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# Schiff base complexes of Mo(VI) immobilized on functionalized graphene oxide nano-sheets for the catalytic epoxidation of alkenes

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#### ABSTRACT

Mo(VI) tetradentate Schiff base complexes were covalently immobilized onto chemically functionalized graphene oxide (GO) using 3-(tri-methoxysilyl) propylamine as a coupler. The resulting heterogeneous catalysts have been characterized by FTIR, DRS, XRD, SEM, TGA, and atomic absorption spectroscopy (AAS). These catalysts were applied in epoxidation of cyclooctene and other olefins. The catalytic procedures with all catalysts were optimized for different parameters such as oxidant, solvent and temperature. Recycling results indicated that the catalysts were highly stable and maintained activity and selectivity even after being used for five cycles.



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#### **KEYWORDS**

Mo(VI) Schiff base complexes; graphene oxide; alkene epoxidation; heterogeneous catalyst

# 1. Introduction

Catalytic epoxidation of alkenes is of interest for the synthesis of fine chemicals. Because of their versatility as intermediates, epoxies have great value in chemical technology and synthetic organic chemistry [1]. Epoxides react to provide industrially important products such as antistatic agents, detergents, corrosion protection agents,



Scheme 1. Preparation of L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> dialdehydes.

surfactants, textiles, lubricating oils and cosmetics [2]. Large epoxides are fine chemicals with interesting chemical properties, *e.g.* cyclooctene oxides are extensively used in the manufacturing of pesticides, pharmaceuticals and polyesters [3]. Mo(VI) Schiff base complexes have been used as oxidation catalysts for organic substrates, because Mo(VI) complexes offer advantages such as environmental, economic and commercially available [4]. The fundamental role of molybdenum-based catalysts for production of both fine chemicals and bulk chemicals has increased attention toward this metal [5]. Dioxomolybdenum(VI) complexes of tetradentate Schiff bases [6], dimethyldioxo Mo(VI) diazabutadiene and dichloro were reported as active epoxidation catalysts [7].

One of the main problems of homogeneous transition metal complexes as catalysts is the formation of oxo and peroxo dimeric and other polymeric species [8]. The formation of these compounds can deactivate catalysts irreversibly. This problem may be solved by supporting of the metal complexes within solid supports so it can separate complexes from each other [9]. Meanwhile, the separation, recycling, inadequate stability of homogeneous catalysts and leaching of the active metal into the solvent are part of serious problems. Heterogenization of homogeneous catalysts onto solid supports has been studied because of the long catalytic lifetime, thermal stability, easy separation, easy recyclability and high selectivity [10]. A main method for heterogenizing of homogenous catalyst is to anchor the soluble catalyst on to large surface area inorganic supports [11].

Many different solid materials have been tested for heterogenization, such as mesoporous silica, carbon materials, organic polymers, clays, metal-organic frameworks, *etc.* [12, 13]. Graphene shows promise as a future material in composite materials, sensors, hydrogen storage, drug delivery, solar cells and catalysis due to its optical, electrical, thermal and mechanical characteristics [14, 15]. Graphene oxide (GO) possesses advantages, including facile synthesis, high surface area, substantial solubility, low toxicity, good hydrophilicity, and excellent biocompatibility [16–18]. Owing to the presence of carboxyl, hydroxyl, carbonyl, and epoxy groups, oxygen functionality modifications can establish sites for anchoring complexes and ions [19]. Therefore, it has been recognized as an ideal candidate for immobilizing various transition metal complexes.

In this study we report the synthesis and characterization of new Mo(VI) tetradentate Schiff base complexes immobilized onto chemically functionalized graphene oxide (GO) using 3-(tri-methoxysilyI) propylamine (Schemes 1 and 2) and their application in epoxidation of different alkene substrates.



R=H, MoO<sub>2</sub>L<sub>1</sub>-GO. R=Br,MoO<sub>2</sub>L<sub>2</sub>-GO. R=OCH<sub>3</sub>, MoO<sub>2</sub>L<sub>3</sub>-GO

Scheme 2. Schematic outline of synthesis of MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO.

