reaction condition: The molar ratio for catalyst : alkene : TBHP are 1 : 200 : 200. The reactions were run for 12 h at 75 °C.

[b] GC conversion based on starting alkene.

quite reasonable epoxide yield of 86% after 12 h. The poorer yields obtained with CH_2Cl_2 are probably caused by the lower reaction temperature at reflux.

Several TBHP sources were tested in oxidation of cyclooctene, TBHP (70%) in water, TBHP (80%) in di-tert-butyl peroxide/water 3:2, TBHP (5.0–6.0 M) in decane and TBHP (70%) in water in the presence of di-tert-butyl peroxide (figure 1) with catalyst **6** in 1,2-dichloroethane. Both TBHP in di-tert-butyl peroxide/water and TBHP in decane show the highest yields (98%) after 12 h at 75 °C; TBHP in water and TBHP in water in the

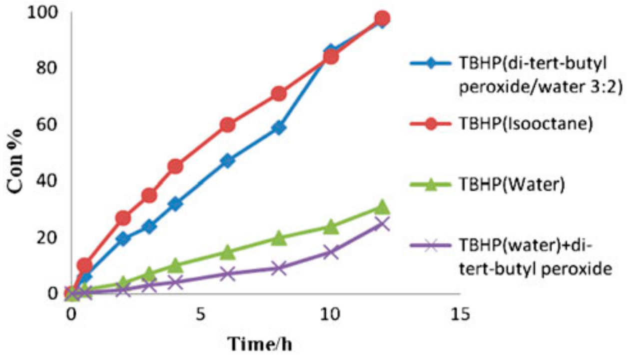
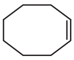
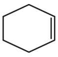
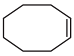
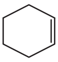
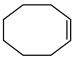
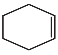
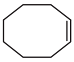
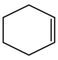


Figure 1. Epoxidation of cyclooctene catalyzed using [piperazinCH_2{MoO_2(Salen)}]$_n$ with various TBHP at 75 °C for 12 h in 2 mL of 1,2-dichloroethane.

Table 2. Catalytic oxidation of various alkenes with TBHP by polymeric [MoO_2(Salen)] complexes[a].

Catalyst	Substrate	Con %[b] (time)	Selectivity to epoxide % (time)
[PiperazinCH_2{MoO_2(Salen)}]$_n$		95 (12 h)	98 (12 h)
		73 (12 h) 94 (18 h)	92 (12 h) 86 (18 h)
[PiperazinCH_2{MoO_2(Salphen)}]$_n$		89 (12 h)	97 (12 h)
		68 (12 h) 92 (18 h)	92 (12 h) 84 (18 h)
[PiperazinCH_2{MoO_2(Salpn)}]$_n$		93 (12 h)	97 (12 h)
		82 (12 h) 97 (18 h)	99 (12 h) 92 (18 h)
[PiperazinCH_2{MoO_2(Salen)}]$_n$[c]		85 (12 h)	98 (12 h)
		60 (12 h)	96 (12 h)

[a] Reaction condition: The molar ratio for catalyst : alkene : TBHP are 1 : 200 : 200. The reactions were run at 75 °C in 2 mL of 1,2-dichloroethane.
[b] GC conversion based on starting alkene.
[c] GC conversion in the presence of the radical scavenger.

presence of di-tert-butyl peroxide show much lower yields (<32%). The significant difference in the cyclooctene oxide yield in case of various oxidants can be explained by an inhibition due to water during the catalytic test. Furthermore, the results show that di-tert-butyl peroxide does not accelerate the oxidation of cyclooctene.

Catalytic activities of the prepared catalysts were studied through oxidation of olefins with TBHP in 1,2-dicholoroethane. The results are given in table 2. Generally, excellent yields and selectivity toward epoxide are observed for cyclooctene and cyclohexene.

