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Enantioselective epoxidation of olefins catalyzed by Mn (salen)/MCM-41 synthesized with a new anchoring method

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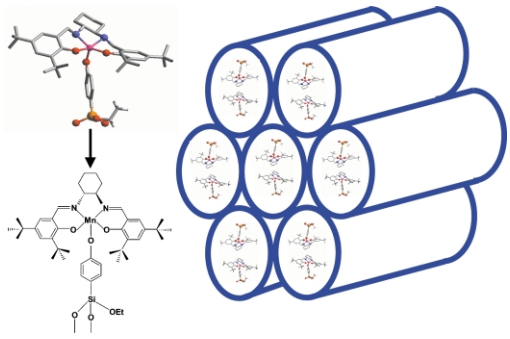
New immobilization of the chiral Mn(salen) complex through the complexation of manganese by oxygen atoms of the phenoxyl groups grafted on the surface of MCM-41 leads to a markedly higher ee than for the free complex.

Enantioselective epoxidation of unfunctionalized olefins is of great importance for the synthesis of chiral intermediates. Chiral Mn^{III}(salen) complexes are excellent catalysts for this reaction.[1] Compared to the homogeneous complexes, heterogeneous systems have the inherent advantages of easy separation and better handling properties,[2] therefore, the heterogenization of chiral Mn^{III}(salen) complexes has received great attention.[3–6] Corma *et al.*[5b] reported that a chiral Mn(salen) complex was synthesized inside the supercages of zeolite Y through the interaction between Mn and the surface oxygen ion. A chiral Cr(salen) complex was immobilised on modified MCM-41 through axial complexation of Cr by NH_2 groups grafted onto the surface of MCM-41.[5d] These salen complexes were immobilised by one coordinative bond.

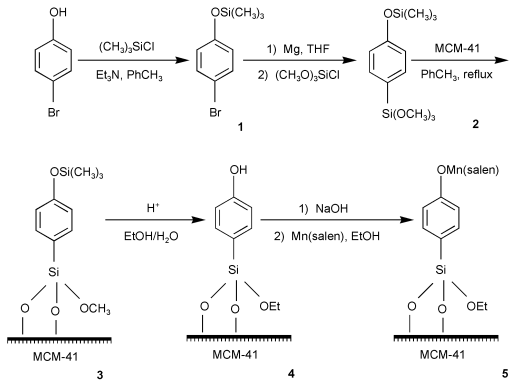
In this work, the chiral Mn^{III}(salen) complex was anchored onto siliceous MCM-41 by a new strategy (Scheme 1). The as-synthesized catalyst, Mn(salen)/MCM-41, shows excellent enantioselectivity for the asymmetric epoxidation of unfunctionalized olefins.

The Mn(salen) complex was synthesized according to the literature.[7] The MCM-41-anchored Mn(salen) catalyst was prepared as shown in Scheme 2. 4-Trimethoxysilylphenoxytrimethylsilane (**2**) was obtained from 4-bromophenoxytrimethylsilane (**1**)[8] and chlorotrimethoxysilane. The appearance of two new bands at 2845 and 1090 cm^{-1} in the FT-IR spectrum indicates the presence of the trimethoxysilyl group. Then **2** was anchored onto MCM-41 (S_{BET}: 747 $m^2\ g^{-1}$, pore size: 33.6 Å), according to the literature,[9] forming a white powder (**3**). The strong band at 1602 cm^{-1} in the IR spectrum confirms the successful grafting of **2** onto MCM-41. The ^1H MAS NMR signal at −0.5 ppm and ^{13}C CP/MAS NMR signal at −1.2 ppm, due to trimethylsilyl groups, together with ^{13}C CP/MAS NMR signals at 157.8, 135.0, 117.0, 114.6, 49.5 ppm, are in good agreement with the proposed structure of **3**.

