ELSEVIER

Epoxidations of olefins catalysed by new Mn(II) salen immobilized mesoporous materials

Boyapati Manoranjan Choudary [a, *], Mannepalli Lakshmi Kantam [a], Balagam Bharathi [a], Pentlavally Sreekanth [a], Francois Figueras [b]

[a] *Inorganic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b] *Institut de Recherches sur la Catalyse, CNRS, 2 av. A. Einstein, 69626, Villeurbanne, Cedex, France*

Abstract

Covalently anchored Mn(II) salen complexes on mesoporous materials have been prepared by direct condensation of prefabricated Mn complex on the support or via ensembling step-wise salen entities on the support and subsequent complexation. The resultant anchored complexes have been compared with the immobilised Mn(II) salen complexes on mesoporous materials prepared by the process of cationic exchange of a Mn(II) salen complex for the epoxidation of styrene and cyclic olefins with different oxidizing agents such as PhIO and *m*-chloroperbenzoic acid. Both types of samples show comparable structures but the anchored complexes can be recycled with perbenzoic acid as oxidant. © 2000 Elsevier Science B.V. All rights reserved.
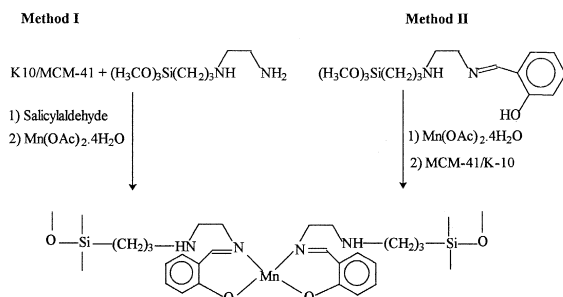
1. Introduction

Epoxides are versatile building blocks in organic syntheses [1,2]. Although Srinivasan et al. [3] reported Mn(II) salen complexes for the epoxidation of olefins for the first time in 1986, the chiral Mn(III) salen complexes reported by Jacobsen [1,2] and Katsuki's groups [4] have emerged as the most promising catalysts of the decade for the enantiomeric epoxidation of the unfunctionalised olefins triggering vigorous research all over the world on Mn(II) salen systems. The immobilisation of transition metal complexes on solid supports can provide catalysts that are easier to handle and possibly exhibit improved activities and selectivities expected to be induced by the support [5–7]. Heterogenized Mn-porphyrin, Mn(II) salen and its analogues using clays [7], microporous zeolites [8–10], MCM-41 [11–15] and polymer supports [16,17] have been reported. Different strategies have been used in these preparations involving ship in the bottle synthesis wherein the complex is formed by reaction of the ligand on a Mn-zeolite [8–10] or Mn-MCM-41 [11], exchange of a cationic Mn complex with montmorillonite [7] or MCM-41 [12,13] or anchoring of a polydentate ligand, which is further reacted

* Corresponding author. Tel.: +91-40-7170921; fax: +91-40-7173387.

E-mail address: choudary@iict.ap.nic.in (B.M. Choudary).

Method I

K10/MCM-41 + $(H_3CO)_3Si(CH_2)_3NH$ NH_2

1) Salicylaldehyde
2) Mn(OAc)$_2$.4H$_2$O

Method II

$(H_3CO)_3Si(CH_2)_3NH$ N= (phenyl with HO)

1) Mn(OAc)$_2$.4H$_2$O
2) MCM-41/K-10

O—Si—(CH$_2$)$_3$—HN N NH—(CH$_2$)$_3$—Si—O Mn complex

Scheme 1.

with a Mn salt [14,15]. However, the turnover number reported so far for the epoxidation of unfunctionalised olefins is relatively low.

