Chiral catalysis in nanopores of mesoporous materials

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This article reviews the recent progress made in asymmetric catalysis in the nanopores of mesoporous materials and periodic mesoporous organosilicas (PMOs). Some examples of chiral catalysts within the nanopores show improved catalytic performance compared to homogeneous catalysts. The factors including the confinement effect, the properties of the linkages and the microenvironment in nanopores, which affect the activity and enantioselectivity of asymmetric catalysis in nanopores, are discussed.

1 Introduction

Chiral compounds are very important for the synthesis of pharmaceuticals, fine chemicals, vitamins and non-linear optical materials. There are several approaches to obtain chiral compounds including chiral resolution, chemical derivatization and asymmetric catalysis. Asymmetric catalysis is

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one of the most attractive methods, because plentiful prochiral substrates can be transformed to chiral compounds with controlled absolute configuration catalyzed usually by a small amount of chiral catalysts. Homogeneous asymmetric catalysis has made great progress in the last few decades. However, most of the homogeneous asymmetric catalysts have not been industrialized yet. One of the major problems is due to the difficulty in the separation and recycling of the chiral catalysts. Recently, heterogeneous asymmetric catalysis has attracted much attention for its potential advantages, such as the easy purification of products, separation and recycling of chiral catalysts, isolation of catalytic centers, and continuous reaction *via* a fix-bed reactor.[1] Heterogeneous chiral catalysts for asymmetric hydrogenation, epoxidation, Aldol reaction and D–A addition have been prepared through immobilization of the homogeneous catalysts on organic or inorganic supports.[1]

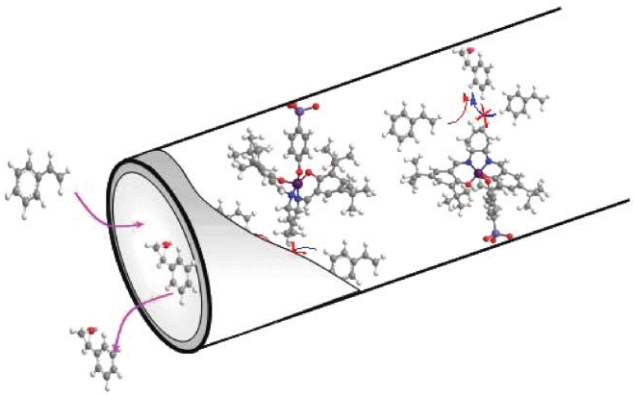
Homogeneous chiral catalysts, usually transition-metal complexes, can be immobilized on various supports through covalent grafting of chiral catalysts on mesoporous materials[2] or carbon materials,[3] encapsulation of chiral catalysts in zeolites,[4] and ion-exchange of catalysts into charged supports.[5] Among different kinds of supports mentioned above, the mesoporous materials have attracted much attention because of their unique properties, such as well-ordered pore arrays, large surface area, uniform pore size distributions and tunable pore diameter (4–15 nm).[6] MCM-41 and SBA-15 are the most frequently used mesoporous materials for the immobilization of homogeneous chiral catalysts.

Recently, the periodic mesoporous organosilicas (PMOs) with an organic moiety bridging in the mesoporous framework are regarded as one of the promising porous materials for assembling chiral catalysts,[7] because PMOs have a uniform distribution of organic moieties in the framework. The nanopores of the PMOs can be used as novel nanoreactors for heterogeneous asymmetric catalysis when the chiral catalysts are assembled in the nanopores of PMOs[8] or incorporated in the framework of PMOs.[9]

This paper will present the progress made in the asymmetric catalysis in nanopores of mesoporous materials and the PMOs, focusing on the work reported mainly in this group with related examples reported in other groups in recent years. We have systemically investigated the asymmetric epoxidation on Mn(salen) catalysts immobilized in the nanopores of mesoporous materials (as shown in Scheme 1), and the factors of the heterogeneous chiral catalysts influencing the asymmetric catalytic performance in nanopores are summarized and discussed in detail.

2 Immobilization of chiral catalysts in nanopores

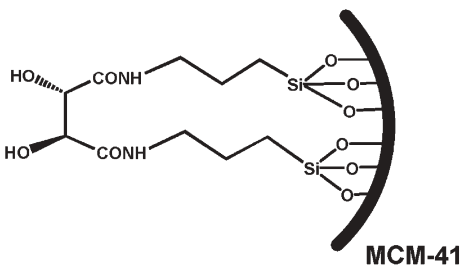
A homogeneous chiral catalyst can be heterogenized on solid supports through various methods, including grafting, ion exchange, or adsorption of a homogeneous catalyst on supports,[1,10] encapsulation of chiral catalysts by ship-in-bottle method[4b] or sol–gel method,[11] and so on.[12] Among these methods, the immobilization of a chiral catalyst into nanopores of inorganic supports is still a challenge. There are several methods usually used for the immobilization of chiral catalysts into the nanopores of mesoporous materials. The most effective one is the post-grafting method.[1] For silica-based supports, the chiral catalysts can be introduced into the nanopores *via* a linkage to attach the catalyst through reacting with the Si–OH functionalities in nanopores. Here is shown our example in which chiral tartrate acid was grafted into nanopores of MCM-41 *via* Si–OH groups using 3-aminopropyltrimethoxysilane as the linkage (Scheme 2).[13] Generally, two grafting methods are used. One is the grafting *via* a chiral ligand;[14] and the other is the grafting *via* the coordination of a grafted ligand to the metal.[15]



Scheme 1 The asymmetric epoxidation of styrene catalyzed by chiral Mn(salen) catalyst immobilized in nanopores.

Some chiral catalysts are grafted inevitably on the external surface of the supports. However, the external surface area of the support is much less than that contributed by the nanopores of the support.[16] Therefore, the amount of Si–OH groups on the external surface is much less compared to that in nanopores and the amount of the chiral catalysts grafted on the external surface is usually not dominant. In order to introduce chiral catalysts exactly into nanopores, the Si–OH groups on the external surface of supports could be first passivated and then the chiral catalysts could be immobilized in the nanopores of supports *via* the reaction of the catalyst with the Si–OH only in the nanopores.[17,18] After immobilization of the chiral catalyst in the nanopores, the pore size and the pore volume of the nanopores are decreased, as confirmed by N_2 adsorption.[2c] The amount of the grafted chiral catalysts depends on the concentration of Si–OH groups of the support.

Alternatively, a chiral catalyst can be synthesized in the nanopores of mesoporous materials *via* a multi-step procedure according to the solid-phase synthesis method.[19] A component of the chiral catalyst is firstly grafted into the nanopores, and then it reacts with other molecules to form the chiral catalyst

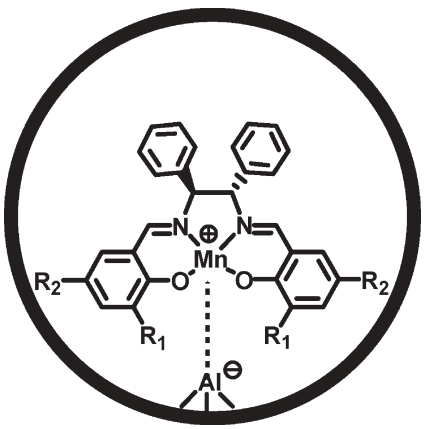


Scheme 2

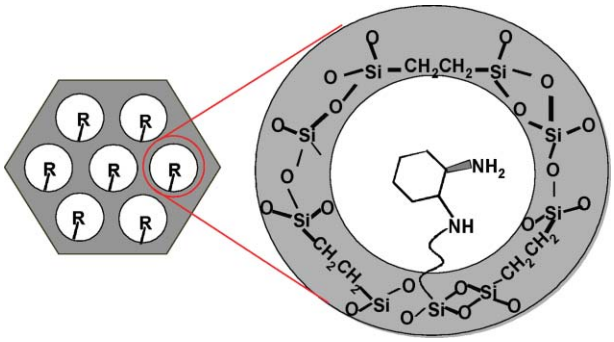
attached in the nanopores. However, it is inevitable that there are some unreacted fragments of the catalysts remaining in the nanopores, which might cause some unexpected catalytic reactions.[20]

