New immobilized chiral Mn(III) salen complexes on pyridine N-oxide-modified MCM-41 as effective catalysts for epoxidation of nonfunctionalized alkenes

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Abstract

We prepared new chiral Mn(III) salen complexes **1′**–**4′** immobilized on pyridine N-oxide-modified MCM-41 through the axial coordination. Epoxidation of styrene and 4-chlorostyrene with the use of these complexes as catalysts in the presence of NaOCl was found to proceed enantioselectively (*ee*, 62–69%) at 0 °C in 8–12 h, which is a significantly higher enantioselectivity than that observed for their homogeneous counterparts (*ee*, 36–51%). These catalysts were also effective for the relatively bulkier alkenes, such as indene and 2,2-dimethylchromene, and have shown a reactivity (82–98%) and an enantioselectivity (69–92%) similar to those observed for their homogeneous system. The catalysts could be recycled several times without loss of performance.
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1. Introduction

The immobilization of homogeneous catalysts, which endows homogeneous systems with attractive features such as easy product separation and catalyst recovery by simple filtration, constitutes a rapidly expanding research area [1–4]. As chiral catalysts are expensive, their recovery from the reaction mixture and re-use are highly desirable. Among the systems developed so far for catalytic enantioselective epoxidation of nonfunctionalized alkenes, chiral Mn(III) salen complexes have proved to be extremely efficient in homogeneous phase [5–8], but the separation of these catalysts from the reaction mixture is problematic. Therefore, several papers have appeared recently on the immobilization of Mn(III) salen complexes on solid supports [9–18]. Considerable progress has been made with the use of poly-

meric supported catalysts [9,10,19–23], but inorganic insoluble supports have scarcely been investigated [14–16,24]. Ordered mesoporous solids like MCM-41, because of their well-defined, uniform mesopores and facile surface modification, are potential solids for the immobilization of chiral homogeneous catalysts [25] and are being explored for the immobilization of chiral metal complexes. For example, Zhou et al. [24] reported the immobilization of Cr(III) salen complex through axial coordination by an NH_2 group covalently bonded to MCM-41, which showed good catalytic activity for the epoxidation of styrene and substituted styrene in the presence of PhIO as an oxidant. Furthermore, Xiang et al. [15] synthesized MCM-41 bearing phenoxy groups that were used to immobilize Mn(III) salen complex by one coordinative bond and demonstrated that the enantioselectivity (*ee*) of the anchored catalyst is higher than that of the corresponding homogeneous catalyst for the epoxidation of α-methyl styrene. However, the catalyst failed to epoxidize bulkier alkenes, like 1-phenylcyclohexene. In

the present study, we have synthesized pyridine N-oxide-modified MCM-41 and used it to support Mn(III) salen complexes **1**–**4** through axial coordination. By incorporating pyridine N-oxide in MCM-41, we have tried to create a catalytic environment of the immobilized catalysts, **1′**–**4′**, akin to that of homogeneous Mn(III) salen complexes **1**–**4** [26]. It is worth mentioning here that no additional pyridine N-oxide is required as an axial base during the epoxidation reaction with anchored catalysts **1′**–**4′**. The epoxidation of styrene with NaOCl catalyzed by immobilized Mn(III) salen complexes, **1′**–**4′**, showed *ee* for styrene oxides in the range of 62–69%, which is significantly higher than the *ee* (36–51%) obtained with homogeneous catalysts **1**–**4**. Furthermore, complexes, **1′**–**4′**, worked well for several cycles, even for relatively bulkier alkenes such as indene and 2,2-dimethylchromene, in contrast to other reported Mn(III) salen complexes anchored on MCM-41, which failed to epoxidize bulkier and nonplanar substrates [15].

