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Chiral Mn(III) salen complexes covalently bonded on modified MCM-41 and SBA-15 as efficient catalysts for enantioselective epoxidation of nonfunctionalized alkenes

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Abstract

Chiral Mn(III) salen complex supported onto modified mesoporous supports (MCM-41 and SBA-15) were prepared using 3-aminopropyltriethoxysilane as a reactive surface modifier by a covalent grafting method. The supported catalysts showed higher chiral induction (ee, 71%) for enantioselective epoxidation of styrene and 4-chlorostyrene in presence of pyridine N-oxide (PyNO) as axial base using aqueous NaOCl (12%) as an oxidant than seen in its homogeneous counterpart **1** (ee, 48%). SBA-15-based catalyst **3**, with a larger pore diameter, was found to be more active than MCM-41-supported catalyst **2**. In addition, bulkier alkenes like indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene were efficiently epoxidized with these supported catalysts (ee up to 96%), and the results were comparable to those for the homogeneous system. The performance of catalysts **2** and **3** was retained for four reuse experiments.

Keywords: Heterogeneous catalysis; Supported chiral Mn(III) salen; Nonfunctionalized alkenes; Epoxidation; MCM-41 and SBA-15

1. Introduction

Chiral salen transition metal complexes have become a matter of current interest [1–7] because of their wide applications as catalysts in asymmetric epoxidation [1–4], cyclopropanation [5], aziridination [6], Knoevenagel condensation [7], and selective hydrogenation [8–10] reactions under homogeneous conditions. Separation and recycling of the homogeneous catalyst is problematic, however, making the entire process economically nonviable for industrial applications, more so for expensive catalysts with low turnover numbers. Therefore, heterogenization of homogeneous catalysts has become an important strategy for obtaining supported catalysts that retain the active catalytic sites of a homogeneous analogue while at the same time providing advantages of easy separation and recycling of the catalyst [11,12]. Several papers have recently appeared on the heterogenization of chiral salen transition metal complexes onto solid supports, including organic polymers [13–17] and inorganic solids of varied porosity [4,18–26] where the metal complexes were supported via axial or apical coordination or through covalent bonding of the ligand to the support with moderate to excellent results for enantioselective epoxidation of nonfunctionalized alkenes. Furthermore, such heterogenization of chiral Mn(III) salen complex revealed that the local environment inside the mesopores and pore size of the support does affect the enantioselectivity of the epoxidation reaction [18,19,21,22]. Therefore, it is prudent to graft the active metal complex onto solid support with varied pore sizes to determine the optimum pore size for efficient diffusion of reactant and product molecules. Ordered mesoporous solids like MCM-41 and SBA-15, with their well-defined uniform mesopores and facile surface modification, are potential materials [27–29] for heterogenization of valuable chiral homogeneous catalysts. Herein, we describe the covalent bonding of a homogeneous system (complex **1**) on modified MCM-41 and SBA-15 using 3-aminopropyltriethoxysilane (APTES) as a reactive surface modifier to give

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supported complexes **2** and **3**. To allow the maximum conformational mobility in the complex needed to obtain a high level of asymmetric induction, the grafting was done through one of the fifth positions of the Mn(III) salen complex. The supported catalysts **2** and **3** effectively catalyzed epoxidation of styrene and 4-chlorostyrene (ee, 68–71%) with aqueous NaOCl. These results are significantly better than those achieved with the catalyst **1** under a homogeneous system (ee, 45–48%) and other reported Mn(III) salen complexes [19,30] anchored on MCM-41. Remarkably, catalysts **2** and **3** worked well for several cycles even with relatively bulkier alkenes such as indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene (ee, 67–96%), and the results are comparable with those of the corresponding homogeneous system.

2. Experimental

Cetyltrimethylammonium bromide (CTAB), manganese(II) acetate (s.d. Fine Chem. Ltd. India), sodium silicate solution, tetraethyl orthosilicate (TEOS), triblock organic copolymer (EO_{20}–PO_{70}–EO_{20}) Pluronic P123 (Aldrich), HCl (Ranbaxy, India), APTES (Fluka), aqueous NaOCl (12%) (National Chemicals, India), and PyNO (Fluka) were used as received. Indene, styrene, 4-chlorostyrene, and 1,2-dihydronaphthalene were passed through a pad of neutral alumina before use. 2,2-Dimethylchromene was synthesized as described previously [31]. A highly ordered hexagonal siliceous MCM-41 was synthesized as described previously [23]. All of the solvents used in the present study were purified by known methods [32].