# 2. Experimental

# 2.1. Materials and physical measurements

Solvents and reagents were purchased from Merck or Fluka and used without further purification. <sup>1</sup>H-NMR spectra were recorded on a Bruker Asend TM 400 MHz spectrometer in DMSO-d<sub>6</sub> and CDCl<sub>3</sub> using tetramethylsilane (TMS) as an internal reference. FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. Diffuse reflectance spectra (DRS) were registered on a Scinco 4100 from 200-1100 nm using 6890 series. XRD patterns were recorded by a Rigaku D-Max C III, X-ray diffract-ometer using Ni-filtered Cu Ka radiation. The metal contents of the catalysts were

measured by Atomic Absorption Spectrophotometer (AAS-Perkin–Elmer 4100-1319) using a flame approach. The purity of the solvents and analysis of the oxidation products were determined by gas chromatography using an Agilent 7890 with a capillary column and FID detector.

# **2.2. Synthesis of L**<sub>1</sub>

To a stirred solution of salicylaldehyde (50 mmol) and  $K_2CO_3$  (3.05 g, 25 mmol) in DMF (75 mL) was added dropwise 1,2-dibromoethane (9.4 g, 50 mmol) in DMF (25 mL). The reaction was continued for 6 h in 150 °C and then 1 h at room temperature. After the addition was completed, 250 mL of distillated water was added and the mixture was put in the refrigerator; 1 h later the precipitate was filtered and washed with 500 mL distilled water, then dried in air and recrystallized from ethanol and dried in vacuum.

**L**<sub>1</sub>. Yield: 4.99 g (76%), m.p: 130 °C, Color: cream. IR (KBr, ν cm<sup>-1</sup>): 1675 ν (C=O), 1484, 1468 ν (Ar-C=C), 1285, 1235 ν (Ar-O), 1173, 1045 ν (R-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ (ppm) d 9.86 (s, 2 H, CHO), 7.93 (d, 4 H, Ar*H*), 7.23 (d, 4 H, Ar*H*), 4.40 (s, 4 H, OCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 190.5, 162.7, 131.2, 129.1, 114.6, 64.2 ppm.

# **2.3.** Synthesis of $L_2$ and $L_3$

5-Bromo-2-hydroxybenzaldehyde or 5-methoxy-2-hydroxybenzaldehyde (50 mmol) was dissolved in 75 mL DMF and potassium carbonate (3.05 g, 25 mmol) was added, and the mixture was stirred at room temperature; 1,2-dibromoethane (9.4 g, 25 mmol) was added dropwise and then the reaction mixture was stirred under reflux for 6 h. The mixture was partitioned between water and ethylacetate. The ethyl acetate layer was collected and concentrated under reduced pressure and then subjected to silica gel 100-200 mesh column chromatography using 1:10 hexane ethylacetate as eluent to afford compounds in pure form.

**L**<sub>2</sub>. Yield: 8.35 g (78%), m.p: 143 °C, Color: cream. IR (KBr, v cm<sup>-1</sup>): 1678 v (C=O), 1491, 1471 v (Ar-C=C), 1289, 1237 v (Ar-O), 1176, 1049 v (R-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ (ppm) 10.20 (s, 2 H, CHO), 7.83 (dd, 2 H, Ar*H*), 7.73 (d, 2 H, Ar*H*), 7.33 (d, 2 H, Ar*H*), 4.58 (s, 4 H, OCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 195.6, 160.6, 139.6, 136.0, 121.8, 120.1, 111.7, 64.8 ppm.

**L**<sub>3</sub>. Yield: 5.78 g (70%), m.p: 118 °C, Color: cream. IR (KBr, ν cm<sup>-1</sup>): 1673 ν (C = O), 1495, 1477 ν (Ar-C = C), 1283, 1234 ν (Ar-O), 1170, 1042 ν (R-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 10.52 (s, 2 H, CHO), 7.41 – 7.45 (m, 2 H, Ar*H*), 7.26 (s, 2 H, ArH), 7.14 (d, 2 H, Ar*H*), 4.50 (s, 4 H, OCH<sub>2</sub>), 3.88 (s, 3 H, OCH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 189.5, 156.1, 153.4, 125.2, 123.3, 114.4, 110.2, 64.7, 55.6 ppm.

