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## 1. Introduction

Catalytic oxidations, especially olefin epoxidation<sup>1</sup> and sulfoxidation<sup>2</sup> reactions, using transition metal complexes,<sup>3,4</sup> are considered to be among the most eco-friendly, most important reactions in industrial chemistry. Oxidation catalysis has played as leading role in this era due to the production of huge quantities of intermediates and monomers for industrial chemistry. Epoxides are versatile precursors in the synthesis of a variety compounds such as resins, cosmetics, surface coatings, sweeteners, perfumes, drugs, *etc.* and sulfoxides are well known valuable building blocks to produce biologically important compounds.<sup>5,6</sup> Schiff-bases<sup>7,8</sup> represent one of the

# Synthesis and characterization of $3-[N,N'-bis-3-(salicylidenamino)ethyltriamine] Mo(vi)O_2@SBA-15: a highly stable and reusable catalyst for epoxidation and sulfoxidation reactions$

Anish Lazar,<sup>a</sup> Werner R. Thiel<sup>b</sup> and A. P. Singh\*<sup>a</sup>

The efficient and reusable oxidation catalyst  $3-[N,N'-bis-3-(salicylidenamino)ethyltriamine] Mo(vi)O_2@SBA-$ 15 has been synthesized by the anchoring of the 3-[N,N-bis-3-(salicylidenamino)ethyltriamine] ligand (L or Salpr) on the inner surfaces of organofunctionalized SBA-15 and subsequent complexation with Mo(vı) O<sub>2</sub>(acac)<sub>2</sub>. The physico-chemical properties of the functionalized catalysts were analyzed by elemental analysis, ICP-OES, XRD, N<sub>2</sub>-sorption measurements, TG & DTA, solid state <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy, FT-IR, Raman spectroscopy, XPS, DRS UV-Vis spectroscopy, SEM and TEM. XRD and N<sub>2</sub> sorption analyses helped to find out the morphological and textural properties of the synthesized catalysts and confirm that an ordered mesoporous channel structure was retained even after the multistep synthetic procedures. The (100), (110) and (200) reflections in SBA-15 provide hints of a good structural stability. the existence of long range ordering and a high pore wall thickness. TG and DTA results reveal that the thermal stability of (L)Mo(vi)O2@SBA-15 was maintained up to 300 °C. The organic moieties anchored over the surface of the SBA-15 support were determined by solid state <sup>13</sup>C NMR and FT-IR spectroscopy. Further, solid state <sup>29</sup>Si NMR spectroscopy provides the information about the degree of functionalization of the surface silanol groups with the organic molety. The electronic environment and the oxidation state of the molybdenum site in (L)Mo(vi)O2@SBA-15 were monitored by Raman spectroscopy, XPS and DRS UV-Vis techniques. Moreover, the morphology and topographic information of the synthesized catalysts were confirmed by SEM and TEM imaging. The synthesized catalysts were evaluated in epoxidation and sulfoxidation reactions, and the results show that (L)Mo(v)O2@SBA-15 exhibits high conversion and selectivity towards epoxidation and sulfoxidation reactions in combination with high stability. The anchored solid catalysts can be recycled effectively and reused several times without major loss in activity. In addition, Sheldon's hot filtration test was also carried out.

> most widely utilized classes of ligands in inorganic chemistry, which are capable to bind various metal ions to give complexes with tunable properties. They are also used as a ligands in industrial chemistry due to the following the facts: (i) there are simple synthetic methods for preparation in large scale (ii) they provide several binding sites for metals and can be designed to leave vacant sites for coordination of substrates (iii) the substitution on the aromatic ring allows a fine-tuning of their properties.

> In recent years, the design and synthesis of catalytically active supported metal complexes has received increasing attention due to the some disadvantages of homogeneous systems compared to heterogeneous catalysts. In the case of molybdenum based catalysts<sup>9-11</sup> derived from Schiff-base ligands, *cis*-dioxomolybdenum species have been particularly investigated because of their good catalytic activity for the selective oxidation of cycloalkenes and sulfides. A variety of Schiff-base ligands such as bidentate-N-donor ligands

<sup>&</sup>lt;sup>a</sup>Catalysis division, CSIR-National Chemical Laboratory, Pune-411008, India. E-mail: ap.singh@ncl.res.in; Fax: +91-20-2590 2633; Tel: +91-20-2590 2497

<sup>&</sup>lt;sup>b</sup>Fachbereich Chemie, Technische Universitat Kaiserslautern, 67663 Kaiserslautern, Germany

(bipyridines,<sup>12</sup> diazabutadienes<sup>13</sup> and pyrazolylpyridines<sup>14</sup>) and tetradentate-N-ligands<sup>15,16</sup> (Salpr) have been used to improve the catalytic activity of these reactions with suitable peroxides. Environmentally benign, safer and economically favorable oxidants such as tert-butyl hydroperoxide (TBHP) and hydrogen peroxide  $(H_2O_2)^{17-19}$  have been used for epoxidation and sulfoxidation reaction with such systems. Out of these ligands, the tetradentate-N-donor ligand, 'Salpr'{3-[N,N-bis-3(salicylidenamino)ethyl triamine]} was used as the ligand for epoxidation and sulfoxidation reactions due to its high chelating ability with molybdenum complexes.<sup>20</sup> To avoid the well known limitations from the homogeneous complexes such as poor recyclability, catalyst contamination in the products, etc., supported complexes of catalytically active metals have been synthesized during the recent years. Mesoporous SBA-15 (ref. 21) shows significant attraction in this context due to its high surface area, its uniform pore sizes, its high wall thickness and its high hydrothermal stability compared to other mesoporous materials like MCM-41, MCM-48. To extend the applicability of SBA-15 materials, it is necessary to modify the surface by organic functional groups for anchoring metals and metal complexes.

The stability and selectivity of catalysts in epoxidation and sulfoxidation reactions were challenging tasks in the last decades. To overcome this limitations, SBA-15 was used as the support to immobilize of neat (L)Mo(vI)O<sub>2</sub> complex than other mesoporous materials, due to its higher wall thickness.<sup>22,23</sup> Further, chelation of molybdenum with Schiff base ligand, Mo(vI) O<sub>2</sub>-3-[*N*,*N*-bis-3(salicylidenamino)ethyltriamine] complex, over SBA-15 provides extra stability to the homogeneous complexes. In this work, we report, the synthesis, characterization and catalytic applications of highly stable (L)Mo(vI)O<sub>2</sub>@SBA-15 for efficient heterogeneous epoxidation and sulfoxidation reactions. The catalyst is recyclable and exhibits high catalytic activities.