The purity of the solvents and alkenes and analysis of the product epoxide were determined by gas chromatography (GC) using a Shimadzu GC 14B instrument equipped with a stainless-steel column (2 m long, 3 mm i.d., 4 mm o.d.) packed with 5% SE 30 (mesh size, 60–80) and having a flame ionization detector (FID). Ultrapure N_2 was used as a carrier gas (rate 30 mL/min) with the injection port temperature set at 200 °C. The column temperature for styrene, 4-chlorostyrene, and indene was in the range of 70–150 °C, whereas for chromene and 1,2-dihydronaphthalene, the isothermal temperature was kept at 150 °C. The racemic epoxides were prepared by the epoxidation of respective alkenes with 3-chloroperbenzoic acid in CH_2Cl_2 and were used to determine conversions by comparing the height and area of the GC peaks. The ee's of styrene, 4-chlorostyrene, and 1,2-dihydronaphthalene oxides were determined by GC on a chiral capillary column (Chiraldex GTA and BDA). For 2,2-dimethylchromene and indene epoxides, the ee's were determined by ^{1}H NMR using the chiral shift reagent Eu(hfc)$_3$ and by HPLC (Shimadzu SCL-10AVP) using a Chiralcel column (AD/OB/OD/OJ).

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 200- and 50-MHz spectrometer (Bruker, F113V), respectively. The IR spectra were recorded on a Perkin–Elmer Spectrum GX spectrophotometer in KBr/nujol mull. Electronic spectra were recorded in dichloromethane on a Varian UV–vis-NIR CARY 500 SCAN spectrophotometer. Diffuse reflectance spectra were obtained from UV–vis-NIR scanning spectrophotometer UV-3101 PC. Microanalysis of the complex was done on a Perkin–Elmer 2400 CHNS analyzer. An inductively coupled plasma (ICP) spectrometer (Perkin–Elmer, Optima 2000 DV) was used for Mn estimation. Poweder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X'Pert MPD diffractometer using Cu-K_α ($\lambda = 1.5405$ Å) radiation with a step size of 0.02° 2θ and a step time of 5 s of curved Cu-K_α monochromator under identical conditions. BET surface area was determined using N_2 sorption data measured at 77 K using a volumetric adsorption setup (Porous Materials; PMI system DET sorptometer). The pore diameter of the samples were determined from the desorption branch of the N_2 adsorption isotherm using the BJH method. Transmission electron microscopy (TEM) analysis was done with a Philips Tecnai 20. Scanning electron microscopy (SEM) analysis of the sample was done with a LEO 1430 VP.

2.1. Synthesis of SBA-15

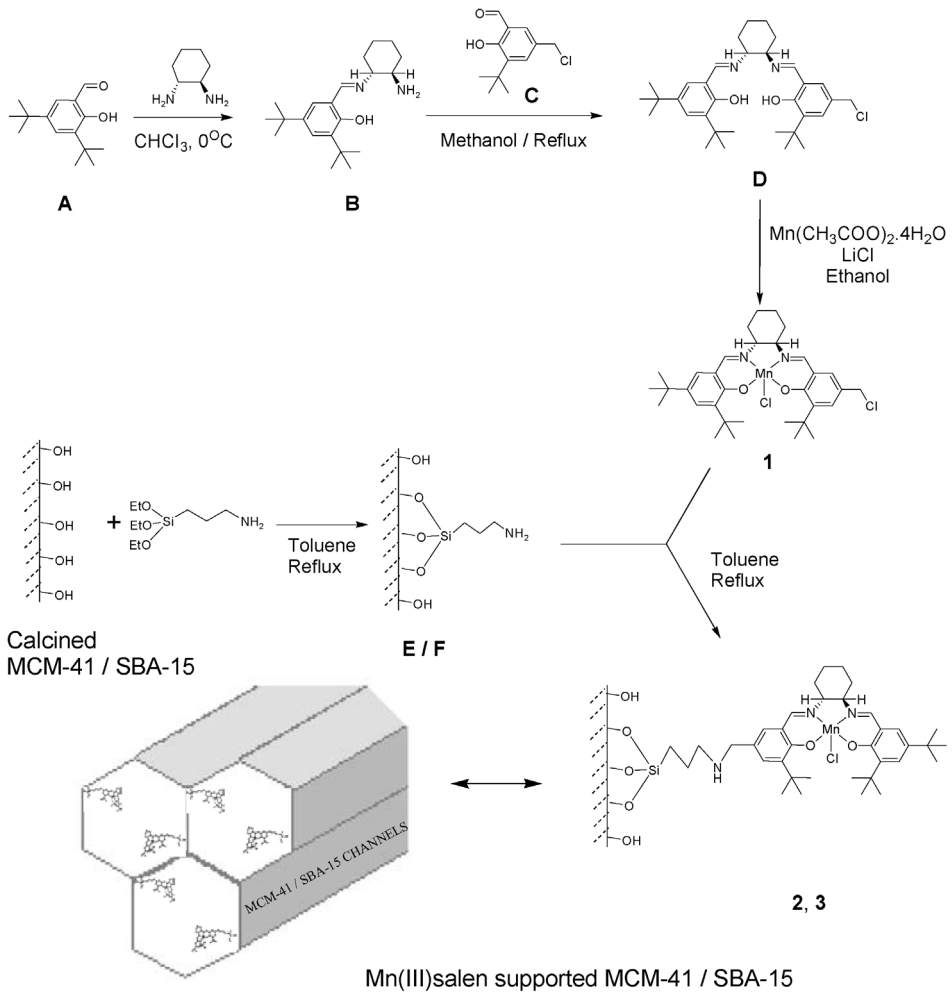
Highly ordered mesoporous SBA-15 was synthesized using a modified procedure reported by Zhao et al. [33] under hydrothermal conditions using a triblock organic copolymer as a template. In a typical synthesis, 12 g of triblock, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{20}–PO_{70}–EO_{20}) (Pluronic P123, mw 5800) was dispersed in 90 g of double-distilled water to which 360 g of 2 M aqueous HCl was added under stirring at ambient temperature (25–30 °C) for 1 h. Finally, 27 g of silica source TEOS was added to the homogeneous solution under stirring to form a gel at 313 K for 24 h, and this was allowed to stand for crystallization under static hydrothermal conditions at 373 K for 48 h in a Teflon Parr reactor. The crystallized product was filtered off, washed with warm distilled water, dried at 383 K, and finally calcined at 813 K in air for 6 h to remove the template. The calcined SBA-15 was characterized by powder XRD.