If a chiral catalyst is an ion or has charged groups, the catalyst can be introduced into the nanopores of the mesoporous materials with the opposite charge *via* ion exchange.[21] The charged supports, Al-MCM-41,[21] clays,[5a] or layered double hydroxides (LDH),[5b] are usually used for the immobilization of chiral catalysts. Non-charged chiral catalysts can also be attached with some charged groups, which are further immobilized into nanopores of the supports. For example, Kim and Shin[21] synthesized the cationic chiral [Mn(salen)][PF_6] catalysts and immobilized them into the nanopores of Al-MCM-41 by ion exchange (Scheme 3). This type of chiral catalysts is immobilized in nanopores by electrostatic interaction. However, these catalysts have some leaching problems during the catalytic reaction if the reaction conditions, including solvent, is not appropriate. Another similar method to prepare chiral catalysts in nanopores is through ion exchange. The metal ions are first pre-exchanged in the nanopores of support and then they coordinate with the chiral ligand to form the chiral catalysts in the nanopores.[22] One of the examples is the modification of the Mn-exchanged Al-MCM-41 catalyst by a chiral salen ligand reported by Hutchings and co-workers.[23] However, the exact coordination mode of the chiral ligand with the pre-exchanged ion has not been thoroughly investigated. It was also found that the Mn ion was stable on the support but the leaching of salen ligands was observed in the asymmetric epoxidation test.[24]

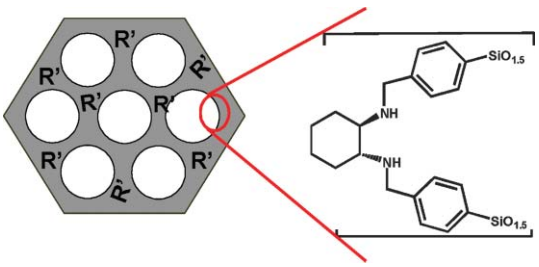
PMOs synthesized from bridged silane precursors, $(R'O)_3Si–R–Si(OR')_3$, have uniformly distributed organic moieties in the mesoporous framework.[7] Compared with mesoporous silicas, they exhibit unique properties, such as tunable surface hydrophobicity/hydrophilicity. Furthermore, their hydrothermal and mechanical stability could be modified by incorporation of different types of organic moiety in the framework. The PMOs may have potential applications as catalysts and catalyst supports especially for the production of fine chemicals. If a chiral center is introduced into the R bridge between the two silicon centers, then chiral PMOs with chiral moieties within the mesoporous framework could be prepared.



Scheme 3



Scheme 4 Chiral PMOs with chiral ligands in the pore.



Scheme 5 Chiral PMOs with chiral ligands in the framework.

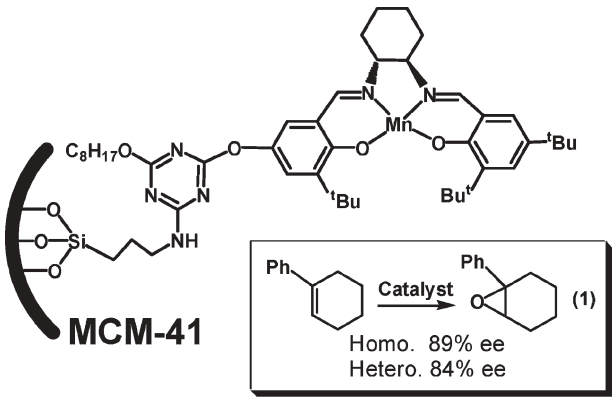
PMOs with large numbers of chiral moieties uniformly distributed in the mesoporous framework provide opportunities for obtaining high chiral induction ability for asymmetric catalysis. The chiral moieties could also be introduced into the pores of PMOs through either grafting method or co-condensation of $(R'O)_3Si–R–Si(OR')_3$ with $R''–Si(OR')_3$ (R″ containing a chiral center). Through adjusting the surface properties of the PMOs, the diffusion rate of the reactant during the catalysis could be enhanced, which may result in a solid catalyst with high catalytic activity. There are a few examples of PMOs with chiral moieties either in the mesopore or in the mesoporous framework prepared by the co-condensation method (Schemes 4 and 5).[8] Such chiral moieties combined with an Rh complex were tested for the asymmetric transfer hydrogenation of ketones.[25]

3 Chiral catalysis for catalysts immobilized in nanopores

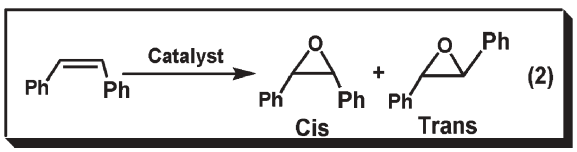
3.1 Chiral catalysis in nanopores of mesoporous materials

Bigi *et al.*[14] reported a chiral Mn(salen) catalyst that was grafted in the nanopores of MCM-41 from the salen ligand through a triazine-based linkage (Scheme 6). The propyl amino group in the pore allows retention of the free conformation of the Mn(salen) catalyst and the triazine group could prevent the possible chain folding. The heterogeneous catalyst showed an enantiomeric excess (ee) of 84%, similar to that of the homogeneous counterpart (89%) for the asymmetric epoxidation of 1-phenylcyclohexene (Scheme 6, reaction (1)).

Hutchings and co-workers[23] prepared a heterogeneous Mn(salen) catalyst by the modification of Mn-exchanged Al-MCM-41 with chiral salen ligand for the asymmetric epoxidation of (*Z*)-stilbene with PhIO as oxygen donor (reaction (2)).



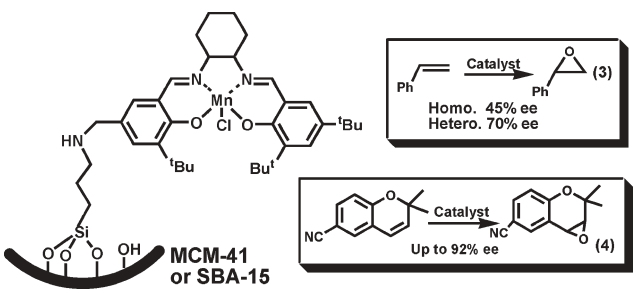
Scheme 6



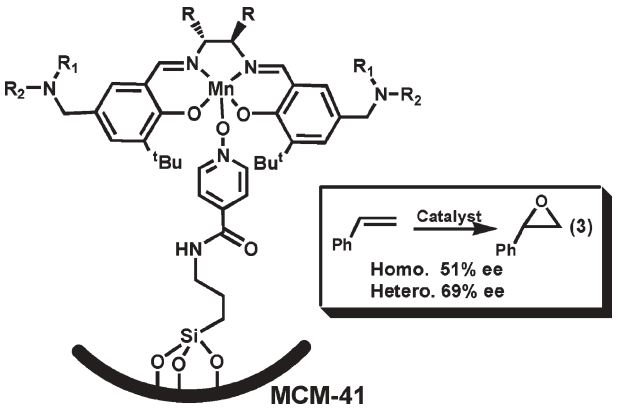
The *cis*/*trans* ratios of the epoxides were increased from 0.4 for the homogeneous catalyst to 4.3 for the heterogeneous catalyst. It was proposed that the nanopores of MCM-41 retarded the rotation of the radical intermediate and produced more *cis* epoxide compared to the homogeneous catalyst.

Kureshy *et al.*[26] reported that chiral Mn(salen) catalyst immobilized in the nanopores of MCM-41 and SBA-15 (Scheme 7) showed higher chiral induction (70% ee) than its homogeneous counterpart (45% ee) for the enantioselective epoxidation of styrene with aqueous NaOCl as oxidant (Scheme 7, reaction (3)). In addition, bulkier alkenes such as 6-cyano-2,2-dimethylchromene (Scheme 7, reaction (4)) were also efficiently epoxidized into their epoxides on these supported Mn(salen) catalysts (up to 92% ee), and the reaction results were comparable to those of the homogeneous counterparts. The heterogeneous catalyst can be used for four times without obvious loss of activity and enantioselectivity.

