Enantioselective epoxidation of unfunctionalised olefins catalyzed by Mn(salen) complexes immobilized in porous materials *via* phenyl sulfonic group†

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Heterogeneous chiral Mn(salen) catalysts axially immobilized on mesoporous materials *via* phenyl sulfonic groups result in remarkably higher ee values (up to 95%) for asymmetric epoxidation of unfunctionalised olefins.

Due to the importance of chiral Mn^{III}(salen) complexes[1] for asymmetric catalytic epoxidation of unfunctionalised olefins, the heterogenization of Mn^{III}(salen) complexes, especially immobilized on mesoporous materials, has received great attention in recent years.[2] These heterogeneous catalysts have the advantages of easy separation and recycling of catalysts, purifying products and better handling. However, for most cases, the immobilized Mn(salen) complexes show lower enantioselectivities than their homogeneous catalysts. Only few of them[3] lead to higher ee values than their corresponding homogeneous counterparts. Recently, this group[3c] reported that a chiral Mn^{III}(salen) catalyst axially immobilized into MCM-41 by phenoxyl groups gives 72% ee, higher than the homogeneous 56% for asymmetric epoxidation of α-methylstyrene.

Mn(salen) complexes have been reported to be immobilized by electrostatic interaction.[3e,4] Mn(salen) containing sulfonic anions intercalated into Zn^{II}–Al^{III} LDH were effective for stereoselective epoxidation of *R*-(+)-limonene.[4e] Herein, we use the phenyl sulfonic anion as an axial linkage to immobilize chiral Mn(salen) complexes on inorganic mesoporous materials. This is a universal immobilization method with inherent advantages of simple operation, high stability, versatile supports and utilization of surface and pore effects of the supports. These heterogeneous catalysts show much higher enantioselectivity and *cis*/*trans* selectivity compared to their homogeneous counterparts for asymmetric epoxidation of unfunctionalised olefins.

Three (*S*,*S*)-Mn(salen)Cl complexes (Fig. 1) were synthesized according to the literature.[5] Four siliceous mesoporous materials were used as supports: MCM-41 (pore sizes 1.6 and 2.7 nm), SBA-15 (pore size 7.6 nm) and activated silica (pore size 9.7 nm, with sharp pore size distribution). These supports were chemically modified with phenyl groups (**1**) (Scheme 1), then sulfonated[6] with 10% fuming sulfuric acid. After converting the phenyl sulfonic groups into sodium sulfonate (**3**), Mn(salen) complexes can be readily anchored on the supports by ion-exchange in refluxing ethanol to give brown **4**. The chloride ions in the resulting solution can be separated and identified by use of an H^+–$AgNO_3$ aqueous solution.

† Electronic supplementary information (ESI) available: CP/MAS ^{13}C NMR, FTIR, UV-vis and PXRD spectra of the catalysts. See http://www.rsc.org/suppdata/cc/b4/b417041e/

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The presence of phenyl groups on **1** was confirmed by FT-IR and ^{13}C CP/MAS NMR spectroscopy. The heterogeneous Mn(salen) catalysts were characterized by FT-IR, UV-Vis, PXRD and ICP. The IR band at 2985 cm^{-1}, associated with *t*-Bu group, together with other IR bands at 1449, 1397 and 1371 cm^{-1} confirmed the successful grafting of the Mn(salen) complexes. The UV-Vis spectra provide further evidence for the presence of Mn(salen) complexes on the supports. The characteristic bands at 326 and 438 nm for Mn(salen-a)Cl are shifted to 321 and 420 nm, respectively, after immobilization, indicating that the electrostatic interaction between the immobilized Mn(salen-a) and the support slightly affects the catalyst. PXRD patterns confirm that the mesoporous structure of the heterogeneous catalysts still retain good periodicity after the immobilization. The amount of Mn(salen) grafted is in the range of 0.02–0.04 mmol g^{-1} based on Mn as analyzed by ICP. As a comparison, a support without grafted phenyl groups was prepared according to an identical method (steps i–iii in Scheme 1) and no Mn was detected based on ICP analysis. This means that the Mn(salen) complexes were anchored on supports *via* the phenyl sulfonic group.