2.2. Preparation of 3-aminopropylsilyl-functionalized MCM-41 (*E*) and SBA-15 (*F*)

A suspension of APTES (4.56 g, 20.63 mmol) and 10 g of calcined MCM-41/SBA-15 in 90 mL of toluene was heated to reflux with stirring under inert atmosphere for 24 h. The resulting masses were cooled to 25–30 °C and filtered. The solids were filtered and washed successively with dry toluene and diethyl ether, then dried under vacuum at ambient temperature. The dried material was subjected to Soxhlet extraction with dry dichloromethane for 24 h. Finally; the solids (**E** and **F**) were dried at 50–55 °C under vacuum for 8 h. The characterization was accomplished by microanalysis (Table 1), IR, diffuse reflectance, UV–vis spectroscopy, XRD, and nitrogen sorption studies. IR (KBr) for **E**: 463, 794, 1079, 1633, 2937, 3437 cm^{-1}. Diffuse reflectance UV–vis: 245, 340 nm; IR (KBr) for **F**: 460, 798, 1076, 1636, 2937, 3437 cm^{-1}. Diffuse reflectance UV–vis: 270, 335, 375 nm.

Table 1
Physico-chemical characterization data of MCM-41, SBA-15, aminopropyl modified MCM-41 (**E**) and SBA-15 (**F**) and supported catalysts **2** and **3**

Compound	Mn loading (mg/100 mg)	BJH pore diameter (Å)	Total pore volume (cm^3/g)	BET surface area (m^2/g)	Micro analysis, found %			
					C	H	N	C/N
1	–	–	–	–	63.02	7.12	4.40	14.13
MCM-41	–	37	0.727	786	–	–	–	–
E	–	28	0.412	464	7.86	1.75	1.89	4.16
2	22	21	0.290	325	10.92	1.42	1.04	10.5
SBA-15	–	68	1.120	662	–	–	–	–
F	–	57	0.719	364	7.65	1.66	1.84	4.16
3	23	49	0.562	235	14.15	1.91	1.38	10.25



Scheme 1. Synthesis of the complexes **1**–**3**.

*2.3. Synthesis of unsymmetrical Mn(III) salen complex **1***

The synthesis sequence for non-C_2-symmetric salen-based Mn(III) salen complex **1** is shown in Scheme 1. This involves the initial preparation of a chiral half unit *N*-(2-hydroxy-3,5-di-*tert*-butylbenzaldehyde)-1-amino-2-cyclohexaneimine (**B**) from 3,5-di-*tert*-butyl salicylaldehyde (**A**) and 1*S*,2*S*-(+)-cyclohexanediamine as described previously [34], followed by condensation of half unit (**B**) with 5-chloromethyl 3-*tert*-butylsalicylaldehyde (**C**) [35] in dry methanol to form a unsymmetrical chiral salen-based ligand (**D**) (Yield, 80–82%), Anal. Calcd. for $C_{33}H_{47}ClN_2O_2$: C, 73.54; H, 8.73; N, 5.20; found: C, 73.48; H, 8.73; N, 5.17; IR (KBr) 3411, 2957, 2863, 1629, 1597, 1470, 1441, 1390, 1361, 1272, 1251, 1204, 1172, 1095, 1044, 878, 827, 712, 644, 590 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ ppm 1.23 (s, 18H), 1.42 (s, 9H), 1.47–2.10 (m, 8H), 3.30–3.48 (m, 2H), 4.56 (s, 2H), 6.85 (d, 1H $J = 1.9$ Hz), 7.05 (d, 2.0 Hz), 7.43 (d, 1H, $J = 2.2$ Hz), 7.52 (d, 1H $J = 2.2$ Hz), 8.32 (s, 1H), 8.44 (s, 1H), 13.50 (bs, 1H), 14.48 (bs, 1H); $^{13}C\{^1H\}$, δ ppm 24.2, 24.8, 26.2, 29.3, 29.6, 29.8, 33.9, 34.1, 35.2, 45.8, 72.3, 78.1, 116.8, 118.2, 122.4, 126.4, 127.4, 127.6, 136.2, 139.8, 157.9, 161.5, 164.8, 165.7. On complexation with $Mn(CH_3COO)_2{\cdot}4H_2O$ and its aerial oxidation in the presence of LiCl, this gave complex **1**.

