Selective epoxidation of olefins catalyzed by oxodiperoxomolybdenum(VI) complexes immobilized over highly ordered 2D-hexagonal mesoporous silica

Swarup K. Maiti [a], Subhajit Dinda [a], Mahasweta Nandi [b], Asim Bhaumik [b,*], Ramgopal Bhattacharyya [a,**]

[a] Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700032, India
[b] Department of Materials Science and Centre for Advanced Materials, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

ARTICLE INFO

ABSTRACT

Two oxodiperoxomolybdenum(VI) complexes of 8-quinolinol have been immobilized over a highly ordered 2D-hexagonal mesoporous silica. The latter has been synthesized hydrothermally by using cationic–non-ionic mixed surfactant templating route. The mesoporous silica and the immobilized materials were thoroughly characterized by powder X-ray diffraction, N_2 sorption, transmission electron microscopy (TEM), UV–vis and FT-IR spectroscopic tools and elemental analyses. Experimental results revealed 6.7–7.1 wt% loading of metal complexes on the mesoporous silica host. The immobilized nanostructured materials showed very good catalytic activity and excellent recycling efficiencies over their respective homogeneous catalysts for the epoxidation of different olefins in the presence of $H_2O_2/NaHCO_3$ system. High catalytic efficiency could be attributed to the heterogenization of soluble metal complexes on the high surface area mesoporous host.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Mo and W containing homogeneous catalysts show excellent catalytic efficiencies towards selective epoxidation of olefins [1–4] under liquid phase condition, where catalyst, reactant and reagent form a single phase with the solvent present in the medium. These homogeneous catalytic systems containing the soluble metal complexes in the reaction medium could not be reused as the efficiency of the subsequent catalytic cycles are very poor. Additionally, the separation of product(s) from the reaction mixture is a cumbersome process. However, for industrial utilization a long self-life (for repeated use) of a catalyst as well as minimum effort to separate the catalyst from the reaction mixture, which is also economical, are required. Thus in spite of excellent catalytic efficiencies the application of these homogeneous catalysts has been restricted in large-scale industrial processes. On the other hand, in porous heterogeneous catalytic systems, the catalyst can be present as a separate solid phase in the reaction mixture under conventional

liquid phase [5] or triphasic [6] condition. These heterogeneous catalysts have gained considerable interest over the last few decades in academia and industry because of their efficiency for repeated use in many catalytic cycles and ease of product separation. In order to achieve the unique advantages of both homogeneous and heterogeneous catalytic systems a large-scale research effort have been focused towards the heterogenization of transition metal containing catalysts onto different solid supports such as silica [7,8] polymers [9] and mesoporous materials [10–16]. Micelle-templated inorganic mesoporous silica and related materials [17,18] have emerged in the past decade as very promising support materials owing to their unique physico-chemical properties (very high surface area, pore volume and narrow pore size distribution) [17]. Jia and Thiel modified the micelle-templated silica MCM-41 with a bidentate pyrazolylpyridine ligand and prepared a covalently anchored complex MoO(O)$_2$L-L, which was active in cyclooctene epoxidation [19]. Similarly, MCM-41 surface has been functionalized with monodentate and bidentate ligands and the resulting materials showed very good catalytic activities in epoxidation reactions [20,21].

In this context a Cu(II)–Schiff base complex was covalently grafted with 3-aminopropyl functionalized silica surface and the resulting material showed good catalytic activity in allylic oxidation of olefins in the presence of tert-butyhydroperoxide (TBHP) [8].

* Corresponding author. Tel.: +91 33 2473 4971; fax: +91 33 2473 2805.
** Corresponding author.
E-mail addresses: msab@mahendra.iacs.res.in (A. Bhaumik), aargibhatta@yahoo.com (R. Bhattacharyya).

Oxo complexes of organomolybdenum(VI) of the type $MoO(O_2)_2L_2$ [22,23] (L = mono or bidentate Lewis base), are also used as catalysts in the heterogeneous epoxidation of olefins with TBHP as oxidant. Corma et al. presented a review about the state of the art concerning the syntheses, reactions and catalytic applications of some zeolite anchored Mo complexes for epoxidation of simple alkenes [24]. The heterogenization was also achieved by reacting a surface fixed linker molecule (synthesized with trimethoxyiodo-propylsilane), bearing a R-CH$_2$I end group with one of the salen nitrogen atoms [25]. The heterogenized complexes were found to be efficient catalysts for the asymmetric epoxidation at room temperature by using TBHP as the oxidizing agent. Recently, Tangestaninejad et al. [26] have reported an epoxidation method on which Mo(CO)$_6$ immobilized in a polymer bound aliphatic amine (prepared from Merrifield resin), gave excellent yields in the epoxidation of cyclic and aromatic olefins, specially *cis*- and *trans*-diphenylethylene in the presence of H$_2$O$_2$/NaHCO$_3$ system as an oxidant.

Herein, we report the immobilization of oxodiperoxo-8-hydroxy-quinolinolato Mo(VI) complexes over highly ordered mesoporous silica. Both the host and the immobilized catalysts were characterized by powder XRD, N$_2$ sorption, electron microscopy and spectroscopic techniques. The heterogenization of these soluble metal complexes resulted excellent catalytic activity and epoxide selectivity in the oxidation of various olefins in the presence of dilute aqueous H$_2$O$_2$ as oxidant and sodium bicarbonate as a co-catalyst.

