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A novel layered organic polymer-inorganic hybrid zinc poly (styrene-phenylvinylphosphonate)-phosphate immobilized chiral salen Mn(III) catalyst large-scale asymmetric epoxidation of unfunctionalized olefins

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1. Introduction

The asymmetric epoxidation of unfunctionalized olefins takes a great importance in synthesis of chiral epoxides, which are widely used in the manufacture of drugs, vitamins, fragrances and other optical materials [1-3]. Chiral Jacobsen-type salen Mn(III) complexes as homogeneous catalysts have emerged extremely efficient systems for the asymmetric epoxidation of the unfunctionalized olefins [4] in the presence of terminal oxidants such as iodosylbenzene, sodium hypochlorite, *m*-Chloroperbenzoic acid, hydrogen peroxide and so on [5-8]. However, the recycle of the expensive homogeneous catalysts is so difficult that limit the practical applications of chiral salen Mn(III) catalysts in both synthetic chemistry and industrial processes [9]. Consequently, the last decades have witnessed an intense research effort to Jacobsentype salen Mn(III) complexes on supports to make them recyclable and enhance their stability, activity, and selectivity [10,11]. For

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ABSTRACT

A novel layered organic polymer-inorganic hybrid zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA) has been synthesized under mild conditions and diphenol-modified ZnPS-PVPA was used to successfully immobilize the chiral salen Mn(III) by axial coordination. The obtained heterogeneous chiral catalysts exhibited excellent activities and enantioselectivities using sodium periodate as an oxidant for asymmetric epoxidation of unfunctionalized olefins, especially for the epoxidation of α -methylstyrene (conversion: up to 97%; *ee*: exceed 99%). Moreover, these synthesized catalysts were relatively stable and could be expediently separated from the reaction system, and could be recycled at least ten times without obvious loss of activity and enantioselectivity. These novel catalysts could be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level, which offer a great possibility for application in industry.

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example, salen Mn(III) complexes have been immobilized onto inorganic supports such as clays [12], SBA-15 [13], MCM-41 [14]; organic poly-systems such as PS [15], *p*-divinylbenzene [16]; and organic polymer-inorganic hybrid solids as zirconium phosphatephosphonate materials reported in our group: ZPS–IPPA [17]; ZPS–PVPA [18] and ZSPP [19]. By contrast, the inorganic materials and organic polymers which were employed for the immobilization of homogeneous catalysts generally exhibited higher or lower catalytic activities than their corresponding homogeneous counterparts, whereas the organic polymer-inorganic hybrid materials as very promising support which were used to immobilize chiral salen Mn(III) complexes and obtained heterogeneous catalysts displayed comparable or even higher conversions and enantioselectivities than those reported in the relevant literatures [17–20].

To the best of our knowledge, there are no reports on hybrid zinc phosphate-phosphonate materials immobilized chiral salen Mn(III) catalysts for the asymmetric epoxidation reaction. Meanwhile, there are relatively few reports using sodium periodate as an oxidant in the system of asymmetric epoxidation. Hence, we have designed and synthesized a novel layered organic polymerinorganic hybrid-zinc poly (styrene-phenylvinylphosphonate)phosphate (ZnPS-PVPA) based on our previous work. This layered compound was prepared under mild conditions in the absence of

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organic template. Noteworthy features of this new compound as support for immobilization of chiral salen Mn(III) complexes are: (1) the hybrid material possesses adjustable of functional organic groups, which allows us to tailor their density, chemical reactivity, and thermal stability [18]; (2) this compound with abundant framework as well as the lavers of the phosphates [21–24]are separated on either side by the pendent organic moieties of the phosphonate groups: (3) the compound can be prepared easily and economically from commercially available sources. Founded on these advantages, the chiral salen Mn(III) complexes were immobilized onto the diphenol-modified layered ZnPS-PVPA through axial coordination for the first time and showed significantly higher enantioselectivities with NaIO₄ as an oxidant system at room temperature for asymmetric epoxidation of unfunctionalized olefins, furthermore, the catalysts could be recycled at least ten times without significant loss of activity and enantioselectivity. Such excellent catalytic effect is likely to attribute to the specific frameworks of ZnPS-PVPA which could provide the advantaged reaction microenvironment for the asymmetric epoxidation. In addition, these novel heterogeneous catalysts could be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level. As far as our information goes, there are scarcely any reports about large-scale reactions in the asymmetric epoxidation of unfunctionalized olefins, which offer a great possibility for application in industry.