Yield 90%; IR (KBr): 3434, 2955, 2866, 1613, 1536, 1436, 1389, 1252, 1202, 1029, 836, 568 cm^{-1}: UV–vis. (CH_2Cl_2) 284, 416, 422, 399, 320, 284 nm; $[\alpha]_D^{30} = +663$ ($c = 0.04$ g, 0.064 mmol/100 mL, CH_2Cl_2).

2.4. Heterogenization of unsymmetrical Mn(III) salen-based complex *1* on aminopropylsilyl-functionalized MCM-41 and SBA-15

The surface-modified MCM-41/SBA-15 (**E**/**F**) (1 g) was added to a solution of the unsymmetrical Mn(III) salen complex (**1**) (352.4 mg, 0.562 mmol) in dry toluene (10 mL), and the resulting suspension was refluxed for 48 h under inert atmosphere. The supported catalyst **2**/**3** was filtered, washed thoroughly with dry toluene and diethyl ether, and extracted repeatedly with methanol and dichloromethane on a Soxhlet extractor until the washings become colorless. All of the washings were combined, the solvent was evaporated, and the residue was dissolved in toluene (10 mL). The difference between the initial and final concentrations as measured by UV–vis spectroscopy gave the Mn(III) salen loadings on modified MCM-41 (**E**) and SBA-15 (**F**). The characterization of chiral Mn(III) salen catalysts **2** and **3** was done by microanalysis (Table 1), UV–vis reflectance spectroscopy (DRS), IR, XRD, ICP, SEM, TEM, and nitrogen sorption studies (Table 1).

Catalyst **2**: Yield, 90%; IR (KBr): 3453, 2960, 1633, 1079, 802, 457 cm^{-1}; diffuse reflectance 275, 330, 430, 530 nm.

Catalyst **3**: Yield, 89%; IR (KBr) 3425, 2958, 1629, 1081, 801, 461 cm^{-1}; diffuse reflectance 280, 350, 427, 540 nm.

2.5. Enantioselective epoxidation of nonfunctionalized alkenes

Enantioselective epoxidation reactions were carried out using catalysts **1**, **2**, and **3** (0.05 mmol) with styrene, 4-Cl-styrene, indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene (1 mmol) as substrates in 1 mL of dichloromethane (for catalyst **1**) and 4 mL of dichloromethane (for catalysts **2** and **3**) under reaction conditions in the presence of PyNO (0.13 mmol) as an axial base with aqueous buffered 2.75 mmol NaOCl (12%, pH = 11.3) as an oxidant. The NaOCl was added in five equal portions at 0 °C, and the reaction mass was stirred using a magnetic stirrer (homogeneous) and a mechanical stirrer (heterogeneous) at 800 ± 20 rpm. The epoxidation reaction was monitored by GC with *n*-tridecane (0.1 mmol) as a GLC internal standard for product quantification. After completion of the reaction, the supported catalysts **2** and **3** were separated by centrifugation, washed thoroughly with dichloromethane, and dried for reuse.

3. Results and discussion

The anchoring of unsymmetrical chiral Mn(III) salen complex **1** was made through the fifth position of the salen complex onto surface-modified MCM-41 and SBA-15, as depicted in Scheme 1. This strategy has considerable advantages over others described in the literature [19] from the standpoint of economy of synthetic steps. Further, the coordination sphere of manganese ion is not involved in the anchoring of the complex **1** to the support, and thus the activity of these supported catalysts **2** and **3** is akin to that of homogeneous complex **1**.

The loading of **1** in supported catalysts was found to be 22–23 mg/100 mg as determined by ICP and spectrophotometry (Table 1). The powder XRD patterns of MCM-41 and SBA-15 show a very intense peak assigned to reflection at (100) and two additional peaks with low intensities at (110) and (200) reflections, which can be indexed to a hexagonal lattice (Figs. 1A and 1B, M-1 and S-1). It is observed that on functionalization with 3-aminopropyltriethoxysilane, the intensities of all of the peaks of (**E** and **F**) decrease marginally with a little shift toward lower 2θ values (M-2 and S-2), demonstrating the occurrence of silylation inside the mesopores of MCM-41/SBA-15. After heterogenization of chiral Mn(III) salen complex **1**, intensities of the peaks at the (110) and (200) reflections were decreased (M-3 and S-3), indicating that the mesoporous structure of the supports remained intact under the conditions used for heterogenization. SEM micrographs (Fig. 2) revealed that MCM-41 (A) and SBA-15 (B) samples consist of small agglomerates whose morphology does not change in the supported catalysts **2** (C) and **3** (D).

TEM micrographs of purely siliceous MCM-41 and SBA-15 revealed hexagonally arranged pore structures when viewed along the pore direction, along with parallel lattice fringes on a side view analysis (Figs. 3A and 3D). Whereas SBA-15 prepared in the acidic medium exhibited mesopores of a one-dimensional channel system, confirming that SBA-15 has a 2D p6mm hexagonal structure. The presence of equidistant parallel fringes demonstrates the nature of separation between layers and the unique well-packed arrangement of such monolayers (Figs. 3C and 3F). The ordered mesoporous structure of the support was unaffected by anchoring of chiral Mn(III) salen complex **1** (Figs. 3B and 3E).

