Heterogeneous enantioselective epoxidation catalyzed by Mn(salen) complexes grafted onto mesoporous materials by phenoxy group

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Abstract

Three chiral Mn(salen) complexes were immobilized into different mesoporous material via phenoxy group by a simplified method and they show high activity and enantioselectivity for asymmetric epoxidation of various substituted unfunctional olefins. The heterogeneous Mn(salen) catalysts show comparable ee values for asymmetric epoxidation of styrene and 6-cyano-2,2-dimethylchromene and much higher ee values for epoxidation of α-methylstyrene (heterogeneous 79.7% ee versus homogeneous 26.4% ee) and *cis*-β-methylstyrene (heterogeneous 94.9% ee versus homogeneous 25.3% ee for *cis*-epoxide) than the homogeneous catalysts. These heterogeneous catalysts also remarkably alter the *cis/trans* ratio of epoxides for asymmetric epoxidation of *cis*-β-methylstyrene (heterogeneous 21 versus homogeneous 0.38). The axial tether group does not make a big effect on ee values and the increase in ee value and change in *cis/trans* ratio are mainly attributed to the axial immobilization mode and the support effect of heterogeneous catalysts. The catalysts keep constant ee values for the recycle tests of eight times for asymmetric epoxidation of α-methylstyrene. And several possibilities were proposed to elucidate the difference in ee values of heterogeneous catalysts from homogeneous catalysts.
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Keywords: Heterogeneous catalysis; Enantioselective epoxidation; Mesoporous material; Unfunctional olefin; Mn(salen) complexes

1. Introduction

Enantioselective epoxidation of unfunctional olefins is of great importance in synthesis of fine chemicals and pharmaceuticals. Chiral Mn^{III}(salen) complexes are excellent catalysts for asymmetric catalytic epoxidation [1]. Compared to the homogeneous catalysts, heterogeneous catalytic systems have the inherent advantages of easy separation, recycling catalysts, purifying products and better handling properties [2]. Therefore, immobilization of chiral metal (salen) complexes onto inorganic support has received great attention in recent years [3]. They have been immobilized into mesoporous molecular sieves [4], mesoporous silica [5], carbon material [6], zeolite Y [7] and Al-MCM-41 [8]. They

were also ion-exchanged into layered double hydroxides [9], encapsulated into zeolite [10] and immobilized into inorganic membrane [11]. However, the heterogeneous Mn(salen) catalysts always give lower ee values for asymmetric epoxidation compared with the homogeneous catalysts. It is urgently needed new and effective heterogeneous Mn(salen) catalysts for asymmetric epoxidation of various unfunctional olefins.

This group has briefly reported that one chiral Mn(salen) complex axially immobilized into MCM-41 via phenoxy group [4c] presents higher ee value than homogeneous catalyst for asymmetric epoxidation of α-methylstyrene. However, the reasons for increase in ee values (due to the bulky axial group and/or the mesoporous effect of the support) were not clear and the preparation of the heterogeneous catalyst is too complicated. In this work, three chiral Mn(salen) complexes were immobilized into various mesoporous materials by a simplified method. The heterogeneous Mn(salen) cata-

lysts give much higher ee values for asymmetric epoxidation of α-methylstyrene (heterogeneous 79.7% ee versus homogeneous 26.4% ee) and *cis*-β-methylstyrene (heterogeneous 94.9% ee versus homogeneous 25.3% ee for *cis*-epoxide), and result *cis*-epoxide as the main product (*cis/trans* is increased from homogeneous 0.38 to heterogeneous 21) for epoxidation of *cis*-β-methylstyrene. The results also show that the axial tether group does not make a big effect on ee values and the increase in ee values can be mainly due to the immobilization mode and the support effect. The catalysts are stable for the recycle tests of eight times. And several possibilities were proposed to elucidate the difference in ee values of heterogeneous catalysts from homogeneous catalysts.

2. Experimental

2,4-Di-*tert*-butylphenol, 2,4-di-*tert*-pentylphenol, D-(−)-tartaric acid, *cis*- or *trans*-1,2-diaminocyclohexane, *cis*- and *trans*-β-methylstyrene, phenyltriethoxylsilane, 6-cyano-2,2-dimethylchromene, 4-phenylpyridine *N*-oxide (PPNO), (*S,S*)-1,2-diphenylethylenediamine and 3-chloroperoxybenzoic acid (*m*-CPBA) were purchased from Acros Chemical Company and used as received. Activated silica (shorted for SiO_2, pore size of 9.7 nm with sharp pore distributing), SBA-15 (pore size of 7.6 and 6.2 nm) and MCM-41 (pore size 2.7 nm) were used as supports. All FT-IR spectra were collected on a Fourier transform infrared spectrometer (Nicolet Nexus 470) with a resolution of $4 \, cm^{-1}$ and 64 scans in the region of $4000-1000 \, cm^{-1}$. IR spectra of free complexes and supported complexes were recorded by making samples into KBr pellets and self-supporting wafers, respectively. NMR spectra were accumulated on a Bruker DRX-400 spectrometer and solid samples were recorded by CP/MAS technology. UV–vis spectra were recorded on a JASCO V-550 spectrophotometer equipped with an integrating sphere. XRD patterns were recorded on a Rigaku D/Max 3400 powder diffraction system using Cu KR radiation (40 kV and 30 mA) over the range $0.5 \le 2\theta < 10°$. EPR spectra were recorded on a JEOL ES-ED3X spectrometer with fixed microwave frequency at 9.239 GHz in power 1 mW. Racemic epoxides were synthesized and detected by GC–MS (GC6890-MS5973N). The products were analyzed by GC–MS and yield (with *n*-nonane as internal standard) and ee values were determined by gas chromatography (6890N, Agilent Co.) using a chiral column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μm, Agilent Co.).
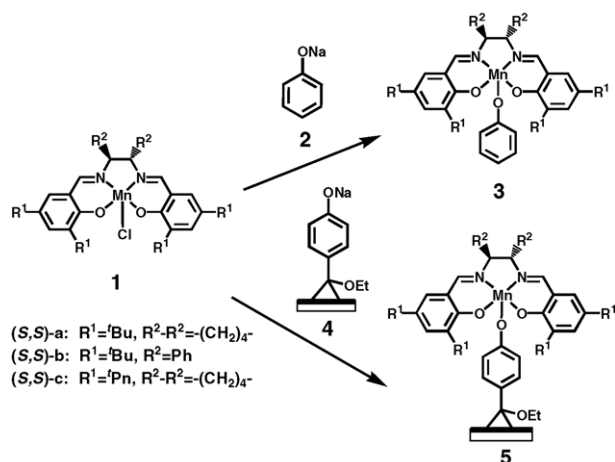
2.1. Synthesis of homogeneous Mn(salen)OPh catalysts (3a–b)

