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Covalently anchored chiral Mn(III) salen-containing ionic species on mesoporous materials as effective catalysts for asymmetric epoxidation of unfunctionalized olefins

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Abstract

A kind of chiral Mn(III) salen-containing ionic species was prepared and covalently anchored on mesoporous materials, including SBA-15, MCM-48, MCM-41, and amorphous SiO_2, via imidazole modification. These catalysts were characterized by N_2 sorption, XRD, FTIR, DR UV–vis, and elemental analysis. The results showed that the chiral Mn(III) salen complex was successfully immobilized inside the channels of the modified mesoporous materials and that the long-range mesoporous ordering of parent supports was maintained after the immobilization. These prepared catalysts were evaluated in the asymmetric epoxidation of unfunctionalized olefins with *m*-chloroperoxybenzoic acid as oxidant. Comparable or even higher enantioselectivity than that of homogeneous counterpart was obtained with similar catalytic activity. Moreover, these heterogeneous catalysts can complete epoxidation rapidly, thus providing notably high turnover frequencies, attributed in part to the ionic property of the active centers. The SBA-15-based catalyst showed the best performance in the epoxidation reaction. Furthermore, these immobilized catalysts were stable and could be recycled five times without loss of activity.

Keywords: Imidazole-modified mesoporous materials; Chiral Mn(III) salen complex; Asymmetric epoxidation; Unfunctionalized olefins

1. Introduction

The asymmetric epoxidation of unfunctionalized olefins is highly significant in the synthesis of chiral intermediates in the pharmaceutical and agrochemical fields. To date, the chiral Mn(III) salen complexes have proven to be extremely efficient homogeneous catalysts for the enantioselective epoxidation of unfunctionalized olefins [1–3]. However, the catalyst suffers some problems in homogeneous medium, including difficulty in separation from the reaction mixture and recycling and decreased catalytic activity due to the formation of inactive dimeric μ-oxo Mn(IV) species. Consequently, over the last decade, intense efforts have been made to heterogenize chiral Mn(III) salen complexes on supports in an attempt to make them recyclable and to enhance their stability, activity, and selectivity [4–10]. Considerable research has centered on the immobilization of chiral Mn(III) salen complex on organic polymers [11–15], as well as on porous inorganic supports [16–29].

The silica-based mesoporous materials have large surface areas, high thermal and mechanical stability, and controllable pore sizes of 2–50 nm, allowing ready diffusion of reactants to the active sites located on the inner surface. Moreover, the abundant silanol groups on their surfaces make them easily organically functionalized and grafted to catalytic active species. Several different strategies have been adopted to immobilize chiral Mn(III) salen complexes on mesoporous materials. A multistep grafting method was reported to immobilize chiral Mn(III) salen complexes on MCM-41 [19] and MCM-48

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[20,21], respectively. The chiral Mn(III) salen complexes were immobilized on MCM-41 [22] and Al-MCM-41 [23,24] via ion-exchange reaction. Zhang et al. [25,26] reported a new method of axially immobilizing the chiral Mn(III) salen complexes through the complexation of manganese with various organic groups grafted on the surface of mesoporous supports, which led to an improved enantiomeric excess (ee) compared with that of the free complex. Bigi et al. [27] successfully bounded the chiral Mn(III) salen complexes on MCM-41 and amorphous silica through a triazine-based linker. Kureshy et al. successfully immobilized some chiral Mn(III) salen complexes on modified mesoporous supports through axial coordination [28] and covalent grafting [29]. In most cases, these heterogenized chiral Mn(III) salen catalysts could be recycled several times; however, in general, they always led to lower activity and/or enantioselectivity compared with their homogeneous counterparts.

Recently, room temperature ionic liquids have attracted attention as important solvents in synthesis and catalysis owing to their strong solvent power for many organic and inorganic substances [30,31]. Some work [32–34] has been done on using ionic liquid to immobilize chiral catalysts, and satisfactory catalytic activities have been obtained. Herein we describe a kind of supported ionic liquid containing chiral Mn(III) salen complex. In this study, four kinds of mesoporous materials, based on SBA-15, MCM-48, MCM-41, and amorphous SiO_2, were chloropropylated and then modified with imidazole, which can react with the chiral Mn(III) salen complex containing chloromethyl groups, leading to the formation of ionic complexes. The 1-(3-triethoxysilylpropyl)imidazole group here not only acts as a linker and spacing group between the catalyst and the support, but also makes the active center a kind of ionic liquid, which may be advantageous for reactant diffusion. Thus, we expected to obtain high activity from these immobilized catalysts. We found that all of these heterogeneous chiral Mn(III) salen catalysts effectively catalyzed the epoxidation reaction of unfunctionalized olefins. A short reaction time (no more than that of the free complex) was demonstrated, and thus notably high turnover frequencies (TOFs) were achieved over these catalysts, owing to the ionic properties of the active centers as well as the large pore sizes of the mesoporous supports. Comparable or even higher ee values than those of homogeneous counterpart were obtained in the asymmetric epoxidation of styrene and α-methylstyrene with similar olefin conversions. Furthermore, the heterogeneous catalysts also showed high chiral induction (up to 89%) in the epoxidation of bulkier olefins like indene, and they could be reused for up to five cycles.