# 2.4. Synthesis of GO

Graphene oxide (GO) was prepared by oxidation and exfoliation of graphite powder according to the modified Hummers method [20]. In a typical experiment, graphite powder (2.0 g) and 46 mL of conc.  $H_2SO_4$  were mixed in a 500 mL flask. The resulting mixture was cooled to 0°C in an ice bath under stirring for 2 h. KMnO<sub>4</sub> (6g) was

added with vigorous stirring and the flask was kept oxidizing at 0 °C for 2 h. Subsequently, the reaction mixture was stirred at 35 °C for 30 min. Deionized water (96 mL) was slowly added into the reaction mixture and then the temperature was raised to 95 °C for 15 min using an oil bath. The mixture was treated by adding hydrogen peroxide (30%) and 240 ml of water. Finally, the solid was filtered off and washed with 5% HCl and deionized water until the pH reached 6. The resulting solid was dried at 80 °C for one week to afford GO.

#### 2.5. Synthesis of GO-NH<sub>2</sub>

GO (1.0 g), APTMS (3 mmol) and toluene (25 mL) were added to a 50 mL two-neck flask and the mixture was refluxed at 110 °C under N<sub>2</sub> for 24 h. Afterwards, the mixture was filtered and the resultant solid was washed with toluene several times to remove the residual APTMS. The resulting solid was dried at room temperature to afford GO-NH<sub>2</sub>.

# 2.6. Synthesis of Schiff base ligands grafted onto GO

1 g of GO-NH<sub>2</sub> in 80 mL of dry ethanol was sonicated for 30 min. Excess dialdehyde ligand ( $L_1$ ,  $L_2$  or  $L_3$ ) (5 mmol) was added and the reaction mixture was refluxed for 24 h. The solid was then filtered, washed thoroughly with ethanol, and dried in an oven at 70 °C for 24 h to provide the GO- Schiff base ligand. The resulting materials are denoted  $L_1$ -GO,  $L_2$ -GO and  $L_3$ -GO, respectively.

#### 2.7. Synthesis of MoO<sub>2</sub> Schiff base complexes grafted onto GO

Immobilized Schiff base ligand onto GO ( $L_1$ -GO,  $L_2$ -GO or  $L_3$ -GO) (1 g) was dispersed in 50 mL ethanol and 6 mmol of MoO<sub>2</sub>(acac)<sub>2</sub> in 50 mL ethanol was added to this reaction mixture and refluxed for 24 h. The solid was filtered and washed with ethanol. To remove the unreacted MoO<sub>2</sub>(acac)<sub>2</sub>, Soxhlet extraction was carried out with ethanol and the resulting nanocatalyst dried at 80 °C for 5 h. The resulting materials were denoted MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO, respectively. The amount of Mo loadings was 0.375, 0.369 and 0.372 mmol·g<sup>-1</sup> for MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO.

#### 2.8. Catalytic epoxidation of alkenes

In a typical procedure, a 25 mL round bottom flask, equipped with a condenser and a magnetic stir bar, was charged with an alkene (5 mmol), 10 mmol of TBHP, the catalyst ( $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO) (20 mg) and 5 mL 1,2-dichloroethane, and the mixture was then refluxed. After reaction the solid catalyst was filtered off, washed with 1,2-dichloroethane and then dried at 80 °C for 12 h. The recovered catalyst was used to investigate its stability and recyclability. Analysis of the oxidation products was determined by gas chromatography with a capillary column and FID detector. Column temperature was programmed between 150 °C and 200 °C (5 °C/min). Nitrogen was used as carrier gas (40 mL/min) at injection temperature and 1,2-dichloroebenzene was used as an internal standard.

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**Figure 1.** <sup>1</sup>H-NMR of (a)  $L_1$  (recorded in DMSO-d<sub>6</sub>), (b)  $L_2$  (recorded in DMSO-d<sub>6</sub>), (c)  $L_3$  (recorded in CDCl<sub>3</sub>).