Homogeneous Mn(salen)Cl (**1a–1c**) were synthesized according to literature [12] and their structures are well confirmed by ^{13}C NMR, ^{1}H NMR, FT-IR, rotational analysis and element analysis. salen-a: ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 165.9, 158.1, 139.9, 136.4, 126.7, 126.0, 118.0, 72.4, 35.0, 34.0, 33.2, 31.4, 29.5, 24.3; IR (KBr, cm^{-1}): $\nu = 2952, 1629, 1468, 1434, 1360, 830$; $[\alpha]_D^{20} = +300$ (c 0.1, CH_2Cl_2); elemental analysis calculated (%) for $C_{36}H_{54}N_2O_2$: C 79.12, H 9.89, N 5.13; found: C 78.85, H 9.90, N 5.23. salen-b: ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 165.3, 158.0, 140.1, 139.8, 136.5, 128.3, 128.1, 127.4, 127.1, 126.3, 117.9, 80.2, 35.0, 34.0, 31.4, 29.5; IR (KBr, cm^{-1}): $\nu = 2959, 1629, 1434, 1354, 1166$; $[\alpha]_D^{20} = +74.5$ (c 0.1, CH_2Cl_2); elemental analysis calculated (%) for $C_{44}H_{56}N_2O_2$: C 81.99, H 8.70, N 4.35; found: C 82.78, H 8.70, N 4.78. Salen-c: ^{13}C NMR ($CDCl_3$, 400 M): δ(ppm) = 166.1, 158.1, 138.1, 134.7, 128.7, 126.8, 117.8, 72.4, 38.5, 37.2, 36.9, 33.3, 32.9, 28.4, 27.5, 24.4, 9.5, 9.1; IR (KBr, cm^{-1}): $\nu = 2959, 2858, 1629, 1461, 1381, 1273, 1173, 877$; mp 152–154 °C, $[\alpha]_D^{20} = +287.5$ (c 0.2, CH_2Cl_2); elemental analysis calculated (%) for $C_{40}H_{62}N_2O_2$: C 79.73, H 10.30, N 4.65; found: C 79.42, H 10.30, N 4.74. Mn(salen-a)Cl (**1a**): IR (KBr, cm^{-1}): $\nu = 2952, 2864, 1609, 1535, 1253, 837$; elemental analysis calculated (%) for $C_{36}H_{52}ClMnN_2O_2$: C 68.13, H 8.20, N 4.41; found: C 70.13, H 8.70, N 4.27. Mn(salen-b)Cl (**1b**): IR(KBr, cm^{-1}): $\nu = 2956, 1610, 1534, 1252, 837$; elemental analysis calculated (%) for $C_{44}H_{54}ClMnN_2O_2$: C 72.08, H 7.37, N 3.82; found: C 73.09, H 7.79, N 4.10. Mn(salen-c)Cl (**1c**): IR (KBr, cm^{-1}): $\nu = 2959, 1609, 1535, 1313, 1166, 561$; elemental analysis calculated (%) for $C_{40}H_{60}ClMnN_2O_2$: C 69.51, H 8.69, N 4.06; found: C 70.62, H 7.97, N 4.11.

Phenol (25 g, 0.265 mol, 1.11 equiv.) as solid was added to distilled water (10 ml) containing NaOH (9.54 g, 0.238 mol) with stirring. After stirring for 30 min at room temperature, the mixture was filtrated and washed thoroughly with toluene until no residual phenol can be detected out by $FeCl_3$ characteristic reaction, followed by 3 × 30 ml of ethanol. The white power PhONa (**2**) was obtained after drying for 8 h at 80 °C under high vacuum (20.71 g, 75%) and was stored under Ar.

Mn(salen)Cl complex (**1a** or **1b,** 0.256 mmol) and PhONa (**2,** 35.9 mg, 0.309 mmol, 1.2 equiv.) were added to ethanol (60 ml), and the mixture was refluxed for 3 h at 80 °C (Scheme 1). After cooling to room temperature, ethanol is removed. To this dark solid, 30 ml of CH_2Cl_2 was added, and the organic phase was washed with 15 ml of distilled water. The water samples were detected by HNO_3–$AgNO_3$ solution until no characteristic white floc was observed (needed about three times). Then the CH_2H_2 solution was washed with 10 ml of saturated NaCl solution and dried over anhydrous Na_2SO_4. Removing CH_2Cl_2 gives brown-dark solid Mn(salen)OPh (**3a–b**). Mn(salen-a)OPh (**3a**): IR(KBr, cm^{-1}): $\nu = 2955, 1612, 1535, 1477, 1312, 1253, 1175, 837$; elemental analysis calculated (%) for $C_{42}H_{57}MnN_2O_3$: C 73.26, H 8.28, N 1.16; found: C 74.09, H 8.37, N 1.04. Mn(salen-b)OPh (**3b**): IR (KBr, cm^{-1}): $\nu = 2956, 1614, 1533, 1252, 1174, 836, 699$; elemental analysis calculated (%) for $C_{50}H_{59}MnN_2O_3$: C 75.95, H 7.47, N 1.01; found: C 76.81, H 7.79, N 1.30.

Scheme 1. Preparation of homogeneous Mn(salen)OPh complexes (**3a–b**) and heterogeneous Mn(salen) catalysts (**5a-c**).

2.2. Synthesis of heterogeneous Mn(salen) catalysts (5a–c)

The modified supports **4** were prepared according to Scheme 2. Pure siliceous support (9 g, SiO_2, SBA or MCM) was dehydrated at 125 °C under 10^{-2} Torr for 4 h. Then fresh $PhSi(OEt)_3$ (21 ml) in dry toluene (450 ml) was added to the solid and the mixture was stirred for 1 h at room temperature then refluxed for 18 h at 120 °C under Ar atmosphere. Then the solid was cooled, filtrated and washed thoroughly by toluene and ethanol. Drying at 100 °C under reduced pressure overnight gives the desired Ph/SiO_2 (**6**) as white power.

Ph/SiO_2 (5 g) was added to distilled water (90 ml) containing concentrated sulfuric acid (1.3 g) and catalyst $FeCl_3 \cdot 6H_2O$ (50 mg) and this suspension was stirred at 50 °C for 30 min [13]. Then H_2O_2 (4 ml) was added to the mixture and it was stirred for an additional 5 h. The solid was filtrated, washed by distilled water to neutral giving $PhOH/SiO_2$ (**7**) as white solid. Distilled water (200 ml) containing NaOH (160 mg, 4 mmol) was added to $PhOH/SiO_2$ (4 g) and this mixture was stirred for 3 h at room temperature. The solid was filtrated and washed with distilled water to neutral producing **4** as white powder.
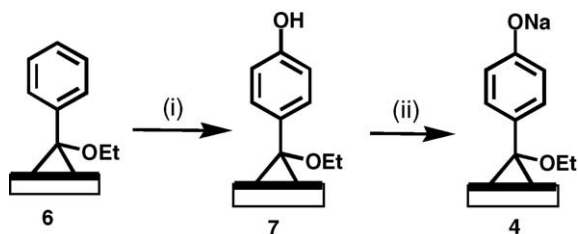
Scheme 2. Preparation of the supports modified by sodium phenolate (**4**). Mesoporous supports: activated Silica (pore size 9.7 nm, with sharp pore size distribution), SBA-15 (pore size 7.6 and 6.2 nm), MCM-41 (pore size 2.7 nm). Reagents and conditions: (i) H_2O_2, H_2SO_4, $FeCl_3 \cdot 6H_2O$, 50 °C, 5 h; (ii) NaOH, r.t., 3 h.