Modified MCM-41 (**4**) was obtained from the acidic hydrolysis of **3**. Neville[8] reported the cleavage of 4-trimethylsilylphenoxytrimethylsilane to 4-trimethylsilylphenol in 95% ethyl alcohol (20 ml) which was acidified with one drop of concentrated hydrochloric acid. It can be seen from the FT-IR spectra (Fig. 1) that the $SiOCH_3$ (2852 cm^{-1}) unreacted with the hydroxyl groups of the supports converts into SiOEt (2982 cm^{-1}) in acidic solution. The band intensity at 2958 cm^{-1} assigned to $Si(CH_3)_3$ decreases gradually. When **3** was stirred for 3 h at 40 °C in 95% ethyl alcohol acidified with two drops of concentrated hydrochloric acid, the peak at 2958 cm^{-1} disappears completely. The disappearance of the ^{13}C CP/MAS NMR signal at −1.2 ppm clearly indicates the removal of $Si(CH_3)_3$ groups (Fig. 2). The elemental analysis data of carbon and hydrogen are 6.97% and 1.20%, respectively. The amount of anchored phenol species is about 0.73 mmol g^{-1} estimated based on the elemental analysis.



Scheme 1 Heterogeneous chiral catalyst, prepared by anchoring of the Mn(salen) complex onto the MCM-41 support.



Scheme 2 The anchoring of the Mn(salen) complex on the MCM-41 support.

The chiral Mn^{III}(salen) complex was then anchored onto **4** through the complexation of manganese by oxygen atoms of the phenoxyl groups. The mixture of **4** (1 g) and sodium hydroxide (0.04 g, 1 mmol) in H_2O (5 ml) was stirred for 1 h at room temperature. The liquid was separated off by centrifugation, and the solid was washed three times with H_2O. The mixture of the Mn(salen) complex (1 mmol) and the solid in ethyl alcohol (20

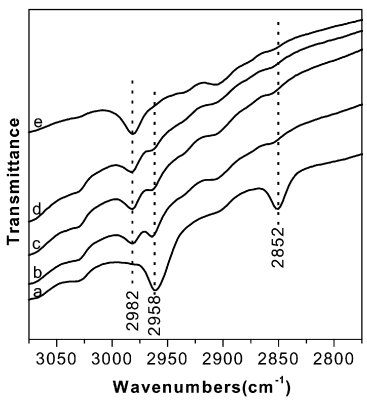


Fig. 1 The FT-IR spectra of the modified MCM-41: (a) before hydrolysis; (b) hydrolysis for 10 h at room temperature; (c) hydrolysis for 15 h at room temperature; (d) hydrolysis for 1 h at 40 °C; (e) hydrolysis for 3 h at 40 °C.

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Table 1 Asymmetric epoxidation of nonfunctional olefins catalyzed by homogeneous Mn^{III}(salen) complex and Mn^{III}(salen) anchored in the mesopores of MCM-41

Entry	Catalyst	Substrate	Solvent	Conversion (%)	E.e. (%)
1	Mn(salen)	α-Methylstyrene	CH_2Cl_2	96	56
2	Mn(salen)/MCM-41	α-Methylstyrene	CH_2Cl_2	60	72
3	Mn(salen)/MCM-41	α-Methylstyrene	Acetone	99	67
4	Mn(salen)/MCM-41 (1st time)	α-Methylstyrene	EtOH	99	70
5	Mn(salen)/MCM-41 (2nd time)	α-Methylstyrene	EtOH	99	70
6	Mn(salen)/MCM-41 (3rd time)	α-Methylstyrene	EtOH	98	73
7	Mn(salen)	1-Phenylcyclohexene	CH_2Cl_2	93	78
8	Mn(salen)/MCM-41	1-Phenylcyclohexene	EtOH	0	0

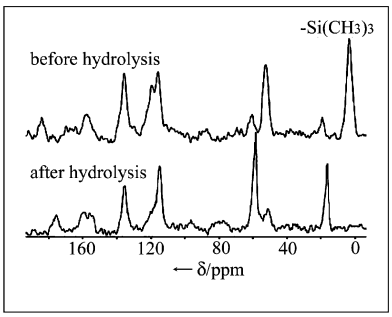

Fig. 2 ^{13}C CP/MAS NMR spectra of the modified MCM-41 before and after hydrolysis.

ml) was stirred for 5 h under reflux, producing a light brown powder. The characteristic imine band at 1635 cm^{-1} in the IR spectrum, the characteristic six well-resolved hyperfine lines in the EPR spectrum, and the UV-Vis absorption spectrum confirm that the Mn(salen) complex is successfully anchored onto MCM-41. The anchored amount of metallic complex on MCM-41 is about equal to the amount of anchored phenol species. Immobilization of the Mn(salen) complex onto unmodified MCM-41, which lacks the anchored phenol species, was unsuccessful.