FTIR spectra (Fig. 4) of supported catalysts **2** and **3** represented as (M-3) and (S-3) show bands at 2960 and 2958 cm^{-1} due to $\nu(CH_2)$ of the propyl arm belonging to the silylating agent, These peaks were absent in the IR spectra of calcined MCM-41 (M-1) and SBA-15 (S-1), confirming the grafting of chiral salen complex **1** onto MCM-41/SBA-15. To further confirm the grafting of the salen unit (structure **1**, Scheme 1) onto modified MCM-41 and SBA-15, the catalysts **2** and **3** were dissolved in HF solution, and the resulting mass was extracted with CH_2Cl_2. After the solvent was completely removed, the resulting brown mass was analyzed by UV–vis and IR spectroscopy, which showed the presence of the Mn(III) salen complex. These observations are in accordance with those reported for the heterogenization of salen on siliceous material [36].

Data on BET surface area, pore diameter, and pore volume are presented in Table 1. A large decrease in BET surface area was observed on functionalization of modified MCM-41 and SBA-15, with a reduction in the mesopore diameter and pore volume (Table 1), suggesting that the complex **1** was present inside the channels of support material. The solid reflectance UV–vis spectra of the supported catalysts **2** and **3** showed characteristic bands in complex **1**, indicating the presence of chiral Mn(III) salen in modified MCM-41 and SBA-15 (Fig. 5) [19].

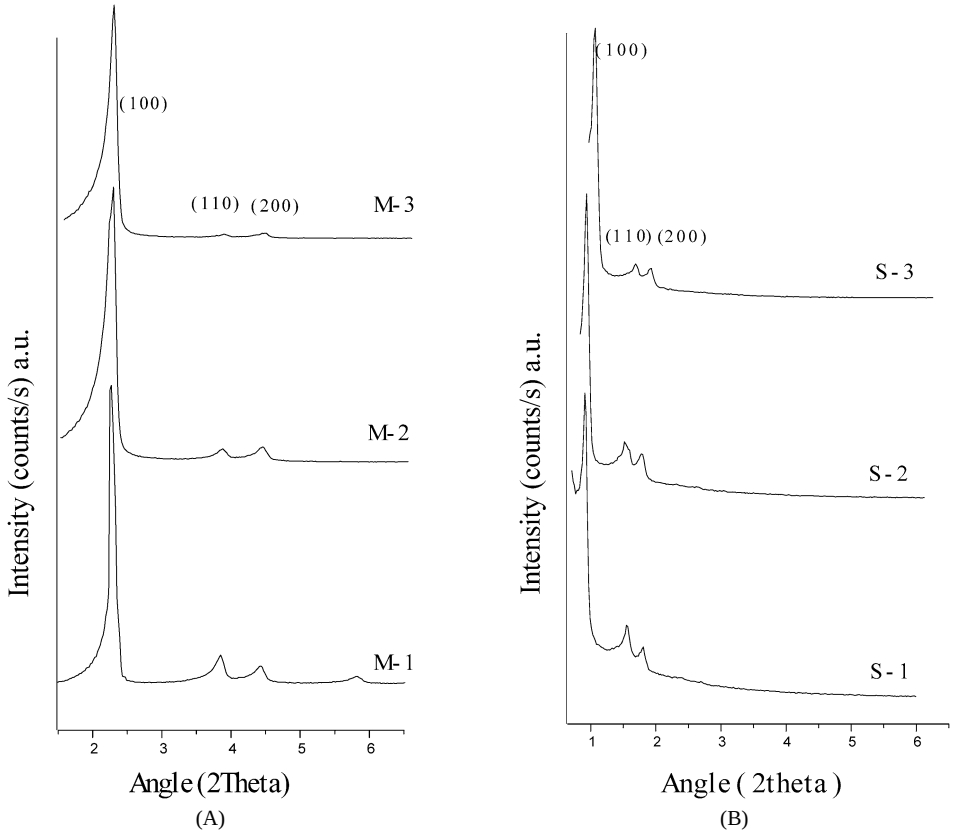


Fig. 1. (A) Powder XRD pattern of calcined MCM-41 (M-1), aminopropyl modified MCM-41 (M-2), supported catalyst **2** (M-3). (B) Powder XRD pattern of calcined SBA-15 (S-1), aminopropyl modified SBA-15 (S-2), supported catalyst **3** (S-3).