The mixture of **1** (1.0 mmol) and modified support **4** (1.0 g) were added to ethanol (60 ml) and this suspension was stirred for 5 h under reflux (Scheme 1). After the solid was filtrated, washed thoroughly with ethanol then CH_2Cl_2 in order to eliminate all the Mn(salen) complexes adsorbed on the supports. The CH_2Cl_2 filtrates were analyzed by UV–vis spectra until no peaks can be detected out (using CH_2Cl_2 as reference for UV–vis detection). After drying, the heterogeneous Mn(salen) catalysts **5** were obtained as brown powder.

2.3. General procedure for asymmetric epoxidation of unfunctional olefins [4c]

A typical epoxidation process with NaClO as oxidant is processed in a solution of CH_2Cl_2 (3 ml) containing olefin (1 mmol), n-nonane (internal standard, 1.0 mmol), PPNO as axial additive (0.38 mmol, if necessary), homogeneous or heterogeneous Mn(salen) catalysts (0.015 mmol, 1.5 mol.%, based on Mn element) and NaClO aqueous solution (pH 11.5, 0.55 M, 3.64 ml, 2 equiv.) at 0 or 20 °C for 6 h or 24 h. After the completion of the reaction, the organic phase was concentrated and purified by flash chromatography for homogeneous catalysts or was filtrated to remove heterogeneous catalysts. The yields and ee values of epoxides were determined by GC. The racemic epoxides were synthesized by epoxidation of corresponding olefins with m-CPBA in $CHCl_3$ at 0 °C and confirmed by GC–MS. The recycling experiments were carried out according to the epoxidation process but the amount was magnified five times. The solid catalysts were filtrated and washed thoroughly with distilled water and ethanol followed by dichloromethane then was used for the next time.

3. Results and discussion

3.1. Synthesis and characterization of Mn(salen)OPh and heterogeneous Mn(salen) catalysts

Mn(salen)OPh complexes were prepared from Mn(salen) Cl complexes and PhONa in refluxed ethanol. The water samples during the preparation process were detected by HNO_3–$AgNO_3$ solution. No white floc was observed for addition of HNO_3–$AgNO_3$ solution to Mn(salen) in CH_2Cl_2 or PhONa aqueous solution. The appearance of characteristic white floc in the water samples proves the presence of isolated chlorine during the process, meaning that Mn(salen)OPh complexes were synthesized via ion-exchange mode. The synthesized Mn(salen)OPh complexes were analyzed by ICP-AES. Mn content accords well with the molecular amount. The ratios of C/H/N based on element analysis accord very well with the calculated results.

The preparation of the heterogeneous Mn(salen) catalysts was greatly simplified. In our early work [4c], the heterogeneous catalysts were prepared via six steps with complicated operation. Now, only three steps were needed and every step is very simple, economical and green. The
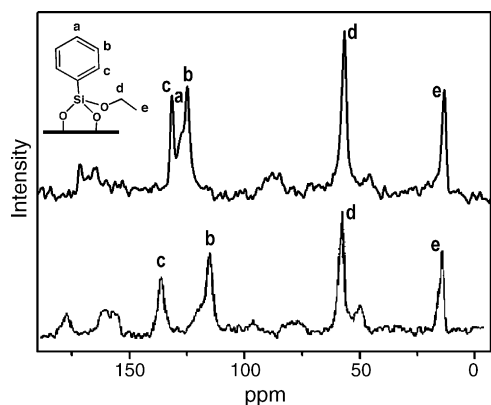
Fig. 1. ^{13}C CP/MAS NMR spectra of Ph/SiO$_2$(9.7) and PhOH/SiO$_2$(9.7).
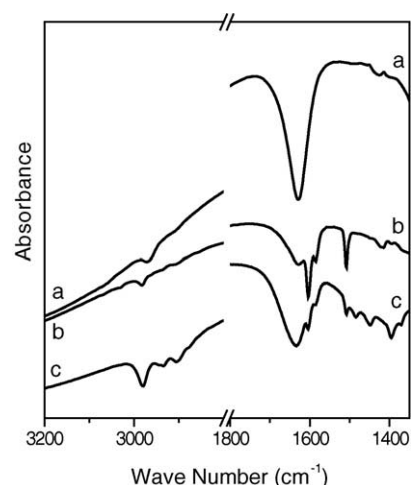

Fig. 2. FT-IR spectra of (a) Ph/SiO$_2$(9.7), (b) PhOH/SiO$_2$(9.7) and (c) Mn(salen-b)/SiO$_2$(9.7).

Mn(salen)Cl complexes were readily immobilized into **4** in ethanol solution under reflux. As comparison, the pure siliceous support without modification by phenyl groups was operated according to Scheme 2 then used for grafting Mn(salen). The support quickly turns to white when it was thoroughly washed with CH$_2$Cl$_2$. And no Mn(salen) complex can be detected out from the support analyzed by ICP-AES based on Mn element. Grafting Mn(salen) onto **6** is also unsuccessful under the same grafting conditions. These results show that Mn(salen) complexes are grafted on the supports via phenoxy group and the Mn(salen) adsorbed on the supports can be completely eliminated by washing with CH$_2$Cl$_2$.

The modified supports (**6**, **7**) were characterized by ^{13}C CP/MAS NMR (Fig. 1), and only carbon atoms attached with hydrogen atom can give characteristic NMR signals. The signals of Ph/SiO$_2$(9.7) (**6**) at 58.2 and 16.2 ppm are assigned to −OCH$_2$CH$_3$ group, and 131.6, 127.4 and 124.9 ppm can be attributed to the three kinds of carbon atoms in phenyl groups. The carbon atom attached with silicon atom has no signals. The appearance of two new bands for **7** at 135.2 and 114.6 ppm, associated with two kinds of carbons atom between the silicon atom and oxygen atom (c and b in Fig. 1), indicates that phenyl groups are hydroxylated at *para* site based on the silica atom. And the chemical shifts agree very well with that of the theory calculation.