## 2. Experimental

## 2.1 Synthesis

Tetraethylorthosilicate (TEOS), Pluronic 123 (P123, average molecular weight: 5800), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 3-chloropropyl trimethoxy silane (3-CPTMS), dimethoxydimethyl silane ((MeO)<sub>2</sub>Me<sub>2</sub>Si), cyclohexene, cyclooctene, cyclohexene oxide, cyclooctene oxide and sulfides were purchased from Aldrich. Diethylene triamine and HCl (36.5%) were purchased from Merck and Thomas Baker (India), respectively. Dry reagent grade solvents were obtained from Merck (India) and further dried before use according to standard methods.

The highly stable and reusable heterogeneous complex, (L)  $Mo(v_1)O_2$ @SBA-15 was synthesized under a nitrogen atmosphere in a step-by-step manner (Scheme 1). The synthesis of mesoporous SBA-15 (ref. 24) was carried out hydrothermally under the autogeneous pressure in an autoclave. The polymer surfactant P123 was used as a template and hydrochloric acid served as a mineralizer. The molecular composition of the gelating mixture was the following:



Scheme 1 Organofunctionalization and immobilization of the neat (L)  $Mo(v_i)O_2$  complex over SBA-15, 1a: synthesis of homogeneous complex [(L)Mo(v\_i)O\_2 complex], 1-b: chloro functionalization of SBA-15 [PrCl@SBA-15], 1-c: capping of PrCl@SBA-15 [-OH protected PrCl@SBA-15], 1-d: heterogenization of homogeneous complex [(L)  $Mo(v_i)O_2@SBA-15$ ].

0.043TEOS-4.4 g P123 
$$M_{\text{avg}} = 5800 = [\text{EO}_{20}-\text{PO}_{70}-\text{EO}_{20}]$$
  
-8.33H<sub>2</sub>O-0.24HCl

Typically, 4.4 g of the tri-block co-polymer was dispersed in 30 g of distilled water and stirred for 1.5 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and the stirring was continued for 2 h. Finally, 9 g of TEOS was added drop wise and the mixture was maintained at 40 °C for 24 h with continuous stirring. The mass was submitted to a hydrothermal treatment (100 °C, 48 h) under static condition. The precipitate was filtered, washed with distilled water, dried in an oven (90 °C, 12 h) and then calcined in the air (500 °C, 6 h) to remove the template completely. The calcined SBA-15 was characterized by powder XRD.

Surface modification of SBA-15 was achieved by a post synthesis grafting method (Scheme 1-b). One gram of SBA-15 was suspended in 50 ml of dry toluene and then heated to reflux together with 3.7 mmol of 3-chloropropyltrimethoxysilane (3-CPTMS) for 8 h under a  $N_2$  atmosphere. The material was filtered after cooling to ambient temperature, washed with dry

#### Paper

toluene and then with dichloro methane. Soxhlet extraction was carried out for 24 h with dichloro methane  $(CH_2Cl_2)$  as the solvent to remove occluded organosilane. The sample was then dried in vacuum for 10 h. The material obtained is designated as PrCl@SBA-15 (Scheme 1-b). It is evident from elemental analysis (C, H, N analysis) that the surface silanol groups on SBA-15 were organofunctionalized by 33% chloropropyl (3-CPTMS) groups as organic modifier. The free –OH groups still present in PrCl@SBA-15 were protected by adding 1.5 mmol of dimethoxydimethylsilane to a stirred suspension of 1 g of PrCl@SBA-15 in dry toluene (50 ml), followed by stirring for 12 h at reflux temperature under an inert atmosphere. The resulting material was filtered off, washed with toluene and was extracted in a Soxhlet with  $CH_2Cl_2$  for 24 h. The obtained material was named as –OH protected PrCl@SBA-15 (Scheme 1-c).

The Salpr ligand 3-[N,N'-bis-3(salicylidenamino)ethyltriamine] was prepared according to a reported procedure<sup>25</sup> (Scheme 1-a). Diethylene triamine (0.5158 g, 5 mmol) was added into an ethanolic solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (2.3433 g, 10 mmol) and the resulting yellow colored solution was heated to reflux for 3 h. After that, the excess of solvent was removed under vacuum and a dark yellow oily product was obtained after purification by column chromatography [silica column, hexane-ethyl acetate (9:1)]. 2 g (0.3732 mmol) of the Salpr ligand were dissolved in 30 ml of ethanol. This solution was added dropwise into an ethanolic solution of Mo(vi)O<sub>2</sub>(acac)<sub>2</sub> (1.384 g in 120 ml) in a 250 ml two neck round bottom flask and the mixture was heated to reflux for 24 h. After filtration, the product was dried and then extracted in a Soxhlet apparatus with a mixture of dichloromethane and ethanol (1:1) to remove unreacted  $Mo(v_1)O_2(acac)_2$ .

To a suspension of –OH protected PrCl@SBA-15 (1 g) in 30 ml of toluene, a solution of the Salpr ligand (L) (1.28 g, 0.0024 mol) in 10 ml of toluene was added, and then the mixture was heated to reflux for 24 h under an inert atmosphere. The resulting suspension was filtered, the residue was washed with toluene and  $CH_2Cl_2$ , and further purified extraction in a Soxhlet apparatus with a mixture of  $CH_2Cl_2$  and diethylether (1 : 1) for 24 h. The final material was designated as 3-[N,N'-bis-3-(salicy-lidenamino)ethyltriamine]@SBA-15 or (L)PrCl@SBA-15. For complexation, an excess of Mo(vi)O<sub>2</sub> (acac)<sub>2</sub> (1 g, 3 mmol) in 100 ml ethanol was added into 2 g of dried (L)PrCl@SBA-15 (Scheme 1-d). After filtration, the product was dried and then extracted in a Soxhlet apparatus with a mixture of dichloromethane and ethanol (1 : 1) to remove unreacted Mo(vi)O<sub>2</sub> (acac)<sub>2</sub>.