We devised and synthesised new covalently anchored Mn(II) salen complexes via ensembling step-wise salen entities and subsequent complexation with Mn or directly condensing silylated prefabricated Mn(II) salen complex onto mesoporous supports, MCM-41 and K10 montmorillonite as described in Scheme 1. The resultant anchored complexes have been compared with immobilised Mn(II) salen complexes on montmorillonite K10 and MCM-41 prepared by cationic exchange process for the epoxidation of unfunctionalised olefins using iodosyl benzene (PhIO) and *m*-chloroperbenzoic acid (mCPBA) as oxidants. The exercise has been undertaken with an objective to evolve the best catalyst system initially suited for epoxidation reactions in general, ultimately to generate heterogeneous chiral catalysts

2. Experimental

2.1. Preparation of Achiral Mn(II) salen exchanged montmorillonite (A) / MCM-41 (B)

Achiral Mn(II) salen exchanged clay (**A**) and MCM-41 (**B**) were prepared by refluxing 2 g of Na–K10 clay or Na–Al–MCM-41 [18] and 1 g of Mn(II) salen in 50 ml of H$_2$O at 100°C for 24 h. The solid catalyst was filtered, washed with ethanol and dried under vacuum at 100°C for 24 h. The complexes were subjected to Soxhlet extraction in ethanol for about 8 h.

2.2. Anchored complexes

Anchored complexes are (Scheme 1) prepared by two methods.

Method I: 3 mmol of 3-trimethoxysilylpropylethylenediamine and 10 g of H$^+$–K10 montmorillonite or pure siliceous MCM-41 [18] were refluxed in toluene followed by filtering, washing with toluene and ether and drying under vacuum for 8 h. The solid encompassing the silylpropyl-ethylenediamine moiety was then refluxed with 6 mmol of salicylaldehyde in 20 ml of ethanol for 8 h to give a Schiff base. The anchored Mn(II) salen K10 (C) and MCM-41 (D) were prepared by reacting the Schiff base anchored on the solid with Mn(OAc)$_2$ · 4H$_2$O in ethanol as described above. The complexes were subjected to Soxhlet extraction in ethanol for about 8 h.

Method II: Following a procedure adopted for the preparation of a heterogeneous silica supported chromium Schiff base complex [19], 6 mmol of salicylaldehyde in 20 ml of ethanol was added to 3 mmol of 3-trimethoxysilylpropylethylenediamine to give a Schiff base. The solution instantly became yellow due to imine formation. Mn(OAc)$_2$ · 4H$_2$O in ethanol was then added to the above solution and the mixture stirred for 30 min to allow the new ligand to complex with manganese. Ten grams of H$^+$–K10 montmorillonite or pure siliceous MCM-41 [18] were then added and stirred overnight in toluene followed by filtering, washing with toluene and ether and drying under vacuum for 8 h. The anchored Mn(II) salen K10 (E) and MCM-41 (F) were subjected to Soxhlet extraction in ethanol for about 8 h.

2.3. Characterisation

The metal (Mn) content analysis was estimated on inductively coupled plasma emission spectrometer, Lab Tam (Australia). X-ray diffraction patterns were determined on a Philips instrument, using Ni-filtered Cu-Kα radiation. Proton nuclear magnetic resonance (^{1}H NMR)

spectra were taken on a Gemini Varian (200 MHz) NMR spectrometer, using TMS as an internal standard. IR spectra were recorded on a Nicolet DX-5 spectrometer. ESR spectroscopic analyses were performed on a Varian spectrometer. UV spectra were recorded at room temperature on a Varian Lamda 9 UV–VIS Spectrometer, after dilution of the sample in MgO (25% of the sample). The products of the reaction were characterised by comparison of their NMR and IR spectra with those reported in the literature.
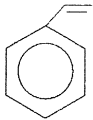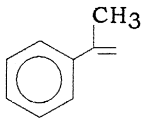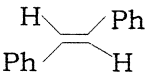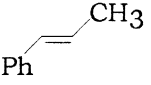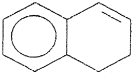
3. Results and discussion

