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Polymer-supported bis (2-hydroxyanyl) acetylacetonato molybdenyl Schiff base catalyst as effective, selective and highly reusable catalyst in epoxidation of alkenes

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ABSTRACT

Polymer-supported bis (2- hydroxylanyl) acetylacetone Schiff base ligand was prepared by reaction of bis (2- hydroxylanyl) acetylacetone with chloromethylated polystyrene in DMF. In the subsequent reaction of this polymer-supported Schiff base ligand with $MoO_2(acac)_2$ the polymer-supported bis (2- hydroxylanyl) acetylacetonato MoO_2 Schiff base complex was prepared. This polymer-supported molybdenum Schiff base catalyst was highly active and selective in epoxidation of various alkenes in the presence of *tert*-buthyl hydroperoxide (TBHP) in CCl_4. It can be recovered and reused for 8 times without any loss in its activity.

In recent years much effort has been devoted to heterogenization of homogeneous catalysts on insoluble supports because homogeneous catalysts suffer from drawback of poor catalyst recovery and product separation [1–3]. Furthermore in homogeneous catalyst systems the formation of μ-oxo dimmers or other polymeric species lead to irreversible catalyst deactivation process. In order to overcome to this shortcoming and combine the advantages of homogeneous and heterogeneous catalyst, homogeneous active catalysts have been immobilized in several heterogeneous organic and inorganic supports [4,5]. In addition to inorganic supports, polymeric counterparts have gained attention because they are inert, nontoxic, nonvolatile, insoluble and recyclable [6,7]. Among the polymeric supports, chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely used supports [8]. Different approaches like encapsulation, intercalation, ion exchange and covalent attachment of homogeneous catalyst on functionalized polymeric surfaces or inorganic solids were used for this strategy [9–13]. Recently immobilization of transition metal complex on polymeric supports through covalent grafting has received wide attention and they were used extensively in organic reactions [14,15].

Oxidation of alkenes to their corresponding epoxides is one of the most important reactions in organic synthesis and it is both of academic and industrial interest. The reaction products–epoxides are used widely as intermediates in organic synthesis, pharmaceuticals as well as polymer production. They are used to provide industrially important products such as surfactants, detergents, antistatic agents and corrosion protection agents, lubricating oils, textiles and cosmetics. On the other hand, they play an important role in the formation of various biologically active compounds [16].

High-valent d^0 transition metal complexes such as Mo^{VI}, V^V and Ti^{IV} are good catalysis for olefin epoxidation reactions, usually by employing *tert*-butyl hydroperoxide (TBHP) as mono-oxygenated oxidant but among these metal complexes molybdenum complexes are considered to be very effective catalysts [17–20]. Numerous attempts have been made to immobilize homogeneous Schiff base complexes, such as, anchoring of them on a polymeric matrix for oxidation reactions [21–23]. Here we report the preparation of polymer-supported molybdenum-based catalyst as efficient heterogeneous catalyst by coordination of Mo^{VI} on anchored Schiff base ligand onto polystyrene.

We have developed convenient catalyst preparation procedures by two simple reactions. Scheme 1 shows the preparation procedures of polymer-supported bis (2- hydroxylanyl) acetylacetonato molybdenyl Schiff base catalyst. In this approach the MoO_2 Schiff base complex is attached via a covalent bond to pendant chloromethyl group on the surface of polymer. Chloromethylated polystyrene resin was reacted with bis (2- hydroxylanyl) acetylacetone Schiff base ligand in DMF [24(a)]. The polymer-supported Schiff base ligand of **1** was used to the immobilization of molybdenyl dication (MoO_2^{2+}) by reaction of this supported Schiff base ligand and $MoO_2(acac)_2$ complex in DMF as a reaction solvent [24(b)]. The principal evidence for anchoring of Schiff base ligand onto polymer (**1**) is appearance and loss of IR peaks that correspond to replace Schiff base ligand on chlorine of chloromethylated polystyrene. In the free Schiff base ligand of $\mathbf{H_2L}$ the imine vibration frequencies appeared in lower frequencies at 1606 cm^{-1} because of existence of strong hydrogen bonding between protons of phenolic OH and nitrogens of imine. In the FT-IR spectrum of polymer-bound Schiff base ligand in similar to unsupported Schiff base ligand ($\mathbf{H_2L}$) a broad band