#### 2.2 Procedure for catalytic reactions

The epoxidation of cycloalkenes such as cyclohexene and cyclooctene were carried out in a 50 ml double necked round bottom flask fitted with a water-cooled condenser and a magnetic stirrer by using anhydrous TBHP as the oxidant. In a typical procedure, anhydrous TBHP (5.0–6.0 M in decane, 1.6 ml, 14.4 mmol) was added into a mixture of (L)Mo(vi)O<sub>2</sub>@SBA-15 (150 mg) or the neat (L)Mo(vi)O<sub>2</sub> complex (75 mg, 0.113 mmol) and 8 mmol of the appropriate cycloalkene in 25 ml of chloroform under a nitrogen atmosphere. The mixture was heated to reflux for 18 h.<sup>25</sup> Samples were withdrawn periodically and analyzed by using a Gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5) and a flame ionization detector (FID).

A 25 ml of round bottom flask was loaded with 5 ml of a suspension responding solution of the appropriate catalysts [25 mg of (L)Mo(vI)O<sub>2</sub>@SBA-15 or 10 mg (0.015 mmol) of the neat (L)Mo(vI)O<sub>2</sub> complex] in CH<sub>3</sub>CN. To this reaction mixture, 1 mmol of the sulfides (thioanisoles) and 1.1 mmol of 30% H<sub>2</sub>O<sub>2</sub> were added at room temperature and stirring was continued for 3 h.<sup>26</sup> Samples were periodically withdrawn from the reaction mixture, filtered off, and analyzed with GCMS. Sulfide conversion (wt%) and selectivity (%) were determined by using a gas chromatograph (Agilent 6890) equipped with a flame ionization detector (FID) and a capillary column (HP-5).

#### 2.3 Analytical procedures and equipment

Elemental analysis (C, H and N) were performed on a Carlo Erba (Model EA 1108) elemental analyzer. The molybdenum content in the material was determined by using an inductively coupled plasma-optical emission spectrometer (ICP-OES) on a Therm IRIS Intrepid II XSP after solubilization of the samples in HF/ HCl solutions. Powder X-ray diffraction (XRD) patterns were measured on a PAN analytical X'pert Pro dual goniometer diffractometer using Ni-filtered CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.5404$  Å) over the  $2\theta$  range of 0.5–10°, with a scan speed of 1° min<sup>-1</sup>. A proportional counter detector was used for the low angle experiments and the data collection was carried out using a flat holder in Bragg-Brentano geometry. N2 adsorption-desorption isotherms, pore size distributions as well as the textural properties of the hybrid materials were determined by using an Autosorb 1C Quantachrome USA. The program consisting of both an adsorption and desorption branch and typically run at -196 °C after the samples were degassed at 150 °C for 4 h. The BET method was applied to calculate the total surface area at relative pressures of  $P/P_{o} = 0.65-0.45$  and the BJH model was applied to the adsorption branch of the isotherm to determine the total pore volume and average pore diameter at a relative pressure of  $P/P_0 = 0.99$ . Pore size distribution (PSD) curves from BJH desorption branch were obtained via the NLDFT model assuming cylindrical pore geometry. Thermal analysis (TG-DTA) of the samples was conducted using a Pyris Diamond TGA analyzer with a heating rate of 10  $^\circ\mathrm{C}$  min $^{-1}$  under an air atmosphere. FTIR spectra of the solid samples were recorded in the range of 4000-400 cm<sup>-1</sup> on a Bruker alpha T FTIR spectrophotometer at room temperatures. Raman spectra of the complexes were recorded with a Horiba Jobin YVON Lab Ram HR spectrometer at 633 nm with a He-Ne laser. Magic angle spinning (MAS) NMR spectra for <sup>29</sup>Si and <sup>13</sup>C nuclei were recorded on BRUKER DSX300 spectrometer at 7.05 T (resonance frequencies: <sup>29</sup>Si, 59.595 MHz, rotor speed 10 000 Hz, external reference Si(OCH<sub>3</sub>)<sub>4</sub>; <sup>13</sup>C, 75.43 MHz, rotor speed 10 000 Hz; contact time: 1.5 ms; pulse delay: 5 µs). XPS measurements were performed on a VG Microtech ESCA 3000 instrument, using nonmonochromatized Mg-Ka radiation at a pass energy of 50 eV

and an electron take off angle of  $60^{\circ}$ . The correction of the binding energy was performed by using the C1s peak of carbon at 284.9 eV, as the reference. DRS UV-Vis spectra of the complexes were analyzed by using a Perkin-Elmer model Lambda 650 spectrophotometer. The scanning electron micrographs of the samples were obtained in a dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. The samples were loaded on stubs and sputtered with a thin gold film to prevent surface charging and also to protect from thermal damaging due to the electron beam. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300 kV were used for HRTEM samples imaging. The samples were crushed and dispersed in isopropanol with low power sonication before putting a drop of this suspension over a carbon coated Cu grid for observation. All synthesized samples were irradiated before the submission of all characterization techniques. The epoxidation reaction of cycloalkenes were performed at 70 °C for 18 h using anhydrous TBHP (5.0-6.0 M in decane) as oxidant and CHCl<sub>3</sub> as solvent. To extend the scope of the catalytic activity, sulfoxidation reactions of sulfides were carried out at 26 °C for 3 h using aqu. H<sub>2</sub>O<sub>2</sub> (70%) as oxidant and CH<sub>3</sub>CN as solvent.

## 3. Results and discussion

### 3.1 Characterization

The morphological and textural properties of all synthesized catalysts were investigated by using powder XRD (Fig. 1a–d) and N<sub>2</sub> adsorption–desorption analysis (Fig. 2A and B). Moreover, these analyses confirmed that the ordered mesoporous channel structure was retained even after the organofunctionalization and the immobilization of the neat (L)Mo(vi)O<sub>2</sub> complex over the SBA-15 support. Fig. 1 exhibits the XRD spectra of (a) assynthesized SBA-15 (b) calcined SBA-15 (c) –OH protected PrCl@SBA-15 (d) (L)Mo(vi)O<sub>2</sub>@SBA-15. The parent SBA-15 shows three reflections at  $2\theta = 0.9^{\circ}$ ,  $1.5^{\circ}$  and  $1.7^{\circ}$ , which are assigned to the (100), (110) and (200) Miller indices, respectively, indicating the formation of a highly ordered hexagonal structure.<sup>27</sup> In all synthesized samples, the (110) reflections are



Fig. 1 XRD pattern of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) –OH protected PrCl@SBA-15 (d) (L)Mo(vi)O<sub>2</sub>@SBA-15.