All the prepared heterogeneous Mn(salen) catalysts were thoroughly washed with CH$_2$Cl$_2$ in order to eliminate Mn(salen) adsorbed on the supports. The IR spectra of the heterogeneous catalysts are shown in Fig. 2. The IR band for Ph/SiO$_2$(9.7) at 1629 cm^{-1} can be due to the adsorbed water species, which overlays the vibration band of C=C in phenyl groups. The IR spectrum of PhOH/SiO$_2$(9.7) shows a pair of new bands at 1604 and 1585 cm^{-1} and another new band at 1508 cm^{-1} due to the *p*-π conjugation of phenyl ring with substituted oxygen atom. The C=O vibration band at about 1200 cm^{-1} was overlayed by SiO$_2$ support. Mn(salen-b)/SiO$_2$(9.7) shows two pairs of bands at 1604, 1586 and 1508, 1449 cm^{-1}, which are attributed to the phenyl

rings conjugated with oxygen atoms. The bands at 2980, 2933 and 2904 cm^{-1}, associated with *tert*-butyl groups, and other bands at 1485, 1396 and 1371 cm^{-1} suggest that the Mn(salen) complex is grafted onto the support.

UV–vis spectra give more obvious evidence for the successful grafting (Fig. 3). Mn(salen-b)Cl and Mn(salen-b)OPh complexes show similar bands at 230, 254, 331 and 446 nm in UV–vis spectra. The bands of Ph/SBA(7.6) at 213 and 263 nm mean the presence of abundant phenyl groups on the support. Grafting Mn(salen-b) onto SBA(6.2) results the characteristic bands of Mn(salen) shifted to 255, 327 and 430 nm, respectively, indicating the presence of inter-
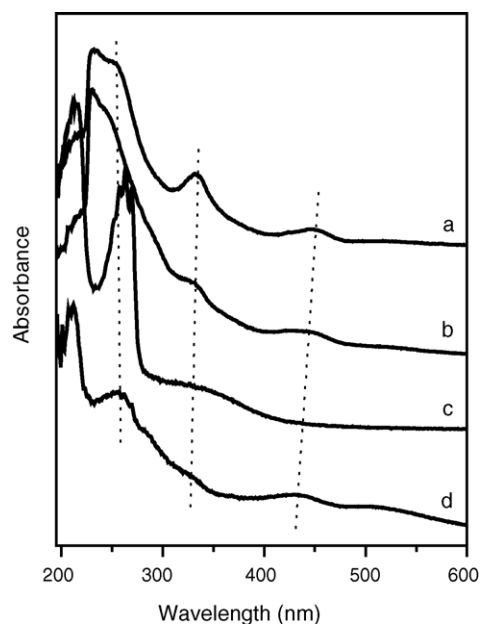

Fig. 3. UV–vis spectra of (a) Mn(salen-b)Cl, (b) Mn(salen-b)OPh, (c) Ph/SBA(6.2) and (d) Mn(salen-b)/SBA(6.2).
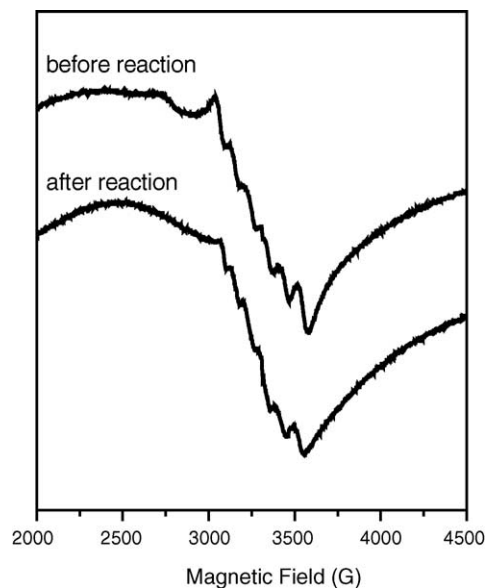
Fig. 4. The EPR spectra of Mn(salen-a)/SiO$_2$(9.7) before and after catalytic reaction.

action of Mn(salen) with the support. The EPR spectrum of Mn(salen-a)/SiO$_2$(9.7) (Fig. 4) gives characteristic six well-resolved hyperfine lines. It was shown that Mn(salen) complexes are located in the heterogeneous catalyst with a well-defined molecular geometry. PXRD patterns of the heterogeneous Mn(salen) catalyst (Fig. 5) show that the structure of the mesoporous materials still keeps good periodicity after immobilization of Mn(salen) complexes. The amount of Mn(salen) grafted onto support is in the range of 0.029–0.055 mmol/g analyzed by ICP-AES based on Mn element.
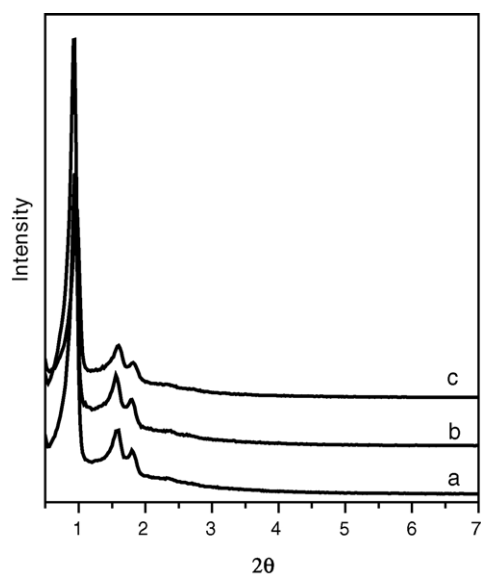

Fig. 5. PXRD spectra of (a) SBA-15 (7.6 nm), (b) Ph/SBA(7.6) and (c) Mn(salen-a)/SBA(7.6).

All the Mn(salen) catalysts used for the asymmetric epoxidation contain the same amount of active centers, 0.015 mmol Mn(salen), and the mass amount of the heterogeneous catalysts was calculated through 0.015 mmol divided by their respective grafting amount of Mn(salen) in the catalysts. *n*-Nonane was used as internal standard due to its stability, inertia and easy handling (bp 151 °C). Five typical olefins, styrene (simple-substituent), α-methylstyrene, *cis*-β-methylstyrene and 6-cyano-2,2-dimethylchromene (di-substituent, substituent groups at one side or two sides of double bond and one cyclic olefin), and 1-phenylcyclohexene (tri-substituent), were chosen as model substrates to investigate the heterogeneous Mn(salen) catalysts. Asymmetric epoxidation of styrene was carried out at 0 °C and other substrates were reacted at 20 °C. PPNO as axial auxiliary was used for asymmetric epoxidation of styrene, 6-cyano-2,2-dimethylchromene and 1-phenylcyclohexene.