2. Experimental

2.1. Preparation of the homogeneous catalysts *I* and *II*

We have prepared two oxodiperoxomolybdenum(VI) complexes following literature procedures [2,27]. Oxodiperoxo molybdenum(VI) adduct [MoO(O$_2$)$_2$·2QOH] [QOH = 8-quinilinol] has been designated as **I**. This complex is neutral. We have prepared an anionic oxodiperoxo-8-quinolinolato-molybdate(VI) complex of tetraphenylphosphonium cation and this has been designated as **II**.

1. Monooxodiperoxomolybdenum(VI) di-8-quinolinolate [MoO(O$_2$)$_2$·2QOH] **I**: An aqueous solution (25 cm^3) of MoO$_3$·2H$_2$O (1.25 g; 6.0 mmol) was dissolved in 30% (w/v) H$_2$O$_2$ (40 cm^3; 13.9 mmol) by stirring at room temperature when a pale yellow solution was obtained. Addition of 8-quinolinol (2.02 g; 13.9 mmol) dissolved in acetic acid (4 M; 10 cm^3) to the above solution with stirring (about 10 min) gave a yellow solid. It was filtered off, washed with water, 95% ethanol and finally with diethylether and dried in vacuuo. Yield, 2.76 g (86%). The compound was moderately soluble in dichloromethane, acetonitrile and acetone but insoluble in ethanol, benzene and diethylether. Found, C, 46.10; H, 3.15; N, 5.78; Mo, 20.32. Calc. for C$_{18}$H$_{14}$N$_2$O$_7$Mo: C, 46.35; H, 3.00; N, 6.01 and Mo, 20.60%. IR (KBr disc; cm^{-1}): 1620 (w), 1590 (w), 1570 (w), 1520 (m), 1480 [s; ν(C–N)], 1380 (s), 1330 (s), 1270 (m), 1100 [s; ν(C–O)], 960 [s; ν(Mo=O)], 850 [s; ν(O–O)], 820 (s), 750 (s), 645 (s), 580 (w), 520 (w), 500 (w), 460 (w). λ_{max} (nm): 318 (sh), 360 ($\in$ = 4635 M^{-1} cm^{-1}).

2. Tetraphenyl phosphonium monooxodiperoxo-unis(8-quinolinolato) molybdenum(VI) [PPh$_4$][MoO(O$_2$)$_2$QO] **II**: **I** (1.17 g; 2.50 mmol) was dissolved in a minimum volume of acetonitrile (20 cm^3) in a conical flask fitted with an air condenser and was stirred (stir-bar) for 1 h after the addition of an excess of H$_2$O$_2$ (30%, w/v; 15 cm^3) when a clear yellow solution was obtained. Addition of an aqueous solution (10 cm^3) of PPh$_4$Cl

(0.86 g; 2.5 mmol) dropwise with constant stirring for another 30 min gave a shining light yellow solid. The compound was found to be soluble in acetonitrile, acetone, dichloromethane and chloroform but insoluble in ethanol and diethylether. The solid was crystallized from dichloromethane–hexane (1:1) solvent system to get rectangular light yellow crystals. Yield, 1.25 g (76%). Found, C, 60.2; H, 4.0; N, 2.2; Mo, 14.4. Calc. for C$_{33}$H$_{26}$O$_6$NPMo: C, 60.0; H, 4.0; N, 2.1 and Mo, 14.6%. IR (KBr disc; cm^{-1}): 3040 (w), 1610 (w), 1600 (w), 1580 (m), 1560 (m), 1490 (s), 1460 (vs), 1455 (s), 1450 (sh), 1375 (s), 1320 (s), 1280 (s), 1100 (vs), 1020 (sh), 1000 (m), 945 (s), [ν(Mo=O)], 845, 810 [m; ν(O–O)], 800 (w), 780 (m), 760 (s), 740 (s), 720 (s), 645 (s), 580 (s), 530 (s), 460 (w), 380 (w), 310 (m). λ_{max} (nm) 357 ($\in$ = 3725 M^{-1} cm^{-1}).

2.2. Preparation of the immobilized catalysts

Highly ordered 2D-hexagonal mesoporous silica has been synthesized using a mixture of cationic (cetyltrimethylammonium bromide, CTAB) and non-ionic (Brij 35, C$_{12}$H$_{25}$-(OC$_2$H$_4$)$_{23}$-OH, a polyether and aliphatic hydrocarbon chain surfactant) mixed surfactant system as the supramolecular structure directing agent (SDA) in the presence of tartaric acid (TA) as a mineralizer [28,29]. Tetraethyl orthosilicate (TEOS, Aldrich) was used as the silica source. In a typical synthesis, 4.44 g CTAB (Loba Chemie) and 2.5 g Brij 35 (Loba Chemie) were dissolved in an acidic aqueous solution of TA (1.17 g TA in 60 g H$_2$O) under vigorous stirring at room temperature for 1 h. This was followed by the addition of 7.0 g TEOS under continuous stirring. After 2 h of continuous stirring, tetramethylammonium hydroxide (TMAOH, 25% aqueous, Sigma–Aldrich) was added dropwise and the pH was maintained at *ca.* 11.2. The resulting mixture was aged overnight under stirring at room temperature and then treated hydrothermally at 353 K for 72 h without stirring. The solid product was collected by filtration, washed several times with water and dried under vacuum at room temperature. The resulting powder was calcined in the flow of air at 723 K for 8 h to remove all the organic surfactants. Immobilization of the metal complexes was carried out by dispersing 1 g of the mesoporous silica in a solution containing 0.5 g of the metal complex dissolved in 25 ml of dry acetonitrile, followed by vigorous stirring at room temperature for 4 h. Then the solid was filtered, washed with acetonitrile and dried under vacuum. Hexagonal mesoporous silica and its corresponding immobilized analogs of **I** and **II** have been designated as HMS, HMS-IC-I and HMS-IC-II, respectively. In Fig. 1, the ortep diagram of oxodiperoxo-bis(8-quinolinolato)molybdenum(VI) **II** obtained by X-ray crystallography is shown.