The heterogeneous catalytic tests were carried out in CH_2Cl_2 (3 ml) containing olefins (1 mmol), *n*-nonane (internal standard, 1 mmol), homogeneous or heterogeneous Mn(salen) catalysts (1.5 mol%) and NaClO solution (pH = 11.3, 0.55 M, 3.64 ml) at 20 °C. The products were analyzed by GC/MS, and yields and ee values were determined by GC with a chiral β-cyclodextrin column. The results of heterogeneous asymmetric epoxidation of α-methylstyrene (Fig. 1) are listed in Table 1. The homogeneous

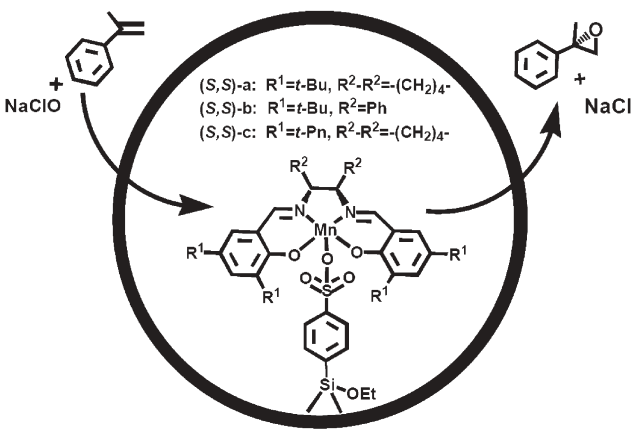
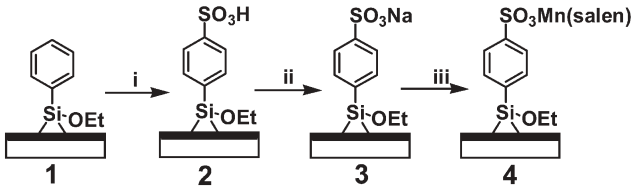


Fig. 1 Schematic illustration of asymmetric epoxidation of α-methylstyrene in the nanopores of heterogeneous Mn(salen) catalysts.



Scheme 1 Preparation of heterogeneous Mn(salen) catalysts immobilized by phenyl sulfonic anions. *Reagents and conditions*: (i) 10% fuming sulfuric acid, 40 °C, 2 h; (ii) $NaHCO_3$, water, r.t., 3 h; (iii) Mn(salen)Cl, ethanol, 80 °C, reflux, 5 h.

Table 1 Asymmetric catalytic epoxidation of α-methylstyrene reactions

Run	Catalyst	Time/h	Yield (%)	Ee[a] (%)
1	Mn(salen-a)Cl	6	100	55.0
2	Mn(salen-a)/MCM(1.6)	24	87.3	78.1
3	Mn(salen-a)/MCM(2.7)	24	78.3	66.4
4	Mn(salen-a)/SBA(7.6)	24	65.6	73.6
5	Mn(salen-a)/SiO_2(9.7)	24	64.2	75.8
6	Mn(salen-a)Cl[b]	6	100	56.6
7	Mn(salen-b)Cl	6	100	26.4
8	Mn(salen-b)/SBA(7.6)	24	50.2	75.4
9	Mn(salen-c)Cl	6	98.4	52.4
10	Mn(salen-c)/SBA(7.6)	24	52.6	73.7
11	Mn(salen-a)/SiO_2(9.7) (4th)	24	35.7	74.6
12	Mn(salen-a)/SiO_2(9.7) (5th)	24	40.5	76.4

[a] (*S*)-Epoxide. [b] Addition of SiO_2(9.7)–$PhSO_3Na$ 100 mg.

Mn(salen-a)Cl catalyst produces epoxide in quantitative yield and 55.0% ee (run 1). Immobilization of Mn(salen-a) on MCM-41 (1.6 nm) gives 87.3% yield and 78.1% ee. Grafting Mn(salen-a) on MCM-41(2.7 nm) gives 66.4% ee and enlarging the pore sizes results in a further increase in ee values (runs 3–5). Using SiO_2 as support presents epoxide in 64.2% yield and 75.8% ee. Adding SiO_2(9.7)–$PhSO_3Na$ solid to the homogeneous system does not affect the reaction and gives the same results as the homogeneous reactions.

Immobilizing the Mn(salen-b) complex on SBA-15(7.6) also leads to ee value of the epoxide being greatly increased from the homogeneous ee value of 26.4% to a value of 75.4%. Similarly, the Mn(salen-c)/SBA(7.6) catalyst also shows a higher ee value of 73.7% compared to its homogeneous ee of 52.4%. All the results show that the enantioselectivities are greatly enhanced by the heterogeneous Mn(salen) catalysts, however, the yields obtained for the immobilized catalysts are usually lower than the homogeneous values, which is mainly due to the diffusion limitation under the heterogeneous conditions. It was also reported[3a] that the ee value was increased from 51 to 59% for asymmetric epoxidation of α-methylstyrene after immobilizing Mn(salen) on MCM-41 by multi-step grafting. Mn(salen-a) axially immobilized on MCM-41 *via* phenoxyl groups[3c] presents a 72% ee value for this substrate whereas the same complex immobilized by the phenyl sulfonic group can give a 78% ee value. The spatial effect including the surface effect originated from the supports as well as the immobilization modes are considered as the main reasons for the increase in ee values.[2d,7]