3.2. The heterogeneous asymmetric epoxidation

The Mn(salen)OPh and the heterogeneous Mn(salen) catalysts display excellent activity and enantioselectivity for asymmetric epoxidation of various olefins (shown in Table 1). Mn(salen-a)Cl and Mn(salen-a)OPh catalysts show completely same reaction results for asymmetric epoxidation of styrene and the heterogeneous Mn(salen) catalysts give the comparable ee values to the homogeneous catalysts (entry 1–4). Mn(salen-a)Cl and Mn(salen-a)OPh catalysts convert 6-cyano-2,2-dimethylchromene to its epoxide with 80.1 and 84.6% ee values, respectively (entry 5–6). Grafting Mn(salen-a) onto AS (9.7) gives 68.8% ee but grafting onto SBA(7.6) results ee increased to 84.9% under same condition (entry 7–8). Mn(salen-a)Cl and Mn(salen-a)OPh give about 50% ee for asymmetric epoxidation of α-methylstyrene (entry 7–8). Notably, immobilizing Mn(salen-a) onto supports results the great improvement in ee value, from homogeneous 53.3% to heterogeneous 72.1 and 73.9% for onto SBA(7.6) and SiO$_2$(9.7) (entry 8–9). As for asymmetric epoxidation of 1-phenylcyclohexene, Mn(salen-a)Cl and Mn(salen-a)OPh give 82.3 and 78.1% ee, respectively (entry 10–11). However, the heterogeneous Mn(salen-a) catalysts immobilized onto SBA(7.6) and SiO$_2$(9.7) present 50.6 and 62.4% ee for this substrate, respectively (entry 12). In addition, the heterogeneous catalysts show high conversions for asymmetric epoxidation of 6-cyano-2,2-dimethylchromene and 1-phenylcyclohexene.

Except for tri-substituent 1-phenylcyclohexene, the heterogeneous Mn(salen) catalysts give the comparable to and even higher ee values for asymmetric epoxidation than the homogeneous catalysts, especially for asymmetric epoxidation of α-methylstyrene. In our previous work [4c], the reasons for the increase in ee values were considered as the bulky axial group and/or the mesoporous effect of the support (MCM-41). The present results show that changing axial ligand from Cl atom to PhO group does not make a

Table 1

Asymmetric epoxidation of various unfunctional olefins catalyzed by homogeneous and heterogeneous Mn(salen) complexes

En	Substrate	Catalyst	T (h)	Yie (%)	Ee (%)	Config.
1		Mn(salen-a)Cl	6	100	37.5	*S*
2		Mn(salen-a)OPh	6	100	37.2	*S*
3		Mn(salen-a)/SBA(7.6)[a]	24	29.8	35.2	*S*
4		Mn(salen-a)/SiO$_2$(9.7)[b]	24	31.2	39.7	*S*
5		Mn(salen-a)Cl	6	97.0	80.1	*(S,S)*
6		Mn(salen-a)OPh	6	100	84.6	*(S,S)*
7		Mn(salen-a)/SBA(7.6)	24	100	84.9	*(S,S)*
8		Mn(salen-a)/SiO$_2$(9.7)	24	84.1	68.8	*(S,S)*
9		Mn(salen-a)Cl	6	100	55.2	*S*
10		Mn(salen-a)OPh	6	100	53.3	*S*
11		Mn(salen-a)/SBA(7.6)	24	53.1	72.1	*S*
12		Mn(salen-a)/SiO$_2$(9.7)	24	50.7	73.9	*S*
13		Mn(salen-a)Cl	6	95.5	82.3	*(R,R)*
14		Mn(salen-a)OPh	6	95.5	78.1	*(R,R)*
15		Mn(salen-a)/SBA(7.6)	24	90.9	50.6	*(R,R)*
16		Mn(salen-a)/SiO$_2$(9.7)	24	93.4	62.4	*(R,R)*

Reactions were performed in CH$_2$Cl$_2$ (3 ml) with olefins (1.0 mmol), *n*-nonane (internal standard, 1.0 mmol), homogeneous or heterogeneous Mn(salen) catalysts (0.015 mmol, 1.5 mol.%), PPNO (0.38 mmol, for entry 1–8 and 13–16) and NaClO aqueous solution (pH, 11.5, 0.55 M, 3.64 ml) at 0 °C (entry 1–4) or 20 °C (entry 5–16).

[a] 89.4% selectivity for epoxide, phenyl aldehyde and acetophenone as by-products.

[b] 95.0% selectivity for epoxide.

great influence on the ee values, but the succedent immobilization as well as the support effect obviously improves the enantioselectivity. That addition of PhONa/SiO$_2$(9.7) to Mn(salen-a)Cl or addition of SiO$_2$ to Mn(salen)OPh gives the completely same results as homogeneous catalysts for asymmetric epoxidation of α-methylstyrene further proves that only immobilization can result higher ee values.

α-Methylstyrene was then chosen to further investigate the heterogeneous Mn(salen) catalysts. The reaction results are listed in Table 2. Homogeneous Mn(salen-b)Cl and Mn(salen-b)OPh still give similar ee values of about 26% (entry 1–2). Mn(salen-b) catalyst immobilized into supports with pore sizes of 2.7, 6.2, 7.6 and 9.7 nm, respectively, gives ee values of 56.3, 71.4, 75.3 and 79.7% (entry 3–6). Similarly, immobilizing Mn(salen-c) onto different supports also gives higher ee values than homogeneous catalyst and the ee values are increased with the increasing the pore sizes of the supports (entry 7–11). This means that the nanopores of the supports indeed affect the asymmetric induction for asymmetric epoxidation. The conversions for the heterogeneous catalysts are somewhat decreased, which may be duo the difficulty in diffusion of reactants into the nanopores of supports [4c,5d].

It was reported [4b] that heterogeneous Mn(salen) catalysts immobilized via multi-step grafting enhanced the asymmetric induction from homogeneous 51% ee to heterogeneous 59% ee for asymmetric epoxidation of α-methylstyrene. This group have reported [4c] that Mn(salen) axially immobilized into MCM-41 through phenoxy group give 72% ee. The axially rigid immobilization mode obviously improves the enantioselectivity. Notably, the present heterogeneous catalysts prepared by the simplified method can give up to 79.7% ee value for asymmetric epoxidation of α-methylstyrene.

The asymmetric epoxidation of *cis*-β-methylstyrene was also tested for the heterogeneous catalysts (Table 3). Homogeneous Mn(salen-a)Cl catalyst produces the *trans*-epoxide as major product (*cis/trans*: 0.38) [14]. But Mn(salen-a)/SiO$_2$(9.7) catalyst gives the *cis*-epoxide as major product and the *cis/trans* ratio is increased from 0.38 to 21 (entry1, 2). Heterogeneous Mn(salen-b)/SiO$_2$(9.7) also results *cis*-

Table 2

Asymmetric catalytic epoxidation of α-methylstyrene catalyzed by homogeneous and heterogeneous Mn(salen) complexes

Run	Catalyst	T (h)	Yield (%)	Ee (%)[a]
1	Mn(salen-b)Cl	6	100	26.4
2	Mn(salen-b)OPh	6	100	23.6
3	Mn(salen-b)/MCM(2.7)	24	70.0	56.3
4	Mn(salen-b)/SBA(6.2)	24	65.6	71.4
5	Mn(salen-b)/SBA(7.6)	24	54.1	75.3
6	Mn(salen-b)/SiO$_2$(9.7)	24	45.3	79.7
7	Mn(salen-c)Cl	6	98.4	52.4
8	Mn(salen-c)/MCM(2.7)	24	77.5	53.3
9	Mn(salen-c)/SBA(6.2)	24	62.1	63.3
10	Mn(salen-c)/SBA(7.6)	24	55.4	69.2
11	Mn(salen-c)/SiO$_2$(9.7)	24	53.2	78.2

Reactions were performed in CH$_2$Cl$_2$ (3 ml) with α-methylstyrene (1.0 mmol), *n*-nonane (internal standard, 1.0 mmol), homogeneous or heterogeneous Mn(salen) catalysts (0.015 mmol, 1.5 mol.%) and NaClO aqueous solution (pH, 11.5, 0.55 M, 3.64 ml) at 20 °C.