All the samples were characterized by powder XRD using a Seifert 3000P X-ray diffractometer on which the small and wide-angle goniometers are mounted. The X-ray source was Cu Kα radiation (α = 0.15406 nm) with an applied voltage and current of 40 kV and 20 mA, respectively. Mesophases of different samples were analyzed using a JEOL, JEM 2010 Transmission Electron Microscope at an accelerating voltage of 200 kV. N$_2$ adsorption measurements were carried out using a Quantachrome Autosorb-1C-TPD at 77 K. Pre-treatment of the samples were done at 473 K for 3 h under high vacuum. Jeol JEM 6700F field emission Scanning Electron Microscopy with an EDS attachment was used for the determination of surface morphology and chemical composition. For the Fourier transform infrared (FT-IR) measurement a Nicolet Magna IR 750 spectrometer Series II was used. A Shimadzu AA-6300 double beam atomic absorption spectrophotometer (AAS) was used for determining the percentage loading of Mo through wet chemical analysis. UV–vis diffuse reflectance spectra (DRS) for the immobilized catalysts were recorded on a Shimadzu 2401PC
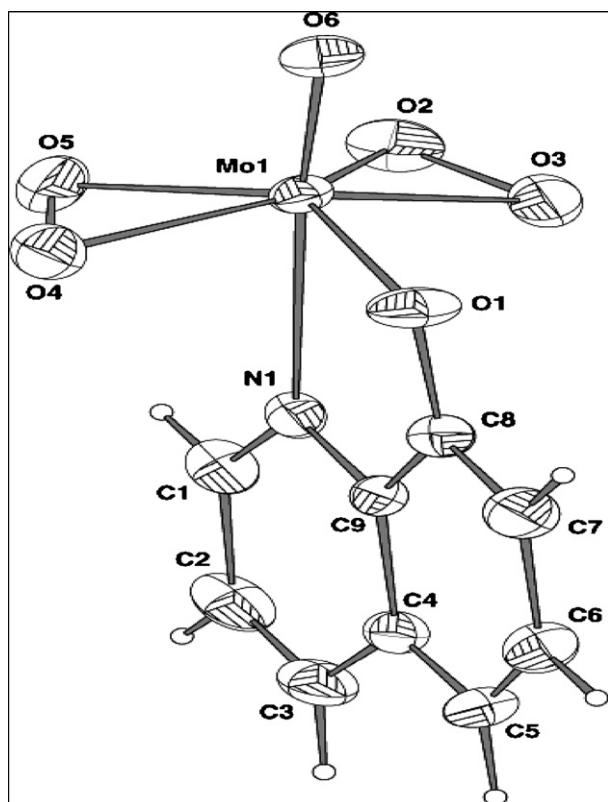
Fig. 1. Molecular structure of the anion $[MoO(O_2)_2(QO)]^-$ **II**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

UV–vis spectrophotometer with an integrating sphere attachment using $BaSO_4$ as the background standard.

Liquid phase oxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and stirred magnetically at room temperature. The substrate and the catalyst were taken previously in the solvent and hydrogen peroxide (30%, w/v) was added immediately before the start of the reaction. To maintain a constant flow of peroxide during the entire period of reaction and also to assure H_2O_2 economy, the oxidant was added periodically. Aliquots from the reaction mixture were withdrawn at various time intervals and H_2O_2 added to the contents of the flask with the help of a syringe through the septum. In a typical operation $0.5\ cm^3$ solution was taken out with the help of a micro-pipette and the solution was subjected to multiple ether extractions and then the extract was concentrated. From this $1\ \mu l$ solution was withdrawn with the help of a gas tight syringe and injected to the GC port (Agilent 6890N, FID). The retention times of the peaks were compared with those of commercial standards and for the calculation of the GC yields nitrobenzene was used as an internal standard.