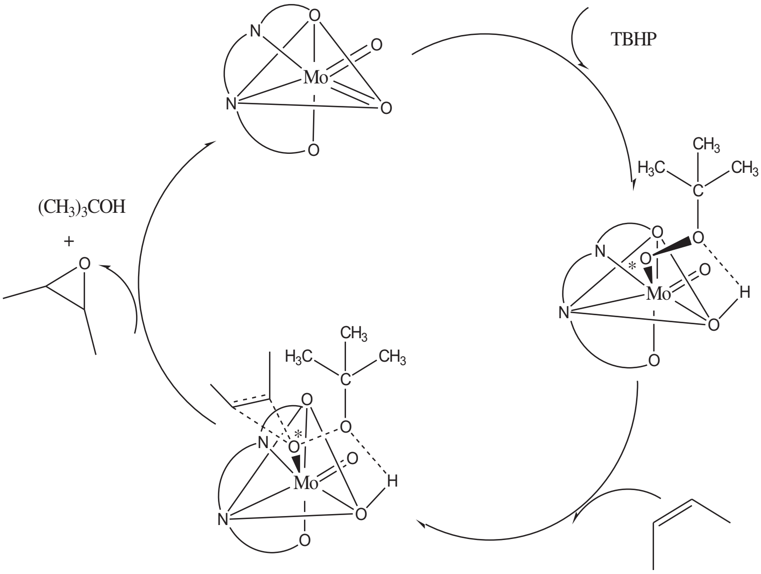
To provide evidence about mechanism, oxygenations of cyclohexene were performed. The data for oxygenation of cyclohexene show very low selectivity with allylic attack, showing that catalytic reaction occurs via nonradical processes [24].

Furthermore, molybdenum catalysis of the oxidation of cyclooctene and cyclohexene was carried out with tert-butyl hydroperoxide in the presence of ionol (2,6-di-tertbutyl-p-cresol) as radical scavenger (table 2). Since the catalytic epoxidation was both slightly inhibited in the presence of ionol, a free radical chain mechanism is excluded.

Based on the result of the study, we suggest a mechanism via a seven-coordinate intermediate (scheme 2) similar to the mechanism outlined [25].

It is assumed that the first step in the proposed sequence is formation of a seven-coordinate species as intermediate (possibly the catalytically active species) containing coordinated peroxide and a protonated oxo. The subsequent step in the sequence proceeds by approach of olefin to coordinated oxygen (*). Herein, the metal center is a Lewis acid, removing charge from the O–O bond, facilitating its dissociation, and activating the nearest oxygen (*) for insertion into the olefin double bond. The intermediate exhibits a hydrogen bond between the oxygen and coordinated OH, favoring formation of epoxide and release of alcohol from the precursor complex.

In the case of styrene epoxidation more than 90% yield was achieved at the end of the first run. However, polymers were decomposed by benzoic acid formed during the oxidation reaction.



Scheme 2. Proposed mechanism for oxidation of alkene with [piperazinCH$_2${MoO$_2$(Salen)}]$_n$ polymer in the presence of TBHP.

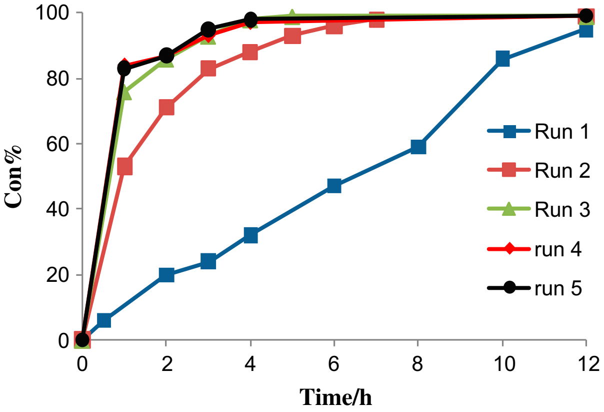


Figure 2. Conversion curves for the epoxidation of cyclooctene catalyzed using $[piperazinCH_2\{MoO_2(Salen)\}]_n$ with TBHP in five consecutive reactions.