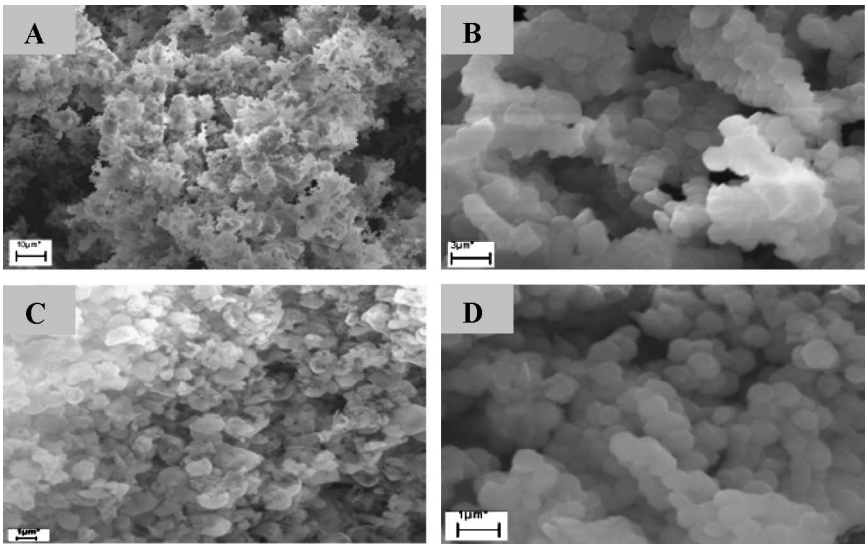


Fig. 2. SEM micrographs of (A) calcined MCM-41, (B) calcined SBA-15, (C) catalyst **2**, (D) catalyst **3**.

The enantioselective catalytic activities of the chiral Mn(III) salen complex **1** (homogeneous) supported catalysts onto modified MCM-41 and SBA-15 (**2** and **3**) were examined for epoxidation of styrene, 4-chlorostyrene, indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene at 0 °C using aqueous NaOCl as an oxidant in the presence of PyNO as an axial base. The data reported in Table 2 show that the supported catalysts **2** and **3** efficiently promoted the enantioselective reaction of styrene and 4-chlorostyrene (entries 2, 3, 7, and 8), producing higher chiral induction (ee, 68–71%) than seen in its homogeneous version **1** (ee, 45–48%). The increase in chiral recognition could arise from unique spatial environment created by both the chiral salen complex and the surface of the supports used. Similar behavior has been reported earlier for the epoxidation of styrenes [18,22,23,37] with chiral Mn(III) and Cr(III) salen complexes. In absence of PyNO, the catalyst **1** epoxidized

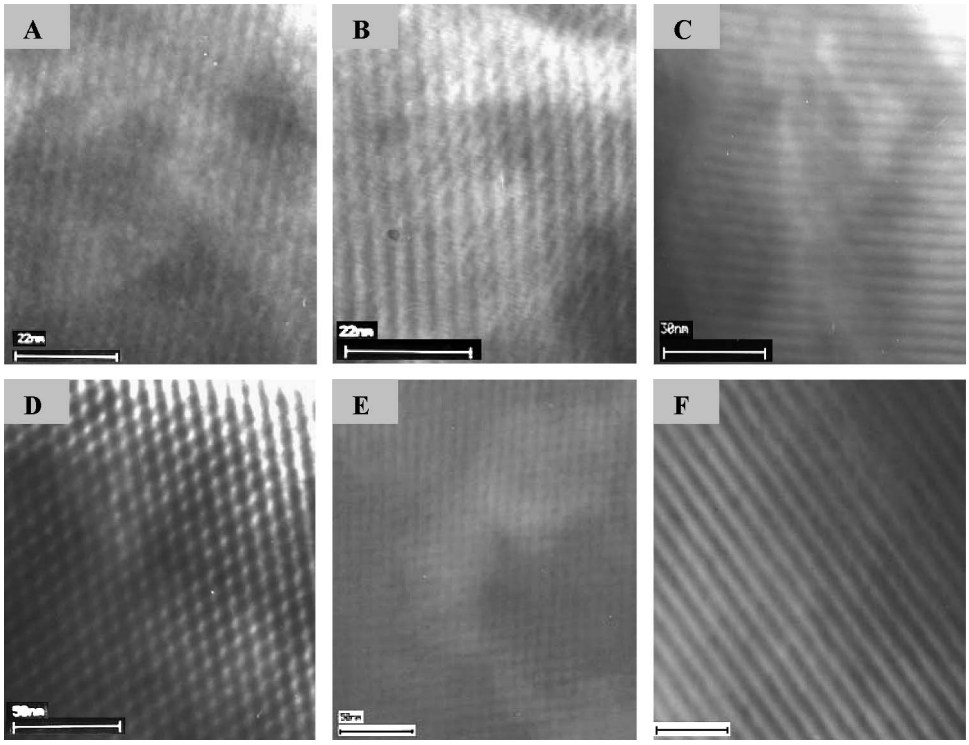


Fig. 3. TEM micrographs of (A) calcined MCM-41, (B) catalyst **2**, (C) pore wall of MCM-41, (D) calcined SBA-15, (E) catalyst **3**, (F) pore wall of SBA-15.

