



Heterogeneous chiral Mn(III) salen catalysts for the epoxidation of unfunctionalized olefins immobilized on mesoporous materials with different pore sizes

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ABSTRACT

Two chiral Mn(III) salen complexes were immobilized onto a series of mesoporous MCM-41 and MCM-48 materials with different pore sizes and the as-synthesized catalysts were active and enantioselective for the asymmetric epoxidation of styrene and indene. The results of XRD, FTIR, DR UV–vis, and N₂ sorption showed that the chiral Mn(III) salen complexes were anchored in the channels of mesoporous materials. The influence of organic silicane dosage on the catalytic performance was studied and the optimum dosage of organic silicane for preparing heterogeneous catalysts was determined. Furthermore, the effect of the fine-tuning of pore size on the performance of heterogeneous catalysts was discussed. In general, larger pore size of the supports could lead to higher conversions and the compatible pore size with substrate may be responsible for the improved enantiomeric excess (ee) values.

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1. Introduction

Chiral Mn(III) salen complexes have proven activity and enantioselectivity for the asymmetric epoxidation of unfunctionalized olefins,^{1,2} which are highly significant in the pharmaceutical and agrochemical fields to synthesize chiral building blocks that could be transformed into other useful chiral compounds through regioselective ring-opening reactions.³ However, the catalyst always suffers from separation and recycling problems in homogeneous system. Consequently, the heterogenization of chiral Mn(III) salen complexes within inorganic matrixes has received great attention^{4–13} over the last decade. The heterogeneous catalysts could be easily separated from the reaction system and simply recycled several times, moreover, the immobilization of chiral Mn(III) salen complexes could effectively decrease the formation of inactive dimeric μ -oxo Mn(IV) species.¹⁴

The mesoporous siliceous materials have large surface areas, controllable pore sizes of 2–50 nm, and abundant silanol groups on the surface, allowing ready material diffusion and easily organically functionalized and grafted to catalytic active species, and thus were widely applied in the immobilization of chiral Mn(III) salen complexes.^{3,15–23} Recently, the influence of pore size

on the catalytic performance of mesoporous material-supported chiral Mn(III) salen complex has been reported. Zhang et al.^{3,15} immobilized the chiral Mn(III) salen complexes into the nanopores of mesoporous supports MCM-41 (1.6 and 2.7 nm), SBA-15 (7.6 nm), and activated silica (9.7 nm) with different pore sizes and the influence of pore size on the catalytic performance was studied. Kureshy et al.^{16,17} supported the chiral Mn(III) salen complex onto the mesoporous materials MCM-41 and SBA-15, and found that the SBA-15-based catalyst, with a larger pore diameter, was more active than MCM-41-supported catalyst. Similarly, Thomas et al.²⁴ and Raja et al.²⁵ also studied the influence of pore size on catalytic performance for other heterogeneous asymmetric reactions.

It is generally believed that the pore size of parent supports could influence the activity and enantioselectivity of the heterogeneous chiral Mn(III) salen catalysts. However, the effect of the fine-tuning of pore size on the catalytic performance of mesoporous material-supported chiral Mn(III) salen complex has seldom been systematically investigated for the heterogeneous asymmetric epoxidation. In this work, the chiral Mn(III) salen complexes were immobilized onto a series of mesoporous MCM-41 and MCM-48 materials, which possess the pore sizes varied on the angstrom length-scale. The as-synthesized catalysts were evaluated in the epoxidation of styrene and indene. The effects of organic silicane dosage and the fine-tuning of pore size on the performance of heterogeneous catalysts were studied.