Fig. 2  $N_2$  adsorption-desorption isotherms and pore size distributions (inset) of (A) calcined SBA-15 and (B) (L)Mo(vi)O<sub>2</sub>@SBA-15.

more intense than the (200) reflection, which favors a more complete condensation of the wall structure due to the high temperatures selected for the hydrothermal synthesis and the further calcination. The existence of the (100), (110) and (200) reflections (Fig. 1) provides a hint for a high structural stability of the material, the existence of a long range ordering and a large pore wall thickness even after a number of treatments with organic molecules. The peak intensities of the (100) reflections are decreasing with broadening from calcined SBA-15 to (L) Mo(vi)O2@SBA-15 due to the proper loading of the organic modifier and the neat (L)Mo(vI)O<sub>2</sub> complex in the calcined SBA-15. Moreover, the decrease in signal intensity may be due to loss of regularity in the 2D hexagonal structure of mesoporous SBA-15. The structural stability and ordered mesoporosity of the samples have retained after incorporation of (L)Mo(vI)O<sub>2</sub> complex in the SBA-15 support.

The N<sub>2</sub> adsorption–desorption isotherms and pore size distributions (inset) of calcined SBA-15 and (L)Mo(v1)O<sub>2</sub>@SBA-15 are shown in Fig. 2A and B, respectively. (L)Mo(v1)O<sub>2</sub>@SBA-15 shows type-IV isotherms with a H1 hysteresis related to capillary condensation steps, a characteristic feature of the highly ordered mesoporous materials (pore size: 2-50 nm).<sup>28</sup> Textural properties of calcined SBA-15 and (L)Mo(v1)O<sub>2</sub>@SBA-15 samples are summarized in Table 1. The mesoporous SBA-15 exhibits a BET

surface area of 601 m<sup>2</sup> g<sup>-1</sup>, a pore volume of 1.02 cm<sup>3</sup> g<sup>-1</sup> and a mean pore diameter of 66 Å. As shown in Table 1, compared to SBA-15, a further reduction of the surface area from 601 to 252 m<sup>2</sup> g<sup>-1</sup> and of the mean pore size from 66 to 56 Å was observed for (L)Mo(vi)O<sub>2</sub>@SBA-15.

The SBA-15 samples exhibit a sharp increase in the N<sub>2</sub> adsorption at a higher  $P/P_{\rm o}$  value (~0.65) indicating the uniformity of the mesoporous structure. In the case of (L)Mo(vı) O<sub>2</sub>@SBA-15, the  $P/P_{\rm o}$  value changed to a lower value of ~0.6, indicative of a minor structural damage of the material after the modifications and being consistent with the XRD results. The significant decrease in surface area, in pore diameter and in pore volume of (L)Mo(vı)O<sub>2</sub>@SBA-15 indicates the successful anchoring of organic modifier group and the further complexation with the molybdenum site occurring on SBA-15, which reduces a part of the textural qualities of the support.

Thermal analysis is a technique for measuring changes in the physico-chemical properties of substances as a function of temperature. The thermal stability of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) -OH protected PrCl@SBA-15 (d) (L)Mo(vi)O2@SBA-15 was determined by TGA (Fig. 3A) and DTA (Fig. 3B) in an atmosphere of air from 30 to 1000 °C with a temperature ramp of 10 °C min<sup>-1</sup>. The TGA curve of the as-synthesized SBA-15 [Fig. 3A(a)] exhibits a 48% weight loss with a corresponding exothermic peak observed in the DTA analysis [Fig. 3B(a)] in the region of 170-220 °C which is assigned to the removal of surfactant from as-synthesized sample. Calcined SBA-15 [Fig. 3A(b)] shows only 13% weight loss from TG curve with no other peak observed in DTA analysis [Fig. 3B(b)]. These evidences support the complete removal of the surfactants from the calcined SBA-15 and the successful formation of a pure siliceous SBA-15 material. The TGA plot of -OH protected PrCl@SBA-15 [Fig. 3A(c)] shows three distinct weight losses corresponding to exothermic peaks in the DTA [Fig. 3B(c)] (i) between 70 and 150 °C corresponding to physisorbed water molecules (ii) between 230 and 310 °C indicating the decomposition of the chloropropyl moiety from PrCl@SBA-15 (iii) between 330 and 450 °C representing the combustion of dimethoxydimethylsilane acting as the capping agent. In the case of (L)Mo(vi)O<sub>2</sub>@SBA-15 [Fig. 3B(d)], one extra peak along with two peaks already observed in the -OH protected PrCl@SBA-15, in the region of 450-510 °C is observed.29 It confirms the high thermal stability of (L)Mo(vI)O2 sites on SBA-15. In some cases the weight loss between 530 and 570 °C arises due to an additional water loss by an ongoing condensation of residual silanol groups.30 The TGA result of the -OH protected



Fig. 3 TGA (A) and DTA (B) pattern of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) -OH protected PrCl@SBA-15 (d) (L)Mo(vi) O<sub>2</sub>@SBA-15.

PrCl@SBA-15 quantitatively shows 26% of weight loss, being greater than in the case of calcined SBA-15. This strongly supports the successful anchoring of 3-CPTMS on the calcined SBA-15. Further, (L)Mo(v1)O<sub>2</sub>@SBA-15 shows 42% of weight loss, which is greater than the loss observed for the –OH protected PrCl@SBA-15, strongly supporting a 16% loading of neat (L)Mo(v1)O<sub>2</sub> sites in the calcined SBA-15. All these results support that the material was synthesized and the (L)Mo(v1)O<sub>2</sub> sites are directly anchored over the modified SBA-15.