2. Experimental

2.1. Material and instruments

(1*R*, 2*R*)-1, 2-diaminocyclohexane, chloromethyl methyl ether (toxic compound), 1-octene, styrene, α -methylstyrene, 4chlorostyrene, indene, *n*-nonane and sodium periodate were supplied by Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers. Styrene was passed through a pad of neutral alumina before use.

FT-IR spectra was recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA), and diffuse-reflectance UV-vis

spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using BaSO₄ as standard. TG analvsis was performed on a SBTQ600 thermal analyzer (USA) with the heating rate of 15 °C · min⁻¹ from 25 to 1000 °C. The Mn content of the catalysts was determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy (AAS). XRD powder pattern was collected on D/MAX-3C diffractometer using graphitemonochromatic Cu K α radiation in the angular range $2\theta = 2-50^{\circ}$ with a step size of 0.02°. Atomic Force Microscope (AFM) was performed on NanoScope Quadrex (USA). The BET surface area was determined with the use of N₂ sorption data measured at 77 K (Quantachrome Autosorb-1). The conversion (with *n*-nonane as internal standard) and the ee value were analyzed by gas chromatography (GC) with Shimadzu GC2014 (Japan) instrument equipped using a chiral column (HP 19091G-B213, $30 \text{ m} \times 30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) or high performance liquid chromatography (HPLC) with Agilent 1200 instrument using Chiralcel OD-H (4.6 mm \times 250 mm) columns.

2.2. Synthesis of zinc poly (styrene-phenylvinylphosphonate)phosphate (ZnPS-PVPA)

The synthesis and characterization of PS-PVPA were accorded to the literature [18] (Scheme 1).

PS-PVPA (6.0 g, 8.5 mmol) was dissolved in 100 ml THF. Hydrated sodium orthophosphate (2.66 g, 17 mmol) dissolved with deionized water was slowly added and vigorously stirred for 1 h. The ratio of polystyrene-phenylvinyl phosphonate parts to inorganic phosphate parts is 0.35: 0.65 in mol stoichiometric. Afterward, this solution of $Zn(Ac)_2 \cdot 2H_2O$ (5.61 g, 25.6 mmol) was slowly added to the reactants with vigorously stirring, accompanied with a step by step temperature rise to 65 °C. The reaction mixture was kept at 65 °C for 72 h. After cooling down to room temperature, the pH of the reaction mixture was adjusted to neutral by addition of triethylamine and then washed with distilled water and ethanol and subsequently dried under vacuum. Primrose yellow solid ZnPS-PVPA was obtained in 90% yield.



Scheme 1. Synthesis of the support.

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2.3. Synthesis of diphenol-modified zinc poly (styrene-
phenylvinylphosphonate)-phosphate (ZnPMPS-PVPA)
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The synthesis of ZnPMPS-PVPA was accorded to the literature [20].

2.4. Grafting chiral salen Mn(III) catalyst onto ZnPMPS-PVPA

The route for preparing the heterogeneous chiral salen Mn(III) catalysts was outlined in Scheme 2. After preswelled in 10 ml of THF for 30 min, ZnPMPS-PVPA (0.50 g) was mixed with chiral salen Mn(III) [4] (1.5 g, 2.36 mmol), sodium hydroxide (adequate amount). And this suspension was stirred for 24 h under reflux. Finally the obtained catalysts were filtered and rinsed thoroughly with THF, CH₂Cl₂, distilled water until the extraction liquid became colorless. The filtrates were collected to be detected until no manganese by atomic absorption spectrometry. After dried in vacuum, the catalysts were yielded with 90–93%. Meanwhile, the manganese contents of the supported catalysts were determined by AAS, which showed values about 0.52–0.65 mmol \cdot g⁻¹ based on the Mn.