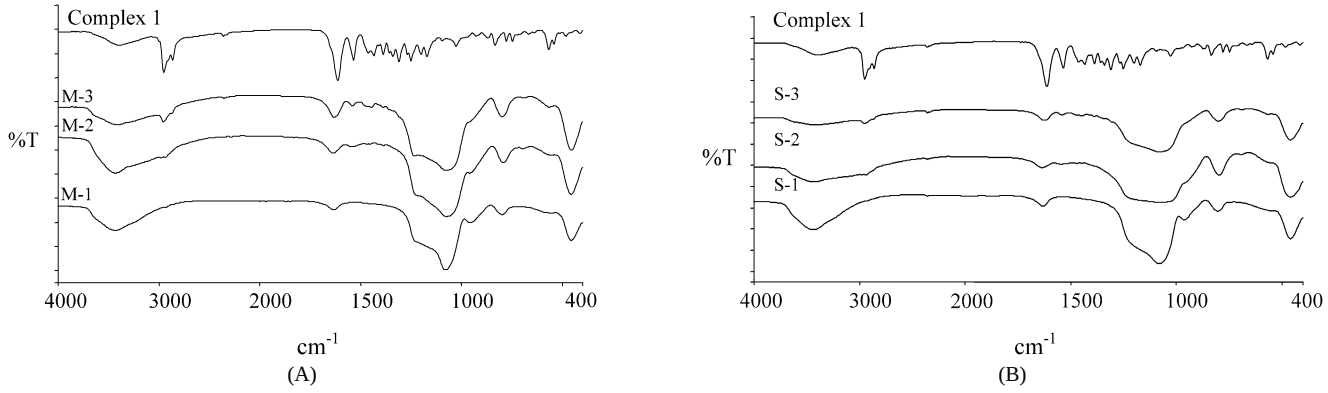


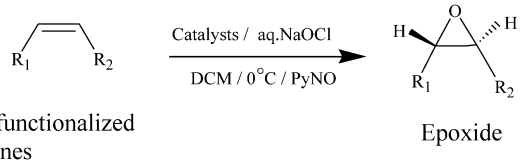
Fig. 4. (A) IR Spectra of calcined MCM-41 (M-1), aminopropyl modified MCM-41 (M-2), supported catalyst **2** (M-3), unsymmetric salen complex **1**. (B) IR Spectra of calcined SBA-15 (S-1), aminopropyl modified SBA-15 (S-2), supported catalyst **3** (S-3), unsymmetric salen complex **1**.

4-chlorostyrene (entry 9; con. 55%, ee 30%), suggesting that the presence of PyNO is essential for catalyst stability and enantioselectivity. The role of PyNO as an axial base was established earlier by other authors [38] and also by us [24,35]. MCM-41 and SBA-15 alone showed negligible catalytic activity toward epoxidation of styrene taken as a representative substrate (2%; entries 4 and 5).

Furthermore, catalysts **2** and **3** were also found to be efficient in the epoxidation of indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene (entries 11, 12, 14, 15, 17, and 18), with results comparable to those from the homogeneous reaction carried out with complex **1** under identical reaction conditions. However, the catalytic reactions were found to be slower (8–12 h) in the supported catalysts **2** and **3** (entries 2, 3, 7, 8, 11, 12, 14, 15, 17, and 18). This behavior is attributed to the diffusional constrains [18] usually present when a catalyst is supported inside the porous materials. Given this effect, materials with larger pore sizes would be expected to face less diffusional resistance. Thus, the higher TOF values obtained with catalyst **3** supported on SBA-15 compared with catalyst **2** supported on MCM-41 **2** are to be expected. The overall performance of catalysts **2** and **3** with varying pore diameters (37–68 Å) is far better in terms of reactivity and enantioselectivity than that of other supported Mn(III) salen systems with 3-mercaptopropyltriethoxysilane as a reactive surface modifier [20,30].

For reusability experiments, catalysts **2** and **3** were recovered from the reaction mixture of the epoxidation of styrene by simple centrifugation. The recovered catalyst was washed thoroughly with CH_2Cl_2 before reuse. The enantioselectivity of the recovered catalysts **2** and **3** did not change much during four reuse experiments; however, the reaction did slow down (Table 3), indicating that although the reactive catalyst

Table 2
Results on the catalytic asymmetric epoxidation[a] of nonfunctionalized alkenes with chiral Mn(III) salen complex **1** and **2**, **3** supported on MCM-41 and SBA-15



Entry	Catalyst	Substrate	Time (h)	Conversion (selectivity)[b] (%)	ee[c] (%)	TOF[d] $\times 10^{-4}$
1	**1**	Styrene	8	100 (100)	45[e]	6.94
2	**2**		12	88 (>99)	68[e]	4.16
3	**3**		9	94 (>99)	70[e]	5.86
4	MCM-41		24	2	–	–
5	SBA-15		24	2	–	–
6	**1**	4-Cl-styrene	7	100 (100)	48[e]	7.93
7	**2**		12	96 (>99)	68[e]	4.53
8	**3**		8	98 (>99)	71[e]	6.87
9	**1**[f]		7	53 (>99)	30[e]	4.36
10	**1**	Indene	8	96 (100)	89[g]	6.73
11	**2**		12	83 (>99)	80[g]	3.93
12	**3**		10	90 (99)	81[g]	5.16
13	**1**	1,2-dihydro-	8	92 (100)	68[g]	6.45
14	**2**	naphthalene	12	85 (>99)	67[g]	4.07
15	**3**		9	94 (>99)	72[g]	5.92
16	**1**	2,2-dimethyl-	8	99 (>99)	99[h]	6.87
17	**2**	chromene	12	94 (>99)	95[h]	4.39
18	**3**		10	96 (>99)	96[h]	5.44