The major advantages of heterogeneous catalysis over its homogeneous counterpart are the ease of recovering and reusability of the catalyst. To confirm that reusability of $[MoO_2(Salen)]_n$ arises from the polymer-bound metal, after completion of the first cycle, the catalyst was recovered from the reaction mixture by centrifugation, washed sequentially with dichloroethane and dried for 3 h at 40 °C. Then, the recovered catalyst was added to fresh substrates under identical conditions for five consecutive runs in the epoxidation of cyclooctene at 75°C. The results are summarized in figure 2, where it is seen that in the first run the catalyst exhibits less activity in epoxide formation in comparison with the following runs. This may be due to swelling of polymeric support which leads to change in the degree of accessibility of catalytically active sites. The conversion curves for runs four and five look very similar. Therefore, it can be concluded that the activity of the catalyst in the epoxidation of cyclooctene remains stable after run four.

To find whether molybdenum leaching occurs during the reaction, we have estimated the amount of molybdenum of the catalyst by ICPAES. In this manner, the filtrates were collected after each run and checked for activity and quantities of Mo (which could have leached from the catalyst) (table 3). Increase in the amount of leached Mo was observed through five runs. The results show the Mo species leached out during the catalytic reaction slightly increase through five cycles.

Furthermore, to understand the nature of catalyst, IR and UV–Vis spectrophotometric measurements were carried out for fresh and used catalyst (after the 5th reaction). figure 3

Table 3. Recycling of catalyst in oxidation of cyclooctene with TBHP[a].

Run	Con % (time)	Selectivity to epoxide[b]	Leaching to Mo (wt.%)[c]
1	95 (12 h)	98	0.071
2	98 (7 h)	98	–
3	99 (5 h)	98	0.143
4	97 (4 h)	98	–
5	98 (4 h)	98	0.178

[a] Reaction condition: The molar ratio for catalyst : cyclooctene : TBHP are 1 : 200 : 200. The reactions were run for 12 h at 75 °C in 2 mL of 1,2-dichloroethane.

[b] GC conversion based on starting styrene.

[c] Determined by ICPAES.

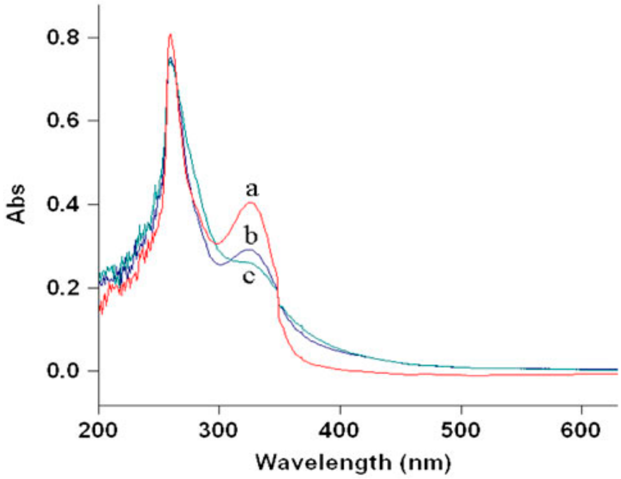


Figure 3. UV–Vis spectra of the samples: (a) fresh catalyst, (b) used catalyst in sulfoxidation after run five, (c) used catalyst in epoxidation after run five.