2.5. Asymmetric epoxidation of unfunctionalized alkenes

To a mixture of olefins (1 mmol), *n*-nonane (internal standard, 1.0 mmol), heterogeneous catalysts (4.7 mol% of the catalysts, based on the Mn amount in the catalyst) in THF (8 ml) was added a solution of NalO₄ (2 mmol) in H₂O (4 ml). The reaction mixture was stirred magnetically at room temperature for 24 h. The catalyst was precipitated from the reaction mixture by adding hexane (10 ml), then the organic phase was separated and purified on a silica gel column, and then analyzed by GC. The progress of the reaction was monitored by GC to find the optimal conversion and selectivity.

2.6. Large-scale asymmetric epoxidation of α -methylstyrene

In order to detect whether the heterogeneous catalysts have the potential of industrial applications, we performed large-scale asymmetric epoxidation reactions with 40 mmol of α -methylstyrene. The corresponding catalysts (1.88 mmol, respectively), *n*-nonane (internal standard, 40 mmol) were added in THF (320 ml) in turn, and then the solution of NaIO₄ (80 mmol) in H₂O (160 ml) was added and stirred continuously at room temperature for 36 h. Afterward the catalysts were precipitated from the reaction mixture by adding adequate amount of hexane, and then the



Fig. 1. UV-Vis spectra of ZnPS-PVPA (a), chiral salen Mn(III) (b) and immobilized catalyst (3d) (c).

organic phase was separated and purified on a silica gel column, and then analyzed by GC.

3. Results and discussion

3.1. Catalysts characterization

The diffuse-reflectance UV-vis spectra (Fig. 1) can provide evidence for the successful immobilization of salen Mn(III) onto the support. The band at 510 nm is due to the d-d transition of salen Mn(III) complex [25]. For the immobilized salen Mn(III) catalysts, all the characteristic bands appeared in their spectra exhibite a blue shift from 259, 335, 433 and 510 nm to 253, 325, 420 and 503 nm, which indicate that an interaction existed between the salen Mn(III) complex and the diphenol-modified ZnPS-PVPA support. Comparing the IR spectra of heterogeneous salen Mn(III) complexes with the neat chiral salen Mn(III) in Fig. 2, it is found that the main characteristic bands of the heterogeneous catalysts were similar to the neat chiral salen Mn(III). The heterogeneous catalysts and chiral salen Mn(III) have the same absorption peak at 1623 cm⁻¹ ascribed to the stretching vibration of C=N bond in the salen ligand, and the strong absorption peak at 530 cm⁻¹ assigned to Mn–N bond of the salen ligand [26.18]. Hence, the observations suggest that the neat chiral salen Mn(III) has been successfully immobilized onto diphenol-modified ZnPS-PVPA support.



Scheme 2. Synthetic route for the supported catalysts.



Fig. 2. FT-IR spectra of chiral salen Mn(III) and immobilized catalysts(3a~3d).

The TG curves for the supported catalyst **3d** (as a representative catalyst) are shown in Fig. 3. There are three stepwise weight losses in the DTG trace for catalyst **3d**. The first section with a weight loss of 4.59% at 60 –200 °C is corresponded to the loss of the surface or interstitial water. In the temperature range 200–600 °C, the DSC curve shows a sharp endothermic peak at 420 °C with weight loss of 38.49%, which is attributed to the decomposition of the appended organic groups and decomposition of the immobilized heterogeneous complex. The third weight loss is with 11.2% because of the dehydrolysis of ZnHPO₄ to Zn₂P₂O₇ [27] in the temperature range of 650–1000 °C. The result showed that the temperature for decomposition of the supported catalyst were much higher than 200 °C. Generally, organic reactions of heterogeneous catalysis were carried out below 200 °C, therefore, these heterogeneous catalysts had favorable thermal stability.

The X-ray diffraction patterns of the pure support ZnPS-PVPA (a) and immobilized catalyst **3d** (b) are compared in Fig. 4. XRD data shows that the crystalline ZnPS-PVPA and immobilized catalyst **3d** are layered complexes whose interlayer distances calculated according to the formula of Bragg equation ($n\lambda = 2d \sin\theta$) are about 21.12 and 40.87 Å [28], respectively. As also can be seen from the XRD patterns, after the diphenol-modified ZnPS-PVPA was used to immobilize the chiral salen Mn(III) complexes, the intensity of diffraction peaks were significantly lower and the diffraction peaks shifted slightly to lower angle with the increase of the interlayer distance remarkably. There has been reported that the molecule



Fig. 3. DSC-DTG curves of immobilized catalyst 3d.