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2. Experimental

2.1. Materials

3-Mercaptopropyltrimethoxysilane, *cis/trans*-1,2-diaminocyclohexane, and 2-*tert*-butylphenol were supplied by Alfa Aesar. *m*-Chloroperbenzoic acid (*m*-CPBA) was purchased from Acros Organics. *N*-Methylmorpholine-*N*-oxide (NMO) was provided by Aldrich. Indene was purchased from Fluka. Alkyltrimethylammonium bromides $C_nH_{2n+1}(CH_3)_3-NBr$ (C_n TAB for brevity, $n=12, 14, 16, 18$; AR) were obtained from Jintan Huadong Chemical Research Institute in Jiangsu. (1*R*,2*R*)-(+)-1,2-Diphenylethylenediamine (>99% ee) was provided by Likai Chiral Tech. Co. Ltd. in Chengdu. (1*R*,2*R*)-(–)-1,2-Diaminocyclohexane was resolved from the technical grade isomers mixture in >99% ee by the reported procedure.²⁶ Tetraethyl orthosilicate (TEOS), 2,2'-azobis(2-methylpropionitrile) (AIBN), and styrene were provided by Jiangtian Co. Ltd. in Tianjin. Racemic epoxides were synthesized by the epoxidation of corresponding olefins with *m*-CPBA in $CHCl_3$ at 273 K²⁷ and detected by gas chromatography (GC). All of the solvents used in the present study were purified before use.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were performed on an R/max-2500 diffractometer with Cu $K\alpha$ radiation at 40 kV and 100 mA in a scan range of $1.5^\circ < 2\theta < 10^\circ$. FTIR spectra were carried out on KBr pellets in a BRUKER VECTOR 22 spectrometer. Diffuse-reflectance UV–vis (DR UV–vis) spectra were obtained on a Shimadzu UV-2550 UV–vis spectrophotometer in the range of 220–800 nm. N_2 adsorption–desorption analysis was carried out at 77 K on a Micromeritics TriStar 3000 apparatus. The analytical data were processed by the BET equation for surface areas and by the BJH model for pore size distributions. Elemental analysis was performed on a Perkin–Elmer 240C analyzer. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, using a Varian Mercury Vx-300 spectrometer. The content of Mn in the heterogeneous catalysts was determined by an ICP-9000 (N+M) spectrometer (TJA Co.), after calcination and solubilization of the samples with hydrogen fluoride and aqua regia. The products of epoxidation reaction were determined by GC with a chiral β -cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m \times 0.25 mm \times 0.25 μ m), using a Rock GC7800 gas chromatograph equipped with a flame ionization detector. Ultrapure nitrogen was used as the carrier gas and the column temperature was programmed in the range of 333–423 K. For each of the epoxidation reactions, the conversion and ee value were determined by averaging the values from two parallel measurements, of which the results should not differ by more than 0.5%, otherwise additional measurements on the same sample need to be done.

2.3. Synthesis of siliceous mesoporous materials

A series of highly ordered siliceous mesoporous materials MCM-41 and MCM-48 with different pore sizes were synthesized according to the literature method,^{28–30} using the alkylammonium salts C_n TAB ($n=12, 14, 16, 18$) with different alkyl chain lengths as templates and TEOS as silica source.

2.3.1. Synthesis of MCM-41 with different pore sizes

The highly ordered hexagonal siliceous MCM-41 materials with different pore sizes were synthesized using a gel (molar) composition of 1TEOS/0.12 C_n TAB/8NH₄OH/114H₂O. In a typical synthesis, the template of C_n TAB was dissolved in warm deionized water. To this solution, ammonia and TEOS were added orderly under vigorous stirring. After stirring at room temperature for 0.5 h, the

resulting gel was allowed to crystallize at 383 K for 52 h in a Teflon-lined autoclave. The solid product was filtered, washed with deionized water, dried at room temperature, and calcined at 823 K in air for 6 h to remove the template. According to the difference in the alkyl chain length of the template, the as-synthesized materials were marked as *n*MCM-41 ($n=12, 14, 16, 18$).