2. Experimental

Cetyltrimethylammonium bromide (CTAB), manganese acetate (s.d. Fine Chem. Ltd., India), sodium silicate solution (Kadvani Chemicals, India), isonicotinic acid (Aldrich, USA), and thionyl chloride (Rankem, India) were used as received. Indene, styrene, and 4-chlorostyrene were passed through a pad of neutral alumina before use. (1*R*,2*R*)-(−)-Cyclohexanediamine (Fluka, USA) was resolved from a technical-grade *cis–trans* mixture according to the reported procedure [27]. 2,2-Dimethylchromene was synthesized by a reported procedure [28]. All of the solvents used in the present study were purified by known methods [29]. The purity of the solvents and alkenes was determined and the product epoxide was analyzed by gas chromatography (GC) with a Shimadzu GC 14B instrument equipped with a stainless-steel column (2 m long, 3-mm inner diameter, 4-mm outer diameter) packed with 5% SE 30 (mesh size 60–80) and a FID detector. Ultrapure N_2 was the carrier gas (rate 30 ml/min), and the injection port temperature was set at 200 °C. The column temperature for styrene, 4-chlorostyrene, and indene was in the range of 70–150 °C, and for chromene the isothermal temperature was kept at 150 °C. The racemic epoxides were prepared by the epoxidation of respective alkenes with *m*-chloroperbenzoic acid in CH_2Cl_2 and were used to determine conversions by the comparison of the GC peak height and area. The *ee* of styrene oxides was determined by GC on a chiral capillary column (Chiraldex GTA). For chromene and indene epoxides, the *ee* was determined by ^{1}H NMR with the chiral shift reagent Eu(hfc)$_3$ and by HPLC (Shimadzu SCL-10AVP) with a Chiralcel column (OD,OJ/OB).

^{1}H and ^{13}C NMR spectra were recorded on a 200- and 50-MHz spectrometer (Bruker, F113V). The IR spectra were recorded on a Perkin–Elmer Spectrum GX spectrophotometer in KBr/nujol mull. Electronic spectra were recorded in dichloromethane on a Hewlett–Packard diode array spectrophotometer (model 8452A). Microanalysis of the complex was done on a Perkin–Elmer CHNS analyzer (model 2400). An inductively coupled plasma spectrometer (Perkin–Elmer, USA; model ICP Optima 3300 RL) was used for Mn estimation. Powder X-ray diffraction patterns of the samples were recorded on a Philips X"pert MPD diffractometer with Cu-K_α ($\lambda = 1.5405$ Å) radiation with a step size of 0.02° 2θ and a step time of 5 s and a curved Cu-K_α monochromator under identical conditions. The BET surface area was determined with the use of N_2 sorption data measured at 77 K with a volumetric adsorption setup (Micromeritics ASAP-2010, USA). The pore diameters of the samples were determined from the desorption branch of the N_2 adsorption isotherm with the Barret, Joyner, and Halenda (BJH) method.

2.1. Synthesis of MCM-41

A highly ordered hexagonal siliceous MCM-41 was synthesized according to the modified procedure of Das et al. [30] by the hydrothermal crystallization method. Sodium silicate (27.34% SiO_2 and 8.05% Na_2O) was used as a silica source and CTAB was used as a template. The composition of the precursor gel used for MCM-41 synthesis was in the following proportions: 1 SiO_2:0.33 Na_2O:0.5 CTAB:74 H_2O. In a typical synthesis, CTAB was dissolved in warm (40–45 °C) deionized water, and to this solution the required quantity of sodium silicate solution was added with stirring. The pH of the obtained mixture was adjusted to 10 with 1:1 H_2SO_4:H_2O (v/v) followed by vigorous stirring. The resulting gel was placed in a Teflon Parr high-pressure reactor for crystallization at 110 °C for 144 h. The solid was filtered and washed thoroughly with deionized water until it reached a pH of 7–8. It was air-dried at room temperature and calcined in air at 550 °C for 6 h.

2.2. Synthesis of immobilized chiral metal complexes **1′**–**4′**

Immobilized chiral Mn(III) salen complexes **1′**–**4′** and their precursors were synthesized as follows.

2.2.1. Synthesis of 4-pyridine carbonyl chloride hydrochloride (**B**)

The isonicotinic acid (**A**) (1 mmol) was precooled in an ice bath, and thionyl chloride (4 mmol) was added slowly. The resulting solution was heated to reflux for 6 h. The excess of thionyl chloride was removed completely by azeotropic distillation with dry benzene (10 ml × 3), and the resulting mass was dried under vacuum to give a white crystalline powder [m.p. 148–152 °C; ^{1}H NMR (200 MHz, CD$_3$OD): 8.57 (*d*, 2H), 9.07 (*d*, 2H); anal. calcd. for C$_6$H$_5$NOCl$_2$: C, 40.44; H, 2.81; N, 7.93; found: C, 40.70; H, 2.89; N, 7.98, IR (KBr) (cm^{-1}) 755, 1090, 1257, 1408, 1602, 1730, 2773, 3102].