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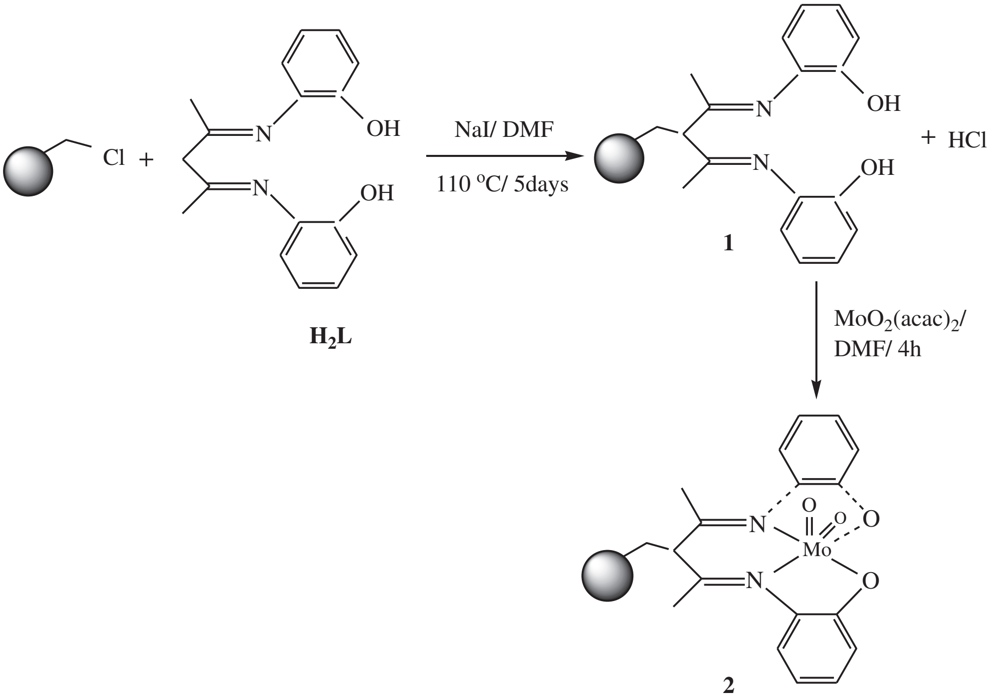


Scheme 1. Preparation procedures of polymer-supported bis (2-hydroxyanyl) acetylacetonato molybdenyl Schiff base catalyst.

appeared in the region of 1620–1560 cm^{-1} that overlapped with C═C stretching vibration frequencies of phenyls of polystyrene support. The N content of resin **1** was also determined by elemental analysis that obtained 2.06% (1.5 mmol/g) which is another evidence of this reaction performance on the resin surface. Further evidence for this reaction on the chloromethylated polystyrene resin noted by decreasing in intensity of the peak at 1266 cm^{-1} in the FT-IR spectrum of the **1**, corresponded to the H–C–Cl wagging modes of the original chloromethylated resin [25].

In the subsequent reaction of $MoO_2(acac)_2$ with polymer-supported Schiff base ligand the molybdenyl dication (MoO_2^{2+}) was coordinated to the supported Schiff base ligand by attracting of two hydrogen bonded protons of resin **1** by two acac^{-1} of $MoO_2(acac)_2$. This coordination has considerable effect on the stretching vibration frequencies of C═N bonds of Schiff base ligand because of the elimination of protons and consequently deleting of strong hydrogen bondings and substitution of MoO_2^{2+} dication instead of two protons. Thus the stretching vibration frequencies of C═N bonds of coordinated Schiff base (resin **2**) shifts to higher frequencies and lies at 1654 cm^{-1} in similar to supported bis (acetylacetone) ethylene diimine Co(II) complex [26]. In the FT-IR spectrum of polymer-supported molybdenyl Schiff base complex (**2**) two new peaks appeared at 908 cm^{-1} and 950 cm^{-1} that corresponded to the Mo═O stretching vibrations. The molybdenum content of the resin **2** was also determined by NAA (neutron activation analysis) that obtained 5.5%. The supported molybdenyl Schiff base complex was firstly tested in epoxidation of cylooctene as a model substrate. The epoxidation reaction was investigated in different solvents and oxidants (Tables 1 and 2, respectively) in the presence of supported molybdenyl Schiff base catalyst **2** [27]. The results showed that in chlorinated solvents such as CCl_4, $CHCl_3$ and CH_2Cl_2 in the presence of TBHP high epoxide yields were observed. The high epoxide yield for CCl_4 in comparison to $CHCl_3$ and CH_2Cl_2 can be related to high boiling point of CCl_4.