2.3.2. Synthesis of MCM-48 with different pore sizes

The mesoporous materials MCM-48 with different pore sizes were synthesized according to the procedures as follows. When C_n TAB ($n=14, 16$) was used as template, C_n TAB was dissolved in warm deionized water, and to this solution the required quantity of TEOS and the aqueous solution of NaOH were added in sequence under vigorous stirring. After stirring for 2 h at room temperature, a gel with a molar composition of 1TEOS/0.46 C_n TAB/0.41NaOH/52.95H₂O was obtained. The resulting gel was allowed to crystallize at 383 K for 72 h in a Teflon-lined autoclave. When C_n TAB ($n=12$) was used as template, the molar composition of the gel was 1TEOS/1.10 C_n TAB/0.46NaOH/112H₂O, and the gel was crystallized at 393 K for 168 h. Then, the solid product was filtered, washed with deionized water, and dried in air at room temperature overnight. The template was removed by calcination at 823 K in air for 6 h. According to the difference in the alkyl chain length of the template, the as-synthesized materials were marked as *n*MCM-48 ($n=12, 14, 16$).

2.4. Synthesis of the homogeneous chiral Mn(III) salen complex

The chiral Mn(III) salen complexes **1** and **2** were obtained through the synthesis sequence given in Scheme 1 according to the literature.³¹

2.4.1. Synthesis of 3-*tert*-butyl-2-hydroxy-5-vinylbenzaldehyde (**D**)

3-*tert*-Butyl-2-hydroxybenzaldehyde (**A**) was synthesized from 2-*tert*-butylphenol as described previously.³² Compound **A** (27.0 g, 0.15 mol), paraformaldehyde (10.0 g, 0.33 mol), and tetrabutylammonium bromide (4.7 g, 14.6 mmol) were stirred in concentrated hydrochloric acid (110 mL) at 313 K for 3 days.³³ The reaction mixture was extracted with diethyl ether (3 \times 150 mL), and the organic phase was washed with 5% NaHCO₃ (2 \times 100 mL), brine (2 \times 100 mL), and dried over MgSO₄. Evaporation of the solvent under vacuum afforded 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde (**B**) as a yellow crystalline solid (34.0 g, 99% yield). 1H NMR (CDCl₃, 300 MHz): δ (ppm) 1.43 (s, 9H), 4.59 (s, 2H), 7.44 (d, $J=1.8$ Hz, 1H), 7.53 (d, $J=1.8$ Hz, 1H), 9.87 (s, 1H), 11.87 (s, 1H).

A mixture of compound **B** (15.9 g, 0.070 mol) and triphenylphosphine (18.3 g, 0.070 mol) was refluxed in cyclohexane (150 mL) for 1 h. After cooling the solution to room temperature, the product was filtered, washed with diethyl ether, and dried under vacuum. Then, 3-*tert*-butyl-5-formyl-4-hydroxybenzyl(triphenylphosphonium) chloride (**C**) (30.9 g, 90% yield) was obtained as a white powder. 1H NMR (CDCl₃, 300 MHz): δ (ppm) 1.13 (s, 9H), 5.66 (d, $J=13.8$ Hz, 2H), 7.32 (d, $J=1.8$ Hz, 2H), 7.62–7.86 (m, 15H), 9.70 (s, 1H), 11.82 (s, 1H).

Compound **C** (24.6 g, 0.050 mol) was stirred in 170 mL of 40% aqueous formaldehyde, and an aqueous solution of 12.5 N NaOH (55 mL) was added, keeping the reaction temperature below 313 K. After stirring at room temperature for 2 h, the mixture was cooled with ice and neutralized with 6 N HCl. At pH \approx 7, the aqueous phase was extracted with cyclohexane. Evaporation of the solvent afforded a semisolid that was purified by flash chromatography (dichloromethane). After distilled under vacuum (380 K, 0.1 mmHg), 3-*tert*-butyl-2-hydroxy-5-vinylbenzaldehyde (**D**) (5.87 g, 57% yield) was obtained as light yellow crystals. 1H NMR (CDCl₃, 300 MHz): δ (ppm) 1.43 (s, 9H), 5.21 (d, $J=11.1$ Hz, 1H), 5.66 (d, $J=17.7$ Hz, 1H), 6.68 (dd, $J=17.4, 10.8$ Hz, 1H), 7.41 (d, $J=2.1$ Hz, 1H), 7.61 (d, $J=2.1$ Hz, 1H), 9.89 (s, 1H), 11.79 (s, 1H).

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