Plasma analysis shows that the solids retain manganese: 2.05% Mn for **A**, 1.09% for **B**, 0.99% for **C**, 1.92% for **D**. Manganese content in the anchored complexes prepared by method II, 1.1% for **E**, 1.81% for **F**. X-ray diffractogram of MCM-41 undergoes no structural change during the preparation of the catalyst [13]. The ESR spectra of the Mn(II)-salen immobilised on K10 and MCM-41 prepared by ion exchange (**A** and **B**) and covalently bound (**C**, **D**, **E** and **F**) show an identical sextuplet signal centered at the position of DPPH, characteristic of Mn(II) ions. Interestingly, this indicates the reduction of Mn(III) complex to Mn(II) for the samples prepared by ion exchange, during the process of ion exchange. No dimerisation was observed even when the complexes were handled in air [11]. The infrared spectrum of the free ligand shows a band at 1630 cm^{-1} attributed to the C = N stretching vibration of the imine. This is reduced to 1600 cm^{-1} in anchored complexes. The UV–VIS spectra of the solids **A**, **B**, **C**, **D**, **E** and **F** of both exchanged and anchored Mn(II) salen montmorillonite, and MCM-41 diluted in MgO, which show bands at 240, 280, 320, 390 and 500 nm recorded a slight variation from the absorption spectra of the corresponding pure Mn(II) salen complex whose bands appeared at 236, 280, 309, 416 and 537 nm. This suggests a slight distortion of the Mn(II) complex immobilised on the surface.

The silylated prefabricated complex prepared as given in Scheme 1 shows identical ESR and UV absorption spectra with pure Mn(II) salen complex indicating that there is no change in coordination. This result substantiates the Mn complexation with two independent salen moieties. The almost identical characterisation data of the anchored complexes on both the supports prepared by step-wise ensembling with the complexes and by direct condensation of silylated prefabricated Mn(II) salen complex demonstrates that the Mn is complexed with two independent salens. Thus, it is established that the complexation of Mn with salen is intermolecular.

All the catalysts (**A**–**F**) thus prepared were employed in the epoxidation of unfunctionalised olefins and the results are reported in Table 1. The extent of conversion of different olefins was estimated by ^{1}H NMR spectroscopy. The effects of various oxidants were studied: PhIO and mCPBA in conjunction with *N*-methylmorpholine-*N*-oxide (NMO).

Whatever the type of preparation, the results are very good for the epoxidation of cyclic olefins or styrene, but these solids display moderate activity for substituted styrenes. The activity changes with the oxidant in the order of PhIO > mCPBA. Recyclability is a real test to determine the efficacy of the catalyst for number of recycles and to establish turn over frequency and number, the factors ultimately decide productivity per hour, total productivity and finally the economics of the process. The major problem of these supported catalysts is the protocol to be adopted for recycling. Indeed, recycling of the catalysts was not very efficient with iodosylbenzene (PhIO) because it was impossible to completely free the catalyst from PhIO$_2$, a disproportionate product of PhIO, insoluble in all the solvents used [17]. Recycling was, however, possible when using mCPBA-NMO as oxidizing system in CH$_2$Cl$_2$ as used by Zhang et al. [20]. This oxidant permits to work at low temperatures and is the best for the enantioselective epoxidation of styrene, there-

Table 1
Epoxidation using Mn(II) salen immobilized mesoporous materials[a]

Entry	Substrate	Catalyst	Yield (%)[b] PhIO	mCPBA[c]
1	(styrene)	A	90	--
		B	70	--
		C	75	68[d], 62[e]
		D	65	65[d], 60[e]
		E	-	68[d], 65[e]
		F	-	67[d], 64[e]
2	(α-methylstyrene)	A	50	--
		B	50	--
		C	45	--
3	(trans-stilbene)	A	35	--
		B	48	--
4	(β-methylstyrene)	A	45	--
		B	33	--
5	(dihydronaphthalene)	A	83	--
		B	73	--
6	(cyclooctene)	A	85	--

a) Reactions were run at 25°C in 10 ml CH_3CN containing 0.100g of catalyst, 1mmol of olefin, 2mmol of PhIO, 0.5 mmol of NMO, 24 h; b) NMR yields based on olefin; c) Reactions were run at 0°C in 10ml DCM containing 0.06mmol of Mn catalyst, 1mmol of olefin, 1.92mmol MCPBA, 4.8mmol of NMO, 2h; d) Recycle 1; e) Recycle 4.