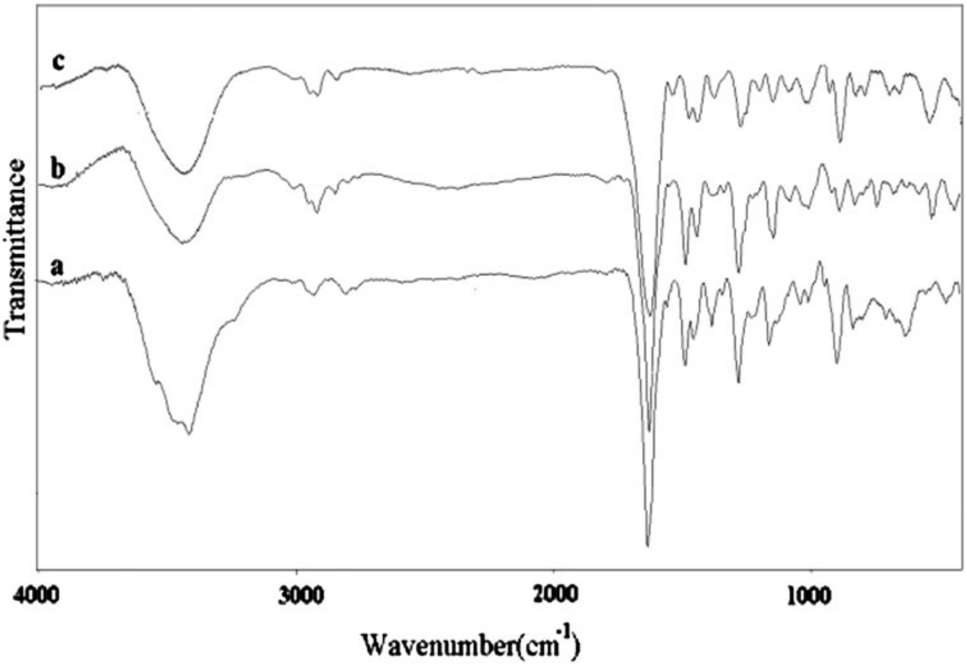


Figure 4. FT-IR spectra of the samples: (a) fresh catalyst, (b) used catalyst in sulfoxidation after run five, (c) used catalyst in epoxidation after run five.

shows the UV–Vis spectra of as-prepared and spent catalyst, lines a and c, respectively. The UV–Vis spectrum of the catalyst after oxygenation shows only the original absorption bands with almost the same intensities.

As shown in figure 4(c), the IR spectrum of the catalyst after use for oxygenation of cyclooctene shows the characteristic ν(C=N), ν(C–H) and $\nu(MoO_2)$ absorption bands, and the positions are in close agreement with the values for the as-prepared sample shown in figure 4(a). The small change in the signal intensity and position is probably due to band overlapping or shifting by coexisting tert-BuOH and cyclooctene oxide. On the basis of these experiments, it appears that heterogeneous catalyst is stable under reaction condition.

3.2.2. Oxidation of sulfide. In order to find optimized conditions for oxidation of sulfides with UHP catalyzed by $[piperazinCH_2\{MoO_2(Salen)\}]_n$, MPS is used as the substrate. The molar ratio 1:600:750 of the catalyst : MPS : UHP is optimum molar ratio for the catalytic system. Different solvents such as acetone, dichloromethane, acetonitrile, DMF, CH_3OH, 1,2-dichloroethane, and mixture of CH_3OH/CH_2Cl_2 were also examined for the oxidation of MPS by UHP. Mixture of CH_3OH/CH_2Cl_2 gave the highest conversion of MPS. Urea hydrogen peroxide (UHP) is not completely soluble in less polar organic solvents such as acetone, dichloromethane, 1,2-dichloroethane, and acetonitrile, so the oxidation yield is low in these solvents (entries 1–4, table 4).

To improve the conversion rate and yield of sulfoxide, various molar ratios of UHP/sulfide in the catalytic oxidation of MPS were examined in mixture of CH_3OH/CH_2Cl_2 (figure 5). The conversion of MPS oxidation improves from 87 to 96% as the

Table 4. The oxidation of sulfide by $[piperazinCH_2\{MoO_2(Salen)\}]_n$ with UHP in various solvents[a].