3. Results and discussion

3.1. General characterization for the mesoporous host HMS and immobilized catalysts HMS-IC-I and HMS-IC-II

Low angle X-ray diffraction patterns of the mesoporous host as well as the immobilized complexes HMS-IC-I and HMS-IC-II are shown in Fig. 2. All four peaks for 1 0 0, 1 1 0, 2 0 0 and 2 1 0 planes of the 2D-hexagonal mesophase [17,28–30] were observed for HMS (a) and the immobilized complexes HMS-IC-I (b) and HMS-IC-II (c), suggesting the retention of highly ordered structures even after the
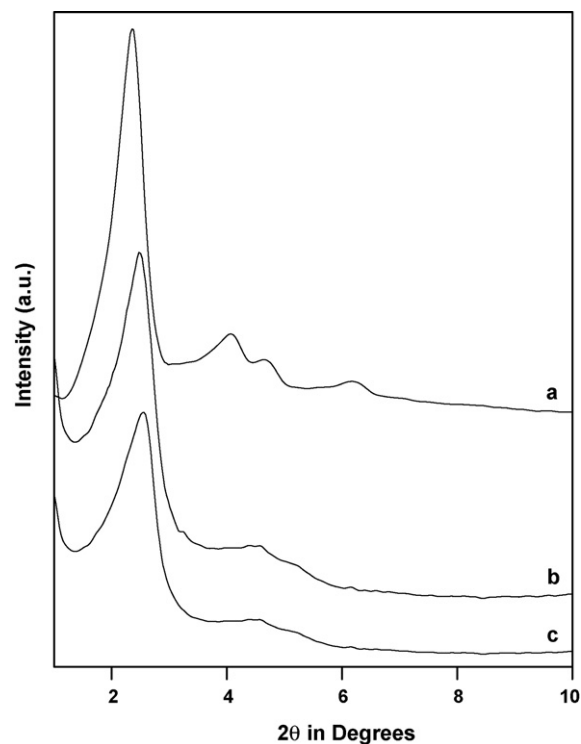

Fig. 2. XRD patterns of calcined HMS (a), HMS-IC-I (b) and HMS-IC-II (c).

loading of metal complexes. In Fig. 3 the N_2 sorption isotherms for HMS sample at 77 K are shown. Typical type IV isotherm with steep rise due to capillary condensation, characteristic of other mesoporous materials [17] was seen. BET surface area and average pore diameter for this sample was $1438\ m^2\ g^{-1}$ and 2.8 nm, respectively. The BJH pore size distribution was calculated from this isotherm, which is shown in the inset of Fig. 3. The pore sizes are distributed within a very narrow range, centered at 2.8 nm for this 2D-hexagonal mesoporous material. Adsorption studies were also carried out over the immobilized complexes HMS-IC-I and HMS-IC-II. The surface area and pore diameters for HMS-IC-I and HMS-IC-II samples were found to be $1055\ m^2\ g^{-1}$ and 2.49 nm and $1025\ m^2\ g^{-1}$ and 2.47 nm, respectively. The surface area for both the samples were found to be little lower than that of the HMS sam-
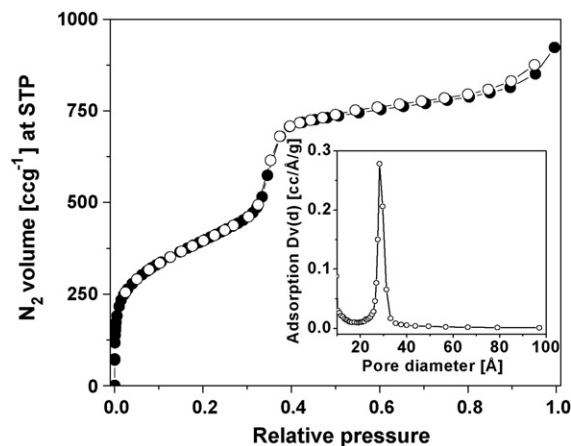

Fig. 3. N_2 adsorption/desorption isotherm for HMS. Adsorption points are marked by filled circles and desorption points are marked by open circle. BJH pore size distribution given in the inset.
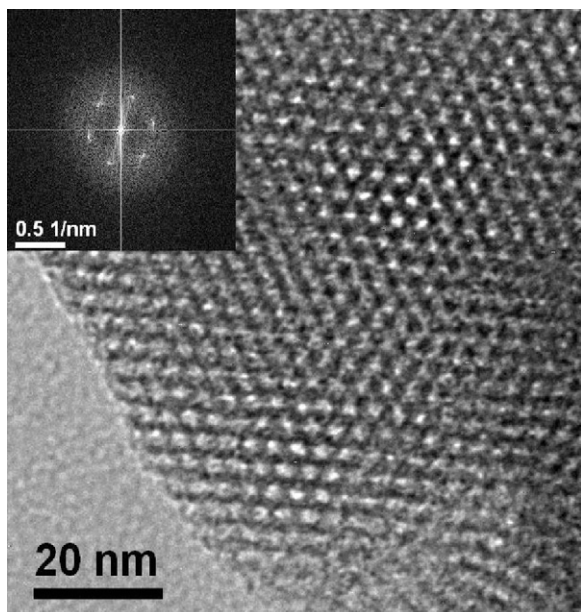
Fig. 4. HRTEM of the HMS sample. FFT pattern is given in the inset.