Mn(salen) catalyst was also axially immobilized in the nanopores of MCM-41 *via* pyridine *N*-oxide by Kureshy′s group (Scheme 8).[2c] These immobilized catalysts showed higher enantioselectivity (69% ee) than its homogeneous counterpart (51% ee) for the asymmetric epoxidation of styrene (Scheme 8, reaction (3)). These catalysts were also effective for the asymmetric epoxidation of bulkier substrates such as indene and 2,2-dimethylchromene (conversion 82–98%, ee 69–92%).



Scheme 7

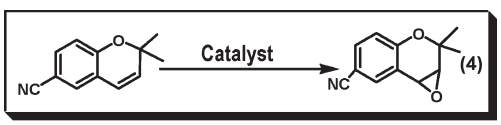


Scheme 8

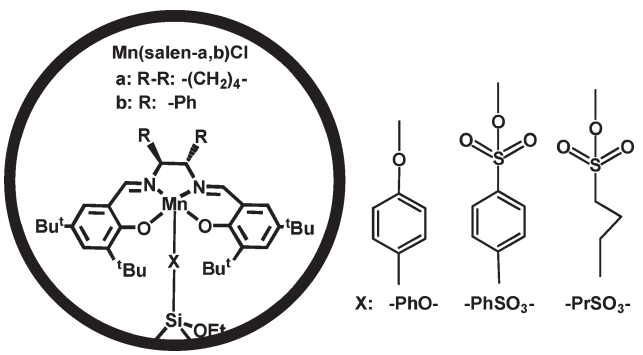
The catalysts could be recycled for at least four times without loss of performance. The increase in ee values was attributed to the unique spatial environment constituted by the chiral salen ligand and the surface of the support.

Recently, our group prepared the axially immobilized chiral Mn(salen) complexes in the nanopores of mesoporous materials *via* the phenoxyl group,[2b,15] phenyl sulfonic group,[27] and propyl sulfonic group. These heterogeneous catalysts were denoted as support-PhO ($PhSO_3$ or $PrSO_3$) Mn(salen) (Scheme 9). The catalysts using activated silica (narrow distribution of pore size at 9.7 nm), SBA-15 (pore size of 7.6 or 6.2 nm), MCM-41 (pore size of 2.7 or 1.6 nm) and insoluble polystyrene resin as support, are abbreviated as 9.7AS, 7.6SBA, 6.2SBA, 2.7MCM, 1.6MCM and PS, respectively.

The phenoxyl-immobilized Mn(salen-a) catalyst,[2b] for example, 6.2SBA-PhOMn(salen-a) shows 84.9% ee for the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene, slightly higher than for the corresponding homogeneous counterpart of 80.1% (reaction (4)).



The 7.6SBA-PhOMn(salen-b) catalyst exhibits 93.5% ee (*cis*-epoxide) for the asymmetric epoxidation of *cis*-β-methylstyrene (reaction (5)), higher than the 25.3% ee obtained for the homogeneous catalyst (entries 1 and 2, Table 1).

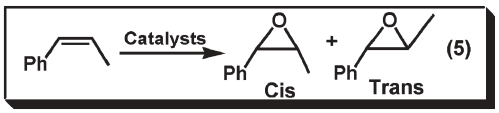


Scheme 9

Table 1 Asymmetric epoxidation of *cis*-β-methylstyrene (reaction (5))

		cis		*trans*		
Entry	Catalyst	Yield (%)	ee (%)	Yield (%)	ee (%)	*cis*/*trans*
1	Mn(salen-b)Cl	25.3	25.3	55.0	93.3	0.46
2	7.6SBA-PhOMn(salen-b)	32.1	93.5	2.9	65.2	11.1
3	7.6SBA-PhSO$_3$Mn(salen-b)	34.7	92.6	4.5	81.4	7.71
4	PS-PhSO$_3$Mn(salen-b)	43.3	68.8	42.5	89.2	1.02

[a] Reactions were performed in CH_2Cl_2 (3 ml) with *cis*-β-methylstyrene (1.0 mmol), internal standard (1.0 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 20 °C.



These results show that the enhancement of enantioselectivity in the asymmetric epoxidation is mainly attributed to the nanopore effect of the supports. The *cis*/*trans* ratios of epoxides are also increased from 0.46 for the homogeneous Mn(salen-b)Cl catalyst to 11.1 for the 7.6SBA-PhOMn(salen-b) catalyst under the same conditions.

Similarly, chiral Mn(salen-b) complex axially immobilized in nanopores of 7.6SBA *via* phenyl sulfonic groups[27] (Scheme 9) also shows higher ee value for the *cis*-epoxide and the *cis*/*trans* ratio than the corresponding homogeneous counterparts for the asymmetric epoxidation of *cis*-β-methylstyrene under the same conditions (entries 1 and 3, Table 1). Polystyrene-supported catalyst, PS-PhSO$_3$Mn(salen-b),[28] still give higher ee value (for *cis*-epoxide) and *cis*/*trans* ratio than those of the homogeneous catalyst (entries 1 and 4, Table 1), but the results are lower than those of 7.6SBA-PhSO$_3$Mn(salen-b) (entries 3 and 4, Table 1), which means that the supports show an obvious effect on the catalytic properties of the heterogeneous asymmetric epoxidation.[18]

In order to increase the catalytic performance, the hydrophobicity of the nanopores of supports was enhanced by the modification with organic groups. The chiral Mn(salen) catalysts were immobilized *via* axial coordination in the nanopores of 9.7AS, the methyl-modified nanopores of 9.7AS(Me), or onto the external surface of 1.6MCM *via* phenyl sulfonic groups with different linkage lengths (the space atom number of R is 0, 1, 2 or 4, and the catalysts are denoted as support-R-PhSO$_3$Mn(salen), shown in Fig. 1).[29,30] The heterogeneous Mn(salen-a) catalysts were tested for the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene (reaction (4), Table 2).[30] 9.7AS(Me)-2-PhSO$_3$Mn(salen-a) catalyst presents TOF of 10.9, which is higher than that obtained for 9.7AS-2-PhSO$_3$Mn(salen-a) catalyst and is similar to the homogeneous counterpart. The activity of Mn(salen-a) catalyst in the nanopores of the methyl-modified catalyst, 9.7AS(Me)-4-PhSO$_3$Mn(salen-a), is greatly increased. The TOF can be as high as 14.8 h^{-1}. Under the same conditions, the TOF of the homogeneous catalyst is 10.8 h^{-1}. The ee value obtained for 9.7AS(Me)-4-PhSO$_3$Mn(salen-a) catalyst is also higher than the corresponding homogeneous counterpart for the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene.

Kureshy *et al.*[5a] immobilized dicationic chiral Mn(salen) catalysts into the anionic montmorillonite clay for the

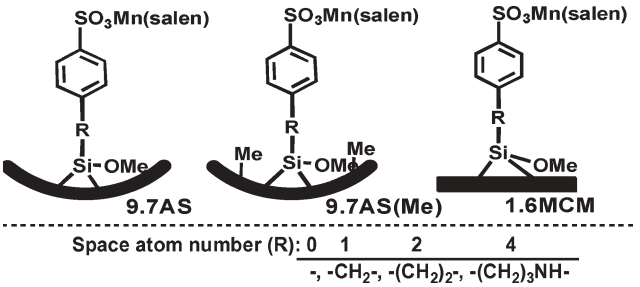


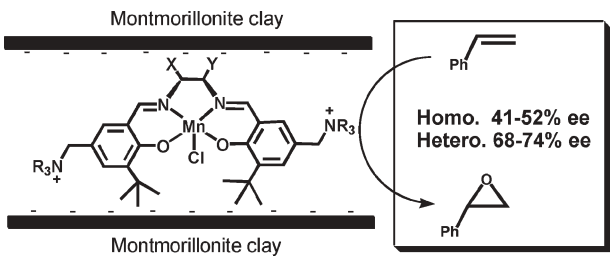
Fig. 1 The Mn(salen) catalysts immobilized in the nanopores of 9.7AS and modified nanopores of 9.7AS(Me) and on the external surface of 1.6MCM *via* different linkage lengths R.