In the recent years many researchers have investigated the mechanistic aspects of molybdenum(VI)-catalyzed epoxidation reaction in the presence of TBHP [28–31]. Generally they believed the TBHP coordination to the molybdenum(VI)-center, activation by it and then oxygen transition to substrate. In addition, the high epoxide yields obtained in the chlorinated solvents such as CCl_4, $CHCl_3$, 1,1,2,2-tetrachloroethane, and 1, 2, dichloroethane [29–32] as we also observed in this research. This can be explained by hard-soft acid–base theory. The solvents such as methanol, acetone, THF, and acetonitrile containing hard coordinate donating atoms (O and N as hard bases) tend strongly to link to the hard metal centers such as Mo(VI) (as hard acid). On the other hand all of chlorinated solvents do not have any coordination ability to the metal (molybdenum(VI)) center. As the coordination ability of the solvent increases, the solvent competes with TBHP for coordination to the molybdenum(VI) and inhibits the TBHP coordination and retards the reaction progress, resulting in decreasing the epoxide yield. The effect of other different reaction media such as $NaIO_4$ and H_2O_2 on the epoxidation of cyclooctene under various conditions was also investigated (Table 2). It was clear that in CCl_4 in the presence of TBHP high epoxide yield was observed. This may be related to the ability of TBHP and the inability of the H_2O_2 and $NaIO_4$ reagents to mix with the organic substrate phase.

Thus the activity of polymer-supported molybdenyl Schiff base catalyst (**2**) in epoxidation of different alkenes was investigated in CCl_4 as a reaction solvent in the presence of TBHP as an oxidant (Table 3). These results showed that the supported molybdenyl Schiff base catalyst (**2**) was very active and selective in epoxidation of different (cyclic and linear) alkenes in the presence of TBHP in CCl_4. It was more active in

Table 1
Epoxidation of *cis*-cyclooctene catalyzed by polymer-supported bis (2- hydroxylanyl) acetylacetonato MoO_2 Schiff base catalyst in different solvents in the presence of *tert*-buthyl hydro peroxide under reflux conditions[a].

Solvent	Time (h)	Epoxide (%)[b]
CH_3COCH_3	3	No reaction
THF	3	No reaction
MeOH	3	3
CH_3CN	3	10
CH_2Cl_2	3	65
$CHCl_3$	3	84
CCl_4	1.5	97

[a] Reaction conditions: *cis*-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.05 g as 0.029 mmol/Mo), reaction solvent (5 mL).

[b] GLC yield based on the starting cyclooctene.

Table 2
Epoxidation of *cis*-cyclooctene catalyzed by polymer-supported bis (2- hydroxylanyl) acetylacetonato MoO_2 Schiff base catalyst with different oxidants under reflux conditions [a].

Solvent	Oxidant	Time (h)	Epoxide (%)[b]
CCl_4	TBHP	1.5	97
CCl_4/H_2O	H_2O_2	3	6
CCl_4/H_2O	$NaIO_4$[c]	3	2
CH_3CN/H_2O	TBHP	3	8
CH_3CN/H_2O	H_2O_2	3	25
CH_3CN/H_2O	$NaIO_4$[c]	3	4

[a] Reaction conditions: *cis*-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.05 g as 0.029 mmol/Mo), reaction solvent (5 mL).
[b] GLC yield based on the starting cyclooctene.
[c] Tetrabuthylphosphoniom bromaid (0.01 g) was used.

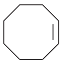
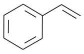
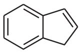
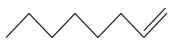
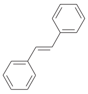
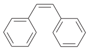
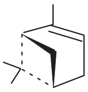
conversion of cyclic than linear alkenes. Furthermore it converts both *cis* and *trans* stylbene to only *cis* stylbene epoxide isomer.