Infrared spectroscopy helped to find out the nature of the surface functional groups being present in the materials and it is furthermore used for monitoring of the multistep assembly of

Fable 1       Textural properties <sup>a</sup> of calcined SBA-15 and (L)Mo(vi)O2@SBA-15								
Sample	Mo content <sup><i>b</i></sup> mmol $g^{-1}$	$a_0^c$ [Å]	BET SA $[m^2 g^{-1}]$	$D_{\mathrm{p}}\left[\mathrm{\mathring{A}} ight]\left(\mathrm{BJH} ight)$	$V_{\rm p} \left[ {\rm cm}^3  {\rm g}^{-1} \right] \left( {\rm BJH} \right)$	$\omega_{\mathrm{t}}^{d}(\mathrm{\AA})$		
SBA-15	_	106.02	601	66	1.02	40.02		
(L)Mo(vi)O2@SBA-15	0.18	105.46	252	56	0.37	49.46		

 $a^{a} a_{0}$ , unit cell parameter; SA, surface area;  $D_{p}$ , pore diameter;  $V_{p}$ , pore volume;  $\omega_{t}$ , pore wall thickness. b From ICP-OES analysis.  $c^{a} a_{0} = 2d_{100}/1.73$ .

the catalyst inside the mesoporous SBA-15 material. FT-IR spectra of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) –OH protected PrCl@SBA-15 and (a) the neat (L)Mo(v1)O<sub>2</sub> complex (b) (L)Mo(v1)O<sub>2</sub>@SBA-15 are shown in Fig. 4A and B, respectively. In the spectrum of the as-synthesized SBA-15 [Fig. 4A(a)], peaks at 2980 cm<sup>-1</sup> and 2895 cm<sup>-1</sup> indicate the stretching vibrations of the –CH<sub>2</sub> groups being present in the surfactant molecules. In calcined SAB-15 [Fig. 4A(b)], a broad band at 3600–3200 cm<sup>-1</sup> and a weak band at 3738 cm<sup>-1</sup> are attributed to the *v*-OH stretching vibrations of hydrogen bonded and isolated surface silanol groups being present in the host materials.<sup>31,32</sup> Further, a sharp band at 1628 cm<sup>-1</sup> is corresponding to the –OH bending vibration of the silanol groups. Moreover, the absence of strong absorptions in calcined SBA-15 at 3000–2700 cm<sup>-1</sup> indicates the complete removal of surfactants.

After the chlorofunctionalization of the SBA-15 [Fig. 4A(c)], the peaks at 3738 cm<sup>-1</sup> and 3600–3400 cm<sup>-1</sup> had disappeared, indicating that the silanol groups on the surface of SBA-15 are transferred into a Si–O–Si framework. Further, peaks at 2980 cm<sup>-1</sup> and 2895 cm<sup>-1</sup> appeared being assigned to the stretching vibrations of the –CH<sub>2</sub> groups in propyl chain of the organic modifiers which evidently supports that the chloropropyl group is attached to the SBA-15. In both compounds, the neat



Fig. 4 FT-IR spectroscopy of (A) [(a) as-synthesized SBA-15, (b) calcined SBA-15, (c) -OH protected PrCl@SBA-15] and (B) [(a) the neat (L)Mo(v<sub>1</sub>)O<sub>2</sub> complex (b) (L)Mo(v<sub>1</sub>)O<sub>2</sub>@SBA-15].

(L)Mo(vi)O<sub>2</sub> complex [Fig. 4B(a)] and in (L)Mo(vi)O<sub>2</sub>@SBA-15 [Fig. 4B(b)], peaks at 755  $\text{cm}^{-1}$  and 1420  $\text{cm}^{-1}$  are assigned to C-H bending and C=C stretching vibrations, respectively, of the arene groups. Moreover, a strong band at 1640 cm<sup>-1</sup> is assigned to the -C=N stretching vibration of the azomethylene group. Characteristic peaks at 940 cm<sup>-1</sup> and 910 cm<sup>-1</sup> are assigned to the symmetric and asymmetric vibrational modes of the ciscoordinated MoO<sub>2</sub> moiety of the neat (L)Mo(vi)O<sub>2</sub> complex, which are not observed for (L)Mo(vi)O2@SBA-15 due to a overlapping of these peaks with  $\nu$ (Si–OH) vibrations. The MoO<sub>2</sub> species prefers to form a *cis* configuration due to a maximized utilization of the  $d\pi$  groups at molybdenum centre.<sup>33</sup> In all these samples, except the neat (L)Mo(vI)O<sub>2</sub> complex, the asymmetric and symmetric stretching vibrations of Si-O bonds in the Si-O-Si framework are observed at 798 cm<sup>-1</sup> and 1080 cm<sup>-1</sup>, respectively [Fig. 4A(a-c) and B(b)]. A strong band at 954 cm<sup>-1</sup> is attributed to the  $\nu$ (Si–OH) vibration,<sup>34,35</sup> indicating the effective formation of siliceous materials.

In addition to this, the results of Raman spectroscopic investigations, being technique complementary to IR spectroscopy, of (a) the neat (L)Mo(vi)O<sub>2</sub> complex (b) (L)Mo(vi)O<sub>2</sub>@SBA-15 are plotted in Fig. 5. The characteristic peaks at 821 and 990 cm<sup>-1</sup>, corresponds to asymmetric and symmetric stretching vibrations of the *cis*-coordinated MoO<sub>2</sub> moiety.<sup>36</sup> This indicates that the oxidation state of molybdenum is VI, which is though retained even after immobilization over SBA-15. Further, results obtained from the Raman spectra are in good agreement with the results of the IR spectroscopic investigations.

The organic moieties anchored over the surface of SBA-15 are further confirmed by NMR techniques. The <sup>13</sup>C solid state NMR spectra of (A) PrCl@SBA-15 (B) –OH protected PrCl@SBA-15 and (C) (L)Mo(v1)O<sub>2</sub>@SBA-15 are depicted in Fig. 6. The presence of peaks at 10, 22 and 43 ppm, assigned to the carbon atoms (C<sub>1</sub>– C<sub>3</sub>) of the propyl chain in organic modifier, indicate the successful chlorofunctionalization of SBA-15 (Fig. 6A). Additionally a sharp peak at –1.7 ppm (C<sub>4</sub>) evidences the presence of –CH<sub>3</sub> groups as result of the capping of residual hydroxyl groups by dimethoxy dimethylsilane in –OH protected SBA-15 (Fig. 6B).



Fig. 5 Raman spectroscopy of (a) the neat (L)Mo(v\_1)O\_2 complex (b) (L)  $Mo(v_1)O_2aSBA-15$ .



Fig. 6 Solid state  ${}^{13}$ C CP MAS NMR spectroscopy of (A) PrCl@SBA-15 (B)-OH protected PrCl@SBA-15 (C) (L)Mo(v)O<sub>2</sub>@SBA-15.