Table 2 Asymmetric epoxidation of 6-cyano-2,2-dimethylchromene (reaction (4)) catalyzed by Mn(salen-a) immobilized in the nanopores of 9.7AS with or without methyl modification

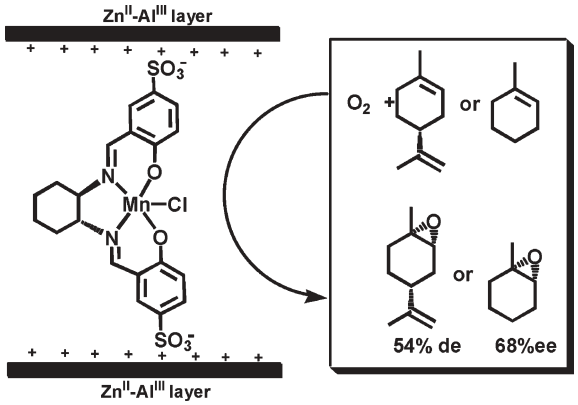
En	Catalyst	*t*/h	Conv. (%)	ee (%)	TOF/h^{-1}
1	Mn(salen-a)Cl	6	97.0	80.1	10.8
2	9.7AS-2-PhSO$_3$Mn(salen-a)	24	88.8	78.7	2.47
3	9.7AS(Me)-2-PhSO$_3$Mn(salen-a)	6	98.3	86.5	10.9
4	9.7AS-4-PhSO$_3$Mn(salen-a)	24	87.3	82.6	2.43
5	9.7AS(Me)-4-PhSO$_3$Mn(salen-a)	4.5	100	90.6	14.8

[a] Reactions were performed in CH_2Cl_2 (3 ml) with 6-cyano-2,2-dimethylchromene (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 20 °C.

preparation of the clay-supported Mn(salen) catalysts (Scheme 10). These heterogeneous catalysts were tested for the asymmetric epoxidation of 6-nitro-2,2-dimethylchromene, indene and styrene with NaOCl as oxidant. The conversions were almost 100% and the ee values were similar to or even higher than those of the corresponding homogeneous ones (74 *vs.* 52% for asymmetric epoxidation of styrene). The increase in ee value was mainly attributed to the unique spatial environment in the nanopores of the support. Furthermore,



Scheme 10

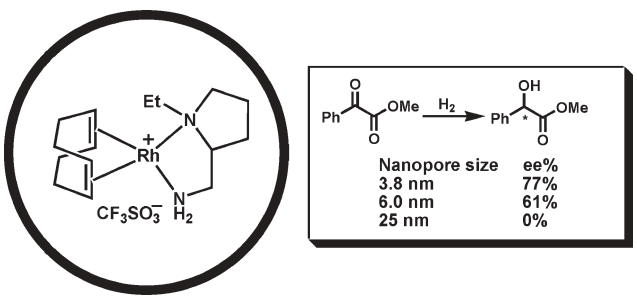


Scheme 11

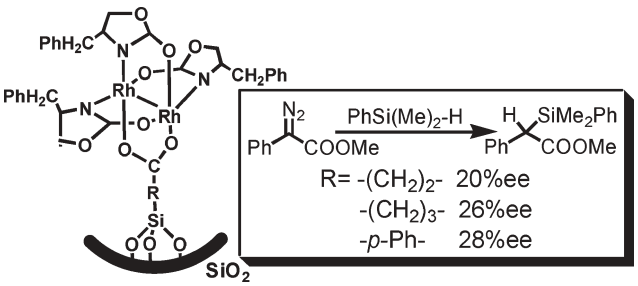
the heterogeneous catalysts could be recovered and recycled four times with constant conversions and ee values.

Similarly, Anderson and co-workers[5b,c] also incorporated a chiral sulfonato-salen-Mn(III) complex in cationic Zn–Al layered double hydroxides (Scheme 11). These catalysts were effective for the stereoselective epoxidation of (*R*)-(+)-limonene using a combination of pivalaldehyde and molecular oxygen as the oxidant. The catalyst could be recycled three times, and retained 100% conversion and 54.0% diastereoisomeric excess. This heterogeneous Mn(salen) catalyst was also found to be highly active and enantioselective for the asymmetric epoxidation of various substituted styrenes and cyclic alkenes.[31] Up to 94% conversion, 68% ee, 90% selectivity and a TOF of 234 h^{-1} were obtained for the asymmetric epoxidation of 1-methylcyclohexene. The catalyst could be recycled without detectable loss of efficiency. These samples suggest that the catalysts immobilized in the nanopores of the layered supports could be as effective as the homogeneous catalysts, and they can be separated and recycled.

Thomas and co-workers[32] reported that a chiral Rh(I) complex could be confined in nanopores by ion exchange method for the heterogeneous asymmetric catalytic hydrogenation of α-ketone (Scheme 12). The chiral catalyst confined in nanopores of 3.8 nm showed 77% ee for the asymmetric hydrogenation; while the homogeneous chiral catalyst gave the racemic products. The increase in the nanopore size from 3.8 to 6.0 nm decreased the ee values from 77 to 61%. When the pore size was further increased to 25 nm, the ee value was decreased to zero, indicating that the nanopore effect plays an important role in the chiral induction.



Scheme 12



Scheme 13

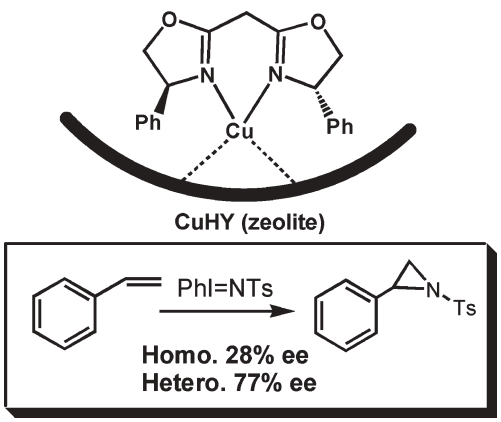
Maschmeyer and co-workers immobilized chiral Rh complexes in nanopores of SiO_2 *via* different linkage groups (Scheme 13) and the catalysts were tested for the asymmetric Si–H insertion reaction.[33] The homogeneous Rh catalysts produced only 2% ee for this reaction. The catalysts immobilized in nanopores of SiO_2 gave higher ee values (20–28% ee) and the asymmetric induction was affected by the linkage groups. When the linkage R was the *p*-C_6H_4 group, the heterogeneous catalyst gave the highest ee value of 28%.

Hutchings and co-workers reported that a Cu catalyst modified with chiral bis(oxazoline) ligand could be introduced into the pores of zeolite Y *via* ion exchange (Scheme 14).[22] This catalyst showed ee value of 77%, higher than 28% obtained for the homogenous catalyst in the asymmetric aziridination of styrene. The asymmetric catalytic reaction was performed in the zeolite cages, in which the confinement effect was considered to improve the asymmetric induction of chiral modifier.