Fig. 4. XRD patterns of ZnPS-PVPA (a) and immobilized catalyst 3d (b).

diameter of Mn(salen)Cl complex is about 16.1 Å [29] which revealed that the chiral salen Mn(III) could easily introduce in the support. The introduction of salen Mn(III) complexes is the most probable cause to make the zinc layer stretched and become broader. The X-ray diffraction patterns of the heterogeneous catalysts ($3a \sim 3c$) are not shown here, because their diffractograms are similar to the diffraction pattern of the heterogeneous catalyst (3d).

The Nitrogen adsorption—desorption isotherms of immobilized catalyst **3d** exhibit representative type IV isotherms with hysteresis loops (Fig. 5.), confirming that the typical catalyst owns different pore size distribution centered around 23.2 Å. The specific surface area and pore volume of the immobilized catalyst **3d** are $62.3 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.19 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. Compared with ZnPS-PVPA, the surface area and pore volume of immobilized catalyst **3d** apparently increased, whereas pore size decreased unnoticeably (Table 1). Different results have been reported [30,31], where the pore sizes, surface areas, and pore volumes all decreased compared to those of the supports after the immobilization of the chiral salen Mn(III). From Fig. 4, we know that the layers of immobilized catalyst and supervalues are stretched observably. Therefore, it could be deduced that



Fig. 5. Isotherms and distribution of pore diameter of immobilized catalyst 3d.

Table 1

The BET surface areas, pore volumes and average pore sizes ZnPS-PVPA and immobilized catalyst ${\bf 3d.}^{\rm a}$

Sample	Surface area (m²/g) ^b	Pore volume $(\times 10^{-1} \text{ cm}^3/\text{g})^{\text{b}}$	Average pore size (Å) ^b
ZnPS-PVPA	4.9	0.1	27.3
3d	62.3	1.9	23.2

^a The samples were out gassed at 150 °C for 6 h.

^b Surface area, Pore volume, Pore size based on the adsorption data of BJH method.

the chiral salen Mn(III) complex are located on the external surfaces or between the layers of ZnPS-PVPA by the increase of surface area and pore volume. Moreover, the increase the surface area of the catalyst can provide enough chance for substrates to access to the catalytic active sites.

The atomic force microscopy (AFM) was used to illustrate the morphologies and particle sizes of the pure support ZnPS-PVPA and immobilized catalyst **3d**. From Fig. 6, the 3D AFM image of the pure support ZnPS-PVPA has shown that the surface is uneven on account of the aggregation of polystyrene segments. Every thin granule of the support is an aggregation of a mass of smaller particulates to some extent [18]. The 2D photograph of the support clearly indicates that the support has various sizes of channels, pores and caves, and the diameters of the pores are ranged in 10–20 nm. Upon the immobilization of chiral salen Mn(III) on the support, the morphologic have greatly changed. The surface of the immobilized catalyst **3d** has become regularly, and the diameter or

height of immobilized catalyst have become smaller than those of the pure support, which may be ascribed to the effect of the entrapment of salen Mn(III) molecules inside the pores. But the average diameters of these pores and secondary channels among the layers of the catalyst are far greater than substrates, it is deduced that more chances will be able to offer substrates to transfer to the internal catalytic active sites.

3.2. Asymmetric epoxidation

To gain a better catalytic effect, the catalyst **3d** was selected as the typical catalyst to investigate the effects of various reaction parameters such as catalyst amount, solvent, oxidant and axial additive on the asymmetric epoxidation of α -methylstyrene.

3.2.1. The effect of the catalyst amount in the asymmetric epoxidation of α -methylstyrene

In order to optimize the catalyst amount, different amounts of catalyst **3d** were used in the asymmetric epoxidation of α -methylstyrene with NaIO₄ as an oxidant. The best results were obtained with 80 mg (0.047 mmol) of the catalyst (Table 2).