Entry	Solvent	Con %[b]	Selectivity to sulfoxide %[b]
1	CH_2Cl_2	2	100
2	$C_2H_4Cl_2$	17	65
3	CH_3CN	64	62
4	CH_3COCH_3	37	67
5	DMF	30	60
6	$CH_2Cl_2 : CH_3OH$	87	89
7	CH_3OH	75	84

[a]Conditions: The molar ratio for catalyst : MPS : UHP is 1 : 80 : 80. The reactions were run for 2 h at room temperature.
[b]GC yields based on the starting MPS.

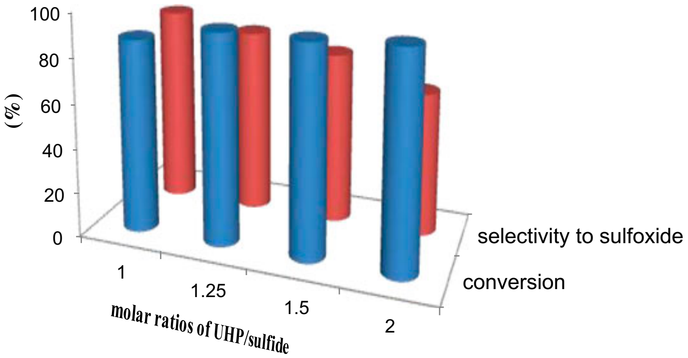


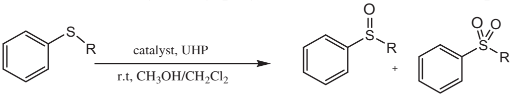
Figure 5. Effect of UHP/sulfide molar ratios on the catalytic performance of $[piperazinCH_2\{MoO_2(Salen)\}]_n$ with UHP in 2 mL of CH_3OH/CH_2Cl_2.

Table 5. Effect of MPS/catalyst molar ratios on the catalytic performance of heterogeneous catalytic systems in sulfide oxidation[a].

Substrate to catalyst ratio	Con %[b]	Selectivity to sulfoxide %[b]	TON[b]
80	94	83	75
100	95	81	95
200	94	81	188
600	95	84	570
1000	87	76	870

[a]Reaction condition: The molar ratio for MPS : UHP is 1 : 25. The reactions were run for 2 h at room temperature in 2 mL of CH_3OH/CH_2Cl_2.
[b]TON is mole of product per mole catalyst. GC conversion based on starting MPS.

Table 6. Oxidation of various sulfides catalyzed by polymeric [MoO_2(Salen)] complexes[b].



Catalyst	R	Con %[b] ()[c]	Selectivity to sulfoxide %[b] ()[c]
[PiperazinCH$_2${MoO_2(Salen)}]$_n$	CH_3	95	84
	CH_3CH_2	77	–
	Ph	20 (55)	85 (88)
	Ph-CH_2	21 (62)	83 (84)
[PiperazinCH$_2${MoO_2(Salphen)}]$_n$	CH_3	96	86
	CH_3CH_2	84	–
	Ph	26 (60)	84 (84)
	Ph-CH_2	28 (66)	86 (88)
[PiperazinCH$_2${MoO_2(Salpn)}]$_n$	CH_3	98	93
	CH_3CH_2	80	–
	Ph	22 (56)	84 (86)
	Ph-CH_2	23 (64)	83 (83)

[a]Conditions: The molar ratio for catalyst : MPS : UHP is 1 : 600 : 750. The reactions were run for 2 h at room temperature in 2 mL of CH_3OH/CH_2Cl_2.
[b]GC yields based on the starting sulfide.
[c]The reactions were run for 6 h.

molar ratio increases from 1 to 2. Simultaneously, the selectivity of sulfoxide drops remarkably from 89 to 64%. Thus, 1.25 ratio of UHP/sulfide that affords sulfoxide as major product is used as optimum condition for oxidation of other substrates.

The effect of substrate to catalyst ratios (S/C) on the turnover number (TON) is illustrated in table 5. The reactions proceed at S/C ratio from 80 to 1000 with increasing TON. The selectivity of sulfoxide increases until substrate to catalyst ratio reach to 600 and then decreases.