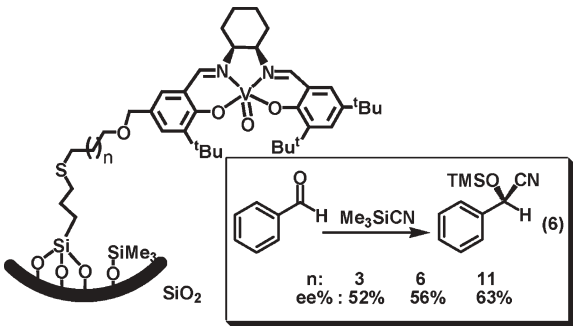
Corma and co-workers[34] studied the asymmetric addition of benzaldehyde with TMSCN (Scheme 15, reaction (6)) on the chiral VO(salen) catalyst grafted from salen ligand *via* different linkage lengths in the nanopores of silica. They found that the ee values of the chiral product cyanohydrin was increased from 52 to 56% and then to 63% when the *n* values in Scheme 15 (chain lengths) were increased from 3 to 6 and 11, respectively. These results indicate that the linkages exerts an effect on the chiral induction for this reaction.

3.2 Chiral catalysis in nanopores of PMOs with chiral moieties either in the mesopore or in the framework

We have synthesized mesoporous ethane-silicas with *trans*-(1*R*,2*R*)-diaminocyclohexane in the nanopores (Scheme 4) by

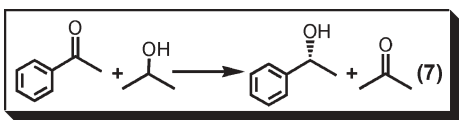


Scheme 14



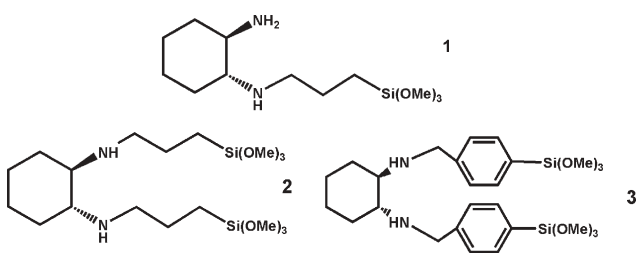
Scheme 15

the co-condensation of 1,2-bis(trimethoxysilyl)ethane and precursor **1** (Scheme 16).[8] The materials have ordered mesoporous structure with pore diameter of 2.5–3.3 nm, BET surface areas in the range 817–890 $m^2\ g^{-1}$, and the loading amount of ligand up to 0.57 mmol g^{-1}. The chiral diamino groups are located in the nanopores of PMOs, which are attached on the pore walls through the propyl linkage. These PMOs after complexing with $[Rh(cod)Cl]_2$ exhibit 82–96% conversion and 19–23% ee values for the asymmetric transfer hydrogenation of acetophenone, which is much higher than a mesoporous silica containing the same chiral moiety in the nanopores (48% conversion and 14% ee value) synthesized also by the co-condensation method (reaction (7)).

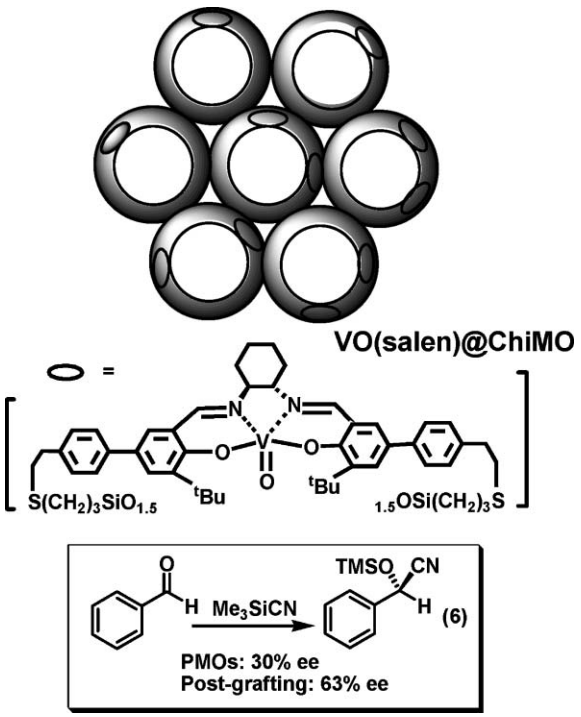


The enhanced catalytic activity of the mesoporous organosilica is mainly contributed to the increased surface hydrophobicity owing to the ethane groups bridged in the mesoporous framework.

The chiral diaminocyclohexane moiety can also be incorporated in the framework of PMOs (Scheme 5) by co-condensation of **2** (or **3**, Scheme 16) with $Si(OMe)_4$ (TMOS).[25] These materials have highly ordered mesostructures with nanopore sizes of 2.0–2.3 nm, BET surface area up to 1071 $m^2\ g^{-1}$, and the ligand loading amount up to 1.02 mmol g^{-1}. The catalyst $[Rh(cod)Cl]_2$ coordinated to the chiral diamino groups in the framework of PMOs with benzyl group as linker exhibits higher conversion (up to 97%) and ee value (up to 30%) than its homogeneous counterparts (45% conversion and 21% ee) for the asymmetric transfer hydrogenation of ketones. For the asymmetric reduction of 2-acetylnaphthalene by ^{i}PrOH, up to 61% ee is obtained. Our results suggest that the PMOs are a



Scheme 16



Scheme 17

novel type of chiral solids which are promising chiral catalysts or chiral catalyst supports.

Corma and co-workers[9b] recently reported that PMOs with a chiral vanadyl Schiff base complex in the framework (Scheme 17) showed enantioselectivity for the asymmetric catalytic cyanosilylation of benzaldehyde with TMSCN (Scheme 17, reaction (6)). The hybrid nanoporous material had an ordered mesostructure with specific surface area of 900 $m^2\ g^{-1}$ and pore diameter of 4.2 nm. The chiral PMO catalyst showed 30% enantioselectivity, which was lower than the 63% obtained for the VO(salen) catalyst covalently grafted in nanopores of mesoporous materials. Their studies showed that the decrease in ee values for the chiral PMOs may be due to the steric constraints imposed on the catalyst originated from the surrounding framework of PMOs.

4 Factors influencing the chiral induction in nanopores

In many cases, the catalysts confined in nanopores show lower conversions than those of homogeneous catalysts in asymmetric reactions under the same conditions.[10] The reasons can be partly attributed to the difficulty in the diffusion of reactants and products in the nanopores. The intrinsic activity of the catalyst might also be decreased after the immobilization. The enantioselectivity in the asymmetric catalytic reactions is usually decreased for the immobilized chiral catalysts compared to the homogeneous counterparts. However, in many cases, the catalysts confined in nanopores show comparable or even higher ee values than the homogeneous catalysts, which are simply attributed to the confinement effect of the nanopores.[1] However, the detailed insights of the confinement effect were not well understood.

When a chiral catalyst is immobilized in a nanopore, there are a number of factors affecting the asymmetric catalytic reaction. Thomas and co-workers[35] proposed that the confinement effect of the nanopores could improve the chiral induction for the asymmetric catalysis in nanopores by strengthening the interaction between the incoming reactant and the chiral ligand, as well as the catalytic metal centre in nanopores. As for the axially immobilized chiral catalysts in nanopores, besides the confinement effect originating from the nanopore, the electronic and steric factors of the linkage may also have some effect on the chiral induction in the nanopores. In addition, the reaction microenvironment in the nanopores may also have an important influence on the catalytic performance.[30] However, the factors originated from the nanopores influencing the chiral catalysis had not been fully investigated.[29] In recent years, we have tried to investigate the confinement effect by specially immobilizing the Mn(salen) catalyst into nanopores of mesoporous materials.