# 3. Results and discussion

# 3.1. <sup>1</sup>H NMR spectroscopic studies

<sup>1</sup>H NMR spectra of L<sub>1</sub> and L<sub>2</sub> were recorded in DMSO-d<sub>6</sub> but spectra of L<sub>3</sub> were recorded in CDCl<sub>3</sub> (Figure 1). Chemical shifts for aldehyde and OCH<sub>2</sub> protons were found at  $\sim$  10.3 and  $\sim$  4.5 ppm, respectively. Aromatic protons were set in the region of 7.09–7.70 ppm for L<sub>1</sub>, 7.33-7.85 for L<sub>2</sub> and 7.14–7.45 ppm for L<sub>3</sub>. Methoxy protons for L<sub>3</sub> are represented with a peak at 3.88 ppm.



Figure 2. FT-IR spectra: (a) GO, (b)  $MoO_2L_1$ -GO, (c)  $MoO_2L_2$ -GO, (d)  $MoO_2L_3$ -GO.

#### 3.2. IR spectroscopy

Figure 2 shows the FT-IR spectra of  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO. The FT-IR spectrum of pure GO support exhibits various vibrational peaks of functional groups such as C-O (1040 cm<sup>-1</sup>), C=O (1730 cm<sup>-1</sup>), C=C (1610 cm<sup>-1</sup>) and =C-H (1382 cm<sup>-1</sup>), revealing the presence of hydroxyl, carboxyl and epoxy groups [21]. After immobilization of the molybdenum Schiff base complex on the graphene oxide surface, the bands at 1106 cm<sup>-1</sup> and 1030 cm<sup>-1</sup> correspond to the stretching vibrations of Si-O-Si and Si-O-C, giving evidence for silylanization of graphene oxide [22]. The band at 1620 cm<sup>-1</sup> can be assigned to the C=N stretch of the imine group. The appearance of two adjacent bands at 902 cm<sup>-1</sup> and 947 cm<sup>-1</sup> in the FT-IR spectra of  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO is characteristic of the presence of *cis*-MoO\_2 group [21]. These results confirm that the molybdenum Schiff base complexes are anchored on the graphene oxide surface.

# 3.3. XRD analysis

XRD spectra are used to investigate the changes in structure of graphene oxide after the immobilization of the MoO<sub>2</sub> Schiff base complexes (Figure 3). The XRD pattern of GO (Figure 3a) shows the characteristic diffraction peak at  $2\theta = 11.4^{\circ}$ , corresponding to (001), which is due to oxidation of graphite powder and trapped water molecules between the graphite layers [23]. After amino functionalization and immobilization of MoO<sub>2</sub> Schiff base complexes on the GO surface, the diffraction peak at  $11.4^{\circ}$  does not disappear, suggesting that the structure of graphene oxide is not destroyed during sample preparation [24]. Moreover, the XRD spectra of MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO show a broad peak at  $2\theta = 23.5^{\circ}$ , verifying that the major oxygen-containing groups of GO have been functionalized.



Figure 3. XRD patterns of (a) GO, (b)  $MoO_2L_1$ -GO, (c)  $MoO_2L_2$ -GO, (d)  $MoO_2L_3$ -GO.

# 3.4. SEM analysis

Scanning electron microscope (SEM) image shown in Figure 4 reveals the nanoscopic features of GO and GO immobilized MoO<sub>2</sub> Schiff base complexes. The similar crumpled nanosheets are in an agglomerated phase in the four structures. These ridges and protrusions due to sp<sup>3</sup> carbon in immobilized GO carry the MoO<sub>2</sub> Schiff base complex on

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Figure 4. SEM image of the (a) GO, (b)  $MoO_2L_1$ -GO, (c)  $MoO_2L_2$ -GO, (d)  $MoO_2L_3$ -GO.

both sides of the GO nanosheets, where reactants can easily approach the catalytic sites. Microstructure of GO is not destroyed through the modification; the small spherical shaped catalyst particles on GO are seen in Figure 4. The size of MoO<sub>2</sub> Schiff base catalysts, mounted on graphene oxide, varies between 50 and 80 nm.

# 3.5. Solid state UV-Visible study

The diffuse reflectance spectra (DRS) of GO, MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO are shown in Figure 5. As-prepared GO exhibits two absorption peaks due to the  $\pi \rightarrow \pi^*$  transition of graphitic carbon double bonds at 242 nm and the  $n \rightarrow \pi^*$  transition of carbonyl groups at 304 nm [25]. The peak at ~570 nm for MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO is ascribed to ligand to metal charge-transfer transitions (LMCT) due to the promotion of an electron from the ligand to the molybdenum empty orbitals [26].