2.2.2. Pyridine-modified MCM-41 (D)

3-Aminopropyl-triethoxysilane (APTS) (**C**) (4.56 g; 20.63 mmol) was added slowly to a solution of 4-pyridine carbonyl chloride hydrochloride (**B**) (3.5 g; 19.66 mmol) in dry DMF (70 ml) under an inert atmosphere at 40–45 °C, and the resulting solution was stirred at 110 °C for 8 h. After 8 h, calcined MCM-41 (10.0 g) was added to the above solution at 110 °C with constant stirring for 24 h. The resulting mass (**D**) was cooled to 25–30 °C and filtered. The solid collected was washed successively with dry DMF and diethyl ether and then dried under vacuum. Dried material was subjected to Soxhlet extraction with dry methanol for 24 h. The off-white solid (**D**) was finally dried at 50–55 °C under vacuum for 8 h. The characterization was done by microanalysis (Table 1), IR spectroscopy, diffuse reflectance UV–vis, and (CPMAS) ^{13}C NMR spectroscopy. [Yield 85%; IR (KBr): 459, 563, 800, 958, 1082, 1389, 1459, 1541, 1656, 2957 cm^{-1}; diffuse reflectance UV–vis: 220, 250, 280 nm; CPMAS ^{13}C, δ (ppm) 172 (amido), 147 (C2 aromatic), 125 (C3, aromatic), 7–45 (3 lines alkyl).]

2.2.3. Pyridine-N-oxide modified MCM-41 (E)

Thirty percent H_2O_2 (6 ml) was added slowly to a suspension of pyridine-MCM-41 (**D**) (2.0 g) in glacial acetic acid (5 ml), and the mixture was heated in a water bath for 3 h. After cooling, the solid was filtered and washed successively with water, 5% aqueous sodium carbonate, and water. The wet mass was dried in vacuum for 10 h at 50–55 °C. The characterization of (**E**) was accomplished by IR, CPMAS ^{13}C NMR, XRD, and solid reflectance UV–vis spectroscopy; the results are in agreement with earlier reports [31,32]. [Yield 87%; IR (KBr) ν(N–O) 1088 cm^{-1}; CPMAS ^{13}C, δ (ppm) 171 (amido), 139 (C2 aromatic), 127 (C3, aromatic) 7–45 (3 lines alkyl); diffuse reflectance UV–vis: 210, 220, 250, 280 nm.]

2.3. Preparation of the homogeneous salen complex

Chiral Mn(III) salen complexes **1**–**4** were synthesized as described earlier [26].

2.4. Synthesis of the supported catalysts 1′–4′

To a solution of the complex **1**–**4** (0.023 mmol) in dry toluene (10 ml) was added pyridine-N-oxide-modified MCM-41 (**E**) (1 g), and the resulting suspension was refluxed for 48 h under an inert atmosphere. The immobilized catalysts **1′**–**4′** were filtered, washed thoroughly with dry toluene, and extracted repeatedly with methanol and dichloromethane on a soxhlet extractor until the extraction liquid became colorless. All of the washings were combined, the solvent was evaporated, and the residue was dissolved in toluene (10 ml). The difference in initial and final concentration as measured by UV–vis spectroscopy gave the amount of complex coordinated to the axial position with oxygen atoms of pyridine N-oxide-modified MCM-41 (**E**). The chiral Mn(III) salen catalysts immobilized on MCM-41 **1′**–**4′** were characterized by microanalysis (Table 1), IR spectroscopy, diffuse reflectance UV–vis spectroscopy (DRS), XRD, ICP, and nitrogen sorption studies (Table 1).

Complex 1′ Yield 88%; IR (KBr) cm^{-1}: 3422, 2958, 1654, 1542, 1457, 1231, 1077, 959, 798; diffuse reflectance UV–vis: 402, 505 nm.

Complex 2′ Yield 89%; IR (KBr) cm^{-1}: 3421, 2953, 1654, 1624, 1544, 1455, 1390, 1232, 1078, 959, 798; diffuse reflectance UV–vis: 400, 500 nm.

Complex 3′ Yield 90%; IR (KBr) cm^{-1}: 3424, 2956, 1656, 1545, 1456, 1234, 1078, 959, 799; diffuse reflectance UV–vis: 404, 503 nm.