The heterogeneous Mn(salen) catalyst was tested for the asymmetric epoxidation of simple olefins. A mixture of solvent (3 ml), 0.4 M NaOCl (pH = 11.5, 5 ml, 2 mmol), and alkene (1 mmol) was cooled to 0 °C. To this mixture was added heterogeneous Mn(salen) catalyst (0.1 g). The mixture was stirred at 0 °C for 24 h. Conversions and enantiomeric excess values were determined by gas chromatography with a chiral β-cyclodextrin column. The results are presented in Table 1. The racemic samples of the epoxides were independently prepared by the epoxidation of the corresponding alkenes with m-CPBA in CH_2Cl_2 and confirmed by GC/MS.

Table1 shows that the Mn(salen) complex is active and enantioselective for the epoxidation of α-methylstyrene in CH_2Cl_2 with NaOCl as oxidant, but the enantioselectivity is not very high (entry 1, conv.: 96%; e.e.: 56%). After anchoring the complex onto the MCM-41 support, the activity of the heterogeneous catalyst is obviously decreased for the epoxidation of this substrate in CH_2Cl_2 with the same oxidant (entry 2, conv.: 60%), however, the enantiomeric excess is notably increased from 56% to 72% for the heterogeneous Mn(salen)/MCM-41 catalyst. Similar results were obtained by Kim[5c] and Che,[5d] respectively. Kim *et al.*[5c] reported that, for the asymmetric epoxidation of α-methylstyrene, the e.e. increased from 51% to 59% after immobilization of Mn(salen) on the siliceous MCM-41 by multi-step grafting. For the enantioselective epoxidation of β-methylstyrene, the e.e. increased from 54% to 73% after immobilization of Cr(salen) through axial NH_2 complexation.[5d] The increase in enantiomeric excess is mainly attributed to the unique spatial environment constituted by the axial bulky group and the mesopores of the MCM-41 support. The decrease in conversion is obviously due to the slow diffusion of the reactant and the oxidant into the mesopores of the MCM-41 in the multiphase reaction system. When acetone was used as the solvent, the conversion can be up to 99%, and the enantiomeric excess is about 67%, still higher than the homogeneous counterpart (entry 3).

The used catalyst was reused for the epoxidation of α-methylstyrene in EtOH and the reaction results are presented in Table 1 (entries 4–6). The results show that the activity and enantioselectivity do not decrease for at least three uses of the catalyst. This indicates that the Mn(salen) complex is strongly bonded to the wall of MCM-41 through the axial complexation of the manganese by oxygen atoms of the phenoxyl group.

A very interesting result is that although the homogeneous complex is active and enantioselective for the epoxidation of 1-phenylcyclohexene (entry 7, conv.: 93%; e.e.: 78%), the anchored Mn(salen) catalyst is inactive for this substrate (entry 8, conv.: 0). This result indicates that for the heterogeneous Mn(salen)/MCM-41 catalyst, the Mn(salen) species are mainly anchored in the mesopores of MCM-41; since 1-phenylcyclohexene is too large to enter the mesopores of MCM-41 containing Mn(salen), no epoxidation of 1-phenylcyclohexene was detected.

The Mn^{III}(salen) complexes are successfully anchored in the mesopores of MCM-41. The anchored catalysts are quite stable and can be recycled. The enantioselectivity of the anchored catalyst is higher than the corresponding homogeneous catalyst because of the bulky axial group and the mesoporous effect of the MCM-41. Our synthesis strategy may provide a general route to anchor Mn^{III}(salen) complexes onto surfaces and mesopores of solid materials.

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