[a] (*S*)-form.

Table 3

Asymmetric epoxidation of *cis*-β-methylstyrene catalyzed by homogeneous Mn(salen) and heterogeneous Mn(salen) catalysts

En	Catalyst	Cis		Trans		Cis/Trans
		Yie (%)	Ee (%)[a]	Yie (%)	Ee (%)[b]	
1	Mn(salen-a)Cl	27.5	54.8	72.5	>99	0.38
2	Mn(salen-a)/SiO$_2$(9.7)	15.7	94.9	0.74	–	21
3	Mn(salen-a)/SiO$_2$(9.7)[c]	20.2	90.1	4.8	>99	4.2
4	Mn(salen-b)Cl	25.3	25.3	54.9	93.3	0.46
5	Mn(salen-b)/SiO$_2$(9.7)	15.6	94.9	0.73	–	21
6	Mn(salen-b)/SBA(7.6)	32.1	93.5	2.9	65.2	11.1
7	Mn(salen-b)/SBA(6.2)	29.3	92.7	4.66	77. 8	6.3
8	Mn(salen-b)/SiO$_2$(9.7)[d]	22.3	93.2	2.1	>99	10.8

Reactions were performed in CH$_2$Cl$_2$ (3 ml) with *cis*-β-methylstyrene (1.0 mmol), *n*-nonane (internal standard, 1.0 mmol), homogeneous or heterogeneous Mn(salen) catalysts (0.015 mmol, 1.5 mol.%) and NaClO aqueous solution (pH, 11.5, 0.55 M, 3.64 ml) at 20 °C.
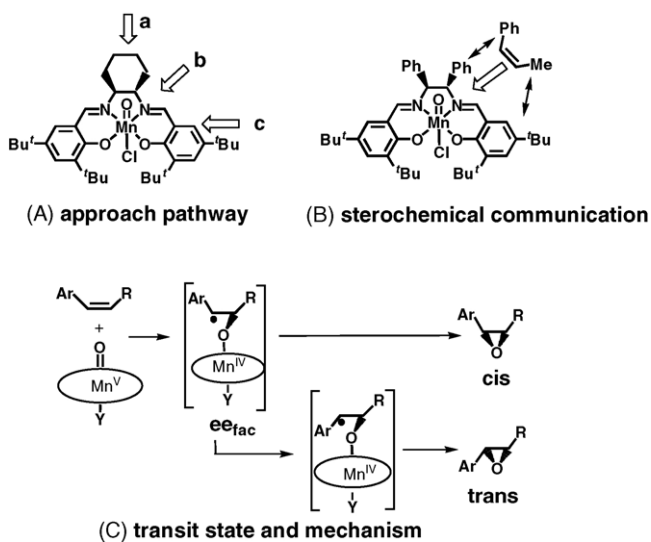
[a] (*S,R*)-form.

[b] (*S,S*)-form.

[c] Addition of PPNO (0.38 mmol).

epoxide as major product (*cis/trans* 21, entry 5). Immobilizing Mn(salen-b) onto other supports, such as SBA(7.6) and (6.2), respectively, gives the *cis/trans* of 11.1 and 6.3 (entry 6, 7). Notably, the addition of axial auxiliary PPNO increases the yield of both the *cis*-epoxide and *trans*-epoxide under the same reaction conditions, but the *cis/trans* ratio is greatly dropped (entry 2, 3 and 5, 8). For example, the *cis/trans* ratio is decreased from 21 to 4.2 for Mn(salen-a)/SiO$_2$(9.7) after addition of PPNO (entry 2, 3). Hutchings and co-workers [8c] also reported that the Mn(salen) immobilized in nanopores of Al-MCM-41 favors the formation of *cis*-epoxide of (Z)-stilbene. In the homogeneous reaction, the radical intermediate can be transferred to *cis*-epoxide via direct collapse or to *trans*-epoxide via rotation then collapse (Scheme 3C) [15]. The heterogeneous catalysts axially immobilized via rigid phenoxy group obviously generate the

cis-epoxide as major product, which may be due to the rotation of the radical intermediate is restricted or the radical lifetime [15b] is shortened not enough for rotation before collapse.

It should be pointed out that the heterogeneous catalysts not only greatly alter the *cis/trans* ratio of epoxides but also remarkably increase the ee values for the *cis*-epoxide. Homogeneous Mn(salen-a)Cl catalyst presents 54.8% ee value for *cis*-epoxide; while the heterogeneous Mn(salen-a)/SiO$_2$(9.7) catalyst results 94.9% ee value (entry 1,2). Homogeneous Mn(salen-b)Cl produces 25.3% ee (for *cis*-epoxide, entry 4). Heterogeneous Mn(salen-b) catalyst immobilized onto SiO$_2$(9.7) gives 94.9% ee value and immobilized onto other supports also gives higher ee values than the homogeneous catalyst (entry 5–7). Addition of PPNO to heterogeneous Mn(salen) catalysts gives slightly lower ee values compared with that without PPNO (for *cis*-epoxide). Che and co-workers [4a] reported that heterogeneous Cr(salen) catalyst axially immobilized via propyl amino group results ee values of the *cis*-product increased from homogeneous 54% to heterogeneous 73%. In this work, Mn(salen) axially immobilized by rigid phenoxy group gives up to 94.9% ee value. Similar with the epoxidation of α-methylstyrene, the axially rigid immobilization mode and the support effect also displays favorable effect on the enantioselectivity (*cis*-epoxide) for asymmetric epoxidation of *cis*-β-methylstyrene.

3.3. The recycling of the heterogeneous Mn(salen) catalyst

When a reaction was over, the heterogeneous catalyst was completely washed by distilled water, ethanol and dichloromethane. The EPR spectra of the recycled heterogeneous catalyst Mn(salen-a)/SiO$_2$(9.7) (Fig. 4) still shows six well-resolved hyperfine lines, just like the fresh heterogeneous catalyst. It means that the molecular geometry of Mn(salen) catalysts keeps well during the epoxi-

Scheme 3. The proposed influence factors for enantioselectivity for asymmetric epoxidation catalyzed by Mn(salen) catalysts.