#### 3.6. TGA analysis

The TG curves of GO,  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO are depicted in Figure 6. The samples were heated at a constant rate of 10 °C min<sup>-1</sup> from 30 °C to 800 °C under N<sub>2</sub> flow. The TG curve of GO shows the first weight loss at 90–180 °C from evaporation of water molecules trapped in the material. Second degradation



Figure 5. DRS spectra of the (a) GO, (b)  $MoO_2L_1$ -GO, (c)  $MoO_2L_2$ -GO, (d)  $MoO_2L_3$ -GO.



Figure 6. TGA patterns of (a) GO, (b) MoO<sub>2</sub>L<sub>1</sub>-GO, (c) MoO<sub>2</sub>L<sub>2</sub>-GO, (d) MoO<sub>2</sub>L<sub>3</sub>-GO.

steps were observed at 200-320 °C which is due to the loss of epoxy and hydroxy functional groups, and the third degradation step (350-650 °C) is the loss of the remaining oxygen-containing groups as well as burning of ring carbon. The TGA curves for MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO and MoO<sub>2</sub>L<sub>3</sub>-GO show three-step weight losses at temperatures from 30 to 800 °C. The weight loss from 200 to 400 °C is attributed to the thermal decomposition of undigested oxygen carrying functionalities and APTMS

				Oxidant/Substrate		Epoxide
Entry	Catalyst (mg)	Solvent <sup>c</sup>	Oxidant	molar ratio	Conversion (%)	selectivity (%)
1	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	CH₃OH	TBHP	2	57.3	100
2	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	CH <sub>3</sub> CN	TBHP	2	72.5	100
3	$MoO_{2}L_{1}-GO(20)$	CH <sub>2</sub> Cl <sub>2</sub>	TBHP	2	53.3	100
4	$MoO_{2}L_{1}-GO(20)$	1,2-DCE	TBHP	2	98	100
5	$MoO_{2}L_{1}-GO(10)$	1,2-DCE	TBHP	2	53.4	100
6	MoO <sub>2</sub> L <sub>1</sub> -GO(15)	1,2-DCE	TBHP	2	79	100
7	MoO <sub>2</sub> L <sub>1</sub> -GO(25)	1,2-DCE	TBHP	2	98	100
8	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	UHP	2	49.8	100
9	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	NalO₄	2	31.8	100
10	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	TBHP	0.5	32	100
11	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	TBHP	1	50.4	100
12	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	TBHP	1.5	69.8	100
13	MoO <sub>2</sub> L <sub>1</sub> -GO(20)	1,2-DCE	TBHP	2.5	97.8	100
14	MoO <sub>2</sub> L <sub>2</sub> -GO(20)	CH <sub>3</sub> OH	TBHP	2	58.5	100
15	MoO <sub>2</sub> L <sub>2</sub> -GO(20)	CH <sub>3</sub> CN	TBHP	2	75.2	100
16	MoO <sub>2</sub> L <sub>2</sub> -GO(20)	CH <sub>2</sub> Cl <sub>2</sub>	TBHP	2	54.7	100
17	MoO <sub>2</sub> L <sub>2</sub> -GO(20)	1,2-DCE	TBHP	2	99.1	100
18	$MoO_2L_2$ -GO(10)	1,2-DCE	TBHP	2	53.8	100
19	MoO <sub>2</sub> L <sub>2</sub> -GO(15)	1,2-DCE	TBHP	2	81.4	100
20	MoO <sub>2</sub> L <sub>2</sub> -GO(25)	1,2-DCE	TBHP	2	98.8	100
21	$MoO_2L_2$ -GO(20)	1,2-DCE	UHP	2	51.3	100
22	$MoO_2L_2$ -GO(20)	1,2-DCE	NalO₄	2	33	100
23	$MoO_2L_2$ -GO(20)	1,2-DCE	TBHP	0.5	31.9	100
24	$MoO_2L_2$ -GO(20)	1,2-DCE	TBHP	1	51.5	100
25	$MoO_2L_2$ -GO(20)	1,2-DCE	TBHP	1.5	71	100
26	$MoO_2L_2$ -GO(20)	1,2-DCE	TBHP	2.5	98.1	100
27	$MoO_2L_3$ -GO(20)	CH₃OH	TBHP	2	55.3	100
28	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	CH₃CN	TBHP	2	71.7	100
29	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	$CH_2CI_2$	TBHP	2	51.6	100
30	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	TBHP	2	96.7	100
31	MoO <sub>2</sub> L <sub>3</sub> -GO(10)	1,2-DCE	TBHP	2	52.2	100
32	MoO <sub>2</sub> L <sub>3</sub> -GO(15)	1,2-DCE	TBHP	2	76.8	100
33	MoO <sub>2</sub> L <sub>3</sub> -GO(25)	1,2-DCE	TBHP	2	96	100
34	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	UHP	2	48.4	100
35	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	NalO <sub>4</sub>	2	30.1	100
36	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	TBHP	0.5	30.5	100
37	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	TBHP	1	48.3	100
38	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	TBHP	1.5	68.3	100
39	MoO <sub>2</sub> L <sub>3</sub> -GO(20)	1,2-DCE	TBHP	2.5	95.7	100