3.2.2. The effect of solvent on the asymmetric epoxidation of α -methylstyrene

In the asymmetric epoxidation of olefins the choice of reaction media is crucially important. Among the mixture of acetonitrile, acetone, tetrahydrofuran, *N*, *N*-dimethylformamide, methanol,



Fig. 6. The AFM images of the pure support ZnPS-PVPA and immobilized catalyst 3d.

Table 2

Optimization of the catalyst ${\bf 3d}$ amounts in the asymmetric epoxidation of $\alpha\text{-methylstyrene.}^{\rm a}$

Entry	Catalyst amount (mg, mmol)	Time (h)	Conv. (%)	ee (%) ^b
1	0 (0)	24	8	5
2	50 (0.029)	24	12	92
3	80 (0.047)	24	97	>99
4	100 (0.059)	24	98	98
5	120 (0.07)	24	98	97

 a $\alpha\text{-methylstyrene}$ (1 mmol), NalO₄ (2 mmol), *n*-nonane (internal standard, 1 mmol), THF (8 ml), H₂O (4 ml), rt. The conversion and the *ee* value were determined by GC with chiral capillary columns HP 19091G-B213 (30 m \times 0.32 mm \times 0.25 μm).

^b Expoxide configuration S.

dichloromethane, chloroform and carbontetrachloride with water were all examined, at the same time, different ratios of tetrahydrofuran/water mixture were also examined. The results are displayed in Table 3, and the data demonstrated that the 2:1 tetrahydrofuran/water mixture was chosen as the best reaction medium, because the higher *ee* was observed. That is due to our support, which contains hydrophobic segments of polystyrene and hydrophilic segments of PVPA in the copolymer [18], make the catalyst possess dual properties which are hydrophobic and hydrophilic. In other words, the heterogeneous catalyst used in mixed solvent has better swelling than either in aqueous solution or in organic solvent. In addition, the heterogeneous catalyst is more readily swelled in tetrahydrofuran than in other solvents, so that they exhibited the higher catalytic activity in tetrahydrofuran/ water mixture solvent.

3.2.3. The effect of the oxidant and axial additive on the asymmetric epoxidation of α -methylstyrene

The effect of various oxidants such as NaOCl, NaIO₄, *m*-CPBA, H₂O₂, and *tert*-BuOOH was investigated in the asymmetric epoxidation of α -methylstyrene catalyzed by the heterogeneous catalyst **3d**. The results are summarized in Table 4. In order to investigate the best oxygen source, we added the suitable axial additive to the reaction mixture for comparison. These axial additives are 4-PPNO for NaOCl, NMO for *m*-CPBA, imidazole for H₂O₂ and NaIO₄ [6,7,32–35]. However, it was also found that the conversions and *ee* values apparently increased in the absence of the axial additives in the asymmetric epoxidation of α -methyl-styrene. These phenomena are not in agreement with other earlier literature reported, in which a good catalytic activity needs an extra axial ligand. When NaOCl, H₂O₂ and *m*-CPBA are used as oxygen source, either in tetrahydrofuran or dichloromethane, only

Table 3

The effect of solvent on the asymmetric epoxidation of α -methylstyrene with NalO₄ catalyzed by the catalyst **3d** at room temperature.^a

Solvent	Time (h)	Conv. (%)	ee (%) ^b
THF/H ₂ O (2:1)	24	97	>99
THF/H ₂ O (1:1)	24	48	95
THF/H ₂ O (1:2)	24	21	94
CH ₃ CN/H ₂ O (2:1)	24	10	99
DMF/H ₂ O	24	66	70
CH ₃ COCH ₃ /H ₂ O	24	20	91
CH ₃ OH/H ₂ O	24	60	90
CH ₂ Cl ₂ /H ₂ O	24	12	76
CCl ₄ /H ₂ O	24	10	30

^a α -methylstyrene (1 mmol), NalO₄ (2 mmol), heterogeneous catalyst **3d** (0.047 mmol), *n*-nonane (internal standard, 1 mmol), rt. The conversion and the *ee* value were determined by GC with chiral capillary columns HP 19091G-B213 (30 m × 0.32 mm × 0.25 μ m).