ple. Also a decrease in the pore diameters were observed for the immobilized complexes vis-à-vis the mesoporous host HMS. The decrease in pore diameter can be attributed to the metal centers adhered to the inner wall of the pores, which resulted in decrease in the pore sizes. HRTEM image of the as-synthesized HMS sample given in Fig. 4, revealed hexagonal arrangement of the pores with different contrast than that of the pore walls. The average pore diameter for this sample agrees well with the N_2 sorption data (2.8 nm) of the calcined HMS sample, considering the fact that little contraction of the unit cell occur during calcination as seen from the respective XRD pattern (Fig. 2). In Fig. 5, solution phase UV–vis spectra of **I** and **II** and UV–vis DRS of HMS-IC-II is
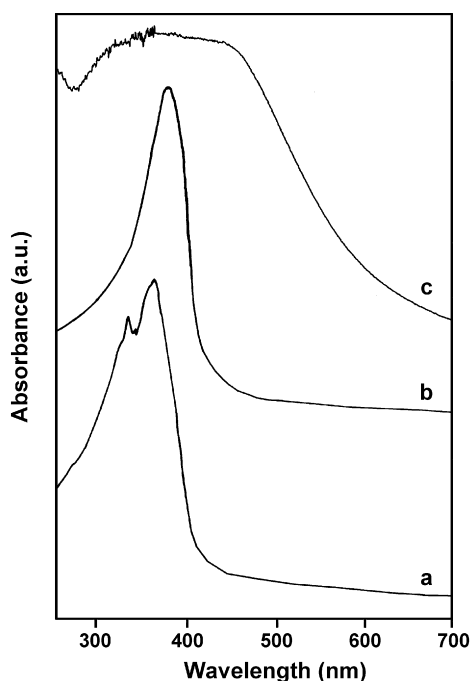

Fig. 5. UV–vis spectra of complex **I** (a), complex **II** (b) and DRS spectrum of HMS-IC-I (c).
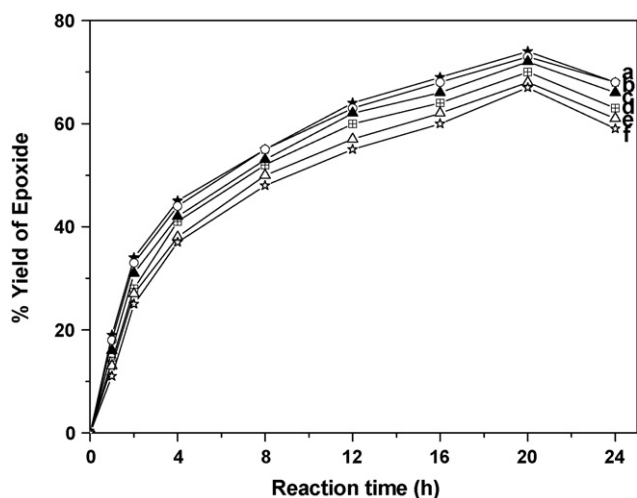

Fig. 6. Reaction profile (yield of epoxide against time) for the heterogeneous epoxidation of styrene using catalyst HMS-IC-I; (a) batch 1, (b) batch 2, (c) batch 3, (d) batch 4, (e) batch 5 and (f) batch 6.

shown. Mo(VI) complexes **I** and **II** showed strong absorption at *ca.* 385 and 390 nm, respectively. These bands could be attributed to the ligand-to-metal charge transfer. On the other hand the immobilized complex showed a very broad absorption ranging from 300 to 500 nm. This broad absorption band could be assigned to immobilization of the Mo(VI) complexes **I** and **II** in the confined nanospace of the mesopores. The UV–vis absorption results further suggested loading of the metal complex on the mesoporous materials. Chemical analysis (AAS) data further indicated loading of 6.7 and 7.1 wt% of complexes in the mesoporous host for **I** and **II**, respectively.

3.2. Catalytic properties of the immobilized complexes

Efficiency for the epoxidation of various olefins over the immobilized catalysts HMS-IC-I and HMS-IC-II is shown in Table 1. We have repeated the catalytic reaction cycles for six times using both the immobilized catalysts HMS-IC-I and HMS-IC-II. The reaction profile for styrene (as a representative case) as brought out by % yield of epoxide against reaction hours was plotted in case of the hydrogenised catalysts for six batches, and these are shown
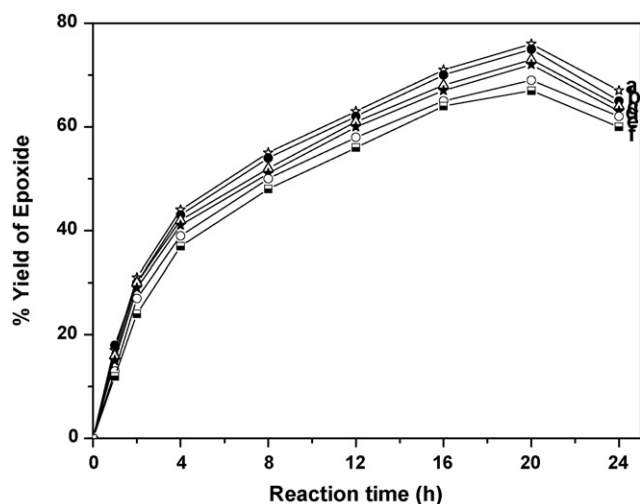

Fig. 7. Reaction profile (yield of epoxide against time) for the heterogeneous epoxidation of styrene using catalyst HMS-IC-II; (a) batch 1, (b) batch 2, (c) batch 3, (d) batch 4, (e) batch 5 and (f) batch 6.