Table 1. Epoxidation of cyclooctene under reflux conditions.<sup>a,b</sup>

 $^a$ The amount of metal loading are 0.375(3.60%), 0.369(3.54%), 0.372(3.57%) (mmol)/g catalyst for MoO\_2L\_1-GO, MoO\_2L\_2-GO and MoO\_2L\_3-GO.

<sup>b</sup>The time of reactions are 60 min for  $MoO_2L_1$ -GO, 45 min for  $MoO_2L_2$ -GO and 90 min for  $MoO_2L_3$ -GO. 'The amount of solvent are 5 mL.

moieties, which have not participated in further chemical functionalization. The last major mass loss observed from 450–550 °C is related to slow decomposition of the Schiff base complex.

# 3.7. Catalytic activity

In order to optimize conditions for the title reaction and also compare the results with previous reports, epoxidation of cyclooctene was examined by changing parameters including the catalyst amount, time, oxidant and solvent. Different oxidants such as tert-butylhydroperoxide, NalO<sub>4</sub> and UHP (urea-hydrogen peroxide) were examined in epoxidation of cyclooctene in various solvents (Table 1, entries 1–4, 14–17 and 27–30).



**Figure 7.** Effect of time on the epoxidation of cyclooctene with TBHP catalyzed by  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO. Conditions: cyclooctene (5 mmol), TBHP (10 mmol), catalyst (20 mg), 1,2-DCE (5 mL).

Tert-butylhydroperoxide has some advantages: (i) It has excellent thermal stability; (ii) It can give high percent of conversion; (iii) environment-friendly.

Solvent plays an important role in oxidation reactions [23]. High epoxide selectivity and conversion were obtained in 1,2-dichloroethane as solvent for  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO catalysts. Other solvents (CH<sub>3</sub>OH, CH<sub>3</sub>CN, and CH<sub>2</sub>Cl<sub>2</sub>) did not show good performance compared to 1,2-dichloroethane (Table 1, entries 1–4, 14–17 and 27–30). Coordinating solvents such as acetonitrile and methanol compete with TBHP to bind Mo [27]. Therefore, in the presence of these solvents, the observed yields are low (Table 1, entries 1–4, 14–17 and 27–30). Lower reflux temperature is important in the lowest conversion in dichloromethane (Table 1, entries 1–4, 14–17 and 27–30).

Catalyst amount also had a role in the reaction. The epoxidation of cyclooctene by TBHP did not proceed in the absence of catalyst. The results in Table 1 (entries 1, 5–7, 14, 18–20, 27 and 31–33) exhibit that increasing the amount of catalyst up to 20 mg increased the yield of cyclooctene epoxide.

The ratio of oxidant to substrate is an important parameter in catalytic oxidation processes. The percent of conversion increased with increasing the molar ratio of [oxidant]:[cyclooctene] from 0.5 to 2 and the conversion of cyclooctene was maximum at 2:1 molar ratio of [oxidant]:[cyclooctene] (Table 1, entries 1–4, 14–17 and 27–30).