[a] Reactions were performed in CH_2Cl_2 1 mL (catalyst **1**), 4 mL (catalysts **2** and **3**) with catalyst 0.05 mmol, substrate 1.00 mmol, PyNO 0.13 mmol, aqueous NaOCl 2.75 mmol at 0 °C.
[b] Based on GC.
[c] By ^{1}H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral capillary column GTA type/chiral HPLC column AD/OB/OD/OJ.
[d] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).
[e] Epoxide configuration *S*.
[f] Reaction conducted in absence of PyNO.
[g] Epoxide configuration 1*S*,2*R*.
[h] Epoxide configuration 3*S*,4*S*.

Table 3
Recycling data for enantioselective epoxidation[a] of styrene as representative substrate using supported catalysts **2** and **3**

Run	Catalyst	Conversion[b] (%)	ee[c]	TOF $\times 10^{-4}$ (s^{-1})
1	**2 (3)**	90 (95)	68 (70)	4.16 (5.86)
2	**2 (3)**	87 (93)	68 (70)	4.02 (5.74)
3	**2 (3)**	82 (89)	68 (70)	3.79 (5.49)
4	**2 (3)**	80 (86)	67 (70)	3.70 (5.30)

[a] Reactions were performed in CH_2Cl_2 (4 mL) with the recovered catalysts **2**, **3** substrate 1.00 mmol, PyNO 0.13 mmol, NaOCl 2.75 mmol for 12 h (catalyst **2**), 9 h (catalyst **3**) at 0 °C.
[b] Based on GC.
[c] By chiral capillary column GTA type.

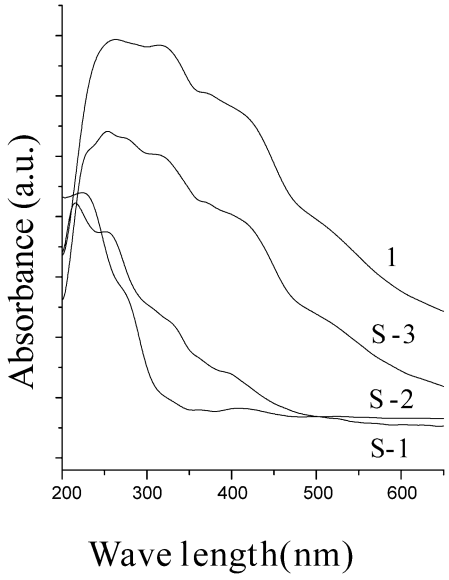


Fig. 5. Diffuse reflectance UV–vis spectra of calcined SBA-15 (S-1), aminopropyl modified SBA-15 (S-2), covalently bonded Mn(III) salen on modified SBA-15 (S-3) and complex **1** (1).

remained intact, diffusional resistance increased due to blockage of some pores with organic matter from previous runs. To check the leaching of the metal complex, fresh reactant was added to the solution obtained after centrifugation of the catalyst that showed no further formation of the epoxide. This same solution did not exhibit any color or the presence of Mn by ICP. This means that the Mn(III) salen complex **1** supported onto modified MCM-41 and SBA-15 was intact and stable in the pore system during the epoxidation reaction.

Characterization of the recycled catalyst (after one cycle) by FTIR spectra, powder XRD, and CHN analysis demonstrated entrapment of some of the reactant within the mesopores, which caused a gradual slowdown of the epoxidation reaction in successive recycle experiments. These observations are in accordance with earlier reports based on a supported Mn(III) salen system [19]. Further, in terms of the transfer of chirality from catalyst to product epoxide, the configuration of the product epoxide was the same as that of the catalyst.

4. Conclusion

Chiral Mn(III) salen catalysts **2** and **3** were prepared by heterogenizing **1** onto modified mesoporous materials MCM-41 and SBA-15 using 3-aminopropyltriethoxysilane as a reactive surface modifier by a covalent bonding method. The supported catalysts demonstrated higher chiral induction (ee, 71%) than its homogeneous counterpart **1** (ee, 48%) for enantioselective epoxidation of styrene and 4-chlorostyrene using NaOCl as an oxidant. The larger-pore size SBA-15 turned out to be a better support, because **3** was found to be more active than **2**. The overall performance of the catalysts **2** and **3** is far better in terms of reactivity and enantioselectivity than that of other supported Mn(III) salen systems with 3-mercaptopropyltriethoxysilane as a reactive surface modifier. To further strengthen our observa-

tions, we are in the process of synthesizing siliceous materials with still-larger pore sizes (>100 Å).

In addition, bulkier alkenes, including indene, 1,2-dihydronaphthalene, and 2,2-dimethylchromene, were efficiently epoxidized with these supported complexes (ee up to 96%), and the results were comparable with those for the homogeneous system. The performance of the catalysts **2** and **3** was retained for four reuse experiments.

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