The reusability of the titled catalyst was also investigated because it can be very important economical criteria in industrial application of catalysts especially in the case of supported one. In Table 4 the results of the reusability experiments of polymer-supported molybdenyl Schiff base catalyst (**2**) in epoxidation of cyclooctene in the presence of TBHP have been reported. These results showed that the reusability and stability of supported catalyst **2** are very high as it converts cyclooctene to its epoxide in 8 times without any decrees in its activity. This stability can be related to the strong binding of catalyst to the polystyrene support via covalent attachment.

The homogeneous liquid phase process yielding propylene oxide (the Halcon process) operated by the Arco company utilizes a soluble Mo(VI) catalyst [20,33]. A heterogeneous catalyst involving a Ti species immobilized on silica particles has also been reported by the Shell company [34] but it is unclear how extensively this catalyst system is used. After that a numerous academic works was published on polymer-supported metal complex alkene epoxidation catalysts with a number of Mo(VI) based systems looking particularly attractive for scale-up and commercial exploitation [35–40]. In comparison to these works the polymer-supported molybdenyl Schiff base catalyst (**2**) have considerable activity, selectivity and reusability.

In conclusion we have reported the simple preparation procedures for immobilization of molybdenyl Schiff base complex on polystyrene support as highly active, selective and reusable polymer-supported molybdenyl Schiff base catalyst.

Table 3
Epoxidation of alkenes catalyzed by polymer-supported bis (2- hydroxylanyl) acetylacetonato MoO_2 Schiff base catalyst with TBHP under reflux conditions [a].

Alkene	Conversion (%)[b]	Epoxide selectivity (%)[b]	Time (h)
	97	100	1.5
	68	100	0.5
	82	100	10
	21	100	10
	62	100	10
	85	100[c] (*cis*)	10
	90	100[c](*cis*)	10
	35	100	0.5

[a] Reaction conditions: *cis*-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.05 g as 0.029 mmol/Mo), reaction solvent (5 mL).
[b] GLC yield based on the starting cyclooctene.
[c] Determined by ^1H-NMR data.

Table 4
Reusability and leaching of polymer-supported bis (2- hydroxylanyl) acetylacetonato MoO_2 Schiff base catalyst in epoxidation of *cis*-cyclooctene with TBHP under reflux conditions [a].

Run	Cyclooctene epoxide (%)[b]	Time (min)	Leaching of Mo (%)[c]
1	97	1.5	1.3
2	97	1.5	0.70
3	97	1.5	0.43
4	97	1.5	0.12
5	97	1.5	–
6	97	1.5	–
7	97	1.5	–
8	97	1.5	–

[a] Reaction conditions: *cis*-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.05 g as 0.029 mmol/Mo), reaction solvent (5 mL).
[b] GLC yield based on the starting cyclooctene.
[c] Determined by ICP analysis.