2. Experimental

2.1. General

Tetraethyl orthosilicate (TEOS; AR), cetyltrimethylammonium bromide (CTAB; AR), triblock organic copolymer (EO_{20}-PO_{70}-EO_{20}) Pluronic P123 (Aldrich), ammonia (25 wt%; AR), sodium hydroxide (NaOH; AR), and hydrochloric acid (HCl; AR) were used to prepare siliceous mesoporous materials. 3-Chloropropyltriethoxysilane, N-methylmorpholine N-oxide (NMO), and α-methylstyrene were purchased from Aldrich. Indene was obtained from Fluka. $(1R,2R)$-(-)-1,2-Diaminocyclohexane and 2-*tert*-butylphenol were supplied by Alfa Aesar. m-Chloroperoxybenzoic acid (m-CPBA) was provided by Acros Organics. Amorphous SiO_2 was purchased from Yu Min Yuan silica–gel reagent factory. All of the solvents used in the present investigation were purified before use.

The content of Mn in the solid catalysts was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an ICP-9000(N + M) spectrometer (TJA Co.). To accomplish this measurement, the sample was quantified with great accuracy and calcined at 823 K for 5 h. The material thus obtained was adequately dissolved with requisite hydrogen fluoride. Then the solution was vaporized to remove silicon fluoride, and the remaining residue was dissolved in aqua regia. The resulting solution was diluted for ICP-AES measurement. C, H, and N contents were evaluated using a Perkin–Elmer 240C analyzer. ^1H and $^{13}C\ \{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, using a Varian Mercury Vx-300 spectrometer. N_2 adsorption–desorption analysis was done at 77 K on a Micromeritics TriStar 3000 apparatus. The surface area was determined using the BET equation, and the pore diameter was estimated using the BJH model. The XRD data were collected on a R/max-2500 diffractometer with $CuK\alpha$ radiation (40 kV and 100 mA) in a scan range of $0.5° < 2\theta < 10°$. FTIR spectra were obtained on a BRUKER VECTOR 22 spectrometer using KBr pellets in the 400–4000 cm^{-1} region. Diffuse-reflectance UV–vis (DRUV–vis) spectra were recorded on a ZASCOV-570 UV–vis spectrophotometer in the range 220–800 nm. Racemic epoxides were synthesized and detected by gas chromatography (GC), using a Rock GC7800 gas chromatograph. The products of epoxidation reaction were determined by GC equipped with a flame ionization detector using ultrapure nitrogen as the carrier gas. The column temperature was programmed between 333 and 413 K. Conversions (with toluene as an internal standard) and ee values were determined by GC with a chiral β-cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m × 0.25 mm × 0.25 μm).

2.2. Synthesis of siliceous mesoporous supports

2.2.1. Synthesis of MCM-41

A highly ordered hexagonal siliceous MCM-41 was synthesized as described previously [35] using TEOS as the silica source and CTAB as the template. A gel (molar) composition of $1TEOS/0.12CTAB/8NH_4OH/114H_2O$ was used. A typical synthetic procedure was carried out as follows, CTAB was dissolved in warm deionized water, and ammonia was added to this solution under vigorous stirring. The required quantity of TEOS was then added dropwise into the solution. After stirring for additional 0.5 h, the resulting gel was transferred into a Teflon-lined autoclave for crystallization at 383 K for 52 h. The solid product was recovered by filtration, washed with deionized water until the filtrate was neutral, and then dried in air overnight. The as-synthesized material was calcined at 823 K in air for 6 h to remove the template.

2.2.2. Synthesis of MCM-48

The purely siliceous MCM-48 was synthesized as described previously [36,37]. In a typical synthesis, CTAB was dissolved in warm deionized water, and to this solution the required quantity of TEOS was added dropwise under vigorous stirring. The aqueous solution of NaOH was then added into the solution. After 2 h of stirring at room temperature, a gel with a molar composition of $1TEOS/0.46CTAB/0.41NaOH/52.95H_2O$ was obtained. This gel was transferred into a Teflon-lined autoclave heated at 383 K for 72 h. The solid product was recovered by filtration, washed with deionized water, and dried in air overnight. The template was removed by calcination at 823 K in air for 6 h.

2.2.3. Synthesis of SBA-15

Parent silica SBA-15 material was synthesized [38,39] using TEOS as the silica source and a triblock organic copolymer Pluronic P123 as the template. In a typical synthesis, 8 g of Pluronic P123 was dispersed in 240 ml of 2 N HCl solution and 60 ml of water under stirring. The resulting solution was heated to 311 K, after which 17 g of TEOS was added under stirring for 20 h to form a gel. The mixture was transferred into a Teflon-lined autoclave for static crystallization at 373 K for 24 h. The solid product was filtered off, washed with deionized water, air-dried at room temperature, and finally calcined at 823 K in air for 6 h to remove the template.

*2.3. Synthesis and heterogenization of chiral Mn(III) salen complex **1***

*2.3.1. Synthesis of the homogeneous chiral Mn(III) salen complex **1***

The chiral Mn(III) salen complex **1** was prepared as follows (Scheme 1).

*2.3.1.1. Synthesis of 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde (**B**)* 3-*tert*-Butyl-2-hydroxybenzaldehyde (**A**) was synthesized from 2-*tert*-butylphenol as described previously [40]. Then the compound **A** (2.7 g, 15.2 mmol) was treated with paraformaldehyde (1.0 g, 33.3 mmol) and tetrabutylammonium bromide (0.47 g, 1.46 mmol) in 11 ml of concentrated hydrochloric acid under vigorous stirring for 72 h at 313 K [41]. The reaction mixture was repeatedly extracted with diethyl ether (3 × 15 ml). The organic phase was washed with 5% $NaHCO_3$ (2 × 10 ml) and brine (2 × 10 ml), then dried over $MgSO_4$. This was further concentrated to give **B** as a yellow crystalline solid (3.4 g, 99% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.43 (s, 9H), 4.59 (s, 2H), 7.44 (d, 1H), 7.53 (d, 1H), 9.87 (s, 1H), 11.87 (s, 1H).