Table 1
Epoxidation of olefins over immobilized catalysts with NaHCO$_3$ as co-catalyst and H$_2$O$_2$ as oxidant[a]

Substrate	Product(s)	Catalyst	Time (h)	Conversion (%)	Yield (%)	TON
Styrene	Styrene oxide (A) + benzaldehyde (B)	HMS-IC-I	20	98	74 + 24	1574 + 510
		HMS-IC-II	20	96	76 + 20	1547 + 387
1-Octene	1,2-Epoxy-octane	HMS-IC-I	16	92	92	1957
		HMS-IC-II	16	88	88	1792
9-Decen-1-ol	9-Epoxy-decane-1-ol	HMS-IC-I	16	79	79	1680
		HMS-IC-II	16	77	77	1568
Norbornene	Norbornene oxide	HMS-IC-I	12	85	85	1808
		HMS-IC-II	12	82	82	1670
Styrene[b]	Styrene oxide (A) + benzaldehyde (B) + others (C)	HMS	20	7.8	60 + 18 + 22[e]	–
1-Octene[c]	1,2-Epoxy-octane (A) + 1,2-Dihydroxy-octane (B)	HMS-IC-I	20	90	67 + 23	1358 + 466
Styrene	Styrene oxide	I[d]	1	99	99	3960
1-Octene	1,2-Epoxy-octane	I[d]	1.25	94	94	4700
9-Decen-1-ol	9-Epoxy-decane-1-ol	I[d]	2	97	97	1940
Norbornene	Norbornene oxide	I[d]	0.17	98	98	9800

[a] Reaction conditions: reaction temperature 298 K, substrate 7.02 mmol; catalyst: HMS-IC-I: 0.0033 mmol, HMS-IC-II: 0.00345 mmol (Mo concentrations); NaHCO$_3$ 1.18 mmol; H$_2$O$_2$ 5.5 mmol/h, total = 110 mmol for styrene, 88 mmol for 1-octene and 9-decen-1-ol, and 66 mmol for norbornene; solvent: acetonitrile 10 ml.

[b] Reaction with HMS, H$_2$O$_2$ and NaHCO$_3$, without the addition of Mo catalyst.

[c] Reaction in absence of NaHCO$_3$.

[d] Reactions were carried out under homogeneous conditions: ratio of substrate:catalyst was 4000:1 (styrene), 5000:1 (1-octene), 2000:1 (9-decen-1-ol) and 10000:1 (norbornene). A slightly higher temperature 313 K was employed for all the reactions in homogeneous catalysis.

[e] Selectivity of products.

in Figs. 6 and 7. As seen from the figure, the catalytic activity of both the catalysts remained almost same even after the sixth reaction cycle. In this case, styrene to styrene oxide is exclusively obtained up to 2 h while the yield of the epoxide is only 30%. Both the immobilized molybdenum catalysts HMS-IC-I and HMS-IC-II (Figs. 6 and 7) showed similar trends. Then from 2 to 20 h interval (epoxide formed at the 20 h = 76%) both the epoxide and benzaldehyde is steadily formed at a constant rate, but during 20–24 h time span the epoxide formation ceases only to undergo the exclusive reaction, namely, styrene oxide to benzaldehyde.

In Table 1, results on the epoxidation of other three olefins, 1-octene, 9-decen-1-ol and norbornene over HMS-IC-I and HMS-IC-II as well as over the unsupported catalysts **I** and **II** are reported. As seen from the results only epoxides are exclusively formed in good