Table 4
The recycles of the Mn(salen-a)/SiO$_2$(9.7) for asymmetric epoxidation of α-methylstyrene

Run	T (°C)	Yield (%)	Ee (%)[a]
1	25	82.1	65.4
2	25	84.7	63.4
3	25	80.1	67.8
4	25	75.3	65.8
5	25	70.5	66.5
6	25	64.6	69.3
7	20	55.1	74.8
8	20	44.3	75.0

Reactions were performed in CH$_2$Cl$_2$ (15 ml) with α-methylstyrene (5.0 mmol), n-nonane (5.0 mmol), Mn(salen-a)/SiO$_2$ (0.075 mmol, 1.95 g, 1.5 mol.%) and NaClO (pH, 11.5, 0.57 M, 17.5 ml) for 24 h.

[a] (S)-form.

dation process. The split is approximately decreased from 92 G for fresh catalyst to 89 G for the recycled catalyst, obviously due to the oxidation of grafted Mn^{III}(salen). Then Mn(salen-a)/SiO$_2$(9.7) was recycled for the epoxidation of α-methylstyrene (Table 4). The former six times were reacted at 25 °C and the later two times were at 20 °C. There is no evident decrease in enantioselectivity even after the catalytic tests for eight times. The conversions show a drop of average 4.7% for every washing and recycle. The TON of the heterogeneous catalyst is estimated to be 371 for the total eight runs, while the TON of homogeneous Mn(salen-a)Cl is about 63, calculated by a homogeneous epoxidation with 1 mol% catalyst. The stability of the heterogeneous Mn(salen) catalysts were enhanced compared with the free ones. It was reported that homogeneous Mn(salen) complexes are prone to oxidative degradation [16] and dimerization to μ-oxo-Mn(IV) species [17], which result in the deactivation of the catalytic species. Immobilization of Mn(salen) onto the supports leads to the isolation of active site and enhancement of the stability.

3.4. The proposed effect factors on enantioselectivity

The ee values obtained from the heterogeneous Mn(salen) catalysts are lower, comparable and even higher than the homogeneous catalysts for he different substrates. The influence factors in the ee values are very complicated for the heterogeneous asymmetric catalysis [3d]. Several main and possible modes were proposed to elucidate the difference in ee values of heterogeneous catalysts from homogeneous catalysts (Scheme 3).

There are several pathways for one olefin to approach the oxo Mn^V(salen) active center (Scheme 3A). One opinion involves pathway **a** as favored approach [18]. Another opinion considers that pathway **b** is reasonable and pathway **c** is also not excluded due to the assumed folded Mn(salen) structure [19]. The different pathway will produce different enantioselectivity for asymmetric epoxidation [18–20]. For

the heterogeneous catalysts, one approach pathway of the substrate to the active center may be restricted or enhanced by the grafting mode and the support. Thomas and co-workers reported that [21] heterogeneous catalysts immobilized on MCM-41 significantly enhance ee value for asymmetric hydrogenation and pore confinement was claimed to control the approach direction of the reactant to the active site.

When olefin approaches the active center via one pathway, the stereochemical communication (chiral recognition) between the olefin and the chiral salen ligand (Scheme 3B) will directly determine ee$_{fac}$ [22], which is the enantiofacial selection in the first C—O band-forming step (shown in Scheme 3C). For the heterogeneous catalysts, the stereochemical communication may be enhanced or reduced by the grafting mode and the surface or nanopores of supports and the heterogeneous catalysts present the different ee values. Corma et al. [23] showed that heterogeneous asymmetric hydrogenation on modified Rh/USY catalyst presents higher ee value and the increase in ee is attributed to the additional interaction of substrate and pore wall. The interaction between chiral ligand and substrate was enforced for catalysts immobilized in the layered materials, which may enhance the enantioselectivity in asymmetric reactions [3d].

The third possibility is that the transition state may be changed upon the heterogenization. It was reported that the early transition state generates lower ee values and stabilizing the oxo Mn^V(salen) intermediate leads a late transition state and affords higher ee values for asymmetric epoxidation catalyzed by homogeneous Mn(salen) catalysts [24]. This group has mentioned in a review [3d] that the energy difference between the R- and S- product transition states is so small that it is very sensitive to the interaction of the Mn(salen) catalysts and grafting modes as well as surface/pore environment for heterogeneous catalysts. Therefore, the enantioselectivity obtained from heterogeneous catalysts can be sensitively changed when the catalyst is assembled in the pores or on the surfaces. For example, the enhanced chiral recognition for asymmetric epoxidation catalyzed by immobilized Cr complex involves the improvement of the stability of catalyst [4a].

The fourth proposal is that the heterogeneous Mn(salen) catalysts react via different process. Just as shown in Scheme 3C, Mn(salen) catalysts produce *cis*-epoxide via direct collapse of radical intermediate and form *trans*-epoxide via rotation then collapse of intermediate. In this work, homogeneous Mn(salen-a)Cl catalysts give the *trans*-epoxide as the major product (*cis/trans* 0.38), but the heterogeneous Mn(salen) catalysts are prone to *cis*-epoxide (*cis/trans* up to 21). The reaction process was altered for the heterogeneous Mn(salen) catalysts. It should be noticed that, for asymmetric epoxidation of terminal olefins (such as styrene or α-methylstyrene), the change in reaction process indeed affects the ee values [22]. Epoxidation via *trans* pathway in fact generates another enantiomer and the observed

ee value can be expressed as follows [22]:

$$Ee_{obs} = ee_{fac} - 2(ee_{trans} \times \%trans)$$

$$or\ Ee_{obs} = (ee_{cis} \times \%cis) - (ee_{trans} \times \%trans)$$

Therefore, the heterogeneous Mn(salen) catalysts, especially for axial and rigid immobilization, restrict the rotation of the radical intermediate, leading to higher *cis/trans* ratio and enhance ee values for asymmetric epoxidation of terminal olefins (α-methylstyrene).

4. Conclusions

Three chiral Mn(salen) complexes were successfully grafted onto various supports via phenoxy group. The heterogeneous Mn(salen) catalysts show comparable ee for asymmetric epoxidation of styrene and 6-cyano-2,2-dimethylchromene and much higher ee for α-methylstyrene and *cis*-β-methylstyrene. The heterogeneous catalysts also remarkably alter the *cis/trans* ratio of epoxides. The axial tether group does not make a big effect on ee values and the increase in ee value and change in *cis/trans* ratio are mainly attributed to the immobilization mode and support effect of heterogeneous catalysts. The catalysts can keep constant ee values for the recycle tests of eight times. And several possibilities were proposed to elucidate the difference in ee values of heterogeneous catalysts from homogeneous catalysts.

Acknowledgments

References

[1] (a) W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801;
(b) R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, Tetrahedron Lett. 31 (1990) 7345;
(c) L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85.