*2.3.1.2. Synthesis of chiral ligand (**C**)* In this procedure, 2.7 g of **B** (12 mmol, 2 equivalent) was refluxed with 0.7 g of $(1R,2R)$-(-)-1,2-diaminocyclohexane (6 mmol, 1 equivalent) in absolute ethanol (45 ml) under stirring for 3 h. The resulting mixture was cooled to room temperature, and 12.5 ml of deionized water was added. The mixture was kept at 277 K in the refrigerator overnight; then the yellow precipitated ligand (2.7 g, 85% yield) was collected by filtration and washed with a small amount of ethanol. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.40 (s, 18H), 1.45–1.99 (m, 8H), 3.30–3.33 (m, 2H), 4.32 (s, 4H), 6.97 (d, 2H), 7.20 (d, 2H), 8.27 (s, 2H), 13.87 (bs, 2H); $^{13}C\ \{^1H\}$ NMR (75 MHz in $CDCl_3$): δ (ppm) 24.5, 29.6, 33.3, 35.0, 65.6, 72.6, 72.9, 118.4, 127.6, 129.7, 137.4, 160.2, 165.7.

*2.3.1.3. Synthesis of chiral Mn(III) salen complex **1*** Chiral ligand **C** (5 mmol) was added to a solution of $Mn(OAc)_2\cdot 4H_2O$ (15 mmol) in absolute ethanol (100 ml). The resulting mixture was refluxed for 0.5 h, after which solid LiCl (15 mmol) was added, and the mixture was refluxed for an additional 2.5 h. The solvent was completely evaporated under reduced pressure on a rotary evaporator, and the residue was extracted with 100 ml of dichloromethane. The organic phase was washed with deionized water (3 × 25 ml) and brine (2 × 20 ml), then dried over $MgSO_4$. This was further concentrated to remove the solvent, and the residue was recrystallized from dichloromethane-hexane to give **1** as a brown solid.

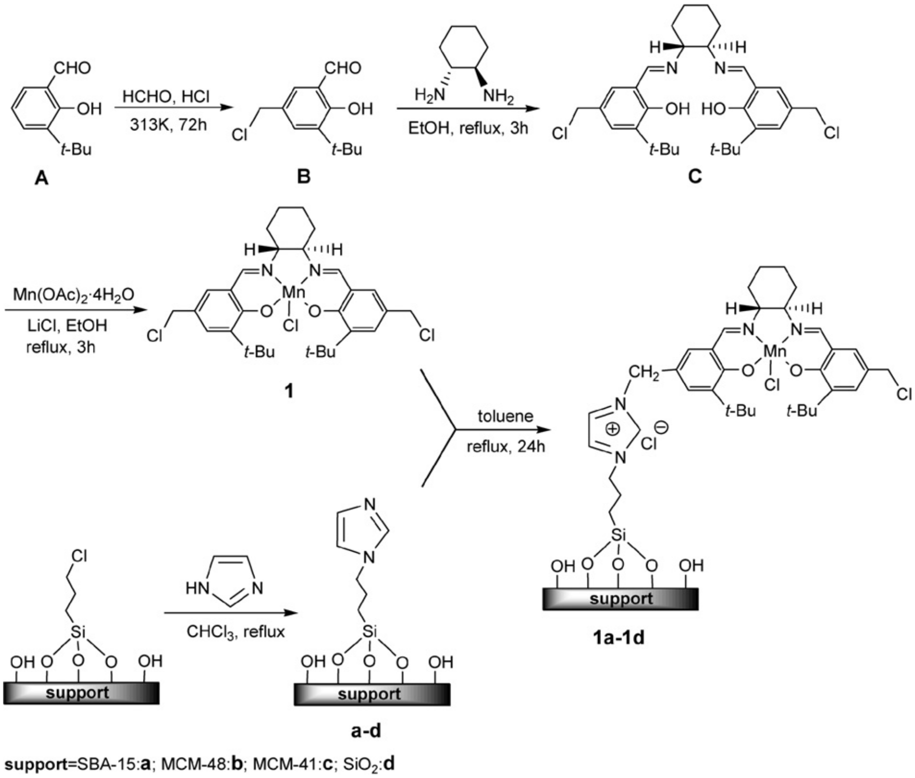
*2.3.2. Heterogenization of chiral Mn(III) salen complex **1***

*2.3.2.1. Preparation of imidazole-modified supports **a–d*** To synthesize the chloropropylated supports, 2.0 g of calcined siliceous mesoporous support was suspended in 60 ml of toluene, and then 1.2 ml of 3-chloropropyltriethoxysilane was added dropwise. The mixture was refluxed for 8 h, and the resulting solid was recovered by filtration and thoroughly washed with ethanol and diethyl ether. The imidazole-modified supports **a–d** were prepared as described previously (Scheme 1) [42]. The chloropropylated supports obtained previously were treated with imidazole (5 mmol) in 100 ml of chloroform under refluxing for 24 h. The modified materials **a–d** were obtained by filtration, washed with diethyl ether, and Soxhlet-extracted with dichloromethane for 20 h.