In the case of (L)Mo(v1)O<sub>2</sub>@SBA-15 (Fig. 6C), resonances in the region between 110 and 150 ppm correspond to the aromatic moieties of the Salpr ligand. Moreover, in the region between 0 and 50 ppm, two extra resonances at 28 ppm and 34 ppm (Fig. 6C), represent the methyl carbon atoms of the *tert*-butyl groups. The small peak at 165 ppm is ascribed to the carbon atoms of the imine groups in (L)Mo(v1)O<sub>2</sub>@SBA-15. Furthermore, one shoulder peak at 56 ppm is assigned to  $-CH_2$  groups of diethylene triamine being present in (L)Mo(v1)O<sub>2</sub>@SBA-15. All the resonance peaks support the successful anchoring of the (L)Mo(v1)O<sub>2</sub> sites on SBA-15.

The degree of functionalization of surface silanol groups with organic moieties on the mesostructured materials can be monitored by means of <sup>29</sup>Si CP-MAS NMR spectroscopy. <sup>29</sup>Si CP-MAS NMR spectroscopy. <sup>29</sup>Si CP-MAS NMR spectra of (A) calcined SBA-15 (B) PrCl@SBA-15 (C) –OH protected PrCl@SBA-15 (D) (L)Mo(vI)O<sub>2</sub>@SBA-15 are depicted in Fig. 7. The spectrum of calcined SBA-15 (Fig. 7A) shows broad resonance peaks from –90 to –115 ppm, indicative for a range of Si–O–Si and Si–OH bonds. The bands centered at –93 ppm, –103 ppm and –113 ppm can be assigned to the Q<sup>2</sup> [germinal silanol, (SiO)<sub>2</sub>Si(OH)<sub>2</sub>], Q<sup>3</sup> [single silanol, (SiO)<sub>3</sub>Si(OH)] and Q<sup>4</sup> [siloxane, (SiO)<sub>4</sub>Si] sites of the silica framework, respectively.<sup>31,32</sup>

Compared to the parent SBA-15, PrCl@SBA-15 (Fig. 7B) shows a decrease in the  $Q^3$  and  $Q^2$  intensities with a corresponding increase in the percentage of Q<sup>4</sup> sites showing that the 3-CPTMS effectively consumes the geminal as well as the single silanol sites. The appearance of the Q<sup>3</sup> signal indicates the presence of some residual non-condensed OH groups attached to the silicon atoms. After chlorofunctionalization (Fig. 7C), two additional peaks at -69 ppm and at -61 ppm were observed and assigned to  $T^3$  [SiR(OSi)<sub>3</sub>] and  $T^2$  [Si(OH)R(OSi)<sub>2</sub>] units, respectively. The existence of the T<sup>3</sup> signal confirms that SBA-15 has been modified by organic moieties. Further, a sharp peak at -22 ppm in the -OH protected PrCl@SBA-15 material indicates the Si atoms of the methoxydimethylsilyl units which are present as capping sites (Fig. 7C). The  $(Q^3 + Q^2)/Q^4$  ratio indicates the presence of silanol groups residing on the support surface, and a lower  $(Q^3 + Q^2)/Q^4$  value for chlorofunctionalized samples suggests that the material contains fewer residual silanols, resulting in a siliceous pore wall structure with a greater degree of condensation and higher hydrothermal stability. Changes in the relative intensities of the Q<sup>4</sup>, Q<sup>3</sup> and  $Q^2$  signals can be explained by the redistribution of the silicon sites during the surface silylation. In the spectrum of (L)Mo(vi)O<sub>2</sub>@SBA-15 (Fig. 7D), peak at -20 ppm decreases with an increase of the Q<sup>3</sup> sites compared to Q<sup>4</sup> indicating the removal of some capping units ongoing with a formation of free silanol groups under the drastic synthetic conditions (Fig. 7D). <sup>29</sup>Si CP-MAS NMR spectra provide direct evidence for the formation of a highly condensed siloxane network with organic group covalently bound to the mesoporous silica and also revealed that both the synthesis process and surfactantextraction treatment did not cause cleavage of the Si-C bonds.

XPS is a surface technique which helps us to find out the oxidation state and chemical environment of atoms due to the shift in binding energies. The XPS spectra of the Mo3d core level of (a) the neat (L)Mo(v1)O<sub>2</sub> complex and (b) (L)Mo(v1)O<sub>2</sub>@SBA-15 are depicted in Fig. 8. The correction of the binding energies was performed by using the C1s peak of carbon at 284.9 eV as the reference. In the neat (L)Mo(v1)O<sub>2</sub> complex (Fig. 8a), peaks at 233 and 236 eV correspond to the  $3d_{5/2}$  and  $3d_{3/2}$  spin–orbit component, which are shifted to higher binding energy values (234 and 237, respectively) in the case of (L)Mo(v1)O<sub>2</sub>@SBA-15 (Fig. 8b). These binding energies correspond to Mo(v1) species and prove the unchanged oxidation state of the metal ion even after heterogenization of the (L)Mo(v1)O<sub>2</sub> sites over SBA-15.



Fig. 7 Solid state  $^{29}Si$  CP MAS NMR spectroscopy of (A) calcined SBA-15 (B) PrCl@SBA-15, (C) –OH protected PrCl@SBA-15 (D) (L)Mo(v) O\_2@SBA-15.

The DRS UV-Vis spectra of (a) calcined SBA-15 (b) the neat (L)Mo(vI)O<sub>2</sub> complex (c) (L)Mo(vI)O<sub>2</sub>@SBA-15 are presented in Fig. 9 to get further information about the coordination environment and the oxidation state of molybdenum in the neat (L)Mo(vi)O<sub>2</sub> complex as well as (L)Mo(vi)O<sub>2</sub>(aSBA-15. The spectra of calcined SBA-15 (Fig. 9a) and (L)Mo(vi)O<sub>2</sub>@SBA-15 (Fig. 9c) exhibit a peak at 225 nm, typical for siliceous materials.<sup>37</sup> In both compounds, namely, the neat (L)Mo(vI)O<sub>2</sub> complex (Fig. 9b) and (L)Mo(vi)O<sub>2</sub>@SBA-15, two bands at 240 and 280 nm are attributed to  $\pi$   $\rightarrow$   $\pi^*$  transitions of the aromatic ring and the azomethine group, respectively. Further, a broad peak at 330 nm is assigned to n  $\rightarrow$   $\pi^*$ transitions of the azomethine group.38 Moreover, a broad band at 440 nm is attributed to  $N \rightarrow Mo(v_1)$  and  $O \rightarrow Mo(v_1)$ ligand to metal charge-transfer transitions (LMCT) due to the promotion of an electron from the ligand centered highest occupied molecular orbital (HOMO) to the molybdenum centered lowest unoccupied molecular orbital (LUMO).39 The absence of a d-d transition in the visible region (400 nm to



Fig. 8 XPS spectra of the Mo3d core level of (a) the neat (L)Mo(vi)O<sub>2</sub> complex (b) (L)Mo(vi)O<sub>2</sub>@SBA-15.