References

[1] N.E. Leadbeater, M. Marco, Preparation of polymer-supported ligands and metal complexes for use in catalysis, Chem. Rev. 102 (2002) 3217–3274.
[2] Q.H. Fan, Y. Ming Li, A.S.C. Chan, Recoverable catalysts for asymmetric organic synthesis, Chem. Rev. 102 (2002) 3385–3466.
[3] A.F. Trindade, P.M.P. Gois, C.A.M. Afonso, Recyclable stereoselective catalysts, Chem. Rev. 109 (2009) 418–514.
[4] K. Ding, Y. Uozumi, Handbook of Asymmetric Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2008.
[5] G. Ertl, H. Kno¨zinger, F. Schu¨th, J. Weitkamp, in: 2nd ed., Handbook of Heterogeneous Catalysis, vols. 1–8, Wiley-VCH, Weinheim, 2008.
[6] J. Lu, T.H. Patrick, Organic polymer supports for synthesis and for reagent and catalyst immobilization, Chem. Rev. 109 (2009) 815–838.
[7] M. Benaglia, A. Puglisi, F. Cozzi, Polymer-supported organic catalysts, Chem. Rev. 103 (2003) 3401–3430.
[8] C.A. McNamara, M.J. Dixon, M. Bradley, Recoverable catalysts and reagents using recyclable polystyrene-based supports, Chem. Rev. 102 (2002) 3275–3300.
[9] A. Choplin, F. Quignard, From supported homogeneous catalysts to heterogeneous molecular catalysts, Coord. Chem. Rev. 178–180 (1998) 1679–1702.
[10] R. Akiyama, S. Kobayashi, "Microencapsulated" and related catalysts for organic chemistry and organic synthesis, Chem. Rev. 109 (2009) 594–642.
[11] J.M. Fraile, J.I. Garca, J.A. Mayoral, Noncovalent immobilization of enantioselective catalysts, Chem. Rev. 109 (2009) 360–417.
[12] Z. Wang, G. Chen, K. Ding, Self supported catalysts, Chem. Rev. 109 (2009) 322–359.
[13] P. Barbaro, F. Liguori, Ion exchange resins: catalyst recovery and recycle, Chem. Rev. 109 (2009) 515–529.
[14] C. Baleizão, H. Garcia, Chiral salen complexes: an overview to recoverable and reusable homogeneous and heterogeneous catalysts, Chem. Rev. 106 (2006) 3987–4043.
[15] D.E.D. Vos, M. Dams, B.F. Sels, P.A. Jacobs, Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations, Chem. Rev. (2002) 3615–3640.
[16] T. Luts, R. Frank, W. Suprun, S. Fritzsche, E.H. Hawkins, H. Papp, Epoxidation of olefins catalyzed by novel Mn(III) and Mo(IV)-salen complexes immobilized on mesoporous silica gel: part II: study of the catalytic epoxidation of olefins, J. Mol. Catal. A Chem. 273 (2007) 250–258.
[17] M.R. Maurya, M. Kumar, U. Kumar, Polymer-anchored vanadium(IV), molybdenum(VI) and copper(II) complexes of bidentate ligand as catalyst for the liquid phase oxidation of organic substrates, J. Mol. Catal. A Chem. 273 (2007) 133–143.
[18] H. Deleuze, X. Schultze, D.C. Sherrington, Reactivity of some polymer-supported titanium catalysts in transesterification and epoxidation reactions, J. Mol. Catal. A Chem. 159 (2000) 257–267.
[19] D.C. Sherrington, Polymer-supported metal complex alkene epoxidation catalysts, Catal. Today 57 (2000) 87–104.
[20] R. Mbeleck, K. Ambroziak, B. Saha, D.C. Sherrington, Stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts, React. Funct. Polym. 67 (2007) 1448–1457.
[21] K.C. Gupta, A.K. Sutar, C.C. Lin, Polymer-supported Schiff base complexes in oxidation reactions, Coord. Chem. Rev. 253 (2009) 1926–1946.
[22] Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation, Chem. Rev. 105 (2005) 1603–1662.
[23] T. Punniyamurthy, S. Velusamy, J. Iqbal, Recent advances in transition metal catalyzed oxidation of organic substrates with molecular oxygen, Chem. Rev. 105 (2005) 2329–2364.
[24] a) Preparation of polymer-supported bis (2- hydroxylanyl) acetylacetone **1**: to a 60 mL DMF in a 100 mL round bottom flask was added 2 g chloromethylated polystyrene, 4 g of bis (2- hydroxylanyl) acetylacetone and 0.03 g NaI and the content was heated in 110 °C for 5 days with stirring. After cooling to room

temperature the mixture was filtered and washed thoroughly with methanol and the resin beads were dried in an oven at 100 °C. b) Preparation of polymer-supported bis (2- hydroxylanyl) acetylacetonato molybdenyl Schiff base catalyst **2**: to a 60 mL DMF in a 100 mL round bottom flask was added 1 g of polymer-supported bis (2- hydroxylanyl) acetylacetone **1**. After stirring for 1 h to swell the polymer, 2 g of $MoO_2(acac)_2$ was added to this mixture and the content was heated for 3 h at 110 °C. Then the content was filtered and the beads were washed thoroughly with chloroform and dried in an oven at 80 °C.

[25] M.D. Angelino, P.E. Laibinis, Synthesis and characterization of a polymer-supported salen ligand for enantioselective epoxidation, Macromolecules 31 (1998) 7581–7587.