Figure 7 reveals the effect of reaction time on epoxidation of cyclooctene with TBHP. Comparing the reactivity of  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO shows that the first two reaches maximum yield after 60 min and 45 min, respectively, so they are more reactive than the third, which needs 90 min to reach this point. The catalytic activity of the complexes is mainly driven by substituent group present on the phenyl rings [28]. Presence of electron withdrawing group on phenyl rings makes the complex more active as catalyst for oxidation [29]; electron releasing group

		MoO <sub>2</sub> L <sub>1</sub> -GO		MoO <sub>2</sub> L <sub>2</sub> -GO		MoO <sub>2</sub> L <sub>3</sub> -GO	
Entry	Alkene	Conversion (epoxide) (%)	Time (min)	Conversion (epoxide) (%)	Time (min)	Conversion (epoxide) (%)	Time (min)
1	$\bigcirc$	88.7 (76)	60	91.9 (81)	45	86 (73)	90
2	$\bigcirc$	98 (100)	60	99.1 (100)	45	96.7 (100)	90
3		91 (95)	210	94.1 (96)	150	90 (91)	240
4	$\sim$	82.8 (100)	210	84 (100)	150	80.2 (100)	240
5	$\sim$	86.6 (100)	210	88.4 (100)	150	82.9 (100)	240
6	.0.L	70.1 (100)	420	75 (100)	420	65.4 (100)	480
7	~X=	65.1 (100)	420	68.5 (100)	420	59.3 (100)	480
8		60.5 (77)	480	64.1 (80)	420	51 (71)	480
9		93.8 (97)	180	96 (98)	150	92.4 (93)	240

Table 2. Epoxidation of some alkenes with TBHP catalyzed by  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO under reflux.<sup>a</sup>

<sup>a</sup>Reaction conditions: alkene (5 mmol), TBHP (10 mmol), catalyst (20 mg), 1,2-DCE (5 mL).

(-OCH<sub>3</sub>) attached on the phenyl rings, the complex loses its activity to a great range. Therefore, the observed trend of activity of the catalysts shows this trend.

These new catalysts,  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO, can be used for the epoxidation of a wide range of substituted alkenes (Table 2). Based on the epoxidation mechanism suggested earlier [30], higher electron donating ability of olefin double bond is anticipated to show more epoxidation reactivity. Therefore, cyclohexene and cyclooctene with inner double bonds should exhibit more activity in comparison to 1-hexene and 1-octene which contain terminal double bonds. Among the endocyclic olefins, cyclooctene was the most reactive (Table 2, entry 2). This reactivity arises from the stability of cyclooctene as well as the high reactivity of its double bond [31]. Steric hindrance on the C = C bond decreased the conversion of the olefins such as 1-methoxy-2-methylprop-1-ene (Table 2, entry 5) and 3,3-dimethylhex-1-ene (Table 2, entry 6) and increased reaction time.

Reusability of solid supported catalysts is an important benefit. Therefore, the reusability of  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO was monitored by sequential epoxidations of cyclooctene (Table 3). After the reaction, the solid catalyst could be easily recovered from the reaction mixture by simple filtration and is ready for reuse after washing with 1,2-dichloroethane and drying at 100 °C. These catalysts show good reusability without significant loss of selectivity after five cycles.

On the basis of Sobczak's ideas [32] and other experimental and theoretical reports [33–35] a reasonable mechanism can be proposed for epoxidation of cyclooctene with tert-butylhydroperoxide by  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO (Scheme 3).

	MoO <sub>2</sub> L <sub>1</sub>	MoO <sub>2</sub> L <sub>1</sub> -GO <sup>a</sup>		MoO <sub>2</sub> L <sub>2</sub> -GO <sup>b</sup>		MoO <sub>2</sub> L <sub>3</sub> -GO <sup>c</sup>	
Number of cycles	Conversion (epoxide) (%)	$TOF^{d}$ $(h^{-1})$	Conversion (epoxide) (%)	$TOF^{d}$ $(h^{-1})$	Conversion (epoxide) (%)	$TOF^{d}$ (h <sup>-1</sup> )	
1	98 (100)	653	99.1 (100)	895	96.7(100)	433	
2	97.2 (100)	648	98.7 (100)	892	96.2(100)	431	
3	96.6 (100)	644	98.1 (100)	887	95.5(100)	428	
4	95.3 (100)	635	97.4 (100)	880	94.7(100)	424	
5	95 (100)	633	96.6 (100)	872	94.1(100)	421	

Table 3. Epoxidation of cyclooctene with TBHP using recycled catalysts.