Complex 4′ Yield 91%, IR (KBr) cm^{-1}: 3429, 2958, 1659, 1542, 1459, 1233, 1079, 960, 802; diffuse reflectance UV–vis 406, 502 nm.
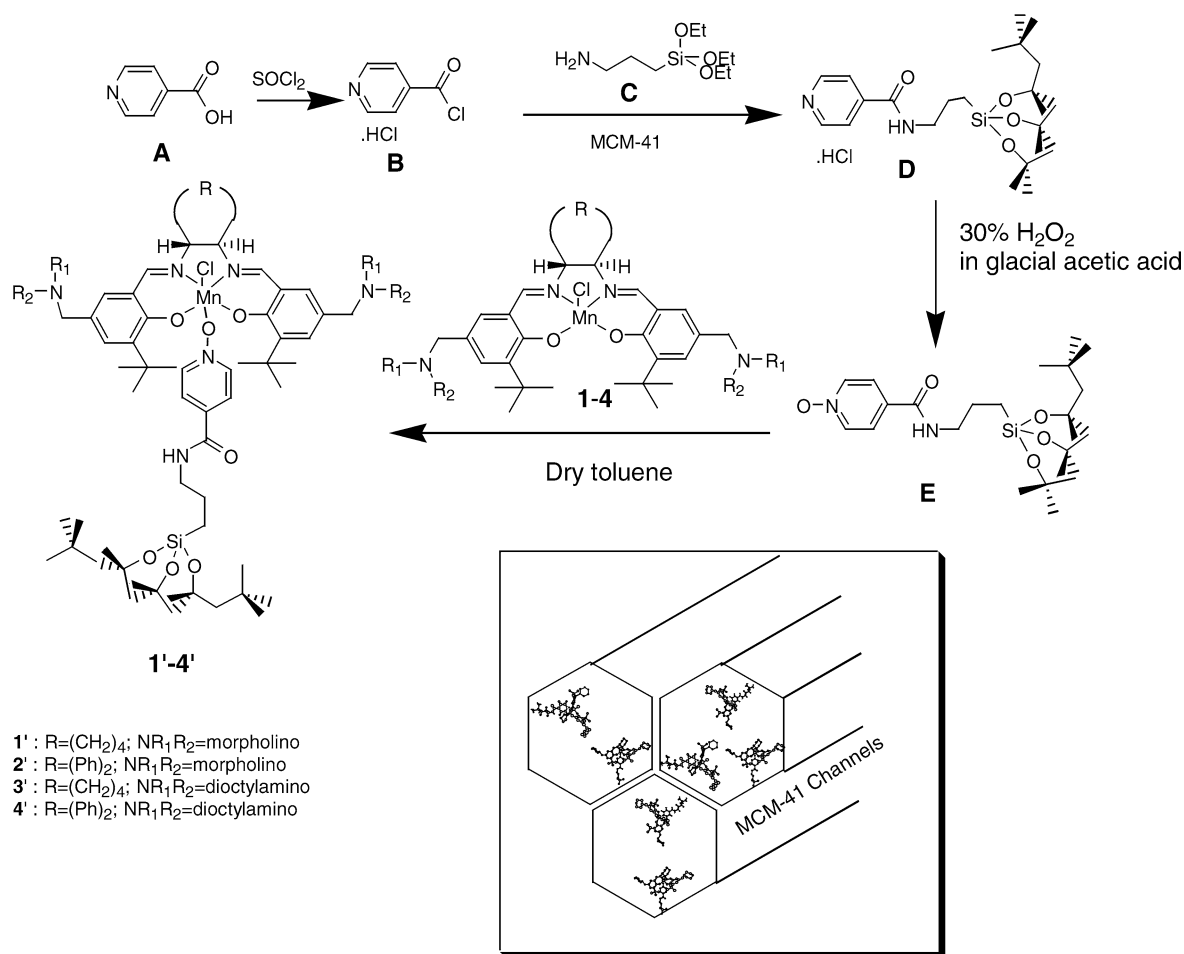
2.5. Enantioselective epoxidation of nonfunctionalized alkenes

Enantioselective epoxidation reactions were carried out with the catalysts **1′**–**4′** (0.05 mmol), with styrene, 4-Cl-styrene, indene, and 2,2-dimethyl chromene (1 mmol) as substrates in 4 ml of dichloromethane and buffered NaOCl (2.75 mmol, pH 11.5) as an oxidant. The addition of NaOCl was done in five equal portions at 0 °C, under heterogeneous reaction conditions. The epoxidation reaction was monitored by GC with *n*-tridecane (0.1 mmol) as the GLC internal standard for product quantification. After completion of the reaction, the immobilized catalysts **1′**–**4′** were centrifuged to separate the product and catalyst from the reaction mixture. The catalysts were washed thoroughly with dichloromethane and dried for re-use.