*2.3.2.2. Synthesis of heterogeneous catalysts **1a–1d*** The imidazole-modified support of **a–d** (1.0 g) was added to a solution of complex **1** (0.4 g) in toluene (60 ml). The mixture was refluxed with vigorous stirring for 24 h (Scheme 1). The brown solids **1a–1d** were collected by filtration, washed with diethyl ether, and then Soxhlet-extracted with dichloromethane for 20 h. The loading of complex **1** in the heterogenized catalyst, based on Mn content, was determined by ICP-AES.

2.4. Asymmetric epoxidation of unfunctionalized olefins

Asymmetric epoxidation reactions were carried out using the heterogeneous catalysts **1a–1d** (0.01 mmol, 1 mol% for **1a** and 0.015 mmol, 1.5 mol% for **1b–1d**, based on Mn element) and homogeneous catalyst **1** (0.01 mmol, 1 mol%, based on Mn element) with styrene, α-methylstyrene, and indene as substrates (1 mmol) and toluene (40 µl) as the internal standard in 10 ml of dichloromethane in the presence of NMO (5 mmol) as an axial base and *m*-CPBA (2 mmol) as an oxidant. The *m*-CPBA was added in five equal portions at 273 K. After the reaction was complete, the supported catalysts were separated by filtra-



Scheme 1. The synthesis of Mn(III) salen complex **1** and immobilized catalysts **1a**–**1d**.

tion, washed with dichloromethane thoroughly, and then dried under vacuum at 333 K for reuse. The filtrate was washed with 10 ml of 1 N NaOH and 10 ml of brine, and then dried over $MgSO_4$. The conversions and ee values were determined by GC. The racemic epoxides were synthesized by the epoxidation of respective olefins in chloroform with *m*-CPBA at 273 K for 24 h [43].

3. Results and discussion

3.1. Characterization of the materials

3.1.1. Chemical analysis

The chiral Mn(III) salen complex **1** was readily anchored onto **a**–**d** through the fifth position of the salen complex, as depicted in Scheme 1. This strategy is simple and economical, and the coordination sphere of manganese ion is preserved in the process of immobilization.

The materials of **a**–**d** were analyzed by elemental analysis. The results, given in Table 1, show that **a**–**d** contained 0.23–0.43 mmol of imidazole groups per gram siliceous support. The manganese contents of the immobilized catalysts were determined by ICP-AES (see Table 1), which revealed that about half of imidazole groups in **a**–**d** participated in covalent bonding to complex **1**. For comparison, pure siliceous materials without modification were used as supports to immobilize the chiral Mn(III) salen complex **1**. However, the complex **1** was leached out readily during extraction by dichloromethane. No product was detected when these materials were used to catalyze olefin epoxidation.

Table 1
Physico-chemical properties of **a**–**d**, **1a**–**1d**, and the parent mesoporous materials

Sample	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore size (Å)	Content of N ($mmol\,g^{-1}$)	Content of Mn ($mmol\,g^{-1}$)
SBA-15	813	1.11	62.3	–	–
a	597	0.83	60.7	0.85	–
1a	482	0.67	52.3	1.09	0.19
MCM-48	1130	0.91	24.4	–	–
b	1003	0.74	23.8	0.46	–
1b	861	0.44	19.3	0.65	0.11
MCM-41	822	0.77	28.8	–	–
c	774	0.69	24.7	0.57	–
1c	626	0.37	19.4	0.81	0.15
SiO_2	347	0.93	86.0	–	–
d	313	0.77	80.1	0.49	–
1d	250	0.61	75.3	0.71	0.12

3.1.2. Nitrogen sorption

All of the parent supports used in this study exhibited type IV isotherms according to the IUPAC [44], with hysteresis loops typical of mesoporous solids. The textural parameters of various materials calculated by N_2 adsorption–desorption isotherms are presented in Table 1. Compared with parent supports, the imidazole-modified samples **a**–**d** exhibited decreased BET surface area, pore volume, and pore size. This indicates that the imidazole groups are located mainly on the inner surfaces of samples **a**–**d**. After immobilization of chiral Mn(III) salen complex **1** on **a**–**d**, a further decrease in BET surface area, pore volume, and pore size was observed, suggesting that complex **1** is present inside the channels of modified materials **a**–**d**.