After a reaction run, the solid catalyst was thoroughly washed with distilled water, ethanol and dichloromethane and then was recycled. Mn(salen-a)/SiO_2(9.7) catalyst was reused for at least five times with constant enantioselectivity of 75%, although the conversion gradually decreased (runs 4, 11, 12). A separate experiment shows that the heterogeneous catalyst can still give the same reaction results even after being soaked in the reaction system for 50 days at room temperature.

The heterogeneous Mn(salen) catalysts were also tested for the asymmetric epoxidation of *cis*-β-methylstyrene (Table 2). The heterogeneous Mn(salen-a)/MCM(1.6) catalyst gives up to 94.6% ee for *cis*-epoxide, higher than the homogeneous result of 54.8% (runs 1 and 2). Immobilizing Mn(salen-a) on SBA-15 or SiO_2 also produces higher ee values for *cis*-epoxide. However, for the *trans*-epoxide, the ee values show a decrease under heterogeneous conditions. Immobilization of Mn(salen-b) or Mn(salen-c) on SBA-15 also leads to higher ee values for *cis*-epoxide and lower ee for *trans*-epoxide compared to the homogeneous results. It was reported that[3b] the ee value increased from 54 to 73% for the *cis*-epoxide for asymmetric epoxidation of this substrate after grafting Cr(salen) *via* axial NH_2 complexation. The unique spatial environment of the heterogeneous catalysts is one of the reasons for the increase in ee value.

In addition, it is interesting to find out that the heterogeneous catalyst also significantly alters the *cis*/*trans* ratio of epoxide product. Homogeneous catalyst Mn(salen-a)Cl produces the *trans*-epoxide as the major product (*cis*/*trans* 0.38) whereas the heterogeneous catalysts give the *cis*-epoxide as the dominant product and the ratio of *cis*/*trans* can reach up to 17.6. Heterogeneous Mn(salen-b) and Mn(salen-c) catalysts also result in similar results in that the *cis*-epoxides are the major product under the heterogeneous conditions. In the homogeneous reaction, the radical intermediate is transformed to the *cis*-epoxide *via* direct collapse or to the *trans*-epoxide *via* rotation followed by collapse.[8] Under heterogeneous conditions, the effect of the supports,

Table 2 Asymmetric epoxidation of *cis*-β-methylstyrene[a]

		cis[b]		*trans*[c]		
Run	Catalyst	Yield (%)	Ee (%)	Yield (%)	Ee (%)	*cis*/*trans*
1	Mn(salen-a)Cl	27.5	54.8	72.5	100	0.38
2	Mn(salen-a)/MCM(1.6)	66.0	94.6	3.76	75.7	17.6
3	Mn(salen-a)/SBA(7.6)	36.2	94.5	2.83	76.5	12.8
4	Mn(salen-a)/SiO_2(9.7)	21.2	94.0	1.30	100	16.2
5	Mn(salen-b)Cl	25.3	25.3	54.9	93.3	0.46
6	Mn(salen-b)/SBA(7.6)	34.7	92.6	4.50	81.4	7.71
7	Mn(salen-c)Cl	27.9	55.8	72.1	98.3	0.39
8	Mn(salen-c)/SBA(7.6)	41.1	94.8	4.76	76.7	8.63

[a] Runs 1, 5 and 7 were conducted for 6 h and the remainder for 24 h. [b] (*S*,*R*)-Epoxide. [c] (*S*,*S*)-Epoxide.

especially the effect of pores, may restrict the rotation of the intermediate, and as a result the *cis*-epoxide becomes the main product. A similar explanation was also given for the results with Mn(salen) complexes immobilized in nanopores of Al-MCM-41 favoring the formation of the *cis*-epoxide of (*Z*)-stilbene.[4d]

In summary, an organic sulfonic group has, for the first time, been used as a linkage to immobilize chiral Mn(salen) complexes on nanopores for asymmetric epoxidation. These heterogeneous catalysts give much higher ee values for asymmetric epoxidation of α-methylstyrene and *cis*-β-methylstyrene than the homogeneous counterparts and display high stability during the catalytic process. *cis*-Epoxide as the major product was achieved for epoxidation of *cis*-β-methylstyrene under heterogeneous conditions. Further studies on the effect of surfaces and nanopores of supports are in progress.

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