Table 1
Physicochemical characterization data of MCM-41, PyN–O modified MCM-41 and immobilized complexes **1′**–**4′**

Compound	Mn loading (mg/100 mg)	BJH pore diameter (Å)	Total pore volume (cm^3/g)	BET surface area m^2/g	Microanalysis (%)			
					C	H	N	C/N
MCM-41	–	37	0.943	1017	–	–	–	–
M-PyN–O	–	31	0.593	757	8.64	2.15	2.34	3.69
1′	16.57	25	0.448	616	6.51	2.49	2.56	6.45
2′	16.83	26	0.435	652	16.90	2.44	2.29	7.38
3′	23.37	25	0.451	618	22.13	3.60	2.33	9.51
4′	25.37	24	0.467	624	24.40	3.05	2.31	10.56

Scheme 1. Synthesis of the complexes **1′–4′**.

1' : R=(CH₂)₄; NR₁R₂=morpholino
2' : R=(Ph)₂; NR₁R₂=morpholino
3' : R=(CH₂)₄; NR₁R₂=dioctylamino
4' : R=(Ph)₂; NR₁R₂=dioctylamino

3. Results and discussion

The preparation of immobilized chiral Mn(III) salen complexes **1′–4′** is depicted in (Scheme 1). The species **B**, **D** and, **E** were characterized by appropriate spectroscopic methods. The interaction of **E** with chiral Mn(III) salen complexes **1–4** [26] in toluene gave immobilized chiral Mn(III) salen complexes **1′–4′**. The loading of the complexes **1′–4′** was found to be 16.5–25.3 mg/100 mg, as determined by ICP and spectrophotometry (Table 1). The XRD pattern of MCM-41 showed an intense peak assigned to reflection at (100) and two additional peaks with low intensities at (110) and (200) reflections, which can be indexed to the hexagonal lattice in Fig. 1a. It was observed that upon functionalization with **D** and **E**, the intensities of all of the peaks decreased marginally with a small shift toward lower 2θ values, as shown in Fig. 1b, which revealed that silylation had indeed occurred inside the mesopores of MCM-41. After immobilization of chiral Mn(III) salen complexes, the intensities of the peaks at the (110) and (200) reflections decreased Fig. 1c, showing that after the immobilization treatment the mesoporous structure of this support remained intact.

The FT IR spectra of MCM-41 showed the characteristic band at 1078 cm^{-1} of Si–O–Si and 3432 cm^{-1} for the Si–OH bond. MCM-41-pyridine N-oxide (**E**) showed an additional band at 2957 cm^{-1} due to ν(CH₂) of the propyl arm belonging to the silylating agent (Fig. 2a). The neat complex (Fig. 2c) showed a medium band at 1608 cm^{-1} due to ν(C=N). This band appeared at 1624 cm^{-1} as a split band and was merged with the band at 1654 cm^{-1} of modified MCM-41 precursor (Fig. 2a). The immobilized complex **2′** (Fig. 2b) (as a representative catalyst) showed all of the characteristic bands of the neat complex **2′** (Fig. 2c) and MCM-41-modified PyN–O (Fig. 2a), indicating the coordination of the complex to modified MCM-41 precursor. The data on BET surface area, pore diameter, and pore volume are presented in Table 1. A large decrease in BET surface area was observed (1017 to 757 m^2/g) upon functionalization of modified MCM-41, represented as **E** in Scheme 1. Similarly, reduction in the mesoporous diameter from 37 to 31 Å (Fig. 3f) and in pore volume from 0.943 to 0.593 cm^3/g was also observed (Table 1). Moreover, a decrease in BET surface area from 757 to 652–616 m^2/g, in pore size from 31 to 26–24 Å (Fig. 3g), and in pore volume from 0.593 to 0.434–0.467 cm^3/g was observed upon immobilization of the complexes **1–4** onto MCM-41-modified PyN–O (**E**),
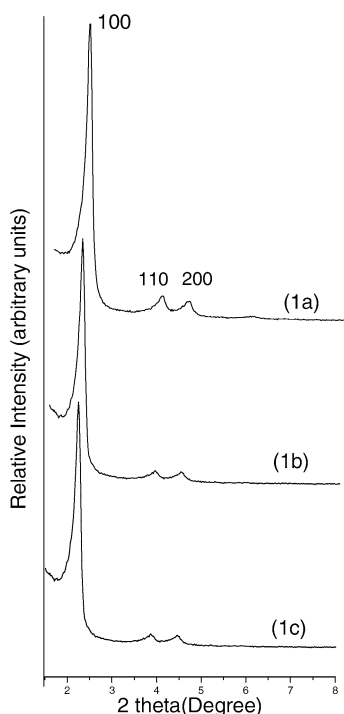
Fig. 1. Powder XRD patterns of calcined MCM-41 (1a), pyridine N-oxide modified MCM-41 (1b), and Mn(III) salen immobilized on Py-N–O modified MCM-41 $\mathbf{2'}$ (1c).