4.1 The effect of the pore sizes

It has been found that the nanopores have an obvious confinement effect on the chiral induction for the asymmetric catalysis in nanopores. For a reaction taking place in a stereo space, such as a pore, layer or cavity, the effect of the space on the reaction can be defined as a confinement effect. Hutchings *et al.*[22,36] found that the confinement effect originated from the zeolite cage could improve the chiral induction for the asymmetric aziridination of styrene in the zeolite cages (Scheme 14). Similarly, the confinement effect resulting from the clay material also improved the enantioselectivity for the asymmetric epoxidation in the interlayers of clays reported by Kureshy′s group (Scheme 10).[5a] It is generally believed that tuning the steric and electronic properties of chiral ligands can alter the enantioselectivity for homogeneous asymmetric catalysis. For example, the use of an unhindered diamine precursor in the chiral Mn(salen) catalyst can open a pathway to olefin approach in which stereochemical communication between the ligand and incoming substrate is maximized, leading to higher enantioselectivity;[37] more electron-donating substitutents on the Mn(salen)-catalyzed epoxidation reaction can stabilize the Mn(V) oxo relative to the Mn(IV) radical intermediate, resulting in a later, more product-like transition state, and higher enantioselectivity.[38] For heterogeneous chiral catalysts in nanopores, the pore effect can provide a way to improve the asymmetric induction by optimizing the nanopores with suitable pore structures and sizes.

In order to study the effect of the nanopores on the asymmetric epoxidation in nanopores, the chiral Mn(salen-a or b) catalysts (Scheme 9) were immobilized into the nanopores of mesoporous materials with different pore sizes and onto the external surface of a support.[2b,29,30] Because the size of the CH_2Cl_2-solvated Mn(salen-a)Cl catalyst is estimated to be 2.05 nm × 1.61 nm by MM2 based on the minimized energy, the catalyst can not enter into the nanopores of 1.6MCM (Fig. 2). The nitrogen sorption results show that the pore size and pore volume remain almost unchanged for 1.6MCM-$PhSO_3Na$ before and after the immobilization of Mn(salen-a) catalyst (Table 3), suggesting

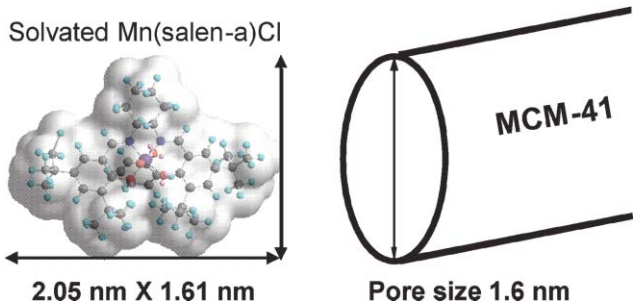


Fig. 2 The sizes of the solvated Mn(salen-a)Cl and nanopores of 1.6MCM.[29]

that Mn(salen-a) complexes are immobilized mainly onto the external surface of MCM(1.6).[29] Mn(salen) catalysts can be immobilized in the nanopores with pore sizes larger than 2.0 nm, as confirmed by BET results.[29]

The Mn(salen-a) catalyst immobilized in the nanopores or on the surface *via* phenyl sulfonic groups was tested for the asymmetric epoxidation of 1,2-dihydronaphthalene (Table 4, reaction (8)).[29]

The ee values obtained for the catalyst in nanopores are increased from 51.7 to 57.5% when the nanopore size is decreased from 9.7 to 2.7 nm, which are higher than that obtained for the same catalyst immobilized on the external surface (45.9% ee). The higher ee values obtained for the catalyst immobilized in the nanopores than that on the external surface can be readily attributed to the enhanced chiral induction by the confinement effect of the nanopores.

The results for the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene (reaction (4)) are listed in Table 5. The Mn(salen) catalyst anchored on the surface of 1.6MCM *via*

Table 3 The results of N_2 adsorption of the catalyst and supports[29]

Entry	Sample	Pore size/nm	S_{BET}/ $m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$
1	MCM-41	1.6	553	0.56
2	1.6MCM-$PhSO_3Na$	1.4	431	0.26
3	1.6MCM-$PhSO_3Mn$(salen-a)	1.4	403	0.27

Table 4 Asymmetric epoxidation of 1,2-dihydronaphthalene (reaction (8)) catalyzed by Mn(salen-a) immobilized on various supports *via* a phenyl sulfonic group

Support-$PhSO_3Mn$(salen-a)	Pore size/nm	*t*/h	Conv. (%)	ee (%)
Activated silica	9.7	24	68.1	51.7
SBA-15	7.6	24	65.9	54.0
MCM-41	2.7	24	73.3	57.5
MCM-41	1.6	24	67.6	45.9

[a] Reactions were performed in CH_2Cl_2 (3 ml) with 1,2-dihydronaphthalene (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 20 °C.

Table 5 Asymmetric epoxidation of 6-cyano-2,2-dimethylchromene (reaction (4)) catalyzed by Mn(salen-a) immobilized on various supports *via* phenoxyl group

Support-PhOMn(salen-a)	Pore size/nm	*t*/h	Conv. (%)	ee (%)
Homo. Mn(salen-a)Cl	—	6	97.0	80.1
MCM-41	1.6	24	76.9	49.0
Activated silica	9.7	24	84.1	68.8
SBA-15	7.6	24	72.6	76.9
SBA-15	6.2	24	100	84.9
MCM-41	2.7	24	31.9	26.4

[a] Reactions were performed in CH_2Cl_2 (3 ml) with 6-cyano-2,2-dimethylchromene (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 20 °C.

phenoxyl group shows 49.0% ee.[30] When the catalyst was immobilized in nanopores, the ee values are increased and reach a maximum (84.9% ee) with the pore size of 6.2 nm, which are also higher than that obtained on the external surface. However, when the pore size is reduced to 2.7 nm, the ee value is remarkably decreased. These results further demonstrate that the confinement effect of the nanopores can change the enantioselectivity of the asymmetric epoxidation, especially the enantioselectivity can be enhanced in the nanopores with the optimized pore size.

Thomas and co-workers[32] also reported the similar phenomenon in the asymmetric hydrogenation of α-ketones on a chiral Rh(I) catalyst confined in nanopores (Scheme 12). The ee values were decreased with increasing the nanopore sizes. When the nanopores became so large that the pore wall was similar to an open surface, the ee value became zero. These results again suggest that the confinement effect originated from the nanopores could enhance the chiral induction for the asymmetric hydrogenation in nanopores.[39]

The above examples show that the asymmetric catalysis in nanopores, compared to that on the surface and in homogeneous media, can significantly increase the enantioselectivity for some asymmetric reactions. When the nanopore size of the support is tuned to a suitable value, the chiral catalysts in the nanopores can give higher ee value in some cases. These results strongly suggest that the confinement effect of nanopores is able to enhance the asymmetric induction as long as the pore size is tuned to a suitable value depending on the catalytic reaction system.

4.2 The effect of the linkages

The linkage for grafting the catalyst in nanopores also has an effect on the asymmetric catalytic performance. Corma *et al.*[34] have found that ee values were increased with increasing the linkage lengths for the asymmetric addition of benzaldehyde with TMSCN (Scheme 15, reaction (6)) in nanopores. It was also found that the linkages affected the asymmetric induction for the asymmetric Si–H insertion reaction (Scheme 13), and the heterogeneous catalyst with *p*-C_6H_4 group as linker gives the highest ee value.[33]

We investigated the effect of the axial linkages on the enantioselectivity for the Mn(salen)-catalyzed asymmetric epoxidation in nanopores with different electronic and steric properties of the linkages. The homogeneous Mn(salen)OPh catalyst was prepared to study the influence of the axial linkage on the catalytic performance.[2b,28] The results show that the Cl could be replaced with OPh in the catalyst and the same reaction results were obtained from the Mn(salen)Cl and Mn(salen)OPh catalysts. Therefore, the electronic effect of the linkages do not show an obvious difference in the chiral induction for the asymmetric epoxidation on Mn(salen) catalysts.