[2] H.U. Blaser, B. Pugin, in: G. Jannes, V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum Press, New York, 1995, p. 33.

[3] (a) C. Bianchini, P. Barbaro, Top. Catal. 19 (2002) 17;
(b) C.-E. Song, S.-G. Lee, Chem. Rev. 102 (2002) 3495;
(c) P. Mcmorn, G.J. Hutchings, Chem. Soc. Rev. 33 (2004) 108;
(d) C. Li, Catal. Rev.-Sci. Eng. 46 (2004) 419.

[4] (a) X. Zhou, X. Yu, J. Huang, S. Li, L. Li, C. Che, Chem. Commun. (1999) 1789;
(b) G.-J. Kim, J.-H. Shin, Tetrahedron Lett. 40 (1999) 6827;
(c) S. Xiang, Y. Zhang, Q. Xin, C. Li, Chem. Commun. (2002) 2696;
(d) D.W. Park, S.D. Choi, S.-J. Choi, C.-Y. Lee, G.-J. Kim, Catal. Lett. 78 (2002) 145;
(e) B. Franca, L. Moroni, R. Maggi, G. Sartori, J. Chem. Soc. Chem. Commun. (2002) 716;
(f) C. Baleizão, B. Gigante, D. Das, M. Alvaro, H. Garcia, A. Corma, Chem. Commun. (2003) 1860;
(g) J.-H. Kim, G.-J. Kim, Catal. Lett. 92 (2004) 123;
(h) I. Domínguez, V. Fornés, M.J. Sabater, J. Catal. 228 (2004) 92;
(i) H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209.

[5] (a) B.M. Choudary, M.L. Kantam, B. Bharathi, P. Sreekanth, F. Figueras, J. Mol. Catal. A 159 (2000) 417;
(b) B.M. Choudary, N.S. Chowdari, M.L. Kantam, P.L. Santhi, Catal. Lett. 76 (2001) 213;
(c) C. Baleizão, B. Gigante, M.J. Sabater, H. Garcia, A. Corma, Appl. Catal. A 228 (2002) 279;
(d) A. Hecked, D. Seebach, Helv. Chim. Acta. 85 (2002) 913;
(e) C. Baleizão, B. Gigante, H. Garcia, A. Corma, J. Catal. 215 (2003) 207;
(f) B.M.L. Dioos, P.A. Jacobs, Tetrahedron Lett. 44 (2003) 8815.

[6] (a) A.R. Silva, J. Vital, J.L. Figueiredo, C. Freire, B.D. Castro, New J. Chem. 27 (2003) 1511;
(b) C. Baleizão, B. Gigante, H. Garcia, A. Corma, J. Catal. 221 (2004) 77;
(c) A.R. Silva, J.L. Figueiredo, C. Freire, B. Castro, Micropor. Mesopor. Mater. 68 (2004) 83;
(d) C. Baleizão, B. Gigante, H. Garcia, A. Corma, Tetrahedron 60 (2004) 10461.

[7] B. Gigante, A. Corma, H. Garcia, M.J. Sabater, Catal. Lett. 68 (2000) 113.

[8] (a) G.-J. Kim, S.-H. Kim, Catal. Lett. 57 (1999) 139;
(b) P. Piaggio, C. Langham, P. McMorn, D. Bathell, P.C.B. Page, F.E. Hancock, C. Sly, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2000) 143;
(c) P. Piaggio, P. McMorn, D. Murphy, D. Bathell, P.C.B. Page, F.E. Hancock, C. Sly, O.J. Kerton, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2000) 2008.

[9] (a) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, I. Ahmael, S. Singh, R.V. Jasra, J. Catal. 221 (2004) 234;
(b) S. Bhattacharjee, J.A. Anderson, Chem. Commun. (2004) 554;
(c) S. Bhattacharjee, T.J. Dines, J.A. Anderson, J. Catal. 225 (2004) 398.

[10] C. Schuster, E. Möllmann, A. Tompos, W.F. Hölderich, Catal. Lett. 74 (2001) 69.

[11] S.-D. Choi, G.-J. Kim, Catal. Lett. 92 (2004) 35.

[12] (a) W. Zhang, E.N. Jacobsen, J. Org. Chem. 56 (1991) 2296;
(b) J.F. Larrow, E.N. Jacobsen, J. Org. Chem. 59 (1994) 1939.

[13] (a) D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, Angew. Chem. Int. Ed. 39 (2000) 4321;
(b) J. Peng, F. Shi, Y. Gu, Y. Deng, Green Chem. 5 (2003) 224.

[14] (a) W. Adam, K.J. Roschmann, C.R. Saha-Möller, Eur. J. Org. chem. (2002) 3519;
(b) W. Adam, K.J. Roschmann, C.R. Saha-Moller, D. Seebach, J. Am. Chem. Soc. 124 (2002) 5068.

[15] (a) S. Chang, N.H. Lee, E.N. Jacobsen, J. Org. Chem. 58 (1993) 6939;
(b) P.O. Norrby, J. Am. Chem. Soc. 117 (1995) 11035.

[16] S.H. Zhao, P.R. Ortiz, B.A. Keys, K.G. Davenport, Tetrahedron Lett. 37 (1996) 2725.

[17] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, Tetrahedron: Asymmetry 6 (1995) 2105.

[18] (a) E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, J. Am. Chem. Soc. 113 (1991) 7063;
(b) B.D. Brandes, E.N. Jacobsen, Tetrahedron Lett. 36 (1995) 5123.

[19] T. Hamada, T. Fukuda, H. Imanishi, T. Katsuki, Tetrahedron 52 (1996) 515.

[20] C.P. O'Mahony, E.M. McGarrigle, M.F. Renehan, K.M. Ryan, M.J. Kerrigan, C. Bousquet, D.G. Gilheany, Org. Lett. 3 (2001) 3435.

[21] (a) M.D. Jones, R. Raja, J.M. Thomas, B.F.G. Johnson, D.W. Lewis, J. Rouzaud, K.D.M. Harris, Angew. Chem. Int. Ed. 42 (2003) 4326;
(b) R. Raja, J.M. Thomas, J. Mol. Catal. A 181 (2002) 3.

[22] (a) M. Palucki, P.J. Pospisil, W. Zhang, E.N. Jacobsen, J. Am. Chem. Soc. 116 (1994) 9333;

(b) J.F. Lorrow, E.N. Jacobsen, Top. Organomet. Chem. 6 (2004) 123;
(c) Y.N. Ito, T. Katsuki, Tetrahedron Lett. 39 (1998) 4325.

[23] A. Corma, M. Iglesias, C. del Pino, F. Sanchez, J. Organomet. Chem. 431 (1992) 233.

[24] (a) M. Palucki, N.S. Finney, P.J. Pospisil, M.L. Güler, J. Am. Chem. Soc. 120 (1998) 948;
(b) L. Cavallo, H. Jacobsen, J. Org. Chem. 68 (2003) 6202.