yields over these immobilized catalysts. For all these substrates very high (more than 1500) TON (turn over numbers = moles of substrate converted per mole of Mo) were obtained. After the reaction the catalysts were recovered by filtration through a Whatman 40 filter paper, washed several times with water and activated at 373 K for 4 h in air. Both the immobilized catalysts have retained their TON values even after many catalytic cycles. Atomic absorption spectrometric analysis shows that molybdenum is not leaching out during oxidation reactions, as no molybdenum was detected in the liquid phase of the reaction mixture after the completion of reaction. Thus these experimental results suggested that the immobilized oxodiperoxo complexes of Mo(VI) catalysts are highly efficient in epoxidation reaction. A control experiment was also carried out with styrene as a representative case, in presence of HMS, hydrogen peroxide and sodium bicarbonate, without the addition of Mo
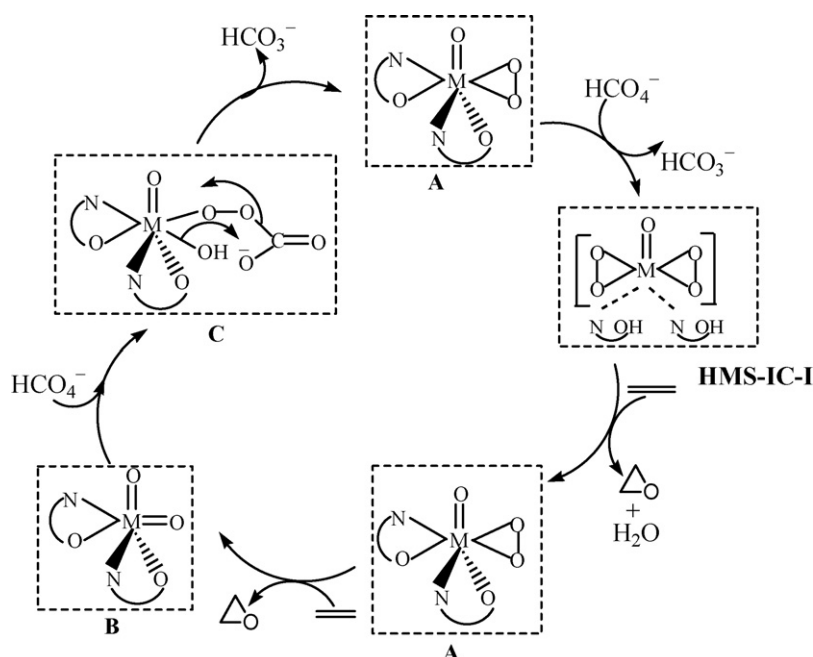
Scheme 1. The dotted rectangular line signifies the mesoporous silica. **A** and **B** have been isolated and spectroscopically characterized in the free form. **C** is the intermediate.
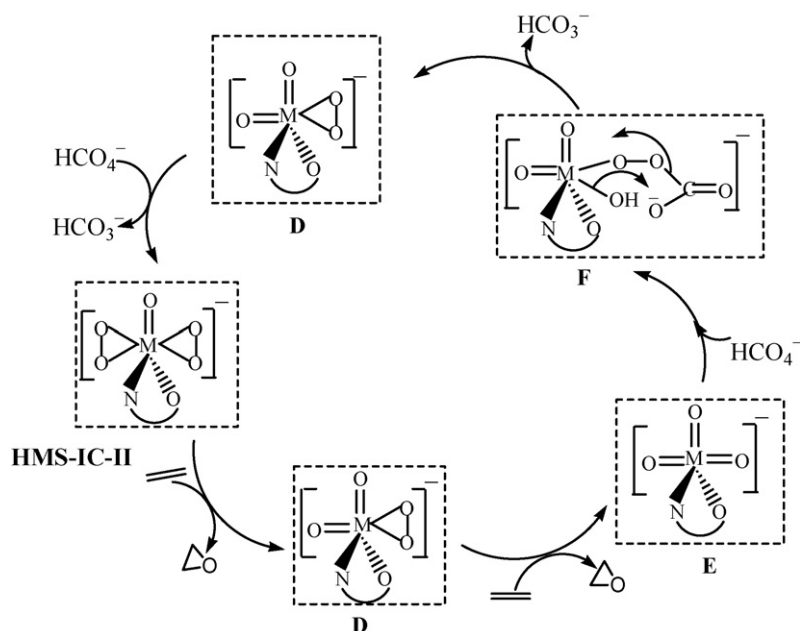
Scheme 2. The dotted rectangular line signifies the mesoporous silica. **D** and **E** have been isolated and spectroscopically characterized in the free form. **F** is the intermediate.

catalyst and the results have been given in Table 1. It is clear that in the absence of any added catalyst the conversion of styrene was very poor viz. 7.8%. For the homogeneous reactions, although % yield of all these oxidation reactions were more than 94% together with the presence of epoxide as the sole product, the recycling efficiency for both the catalyst was very poor as the catalysts get deactivated after one reaction cycle.

When the reactions were carried out in absence of $NaHCO_3$, much lower epoxide selectivity together with undesired diols was formed for all the substrates and result for 1-octene has been given in Table 1 as a representative case. Thus the role of $NaHCO_3$ in these reactions is to retard the hydrolysis of the epoxide products. It is pertinent to mention that sodium bicarbonate has been rarely used as a co-catalyst in a heterogeneous catalytic system in the presence of dilute aqueous H_2O_2 as oxidant [31–33]. Interestingly, $NaHCO_3$ alone can produce epoxides with low to moderate yields. This signifies that these epoxidation reactions are catalytic in the presence of bicarbonate. Use of catalytic amount of bicarbonate in absence of metal catalyst fails to produce any epoxide. Bicarbonate activated H_2O_2 shows enormous efficiency of epoxidation than H_2O_2 alone, because of the formation of peroxymonocarbonate (HCO_4^-) [34,35], which is a more reactive nucleophile than H_2O_2 and speeds up the reaction. This peroxymonocarbonate species is very stable and it remains in this form at the end of the reaction. In Schemes 1 and 2 mechanism of the epoxidation reactions over the immobilized complexes HMS-IC-I and HMS-IC-II have been illustrated. Each mole of olefin can be epoxidized in the presence of monooxodiperoxo species and the intermediate dioxo and trioxo species formed returned back to monooxodiperoxo centers in the presence of HCO_4^-. Since one mole of HCO_3^- is generated during the reaction from each mole of HCO_4^- consumed, concentration of bicarbonate remained unaltered after the reaction. Thus bicarbonate can be recycled for further uses. These catalytic cycles go on over these HMS-IC-I and HMS-IC-II surfaces resulting in high TONs for both the immobilized catalysts. Thus our experimental data revealed that in presence of the immobilized heterogeneous catalyst $NaHCO_3$ could work very efficiently as a co-catalyst. This could open a new application area in heterogeneous catalytic system in future.