Then we selected phenyl and propyl sulfonic groups ($PhSO_3$ or $PrSO_3$) as linkages for grafting chiral Mn(salen) catalysts with the aim to study the effect of the steric property of the axial linkages on the asymmetric epoxidation (Table 6). The propyl linkage is less rigid compared to the phenyl one due to the flexible chain of the propyl group. The Mn(salen-a) catalyst immobilized in the nanopores of 7.6SBA *via* a $PrSO_3$ group gives higher ee value than that obtained for the same catalyst grafted *via* a $PhSO_3$ group for the asymmetric epoxidation of 1,2-dihydronaphthalene (entries 2 and 3). Mn(salen-a) catalyst anchored on the surface of 1.6MCM *via* $PrSO_3$ or $PhSO_3$ group also shows a similar tendency (entries 4 and 5). As for the asymmetric epoxidation of 1-phenylcyclohexene, Mn(salen-b) catalyst immobilized *via* the $PrSO_3$ also exhibits higher ee value than that obtained for the same catalyst grafted *via* the $PhSO_3$ group (entries 7 and 8). These results show that the flexible grafting mode is helpful for the improvement of the enantioselectivity. This may be due to the fact that the flexible grafting mode can maintain the optimized configuration of chiral Mn(salen) catalyst under reaction conditions.[14,40]

The effect of the linkage lengths on the asymmetric epoxidation in nanopores and on the external surface was also studied.[29] The heterogeneous Mn(salen-b) catalysts with different linkage lengths (Fig. 1) were tested for the asymmetric epoxidation of styrene (Table 7). When the Mn(salen-b) catalyst is immobilized in the nanopores of 9.7AS, the chemical selectivities and ee values are increased with increasing the linkage lengths. For the same catalyst anchored on the surface of 1.6MCM, the chemical selectivities are increased with linkage lengths but the ee values are essentially unaffected by the linkage lengths. A similar tendency is also observed for the asymmetric epoxidation of 1-phenylcyclohexene on the heterogeneous Mn(salen-a) catalysts (Fig. 3). The ee values obtained for the catalyst in the nanopores of 9.7AS are

Table 6 Asymmetric epoxidation (reactions (8) and (1)) catalyzed by Mn(salen) catalysts immobilized *via* phenyl or propyl sulfonic groups

Entry	Reaction	Catalyst	*t*/h	Conv. (%)	Ee (%)
1	8	Mn(salen-a)Cl	6	67.4	79.7
2	8	7.6SBA-$PhSO_3$Mn(salen-a)	24	65.9	54.0
3	8	7.6SBA-$PrSO_3$Mn(salen-a)	24	66.2	69.3
4	8	1.6MCM-$PhSO_3$Mn(salen-a)	24	67.6	45.9
5	8	1.6MCM-$PrSO_3$Mn(salen-a)	24	75.6	55.6
6	1	Mn(salen-b)Cl	6	95.6	84.2
7	1	7.6SBA-$PhSO_3$Mn(salen-b)	24	79.5	18.1
8	1	7.6SBA-$PrSO_3$Mn(salen-b)	24	87.6	44.1

[a] Reactions were performed in CH_2Cl_2 (3 ml) with olefin (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 20 °C.

Table 7 Asymmetric epoxidation of styrene (reaction (3)) catalyzed by Mn(salen-b) immobilized *via* phenyl sulfonic groups with different linkage lengths

Catalyst	*t*/h	Conv. (%)	Sel. (%)	Ee (%)
Mn(salen-b)Cl	6	100	100	58
9.7AS-$PhSO_3$Mn(salen-b)	24	31	63	49
9.7AS-1-$PhSO_3$Mn(salen-b)	24	36	67	53
9.7AS-2-$PhSO_3$Mn(salen-b)	24	38	84	57
9.7AS-4-$PhSO_3$Mn(salen-b)	24	42	90	58
1.6MCM-$PhSO_3$Mn(salen-b)	24	55	62	39
1.6MCM-1-$PhSO_3$Mn(salen-b)	24	63	64	40
1.6MCM-2-$PhSO_3$Mn(salen-b)	24	73	65	39
1.6MCM-4-$PhSO_3$Mn(salen-b)	24	78	74	40

[a] Reactions were performed in CH_2Cl_2 (3 ml) with styrene (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.015 mmol, 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 0 °C.

increased from 14 to 65% when the space atom number (R) is increased from 0 to 4. However, the ee values obtained for the same catalyst anchored on the external surface of 1.6MCM are nearly unchanged with the linkage lengths (about 45%).

The effect of the linkages on the asymmetric induction is observed not only for the chiral catalysts immobilized in nanopores of mesoporous materials but also for the PMOs with chiral catalysts incorporated in the framework.[25] We found that after coordination of $[Rh(cod)Cl]_2$ to the PMOs containing chiral amino groups, the PMOs with benzyl groups as linkages exhibit 93–97% conversion and 26–30% ee; while the PMOs with propyl groups as linkages show 16% conversion and only 8% ee for the asymmetric transfer hydrogenation (reaction (7)).[25] The phenyl groups with spatial rigidity and electron-withdrawing ability is found to improve the catalytic activity and enantioselectivity for the asymmetric transfer hydrogenation.

The above examples clearly show that the linkage groups of the heterogeneous chiral catalysts have a remarkable effect on the performance of asymmetric catalysis. The electronic and steric properties of the linkages may affect the configuration of the transition state for the asymmetric reactions.

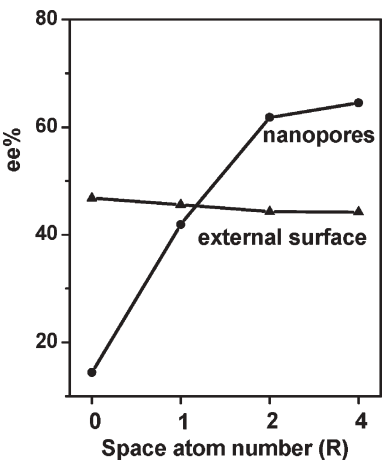


Fig. 3 The ee values obtained for Mn(salen-a) catalyst grafted into the nanopores of AS(9.7) and onto the external surface of MCM(1.6) for the asymmetric epoxidation of 1-phenylcyclohexene.

4.3 The effect of the microenvironment in nanopore

Generally, the organic reactants considered in this article are hydrophobic and the silica-based mesoporous nanopores are hydrophilic. The difficulty in the diffusion of reactants and products in nanopores may result in lower reaction conversions.[1,10] In order to improve the conversion, the nanopores of the mesoporous materials can be modified with nonpolar organic groups.[34,41] More importantly, the change in the reaction microenvironment in nanopores may also have an influence on the enantioselectivity for the asymmetric catalysis in nanopores.[30] Microenvironment here refers to the reaction environment surrounding a catalytic reaction, such as solvent and nanopores in which the reaction takes place. For example, for homogeneous asymmetric catalysis, the reaction microenvironment is mainly the solvent which often exerts a strong influence on reaction results. For asymmetric catalysis in nanopores, the catalytic microenvironment is different from the homogeneous one, which might affect the asymmetric induction in nanopores. Tunable characteristics of the microenvironment for nanopores may be the hydrophilic/hydrophobic property and the rigid surroundings, which are closely associated with the chiral catalytic reactions.

For the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene[30] (Table 2), 9.7AS(Me)-2-$PhSO_3$Mn(salen) catalyst with nanopores modified with methyl groups exhibits TOF of 10.9; while the unmodified 9.7AS-2-$PhSO_3$Mn(salen) catalyst gives a TOF of 2.47 under the same conditions. 9.7AS(Me)-4-$PhSO_3$Mn(salen) catalyst gives even higher TOF than that of the corresponding homogeneous TOF (10.8). The increase in TOF is mainly due to the increased diffusion of the reactants and products in the modified nanopores. The asymmetric inductions are also enhanced for the catalysts in the modified nanopores, for example, the ee values are increased from 82.6% for 9.7AS-4-$PhSO_3$Mn(salen-a) catalyst to 90.6% for 9.7AS(Me)-4-$PhSO_3$Mn(salen-a) catalyst, which could be attributed to the hydrophobic microenvironment in the nanopores.