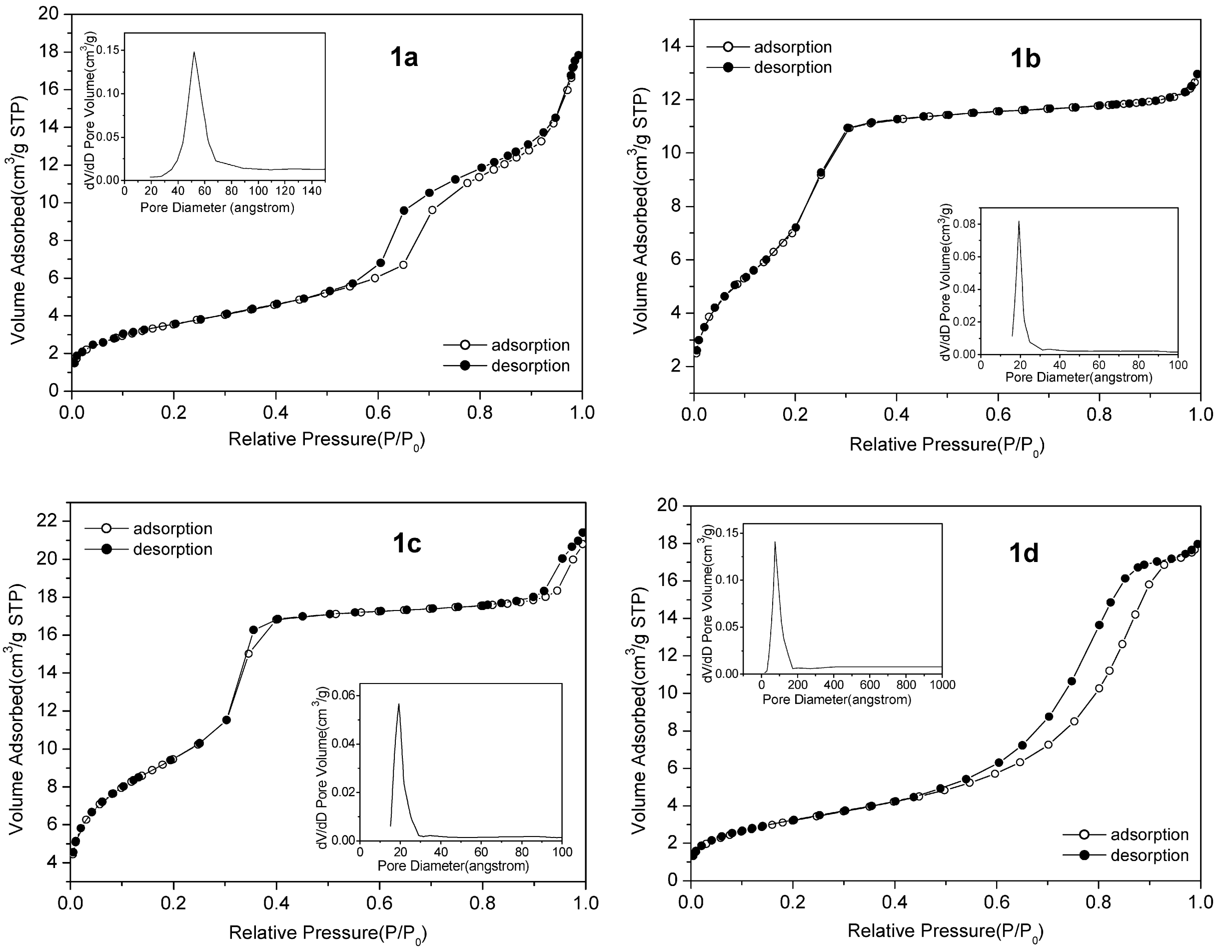


Fig. 1. N_2 adsorption–desorption isotherms and pore size distribution profiles (insert) of immobilized catalysts **1a**–**1d**.

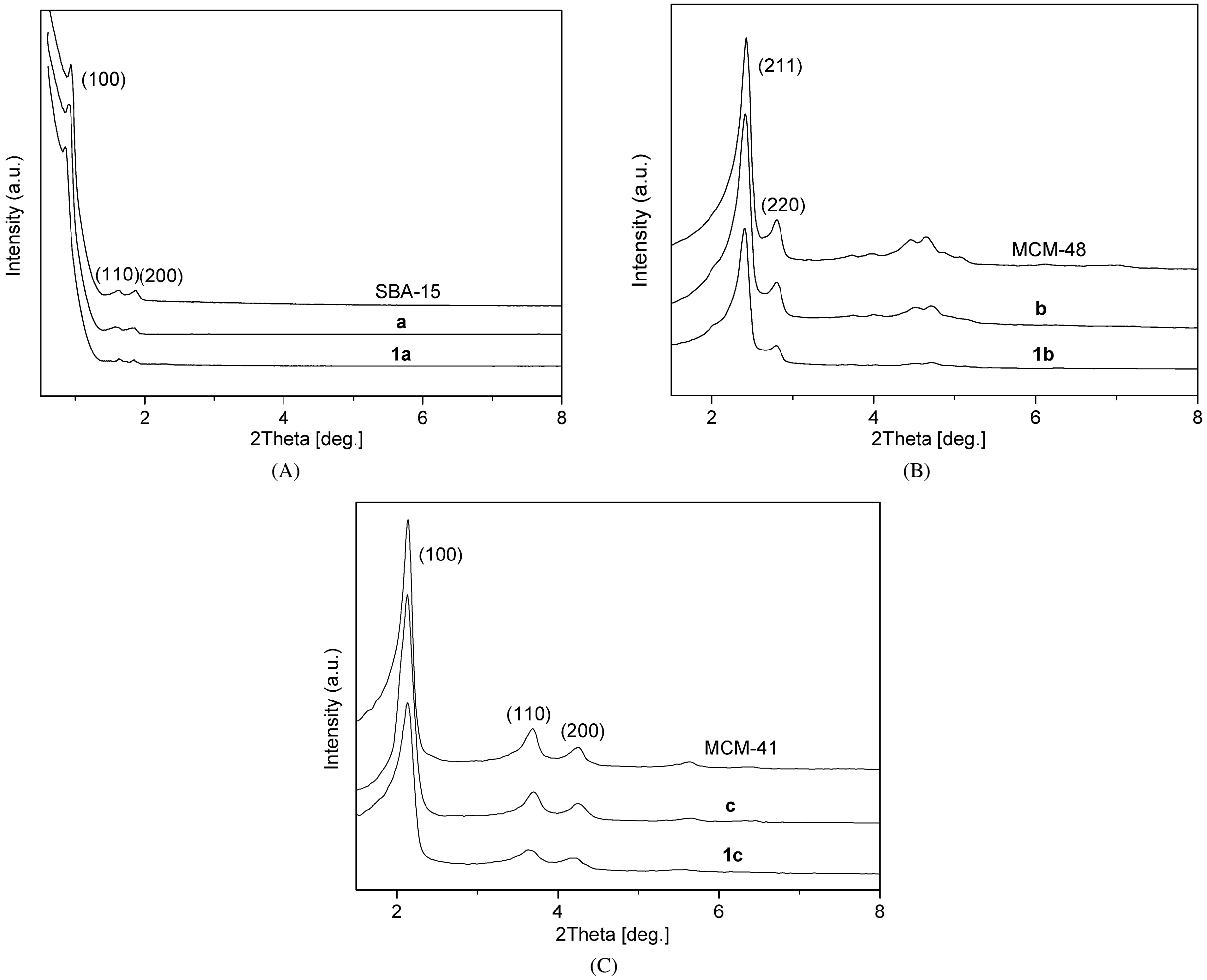
Fig. 1 shows the low- temperature N_2 adsorption–desorption isotherms of immobilized catalysts **1a**–**1d**. These isotherms are of type IV with well-defined sharp inflections observed in p/p_0 ranges 0.5–0.9 for **1a** and **1d** and 0.2–0.4 for **1b** and **1c**, which represent spontaneous filling of the mesopores due to capillary condensation. This indicates that the mesoporous structure of parent support was retained in the immobilized catalysts **1a**–**1d**.