4. Conclusion

We have immobilized neutral and anionic oxodiperoxo-8-quinolinolato Mo(VI) complexes over highly ordered mesoporous silica. Powder XRD data demonstrated retention of 2D-hexagonal mesophase and spectroscopic results revealed moderate loading of the metal complexes in the mesoporous host. The heterogenization of these soluble metal complexes resulted excellent catalytic activity and epoxide selectivity in the oxidation of various olefins in the presence of H_2O_2 as oxidant. Our experimental results suggested considerable enhancement of catalytic efficiency while heterogenizing the Mo(VI) containing homogeneous catalytic systems. After many cycles the immobilized catalysts retained their catalytic efficiency and selectivity, indicating the potential application of the immobilized catalysts in large-scale processes.

References

[1] J. Zhao, A.M. Santos, E. Herdtweck, F.E. Kühn, J. Mol. Catal. A: Chem. 222 (2004) 265.
[2] R. Bandyopadhyay, S. Biswas, S. Guha, A.K. Mukherjee, R. Bhattacharyya, Chem. Commun. (1999) 1627.
[3] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
[4] M. Vasconcellos-Dias, C.D. Nunes, P.D. Vaz, P. Ferreira, M.J. Calhorda, Eur. J. Inorg. Chem. (2007) 2917.
[5] P. Wu, T. Tatsumi, J. Phys. Chem. B 106 (2002) 748.
[6] A. Bhaumik, R. Kumar, J. Chem. Soc. Chem. Commun. (1995) 349.
[7] Y. Liu, K. Murata, M. Inaba, N. Mimura, Catal. Commun. 4 (2003) 281.
[8] S. Mukherjee, S. Samanta, A. Bhaumik, B.C. Ray, Appl. Catal. B: Environ. 68 (2006) 12.
[9] H.U. Blaser, B. Pugin, F. Spinder, J. Mol. Catal. A: Chem. 231 (2005) 1.
[10] B. Viswanathan, B. Jacob, Catal. Rev. Sci. Eng. 47 (2005) 1.
[11] P. McMorn, G.J. Hutching, Chem. Soc. Rev. 33 (2004) 108.

[12] S.M. Bruno, B. Monteiro, M.S. Balula, F.M. Pedro, M. Abrantes, A.A. Valente, M. Pillinger, P. Ribeiro-Claro, F.E. Kühn, I.S. Gonçalves, J. Mol. Catal. A: Chem. 260 (2006) 11.
[13] P. Célestin Bakala, E. Briot, L. Salles, J.-M. Brégeault, Appl. Catal. A: Gen. 300 (2006) 91.
[14] S.M. Coman, M. Florea, V.I. Parvulescu, V. David, A. Medvedovici, D. De Vos, P.A. Jacobs, G. Poncelet, P. Grange, J. Catal. 249 (2007) 359.
[15] T. Luts, W. Suprun, D. Hofmann, O. Klepel, H. Papp, J. Mol. Catal. A: Chem. 261 (2007) 16.
[16] J. Chakraborty, M. Nandi, H. Mayer-Figge, W.S. Sheldrick, L. Sorace, A. Bhaumik, P. Banerjee, Eur. J. Inorg. Chem. (2007) 5033.
[17] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[18] T. Kimura, Micropor. Mesopor. Mater. 77 (2005) 97.
[19] M. Jia, W.R. Thiel, Chem. Commun. (2002) 2392.
[20] C.D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romão, J. Rocha, I.S. Gonçalves, J. Mater. Chem. 12 (2002) 1735.
[21] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 243 (2006) 170.
[22] P. Ferreira, I.S. Gonçalves, F.E. Kühn, A.D. Lopes, M.A. Martins, M. Pillinger, A. Pina, J. Rocha, C.C. Romão, A.M. Santos, T.M. Santos, A.A. Valente, Eur. J. Inorg. Chem. (2000) 2263.

[23] A.A. Valente, Ž. Petrovski, L.C. Branco, C.A.M. Afonso, M. Pillinger, A.D. Lopes, C.C. Romão, C.D. Nunes, I.S. Gonçalves, J. Mol. Catal. A: Chem. 218 (2004) 5.
[24] A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, J. Mol. Catal. A: Chem. 107 (1996) 225.
[25] A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, M. Hanzlik, A.S.T. Chiang, F.E. Kühn, Appl. Catal. A 281 (2005) 267.
[26] S. Tangestaninejad, V. Mirkhani, M. Moghadam, G. Grivani, Catal. Commun. 8 (2007) 839.
[27] S.K. Maiti, S. Banerjee, A.K. Mukherjee, K.M. Abdul Malik, R. Bhattacharyya, New J. Chem. 29 (2005) 554.
[28] D. Chandra, N.K. Mal, M. Mukherjee, A. Bhaumik, J. Solid State Chem. 179 (2006) 1802.
[29] D. Chandra, A. Bhaumik, Ind. Eng. Chem. Res. 45 (2006) 4879.
[30] T. Kang, Y. Park, J. Yi, Ind. Eng. Chem. Res. 43 (2004) 1478.
[31] R. Kumar, P. Mukherjee, A. Bhaumik, Catal. Today 49 (1999) 185.
[32] N.A. Stephenson, A.T. Bell, J. Mol. Catal. A: Chem. 258 (2006) 231.
[33] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
[34] H. Yao, D.E. Richardson, J. Am. Chem. Soc. 122 (2000) 3220.
[35] B.S. Lane, M. Vogt, V.J. DeRose, K. Burgess, J. Am. Chem. Soc. 124 (2002) 11946.