Compared to the inorganic supports, organic polymer supports show more hydrophobic property. As for the asymmetric epoxidation of styrene, polystyrene-supported Mn(salen) catalyst, PS-PhOMn(salen-a),[28] presents obviously higher conversions and chemical selectivities than those obtained for the same catalyst immobilized in nanopores of 7.6SBA or on the external surface of 1.6MCM *via* phenoxyl group or phenyl sulfonic group (Table 8).[2b,27] A similar tendency is also observed for the enantioselectivity. These

Table 8 Asymmetric epoxidation of styrene (reaction (3)) catalyzed by Mn(salen-a) immobilized on inorganic or organic supports

Catalyst	Catal. (%)	*t*/h	Conv. (%)	Sel. (%)	ee (%)
Mn(salen-a)Cl	1.5	6	100	100	37.5
7.6SBA-PhOMn(salen-a)	1.5	24	33.3	89.4	35.2
1.6MCM-PhOMn(salen-a)	1.5	24	50.0	71.2	27.3
1.6MCM-$PhSO_3$Mn(salen-a)	1.5	24	67.1	75.4	29.5
PS-PhOMn(salen-a)	0.5	24	81.4	94.2	41.1

[a] Reactions were performed in CH_2Cl_2 (3 ml) with styrene (1.0 mmol), internal standard (1.0 mmol), PPNO (0.38 mmol), catalysts (0.005 or 0.015 mmol, 0.5 or 1.5 mol%) and NaOCl (pH = 11.5, 0.55 M, 3.64 ml) at 0 °C.

results indicate that the hydrophobic microenvironment of the polymer surface favours the asymmetric epoxidation of styrene on Mn(salen) catalysts.

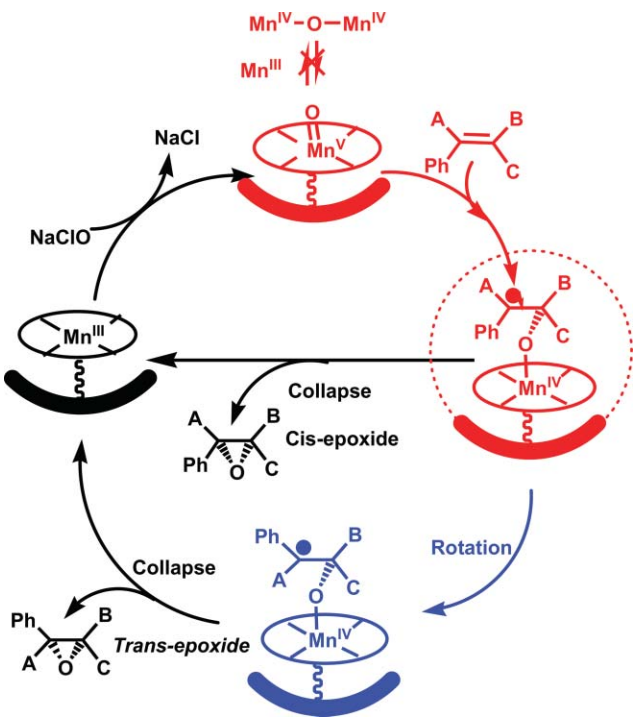
The effect of the reaction microenvironment on the catalytic performance is also observed for the asymmetric catalysis in nanopores of PMOs.[8] It is interesting to note that chiral diamino groups located in nanopores of the mesoporous ethane-silicas exhibit higher catalytic activity and enantioselectivity than those in the nanopores of the mesoporous siliceous materials for the asymmetric transfer hydrogenation (reaction (7)).[9] The increase in the catalytic activity is mainly attributed to the enhanced surface hydrophobicity of mesoporous ethane-silicas compared to that of mesoporous silica.

Therefore, the reaction microenvironment is important for the asymmetric catalysis. An optimized microenvironment may increase the conversion and enantioselectivity for chiral catalysis in nanopores.

4.4 Reaction mechanism in nanopores

The asymmetric catalytic mechanism in nanopores might be different from that in homogeneous systems due to the presence of effects of the nanopores, the linkages, and the reaction microenvironment in nanopores. Here we give the Mn(salen)-catalyzed asymmetric epoxidation in nanopores as an example to discuss the asymmetric epoxidation mechanism in nanopores.

According to the reported mechanism of the homogeneous Mn(salen)-catalyzed asymmetric epoxidation[42] and the experimental results of the catalysis in nanopores,[2b,23,29] a mechanism of the asymmetric epoxidation in nanopores can be proposed in Scheme 18. The olefin approaches the immobilized Mn(V) active sites to form the radical intermediate, which directly collapses to form *cis*-epoxide or first rotates and then collapses to form *trans*-epoxide.



Scheme 18

Several points should be emphasized about the asymmetric epoxidation mechanism in the nanopores. The immobilization of Mn(V) complexes on surface effectively prevents the formation of inactive dimer Mn(IV)–O–Mn(IV), which are reported to be generally formed in the homogeneous asymmetric epoxidation.[43] Therefore, the isolated active sites immobilized in the nanopores result in higher apparent TOF for the immobilized Mn(salen) catalyst than that for the homogeneous catalyst in the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene (14.8 *vs.* 10.8 h^{-1}, entries 5 and 1, Table 2).[30] The chiral recognition between chiral ligand and the pro-chiral olefin may be enhanced or weakened due to the stereo effect of nanopores.[44] The surface and the axial grafting modes may retard the coordination of some axial additives to the Mn atom, which may reduce the asymmetric catalytic performance.[29] The reaction microenvironment, including the nanopores and the grafting modes, may have an influence on the stability and lifetime of the radical intermediate in nanopores.[30] Notably, the rotation of the radical intermediate may be greatly retarded by the nanopores, which results in the production of more *cis*-epoxide (higher *cis*/*trans* ratio) compared to the homogeneous reaction conditions (for example, reactions (2) and (5)).[2b,23,27]

5 Summary and outlook

This article mainly reviews the chiral catalysis in nanopores of the mesoporous materials and the chiral PMOs reported in recent years. The chiral catalysts can be introduced into the nanopores *via* a number of methods, including some novel methods such as co-condensation of chiral catalysts into the framework of PMOs. It is interesting to note that some catalysts in nanopores show improved catalytic performance and altered regioselectivities compared to the homogeneous catalysts for some asymmetric reactions. The factors influencing the chiral catalysis in nanopores are studied in detail for the asymmetric epoxidation of unfunctionalized olefins on Mn(salen) catalysts immobilized in the nanopores of silica-based mesoporous materials. It is found that chiral Mn(salen) catalysts immobilized in the nanopores generally exhibit higher chemical selectivity and enantioselectivity than those anchored on the external surface of supports for the asymmetric epoxidation, especially in the nanopores with the optimized pore size. Our examples clearly suggest that the confinement effect from the nanopores can improve the chiral induction for the asymmetric catalysis. The stereo properties of the linkages of the heterogeneous chiral catalysts also affect the asymmetric catalytic performance. The ee values are increased with increasing the linkage lengths for the asymmetric epoxidation on Mn(salen) catalysts immobilized in nanopores, but the ee values are not affected by the linkage lengths for the catalysts anchored on the external surface. The hydrophobic microenvironment in the nanopores is found to be favorable for the improvement of the asymmetric catalytic performance for hydrophobic substrates.

The asymmetric catalysis in nanopores has important scientific significance and potential application advantages.

However, the research in this direction is still in an early stage and there are many opportunities to be further explored. New strategies should be developed to prepare the materials with nanoreactors available for the chiral catalytic synthesis, such as chiral PMOs with chiral catalysts incorporated in their framework, mesoporous materials with large nanopores and small entrances. Various novel approaches to introduce the chiral catalysts into nanopores are highly desirable for the preparation of new heterogeneous chiral catalysts with high activity, selectivity and stability for the asymmetric catalysis. The factors influencing the chiral catalysis in nanopores should be further investigated, *e.g.* to optimize the size of nanopores, to change the grafting modes, and to tune the reaction microenvironment in nanopores. Theoretical studies on the asymmetric catalysis in nanopores are also absolutely necessary.

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