<sup>a</sup>Reaction conditions: 5 mmol cyclooctene, 10 mmol TBHP, 5 mL 1,2-DCE, 20 mg catalyst during 60 min. <sup>b</sup>Reaction conditions: 5 mmol cyclooctene, 10 mmol TBHP, 5 mL 1,2-DCE, 20 mg catalyst during 45 min. <sup>c</sup>Reaction conditions: 5 mmol cyclooctene, 10 mmol TBHP, 5 mL 1,2-DCE, 20 mg catalyst during 90 min. <sup>d</sup>TOF = (mole of reactant)(yield)/(mole of catalyst)(time).



Scheme 3. Proposed mechanism for the epoxidation of olefin with TBHP and  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO.

According to our experimental results, reaction rates are first order depending on substrate and catalyst concentrations. The first step involves transferring tert-butylhydroperoxide proton to a terminal oxygen of the oxo complex which resulted in coordination of tertbutylperoxide to Mo(VI). Then, alkene substrate coordinated to metal and, as a nucleophile, inserted into the metal oxygen bond of coordinated peroxide. This mechanism describes the faster reaction of electron-rich alkenes in comparison to electron-poor alkenes.

Many molybdenum complexes have been reported for catalytic epoxidation of alkenes with tert-butylhydroperoxide. However, the catalytic systems which have been prepared in this research are superior in terms of turnover frequency (TOF). Very recently, Yang *et al.* immobilized a molybdenum Schiff base complex onto SBA-15 and reported a TOF of 25.6 [36]. Mohammadikish *et al.* have immobilized the molybdenum complex onto nano-magnetite and reached a TOF of 19 [37]. Moghadam *et al.* achieved a TOF of 84 for the molybdenum complex supported onto multi-walled carbon nanotubes [38]. Table 4 compares the efficiency of our catalysts with those in the literature. All of these reports have lower TOF values than MoO<sub>2</sub>L<sub>1</sub>-GO, MoO<sub>2</sub>L<sub>2</sub>-GO

Catalyst	Conversion (%)	Epoxide (%)	TOF $(h^{-1})$	References
MoO <sub>2</sub> salen-SBA-15	49.1	49.1	25.6	[36]
MoO <sub>2</sub> -Thio-SCMNPs	97	99	19	[37]
Mo(CO) <sub>6</sub> @DAB-MWCNT	97	100	84	[38]
$[Mo(O)(O_2)_2(dmpz)_2]$	100	86	_	[39]
Mo-Im-BNPs	97	97	126	[40]
Mo-A-BNPs	97	97	89	[40]
$Fe_3O_4@APTMS/CM-SalophMoO(O_2)$	97	100	133	[41]
MoO <sub>2</sub> L <sub>1</sub> -GO	98	100	653	Present work
MoO <sub>2</sub> L <sub>2</sub> -GO	99.1	100	895	Present work
MoO <sub>2</sub> L <sub>3</sub> -GO	96.7	100	433	Present work

Table 4. Comparison of different Mo-containing catalysts for the epoxidation of cyclooctene.

and  $MoO_2L_3$ -GO in the present research. So, the comparison of epoxidation reaction time of our catalysts (45, 60 and 90 min) with the other reports (18 h) [39], (12 h) [5, 36] and (3.5 h) [40] is significant.

# 4. Conclusion

We prepared new hybrid heterogeneous catalysts by immobilizing Schiff base di-oxo molybdenum complexes onto GO which are functionalized with 3-(tri-methoxysilyl) propylamine. These are active catalysts for the epoxidation of various substituted ole-fins under heterogeneous conditions. The heterogeneous  $MoO_2L_1$ -GO,  $MoO_2L_2$ -GO and  $MoO_2L_3$ -GO catalysts are recyclable and retain a high level of catalytic activity during many cycles.

#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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