Fig. 9 DRS-UV-Vis spectroscopy of (a) calcined SBA-15 (b) the neat (L)  $MO(v_1)O_2$  complex (c) (L) $MO(v_1)O_2@SBA-15$ .

800 nm) confirms the 4d<sup>0</sup> electron configuration of the molybdenum sites.<sup>40</sup>

Scanning electron microscopy (SEM) is an important tool for the morphological characterization of mesoporous molecular sieve materials. Fig. 10(A and B) shows the SEM images of calcined SBA-15 and (L)Mo(vi)O2@SBA-15 with a 2D p6mm hexagonal type structure. The particle size of both materials was found to be in the range between 1.15 and 1.25 µm. Furthermore, the morphology of (L)Mo(vi)O2@SBA-15 was retained after anchoring of the (L)Mo(vI)O2 sites over the functionalized SBA-15 support. Transmission electron microscopy (TEM) is typically used for high resolution imaging of thin films of solid samples for microstructural and compositional analysis. It has been used to obtain topographic information about the mesoporous matrices at nearly atomic resolution. The TEM images of calcined SBA-15 and (L)Mo(vi)O2@SBA-15 shown in Fig. 11(A and B) revealed the formation of a regular hexagonal array of uniform channels having a long-range ordering and well defined 1-D channels. These results are further supported by XRD results presented earlier.

## 3.2 Catalytic activity

The catalytic activity and selectivity of the synthesized catalysts were evaluated in the epoxidation cycloalkenes and in the oxidation of sulfides. The results of the epoxidation reactions catalysed by (L)Mo(v1)O<sub>2</sub>@SBA-15 and by the neat (L)Mo(v1)O<sub>2</sub> complex together with a blank experiment (absence of catalyst) are depicted in Table 2. In the epoxidation reaction, cyclooctene and cyclohexene were used as substrates together with anhydrous TBHP (5.0–6.0 M in decane) as the oxidizing agent and CHCl<sub>3</sub> as the solvent. In the case of (L)Mo(v1)O<sub>2</sub>@SBA-15, results in Table 2 reveal that cyclooctene exhibits higher conversion (93%) and selectivity (97%) than cyclohexene (86% of



Fig. 10 SEM images of (A) calcined SBA-15 (B) (L)Mo(vi)O<sub>2</sub>@SBA-15.



Fig. 11 TEM images of (A) calcined SBA-15 (B) (L)Mo(vi)O<sub>2</sub>@SBA-15.

conversion and 95% of selectivity), due to the presence of a more electron rich C=C double bond.<sup>41</sup> The neat  $(L)Mo(v_1)O_2$  complex gave 88% and 78% conversion for cyclooctene and cyclohexene, respectively. The corresponding selectivities for both epoxides were found to be 96%. The blank experiment showed a very low cycloalkene conversion with a poor epoxide selectivity even after 18 h of reaction time.

To find out the widespread application of the heterogeneous catalyst, (L)Mo(vi)O2@SBA-15, sulfoxidation reactions of various sulfides such as thioanisole, 4-chlorothioanisole, 4-bromothio anisole, ethyl methyl sulfide and diethyl sulfide were carried out with H2O2 as the oxidizing agent and CH3CN as the solvent (Table 3). Normally, sulfides like methyl phenyl sulfide (thioanisole), ethyl phenyl sulfide and diethyl sulfide exhibit slightly higher conversions and comparative selectivities than substituted thioanisoles (-Cl & -Br) due to the electronic effects of -chloro and -bromo substituents in the substrates. As can be seen in Table 3, (L)Mo(vi)O2@SBA-15 catalyst gives slightly better conversions (80% to 100%) and selectivities (85% to 91%) for various alkyl aryl sulfides than the neat  $(L)Mo(v_1)O_2$  complex (conversion, 75% to 100% and selectivity, 84% to 88%). In the absence of the catalyst, lower conversion (10% to 15%) and selectivities (82% to 88%) for various alkyl aryl sulfides were obtained.

### 3.3 Heterogeneity tests

To check the stability and recyclability of the catalyst, (L)Mo(v1)O<sub>2</sub>@SBA-15 was recycled four times (fresh + three cycles) in the epoxidation of cyclooctene and five times (fresh + four cycles) in the sulfoxidation of thioanisole (Table 4). After each cycle, the catalyst was removed by simple centrifugation, washed several times with a suitable solvent like CHCl<sub>3</sub> or CH<sub>3</sub>CN (each time in 5 ml at 26 °C) and dried under vacuum. In every cycle, it can be seen that there is no considerable change in the conversion of the cyclooctene or the thioanisole and for the selectivity of the products. Finally, after the last cycle, the ICP-OES analysis of the used catalyst showed 0.04 mmol  $g^{-1}$  molybdenum metal lost from the fresh catalyst, which confirms that the stability of the (L)Mo(v1)O<sub>2</sub>@SBA-15 was largely retained upto the third (in the epoxidation) or the fourth (in the sulfoxidation) cycle.