fore, the stability was carefully studied in that case. The activity of the catalysts prepared by ion exchange considerably decreased on each recycle due to substantial leaching of Mn(II)

salen during the epoxidation reactions as is observed in zeolites [9]. In effect, it is the neutral complex that adhered onto support, since this complex is reduced during the process of ion exchange from trivalent to divalent. Further, the redox catalyst cycle, which involves Mn(II) ↔ Mn(III) in the epoxidation reaction, does not have any residual charge left on reduced Mn(II) to bind with the support. This accounts for the faster leaching of Mn complexes prepared by ion exchange process observed during epoxidation reactions. The manganese-salen exchanged MCM loses its complex faster than K10, probably due to its lower acidity. By contrast, the anchored catalyst preserved its efficiency even after four recycles. The turnover number of the anchored catalysts per Mn cation is close to 240.

4. Conclusion

Therefore, the design of anchored catalysts via covalent linkage reported earlier [5,21] to overcome the leaching of the complex is successful in the present endeavour. These Mn(II) salen complex anchored on mesoporous materials through an intermolecular Schiff base can be synthesised very easily and show greater potential due to their tuneable larger pore size. The present studies are directed to the synthesis of chiral covalently bound mesoporous systems in the future.

Acknowledgements

References

[1] R.A. Johnson, K.B. Sharpless, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, Chap. 4.1.
[2] E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, Chap. 4.2.
[3] K. Srinivasan, P. Michaud, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
[4] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[5] K.R. Kumar, B.M. Choudary, Z. Jamil, G. Thyagarajan, J. Chem. Soc., Chem. Commun. (1986) 130.
[6] K.J. Balkas, A.G. Gabrielor, S.L. Bell, F. Bedioui, L. Roue, J. Devyank, Inorg. Chem. 33 (1994) 67.
[7] L. Barloy, P. Battioni, D. Mansuy, J. Chem. Soc., Chem. Commun. (1990) 1365.
[8] C. Bowers, P.K. Dutta, J. Catal. 122 (1990) 271.
[9] P.P. Knops-Gerrits, M.L. Abbe, P.A. Jacobs, Stud. Surf. Sci. Catal. 108 (1997) 445.
[10] P.P. Knops-Gerrits, D.E. de Vos, P.A. Jacobs, J. Mol. Catal. 117 (1997) 57.
[11] L. Frunza, H. Kosslick, H. Landmesser, E. Hoft, R. Fricke, J. Mol. Catal. 123 (1997) 179.
[12] G.-J. Kim, S.-H. Kim, Catal. Lett. 57 (1999) 139.
[13] S.-S. Kim, W. Zhang, T.J. Pinnavaia, Catal. Lett. 43 (1997) 149.
[14] Y.V. Subba Rao, D.E. de Vos, T. Bein, P.A. Jacobs, J. Chem. Soc. Chem. Commun. (1997) 355.
[15] P. Sutra, D. Brunel, J. Chem. Soc., Chem. Commun. (1996) 2485.
[16] F. Mimitolo, D. Pini, P. Salvadori, Tetrahedron Lett. 37 (1996) 3375.
[17] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, Tetrahedron: Asymmetry 6 (1995) 2105.
[18] A. Tuel, S. Gontier, Chem. Mater. 8 (1996) 114.
[19] I.C. Chisem, J. Raflet, M.T. Shieh, J. Chisem, J.H. Clark, R. Jachuck, D. Macquarrie, C. Ramshaw, K. Scott, J. Chem. Soc., Chem. Commun. (1998) 1949.
[20] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801.
[21] K.R. Kumar, B.M. Choudary, M.L. Kantam, J. Catal. 130 (1991) 41.