Encouraged by the excellent catalytic performance for the MPS oxidation to sulfoxide, the oxidations of various sulfides were carried out with UHP catalyzed by polymeric complexes of molybdenum. All polymeric complexes are active (table 6) in the oxidation of sulfides with similar reactivity; changing diamine moieties does not have significant effect on the catalyst activity.

Based on Chand *et al*. [26], organic sulfides are oxidized by hydrogen peroxide in a catalytic cycle involving nucleophilic attack of sulfur on oxygen in the oxoperoxo intermediate where positive charge is induced by the Lewis acidic metal center or coordination of

Table 7. Recycling of catalyst in oxidation of MPS with UHP[a].

Run	Con %[b]	Selectivity to sulfoxide %[b]	Leaching to Mo (wt.%)[c]
1	95	84	0.191
2	94	82	–
3	90	81	0.178
4	88	74	–
5	86	65	0.036

[a] Conditions: The molar ratio for catalyst : MPS : UHP is 1 : 600 : 750. The reactions were run for 2 h at room temperature in 2 mL of CH_3OH/CH_2Cl_2.
[b] GC yields based on the starting MPS.
[c] Determined by ICPAES.

the sulfide to the metal. Obviously, the rate of reaction can be controlled by sulfide electronic and steric effects. The yield of the oxidation of sulfides increases with nucleophilic addition of sulfur on oxoperoxo intermediate. Then, replacement of phenyl or benzyl with alkyl decreases the reaction rate.

In order to evaluate the stability of the catalyst, a sample of the catalyst was employed in five consecutive runs in the reaction of MPS with UHP in mixture of CH_3OH/CH_2Cl_2 at room temperature for 2 h (table 7). The heterogenized catalyst was reused several times with a conversion ranging from 95% at the beginning to 86% at the fifth run, with a decrease in the selectivity of sulfoxide. In addition, filtration of $[piperazinCH_2\{MoO_2(Salen)\}]_n$ from the reaction mixtures followed by ICPAS of the reaction solution showed that Mo leaching into solution amounted to < 0.2 wt.%. Therefore, metal loss should not be the main factor responsible for the observed decrease in catalytic activity and sulfoxide selectivity. It is probably due to competitive adsorption of reactant and product at the catalytically active sites. Furthermore, blocking of the active sites of catalyst by the solvent may also contribute to the reduction in conversion with recycling.

We examined the filtrate of reactions without adding fresh catalyst to see whether these display catalytic activity (figure 6). The conversion of curves derived from sulfoxidation using the filtrate as a potential catalyst show that active Mo species are present in all the filtrates. For run one, MPS could be converted at a relatively high rate in filtrates, which means that leaching of active species occurs during the reaction and thus plays an impor-

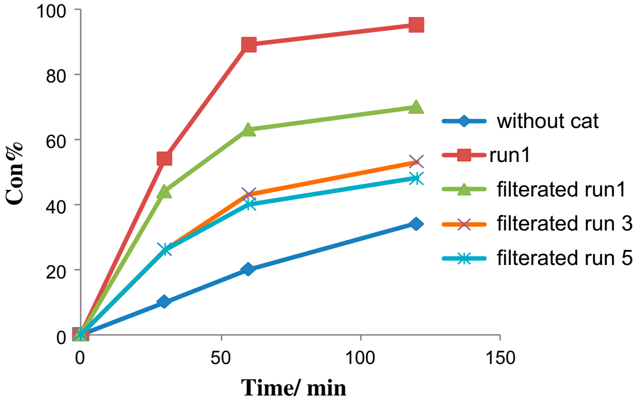


Figure 6. Conversion curves for the oxidation of methylphenylsulfide at room temperature catalyzed using filtrates with UHP.

Table 8. Comparison of literature reports on the selective oxidation of MPS and oxidation of cyclooctene under various conditions.