Table 2
Product yields, *ee*'s, and TOF for enantioselective epoxidation[a] of nonfunctionalized alkenes catalyzed by $\mathbf{1'}$–$\mathbf{4'}$

Entry	Catalyst	Substrate	Time (h)	Yield [b] (%)	*ee* [c] (%)	TOF [k] ($\times 10^{-4}$)
1	$\mathbf{1'}$	Styrene	8	92	66[d]	6.38
2	$\mathbf{2'}$		12	78	69[e]	3.61
3	$\mathbf{3'}$		12	94	65[d]	4.35
4	$\mathbf{4'}$		12	96	69[e]	4.44
5	$\mathbf{1'}$		24	2[j]	–	–
6	$\mathbf{1'}$	4-Cl-styrene	12	75	65[d]	3.47
7	$\mathbf{2'}$		12	99	67[e]	4.58
8	$\mathbf{3'}$		12	85	62[d]	3.93
9	$\mathbf{4'}$		12	90	65[e]	4.16
10	$\mathbf{1'}$	Indene	12	82	69[f]	3.33
11	$\mathbf{2'}$		12	79	80[g]	3.65
12	$\mathbf{3'}$		12	86	86[f]	3.98
13	$\mathbf{4'}$		12	87	85[g]	3.61
14	$\mathbf{1'}$	2,2-dimethyl	12	89	82[h]	3.65
15	$\mathbf{2'}$	chromene	12	98	92[i]	4.54
16	$\mathbf{3'}$		12	87	87[h]	3.80
17	$\mathbf{4'}$		12	86	91[i]	3.98

[a] Reactions were performed in CH_2Cl_2 (4 ml) with catalyst 0.05 mmol, substrate 1.00 mmol, NaOCl 2.75 mmol.
[b] Isolated epoxide.
[c] By ^1H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral capillary column GTA type/chiral HPLC column OJ,OB.
[d] Epoxide configuration *S*.
[e] Epoxide configuration *R*.
[f] Epoxide configuration 1*S*,2*R*.
[g] Epoxide configuration 1*R*,2*S*.
[h] Epoxide configuration 3*S*,4*S*.
[i] Epoxide configuration 3*R*,4*R*.
[j] PyN–O modified MCM-41 without Mn(III)salen.
[k] Turnover frequency is calculated by the expression [product]/[catalyst] $\times$ time (s^{-1}).

which suggests that the complexes **1–4** are present inside the channels of modified MCM-41.

The solid reflectance UV–vis spectra of the immobilized complexes, $\mathbf{1'}$–$\mathbf{4'}$, showed features similar to those of neat complexes, **1–4**, indicating that the coordination of chiral Mn(III) salen to PyN–O-modified MCM-41. Solid reflectance spectra for a representative immobilized Mn(III) salen complex $\mathbf{2'}$(**Z**) PyN–O-modified MCM-41 **E** (**Y**), and calcined MCM-41 (**X**) are shown in Fig. 4, where there is a characteristic charge transfer band near 430 nm and a *d*–*d* band at 500 nm of the Mn(III) salen system [16].

The catalytic activity of the immobilized catalysts, $\mathbf{1'}$–$\mathbf{4'}$, for the epoxidation of styrene, 4-Cl styrene, indene, and 2,2-dimethylchromene was studied in CH_2Cl_2 at 0 °C, with NaOCl as an oxidant; the data obtained are summarized in Table 2. Interestingly, the observed epoxide conversions for all of the alkenes with immobilized catalysts, $\mathbf{1'}$–$\mathbf{4'}$ (75–99%), and respective homogeneous catalysts, **1–4** (97–99%), are comparable [26]. However, the reaction took a relatively longer time with immobilized catalysts. This behavior may be attributed to slower diffusion of the reactants and the oxidant to the active catalytic sites situated in the channels of MCM-41. Significantly, the enantioselectivity for styrene (*ee*, 65–69%, entries 1–4) and 4-Cl styrene (*ee*, 62–67%, entries 6–9) was higher with immobilized catalysts as compared with homogeneous catalysts, **1–4** (*ee*, 36–51%) under identical reaction conditions [26]. A similar trend was reported earlier for Mn(III) and Cr(III) salen complexes immobilized on MCM-41 for 4-Cl styrene