3.1.3. Powder XRD

The powder XRD patterns of **a**–**c**, **1a**–**1c**, and the corresponding parent supports are shown in Fig. 2. Parent MCM-41 and SBA-15 exhibited three XRD peaks assigned to reflections at (100), (110), and (200), which are characteristic of 2D hexagonal lattice (Figs. 2A and 2C). The XRD patterns of MCM-48 (Fig. 2B) showed an intense peak corresponding to (211) reflection along with a shoulder peak at (220) reflection, which are typical for cubic cells. On imidazole modification, a marginal decrease in the relative intensities of the XRD reflections was observed. The well-resolved (110) and (200) reflections for **a** and **c**, and the (220) reflection together with sextet patterns between 2θ angles of 3°–6° for **b**, indicate that no considerable distortion occurred on the channels of the parent supports after modification with the imidazole group. On immobilization of chiral Mn(III) salen complex **1**, the intensities of all of the peaks decreased. However, the XRD patterns clearly indicate that the mesoporous structure of the support retained good periodicity after the immobilization. Thus, imidazole modification and chiral Mn(III) salen complex **1** immobilization had little effect on the long-range mesoporous ordering of parent supports.

3.1.4. FTIR spectroscopy

The FTIR spectra of parent supports showed specific bands at around 1080, 780, and 470 cm^{-1} assigned to characteristic vibrations of the mesoporous framework (Si–O–Si) and a broad band around 3450 cm^{-1} for the adsorbed H_2O molecules. These absorption peaks were maintained after organic modification and chiral Mn(III) salen complex immobilization. Fig. 3 depicts the representative FTIR spectra in the scan range 1300–3300 cm^{-1} for SBA-15, imidazole-modified SBA-15 (**a**), and SBA-15 immobilized chiral Mn(III) salen catalyst (**1a**). In the spectrum of **a**, the IR bands at 3158 and 3110 cm^{-1} were assigned to C–H stretching vibrations of aromatic imidazole rings, and the bands near 3000 cm^{-1} were due to C–H stretching vibrations of alkyl groups belonging to the silylating agent. The IR bands at 1566 and 1454 cm^{-1} can be attributed to C=C stretching vibrations of imidazole rings and C–H deformation vibrations of alkyl groups, respectively. Besides these, the IR band assigned to C=N stretching vibrations was seen at around



(A)

(B)

(C)

Fig. 2. (A) Powder XRD patterns of calcined SBA-15, imidazole-modified SBA-15 **a**, immobilized catalyst **1a**. (B) Powder XRD patterns of calcined MCM-48, imidazole modified MCM-48 **b**, immobilized catalyst **1b**. (C) Powder XRD patterns of calcined MCM-41, imidazole-modified MCM-41 **c**, immobilized catalyst **1c**.

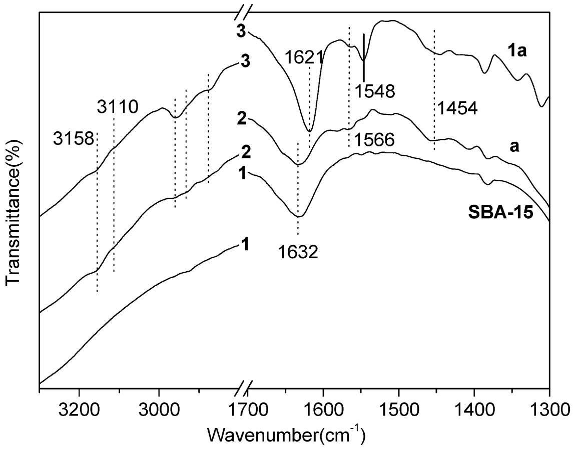


Fig. 3. Representative FTIR spectra of calcined SBA-15, imidazole-modified SBA-15 **a**, immobilized catalyst **1a**.