Entry	Catalyst	Molar ratio cat : sub : ox	Substrate	Temp. (°C)	Time (h)	Conv. %	Selectivity[a] %	Refs.
1	6	1 : 200 : 200	Cyclooctene	75	12(4)[b]	95	98	This work
2	Mo-MCM-41	1 : 68 : 205	Cyclooctene	40	3	97	90	[28]
3	[Ni(L1)]@Mont	1 : 150 : 150	Cyclooctene	Reflux (CH_3CN)	12	67.6	65	[29]
4	PMO-phMo$(CO)_3$	1 : 100 : 154	Cyclooctene	55	0.5	100	100	[30]
5	LP-TEPPPO-Mo	0.1 : 42 : 64	Cyclooctene	55	24	87	100	[31]
6	6	1 : 600 : 750	MPS	r.t	2	95	84	This work
7	MCM-Mo	1 : 200 : 300	MPS	40	1	99	99	[32]
8	Fe_3O_4@SiO_2@VO(salen)	1 : 12.9 : 14.5	MPS	r.t	6	93	95	[33]
9	Silica-based tungstate interphase	1 : 50 : 75	MPS	r.t	1.5	99	82	[34]

[a] Selectivity to cyclooctene epoxide for cyclooctene; selectivity to methyl phenyl sulfoxide for MPS.

[b] Reaction time for fifth run.

tant role for catalytic performance of this material. For runs three and five, sulfoxidation is continued at low rate after the solid catalyst is removed, which means that a small part of the active species is leached from the catalyst. In general, the activity displayed by the filtrates decreases progressively, so that conversions achieved in the fifth run are typically only 20% above that of the control reaction measured in the absence of the catalyst. It seems clear that in MoO_2(Salen) catalysis arises from heterogeneous complex incorporated in polymer and Mo species lost from the support. However, contribution of the heterogeneous catalyst to species lost from the support increases through five cycles. Similar behavior has been observed for polybenzimidazole-supported molybdenum catalysts for oxidation of alkene by Sherrington *et al.* [27] Therein, both polymer-supported Mo and Mo species leached out during the reaction contribute to catalysis after ten runs.

IR and UV–Vis spectra confirm the similarity of structures of the starting and recovered materials. UV spectra of the fresh and used catalysts show two broad bands at 260 and 327 nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions and IR spectra of the spent catalyst show a similar pattern to fresh catalyst, indicating the stability of the catalyst under relatively harsh reaction conditions.

For comparison, some of the most relevant systems reported to date have been included in table 8. These results clearly point out the efficiency of the proposed catalytic systems (table 8, first and sixth entries) in both activity and selectivity in epoxidation and oxidation of sulfide reactions as compared to literature reports involving several heterogeneous systems under various conditions (table 8, entries 2–5 and entries 7–9).

4. Conclusion

Mo-Schiff base polymers, where the polymer linkage is formed by piperazine, have been synthesized and characterized by elemental analyses and IR, UV–Vis, and ^{1}H NMR spectroscopies. Linked Schiff base polymers have been studied as hetereogeneous catalysts for epoxidation of olefins and sulfoxidation. All compounds were active and selective catalysts. According to our data for oxidation of alkenes and sulfides with catalysts precursors **6–8**, no clear trend of different catalytic reactivity was found upon change of the diamine of the Schiff base. Investigation about reusability of [piperazin$CH_2\{MoO_2$(Salen)$\}]_n$ indicated that in the first run the incorporated catalyst exhibited a smaller activity in epoxide formation in comparison with following runs. The polymeric complex could be reused at least five times with a decrease in activity and selectivity in sulfoxidation. On the basis of MPS oxidation results, in addition to polymer-supported Mo, species leached out in solution contribute to catalysis but decrease through consecutive runs. Furthermore, the fresh and recovered catalysts were studied by IR and UV–Vis spectra with little differences in the IR and UV–Vis spectra, indicating that the catalyst has a similar composition and good stability after recycle.

Acknowledgment

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