[12], *α*-methylstyrene [15], and *cis*-*β*-methylstyrene [24], and this increase in *ee* was attributed to the unique spatial environment constituted by chiral salen ligand and the surface of the support. Furthermore, the catalytic activity and enantioselectivity (*ee*, 69–92) of immobilized complexes $\mathbf{1'}$–$\mathbf{4'}$ for the relatively bulkier alkenes like indene and 2,2-dimethylchromene (Table 2, entries 10–17) were found to be comparable to those of the neat complexes **1–4** (*ee*, 68–81%) (Scheme 1) [26]. This shows that the catalytic centers in the MCM-41 channels are easily accessible to the bulkier reactants too. Control experiment with pyridine N-oxide-modified MCM-41 showed negligible catalytic activity (conversion: 2%; Table 2, entry 5) toward the epoxidation of styrene. Hence we can conclude that the catalytic activity is entirely attributed to the salen complex immobilized on the pyridine N-oxide-modified MCM-41. To study the leaching of the metal complex from the immobilized catalyst into the reaction medium and the recyclability of the immobilized catalyst during epoxidation of alkenes, we carried out a few epoxidation reactions with catalyst $\mathbf{1'}$ and styrene as a representative substrate. After the first run of the epoxidation reaction, the catalyst was separated by centrifugation. Fresh reactants were added to the supernatant. Gas
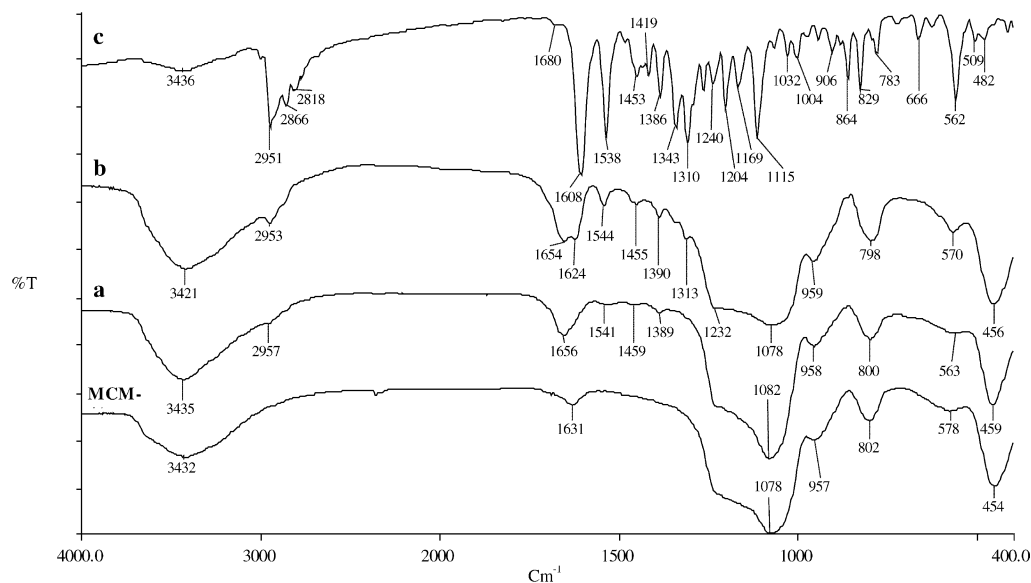
Fig. 2. IR spectra of calcined MCM-41, PyN–O modified MCM-41 (a), immobilized Mn(III) salen **2′** on modified MCM-41 (b), and Mn(III) salen complex 2 (c).
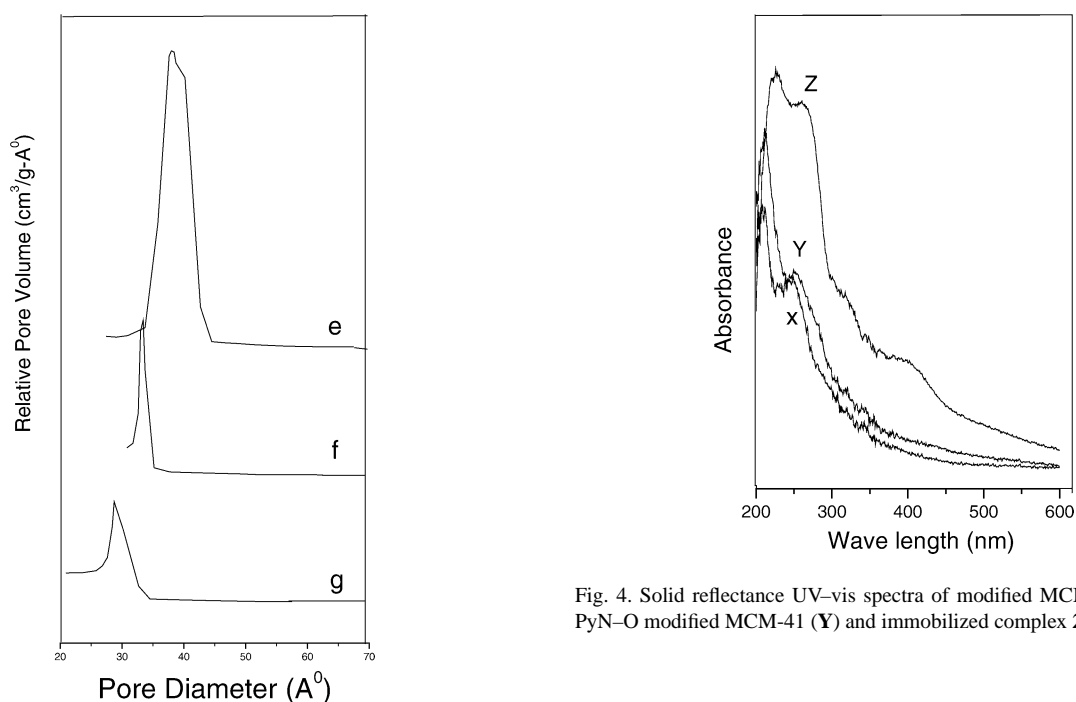