1632 cm^{-1}, overlapped by the O–H bending vibrations of adsorbed water. The IR spectrum of **a** indicated the successful modification of imidazole groups onto the surface of SBA-15. After the modified support was further immobilized with chiral Mn(III) salen complex **1**, the intensity of the bands around 3000 cm^{-1} increased due to the presence of *tert*-butyl groups. The band at 1632 cm^{-1} shifted to 1621 cm^{-1}, attributed to the presence of C=N in salen ligand, which participated in coordination with manganese ions. Furthermore, a new characteristic band of Mn(III) salen at 1548 cm^{-1} appeared in spectrum of **1a**, indicating that the chiral Mn(III) salen complex **1** was immobilized on the support. Similar results were obtained for the other three parent supports.

3.1.5. DR UV–vis spectroscopy

The diffuse reflectance UV–vis spectra of complex **1** and the immobilized catalysts **1a**–**1d** are given in Fig. 4. The spectra of **1a**–**1d** show features similar to those of complex **1**. The bands at 259 and 332 nm can be attributed to the charge transfer transition of salen ligand. The band at 438 nm is due to ligand-to-metal charge transfer transition, and the bands at 509 nm may be assigned to the *d*–*d* transition of Mn(III) salen complex. On immobilization of Mn(III) salen complex, all of the characteristic bands appeared in their spectra, but a blue shift from 332, 438, and 509 nm to 321, 420, and 498 nm, respectively, indicates an interaction between the Mn(III) salen complex and the support. The DR UV–vis spectra further confirmed the immobilization of chiral Mn(III) salen complex **1** on the supports.

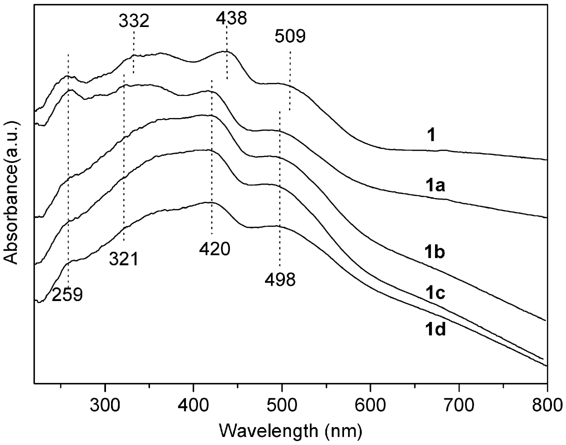


Fig. 4. Solid reflectance UV–vis spectra of homogeneous Mn(III) salen complex **1** and immobilized catalysts **1a**–**1d**.

3.2. *Catalytic properties of the immobilized catalysts*

The heterogeneous catalysts **1a**–**1d** were evaluated in the epoxidation of styrene, α-methylstyrene, and indene at 273 K using m-CPBA and NMO as an oxidant and an axial base, respectively. For comparison, the chiral Mn(III) salen pre-catalyst **1** was also investigated under the same reaction conditions. The results, given in Table 2, show that catalyst **1a** had high catalytic activity in the epoxidation of styrene and α-methylstyrene. Comparable conversions and ee values to homogeneous catalyst **1** were obtained (entries 1, 2, 6, and 7). In particular, in the epoxidation of α-methylstyrene, a higher ee value than the homogeneous ee (44 vs 39%) was achieved by **1a** with no decrease in olefin conversion (entries 6 and 7). This may be due to the higher asymmetric induction resulting from the spatial environment between the chiral Mn(III) salen complex and the channels of the supports. For comparison, the imidazole-modified SBA-15 (**a**) was applied to epoxidize α-methylstyrene under identical conditions. No olefin conversion was observed (entry 8), indicating that the imidazole-modified support was catalytically inactive for the epoxidation of olefins.

Along with the smaller olefin substrates, the heterogenized catalyst **1a** also showed satisfactory catalytic activity and enantioselectivity for relatively bulkier olefins, like indene. An ee value of 89% was achieved by **1a** with an indene conversion similar to that of complex **1** (entries 12 and 13). This indicates that the active sites in the channels of immobilized catalyst also can be accessed readily by the bulkier reactant.

Significantly, the TOF values for all of the immobilized catalysts **1a**–**1d** were notably high (ca. 1.63–2.78 × 10^{-2} s^{-1}) in the epoxidation of the three kinds of olefins used in this work. The epoxidation reactions with immobilized catalysts **1a**–**1d** took no longer than 1 h. It is noteworthy that these TOF values are significantly higher than those of the immobilized catalysts based on the similar supports reported in Refs. [19,22,28,45]. In most cases, catalytic reactions take relatively longer with immobilized catalysts, due to diffusional constraints [19,22–29,45]. This may be explained by the fact that the imidazole-anchored salen Mn(III) complex is indeed a kind of ionic liquid that may tend to contact with the organic phase, thus facilitating entry of reactants and oxidants into the channels of the catalysts and contact with the active sites. This leads to decreased reaction time and increased catalytic activity (TOF).