[26] K.C. Gupta, H.K. Abdulkadir, S. Chand, Polymer-immobilized N, N′-bis(acetylacetone) ethylenediamine cobalt(II) Schiff base complex and its catalytic activity in comparison with that of its homogenized analogue, J. Appl. Polym. Sci. 90 (2003) 1398–1411.

[27] Typical procedure for epoxidation reactions catalyzed by polymer-supported bis (2- hydroxylanyl) acetylacetonato molybdenyl Schiff base catalyst **2**: to a 25 mL round bottom flask equipped with a magnetic stirring bar was added 5 mL CCl_4, 0.5 mmol alkene, 1.5 mmol tert-butylhydroperoxide, 0.05 g (0.029 mmol/Mo) catalyst and was refluxed. The progress of reaction was monitored by GLC.

[28] M. Groarke, I.S. Gonçalves, W.A. Herrmann, F.E. Kühn, New insights into the reaction of *t*-butylhydroperoxide with dichloro- and dimethyl(dioxo)molybdenum(VI), J. Organomet. Chem. 649 (2002) 108–112.

[29] S. Rayati, N. Rafiee, A. Wojtczak, cis-Dioxo-molybdenum(VI) Schiff base complexes: synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins, Inorg. Chim. Acta 386 (2012) 27–35.

[30] Y. Li, X. Fu, B. Gong, X. Zou, X. Tu, J. Chen, Synthesis of novel immobilized tridentate Schiff base dioxomolybdenum(VI) complexes as efficient and reusable catalysts for epoxidation of unfunctionalized olefins, J. Mol. Catal. A Chem. 322 (2010) 55–62.

[31] M. Bagherzadeh, R. Latifi, L. Tahsini, V. Amani, A. Ellern, L.K. Woo, Synthesis, characterization and crystal structure of a dioxomolybdenum(VI) complex with a N,O type bidentate Schiff base ligand as a catalyst for homogeneous oxidation of olefins, Polyhedron 28 (2009) 2517–2521.

[32] K. Ambroziak, R. Pelech, E. Milchert, T. Dziembowskaa, Z. Rozwadowski, New dioxomolybdenum(VI) complexes of tetradentate Schiff base as catalysts for epoxidation of olefins, J. Mol. Catal. A Chem. 211 (2004) 9–16.

[33] J. Kollar, US Patent No. 3,350,422 (1967); 3,351,635 (1967); 3,507,809 (1970); 3,625,981 (1971) to Halcon International.

[34] H.P. Wulff, Brit. Patent No. 1,249,079 (1971); US Patent No.3,923,843 (1975) to Shell Oil.

[35] K. Ambroziak, R. Mbeleck, Y. He, B. Saha, D.C. Sherrington, Investigation of batch alkene epoxidations catalyzed by polymer-supported Mo(VI) complexes, Ind. Eng. Chem. Res. 48 (2009) 3293–3302.

[36] S. Leinonen, D.C. Sherrington, A. Sneddon, D. McLoughlin, J. Corker, C. Canevali, F. Morazzoni, J. Reedijk, S.B.D. Spratt, Molecular structural and morphological characterization of polymer supported Mo(VI) alkene epoxidation catalysts, J. Catal. 183 (1999) 251–266.

[37] J.H. Ahn, J.C. Kim, S.K. Ihm, C.G. Oh, D.C. Sherrington, Epoxidation of olefins by molybdenum(VI) catalysts supported on functional polyimide particulates, Ind. Eng. Chem. Res. 44 (2005) 8560–8564.

[38] M.M. Miller, D.C. Sherrington, Alkene epoxidations catalyzed by Mo(VI) supported on imidazole-containing polymers I. Synthesis, characterization, and activity of catalysts in the epoxidation of cyclohexene, J. Catal. 152 (1995) 368–376.

[39] M.M. Miller, D.C. Sherrington, S. Simpson, Alkene epoxidations catalysed by molybdenum(VI) supported on imidazole-containing polymers. Part 3. Epoxidation of Oct-1-ene and propene, J. Chem. Soc. Perkin. Trans. 2 (1994) 2091–2096.

[40] K.C. Gupta, Alekha Kumar Sutar, Chu-Chieh Lin, Polymer-supported Schiff base complexes in oxidation reactions, Coord. Chem. Rev. 253 (2009) 1926–1946.