Fig. 3. N_2 sorption pore diameter and relative pore volume of calcined MCM-41 (e), pyridine N-oxide modified MCM-41 (f) and immobilized complex **2′** (g).

Fig. 4. Solid reflectance UV–vis spectra of modified MCM-41 itself (**X**), PyN–O modified MCM-41 (**Y**) and immobilized complex **2′** (**Z**).

Table 3
Recycling data for enantioselective epoxidation of styrene as representative substrate using immobilized catalyst **1′**

Run	Time (h)	Yield (%)	*ee* (%)
1	8	92	66
2	12	90	65
3	16	89	66
4	18	88	66

chromatographic analysis of the reaction mixture showed no further increase in the conversion of the substrate styrene. Moreover, the supernatant showed no trace of the metal complex on UV–vis or leaching of Mn by ICP.

The separated catalyst was washed thoroughly with dichloromethane, dried, and subjected to another cycle with fresh reactants under similar epoxidation conditions. It was observed that enantioselectivity with the styrene was nearly the same, but reaction took longer (Table 3). The above procedure was repeated for three cycles, and we did not observe any substantial loss in the catalytic activity of the immobilized catalyst. This indicates that the chiral Mn(III) salen

complex is strongly bonded to the oxygen atom of PyN–O-modified MCM-41 through the axial coordination.

The characterization of the recycled catalyst (after one cycle) was accomplished by FTIR spectrographic, XRD, and CHN analysis, which suggested the partial degradation of the complex and the entrapment of reactant within the silica matrix, and this could be the reason for the gradual slow-down of the epoxidation reaction in the subsequent recycle experiments. These observations are in agreement with earlier reports on the immobilized Mn(III) salen system [16]. Regarding the transfer of chirality from catalyst to the epoxide product, the configuration of the epoxide product was the same as that of the catalyst.

4. Conclusion

Highly ordered hexagonal pores of pyridine N-oxide-modified MCM-41 were used to prepare new immobilized chiral Mn(III) salen complexes through axial coordination. These immobilized catalysts **1′**–**4′** have shown high enantioselectivity in the epoxidation of styrene and 4-Cl styrene compared with their homogeneous counterparts. These catalysts were also effective for relatively bulkier substrates such as indene and 2,2-dimethylchromene and could be recycled three times without loss of performance.

Acknowledgments

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