Among the four immobilized catalysts **1a**–**1d**, the SBA-15-based catalyst **1a** showed the highest catalytic activity for epoxidation; for example, the TOF of 2.78 × 10^{-2} s^{-1} for styrene and α-methylstyrene was as high as that for homogeneous catalyst **1**. This is due to the larger pore size of **1a**, which can minimize the diffusional resistance of the reactants to the active sites in the catalyst. The MCM-48-supported catalyst **1b**, with a

Table 2
Asymmetric epoxidation of unfunctionalized olefins catalyzed by homogeneous complex **1** and immobilized catalysts **1a**–**1d**[a]

Entry	Catalyst[b]	Substrate	Time (h)	Conversion (%)[c]	Ee (%)[d]	TOF ($\times 10^{-2}$ s^{-1})[e]
1	**1**	Styrene	1	>99	44(*R*)	2.78
2	**1a**		1	>99	45(*R*)	2.78
3	**1b**		1	>99	46(*R*)	1.85
4	**1c**		1	90	42(*R*)	1.67
5	**1d**		1	>99	44(*R*)	1.85
6	**1**	α-Methylstyrene	1	>99	39(*R*)	2.78
7	**1a**		1	>99	44(*R*)	2.78
8	**a**		1	–	–	–
9	**1b**		1	>99	42(*R*)	1.85
10	**1c**		1	88	38(*R*)	1.63
11	**1d**		1	>99	42(*R*)	1.85
12	**1**	Indene	1	99	91(1*R*, 2*S*)	2.75
13	**1a**		1	98	89(1*R*, 2*S*)	2.72
14	**1b**		1	98	89(1*R*, 2*S*)	1.81
15	**1c**		1	91	88(1*R*, 2*S*)	1.69
16	**1d**		1	97	87(1*R*, 2*S*)	1.80

[a] Reaction conditions: reaction temperature 273 K, solvent: CH_2Cl_2, oxidant system: m-CPBA/NMO, substrate 1.00 mmol, substrate/m-CPBA/NMO = 1:2:5.

[b] Catalyst was 1 mol% of olefins for **1** and **1a** while 1.5 mol% for **1b**, **1c**, and **1d**.

[c] Conversion % determined by GC with chiral column using toluene as internal standard.

[d] Ee % determined by GC with RESTEK RT-BetaDEXse chiral column.

[e] Turnover frequency (TOF) is calculated by the expression [product]/[catalyst] × time (s^{-1}).

Table 3
The recycling studies of immobilized catalyst **1a** in the asymmetric epoxidation of α-methylstyrene as a representative substrate[a]

Run	Time (h)	Conversion (%)	Ee (%)	TOF ($\times 10^{-2}$ s^{-1})
1	1	>99	44(*R*)	2.78
2	1	99	43(*R*)	2.75
3	1	97	44(*R*)	2.69
4	1	95	43(*R*)	2.64
5	1	99	42(*R*)	2.75

[a] Reactions were performed in CH_2Cl_2 at 273 K with *m*-CPBA/NMO and in the presence of 1 mol% of the catalysts.

smaller pore size than **1a**, exhibited similar conversions and ee values for olefin epoxidation (entries 3, 9, and 14). This can be attributed mainly to this catalyst's three-dimensional topological structure, which favors material transmission. But **1b** had lower TOF values than **1a**, possibly due to its relatively smaller pore size. With the same reaction time, the MCM-41-based catalyst **1c** gave relatively lower conversions and ee values compared with the other three immobilized catalysts (entries 4, 10, and 15). This may be due to the smaller pore size and one-dimensional channel structure of **1c**, which increase diffusional resistance. In addition, the conversions and ee values obtained by **1c** exhibited no obvious change while prolonging the reaction time. The SiO_2-supported catalyst **1d** had a larger pore size but a lower surface area than the other three catalysts. Comparable conversions and ee values with those of **1a** and **1b** were provided by **1d**, but with lower TOF values compared with **1a** (entries 5, 11, and 16).

To study the stability of the immobilized catalysts during the epoxidation of olefins, we applied catalyst **1a** in repeated epoxidation reactions with α-methylstyrene as a model substrate. At the end of each cycle, the catalyst was filtered, washed thoroughly with dichloromethane, dried under vacuum at 333 K, and then subjected to a run with fresh reactants under similar epoxidation conditions. As shown in Table 3, the catalytic activity and enantioselectivity exhibited no obvious decrease for at least four runs. No leaching of Mn was observed in the filtrates by ICP-AES, indicating that the chiral Mn(III) salen complex **1** was strongly bonded to the imidazole-modified supports. Considering the gradual slowdown of conversion, the catalyst was thoroughly Soxhlet-extracted with dichloromethane after four cycles of reuse. Enhanced conversion was again seen in the fifth run (entry 5), indicating that the catalyst remained intact and that the activity reduction should be attributed to the blockage of some pore channels by organic species from previous runs. After five catalytic runs, as expected, the total turnover number (TON) of the heterogeneous catalyst **1a** (ca. 490) was much higher than that of the homogeneous complex **1** (100), which could not be recovered after reaction.

4. Conclusion

A supported ionic liquid containing chiral Mn(III) salen complex was prepared with imidazole-modified mesoporous materials. These heterogeneous catalysts exhibited comparable catalytic activity and enantioselectivity to those of their homogeneous counterparts in the asymmetric epoxidation of unfunctionalized olefins. In particular, notably high TOF values were obtained over these catalysts for their demanded reaction time was as short as the homogeneous one, due in part to the ionic properties of the active centers. The SBA-15-based catalyst showed the best catalytic activity in the epoxidation reaction, and higher TOF values (e.g., 2.78×10^{-2} s^{-1} for styrene and α-methylstyrene) were obtained. Furthermore, these immobilized catalysts were stable and could be easily recovered for reuse at least five times.

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