In addition, to confirm the heterogeneity and stability of  $(L)Mo(vi)O_2@SBA-15$  complex, Sheldon's hot filtration test was carried out, indicating that there is virtually no molybdenum content leaching into the reaction solution under the applied reaction conditions. At first, epoxidation reaction of cyclooctene (Fig. 12) and sulfoxidation reaction of thioanisole (Fig. 13) were performed over  $(L)Mo(vi)O_2@SBA-15$  complex under appropriate reaction conditions (fresh cycle), which are already mentioned in the bottom of the Table 4. To perform the Sheldon's hot filtration test in epoxidation of cyclooctene at 70 °C for 18 h (Fig. 12), heterogeneous catalyst like  $(L)Mo(vi)O_2@SBA-15$  was filtered out from the reaction mixture after 6 h during the reaction, and the filtrate was again charged into round bottom flask for the continuation of the reaction in the absence of catalyst upto 18 h. The results show that 53% cyclooctane oxide

#### Table 2 Epoxidation of cycloalkenes<sup>a</sup>

		Cyclooctene			Cyclohexene			
No	Catalyst	Con. (%)	Oxide	Others	Con. (%)	Oxide	Others	
1	No catalyst	6	88	12	5	86	14	
2	$(L)Mo(vi)O_2$ complex	88	96	4	78	96	4	
3	(L)Mo(vi)O <sub>2</sub> @SBA-15	93	97	3	86	95	5	

<sup>*a*</sup> Reaction conditions: (L)Mo(vı)O<sub>2</sub>@SBA-15, 150 mg or (L)Mo(vı)O<sub>2</sub> complex, 75 mg; substrate, 8 mmol; TBHP (5.0–6.0 M in decane), 14.4 mmol; CHCl<sub>3</sub>, 25 ml; reaction temperature, 70 °C; reaction time, 18 h.

#### Table 3 Sulfoxidation of various sulfides<sup>a</sup>

	No catalyst		rst	(L)Mo(vi)O <sub>2</sub> complex			(L)Mo(vı) O <sub>2</sub> @SBA-15		
Substrate	A	В	С	А	В	С	А	В	С
Thioanisole	14	87	13	100	85	15	100	89	11
4-Chloro thioanisole	10	82	18	75	84	16	80	90	10
4-Bromo thioanisole	15	88	12	84	87	13	92	90	10
Ethyl methyl sulfide	13	87	13	90	88	12	95	91	9
Diethyl sulfide	12	85	15	92	86	14	96	85	15

 $^a$  A, conversion; B, sulfoxide; C, sulfone; reaction conditions: (L)Mo(v1) O<sub>2</sub>@SBA-15, 25 mg or (L)Mo(v1)O<sub>2</sub> complex, 10 mg; substrate, 1 mmol; H<sub>2</sub>O<sub>2</sub>, 1 mmol; CH<sub>3</sub>CN, 5 ml; reaction temperature, 26 °C; reaction time, 3 h.

Table 4 Recycling study of (L)Mo(vi)O<sub>2</sub>@SBA-15 in epoxidation<sup>a</sup> and sulfoxidation<sup>b</sup> reactions

	Epoxidation	(cyclooctene)	Sulfoxidation (thioanisole)		
No of cycles	Conversion	Selectivity	Conversion	Selectivity	
Fresh	93	97	100	89	
I cycle	92	96	99	87	
II cycle	88	95	97	86	
III cycle	80	93	92	85	
IV cycle	_	_	85	85	

<sup>*a*</sup> Reaction conditions: (L)Mo(v1)O<sub>2</sub>@SBA-15, 150 mg; cyclooctene, 8 mmol, 0.8816 g; TBHP (5.0–6.0 M in decane), 14.4 mmol, 1.6 ml; CHCl<sub>3</sub>, 25 ml; reaction temperature, 70 °C; reaction time, 18 h. <sup>*b*</sup> Reaction conditions: (L)Mo(v1)O<sub>2</sub>@SBA-15, 25 mg; thioanisole, 1 mmol, 0.1242 g; H<sub>2</sub>O<sub>2</sub>, 1.1 mmol, 0.1245 g; CH<sub>3</sub>CN, 5 ml; reaction temperature, 26 °C; reaction time, 3 h.



Fig. 12 Sheldon's hot filtration test in epoxidation of cyclooctene.



Fig. 13 Sheldon's hot filtration test in sulfoxidation of thioanisole.

was formed (from the GC analysis) after 6 h and there is no changes in the conversion of cyclioctene was observed after 18 h. For the hot filtration test in sulfoxidation reaction of thioanisole (Fig. 13) at 26 °C for 3 h, (L)Mo(v1)O<sub>2</sub>@SBA-15 catalyst was filtered from the reaction mixture after 1 h during the reaction and the reaction continued uninterrupted in the absence of catalyst upto 3 h. It was observed that 65% methyl phenyl sulfide was converted after 1 h (from the GC analysis) and the conversion of methyl phenyl sulfide remained similar upto 3 h. In both reactions, results show that leaching of the molybdenum atoms was not occurred.

## 4. Conclusion

In summary, the heterogenization of the (L)Mo(v<sub>1</sub>)O<sub>2</sub> complex over SBA-15 was achieved by a multistep synthetic procedure, using the 3-[N,N-bis-3(salicylidenamino)ethyltriamine] ligand (L) and Mo(v<sub>1</sub>)O<sub>2</sub>(acac)<sub>2</sub>. The physico-chemical properties of the functionalized catalyst were analyzed by a series of characterization techniques like elemental analysis, ICP-OES, XRD, N<sub>2</sub> sorption measurements, TG & DTA, solid state <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy, FT-IR, Raman spectroscopy, XPS, DRS UV-Vis spectroscopy, SEM and TEM. The integrity and textural

properties of mesoporous support and synthesized catalysts were obtained from the XRD and N2 adsorption-desorption analysis. Thermal stabilities of the complexes were confirmed by thermal analyses like TG and DTA. The organic moieties anchored over the surface of SBA-15 were investigated by solid state <sup>13</sup>C NMR and FT-IR spectroscopy. The degree of functionalization of surface silanol groups with organic moieties on the mesostructured materials can be monitored by means of <sup>29</sup>Si CP-MAS NMR spectroscopy. The oxidation state and the chemical environment of molybdenum atoms were determined by Raman spectrascopy, XPS and DRS UV-Vis spectroscopy and the morphology and topographic information of the synthesized catalysts were confirmed by SEM and TEM imaging. (L)Mo(vi)O2@SBA-15 complex was found to be highly active, selective and recyclable in the epoxidation and sulfoxidation reactions of various cycloolefins and alkyl aryl sulfides, respectively, compared to the neat  $(L)Mo(v_1)O_2$  sites and the blank reaction. Further, to confirm the heterogeneity of (L)Mo(vi)O<sub>2</sub>@SBA-15 complex, Sheldon's hot filtration test was carried out, and the results show that molybdenum metal does not leach out from the (L)Mo(vi)O<sub>2</sub>@SBA-15 complex.

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