^b Expoxide configuration S.

Table 4

The effect of various oxidants on the asymmetric epoxidation of α -methylstyrene catalyzed by the catalyst **3d** at room temperature.^a

Oxidant	Solvent	Conv. (%)	ee (%) ^b
NaIO ₄ (2 mmol)	THF/H ₂ O	97	>99
NaIO ₄ (1 mmol)	THF/H ₂ O	77	89
NaIO ₄ (2 mmol)/imidazole	THF/H ₂ O	70	88
H_2O_2 (2 mmol)	THF	16	74
H ₂ O ₂ (2 mmol)/imidazole	THF	10	60
NaOCl (2 mmol)	CH ₂ Cl ₂	95	63
NaOCl (2 mmol)/4-PPNO	CH_2Cl_2	77	16
tert-BuOOH (2 mmol)	CH_2Cl_2	37	20
m-CPBA	CH ₂ Cl ₂	>99	20
<i>m</i> -CPBA/NMO	CH_2Cl_2	>99	7

^a α-methylstyrene (1 mmol), axial additives (0.2 mmol), heterogeneous catalyst **3d** (0.047 mmol), *n*-nonane (internal standard, 1 mmol), THF (8 ml), H₂O (4 ml), CH₂Cl₂ (8 ml), 24 h, rt. The conversion and the *ee* value were determined by GC with chiral capillary columns HP 19091G-B213 (30 m × 0.32 mm × 0.25 μm).

^b Expoxide configuration S.

7–74% *ee* values of α -methylstyrene were obtained. The results showed that NaIO₄ is the best oxygen source because this oxidant can give better conversion (97%) and *ee* value (excess 99%). In addition, different equivalents of the oxidant were tested, and the data showed that the higher catalytic activity obtained with 2 equivalents of the oxidant than that with 1 equivalent of the oxidant. From Table 3, the 2:1 tetrahydrofuran/water mixture was chosen as the best reaction medium. This is because the oxidant sodium periodate only has certain solubility in tetrahydrofuran. The more ratios we add, the more sodium periodate will dissolve. When 2 equivalents NaIO₄ was used, the oxidant could provide moderate source of oxygen for the catalytic reaction, and excellent activity and enantioselectivity were obtained. Consequently, the optimum molar ratio of olefin to oxidant is 1: 2.

3.2.4. Enantioselective epoxidation of unfunctionalized olefins

The catalytic activity and selectivity of catalysts $(3a \sim 3d)$ were explored for the asymmetric epoxidation of various olefins using NaIO₄ as an oxidant system under optimized conditions (with *n*-nonane as internal standard). The optimum conditions used for the asymmetric epoxidation of olefins with this heterogenized system were catalyst, oxidant and substrate in a molar ratio of 0.047: 2: 1. Meanwhile, in order to investigate the effect of the support on the catalytic activity of these supported catalysts, the homogeneous chiral salen Mn(III) catalyst **3** was examined for comparison under the same conditions. The catalytic results, summarized in Table 5, show that the heterogeneous catalysts (**3a** ~ **3d**) effectively catalyze the epoxidation of the various olefins in comparable or even higher conversion and enantioselectivity than those of homogeneous catalyst.

As can be seen from Table 5, when nonactivated terminal 1octene was used as a substrate, there was a significant improvement in enantioselectivity (ee: 50-75%, entries 2-5) over the homogeneous system (ee: 40%, entry 1). In the epoxidation of aromatic olefins, the catalytic system showed excellent catalytic performance. Obviously, the enantioselectivity for styrene (ee: 60-67%, entries 7-10) and 4-chlorostyrene (ee: 62-79%, entries 17–20) were higher with immobilized catalysts compared with homogeneous catalyst (ee: 49, 48%, entries 6, 16; respectively) under identical reaction conditions. Especially, in the case of α -methylstyrene, the conversion could reach 97% and *ee* values could exceed 99% (Table 5, entry 15), in which the ee values are outstanding higher than 34% ee for the homogeneous catalyst. Notably, the influence of the support could not be ignored to the chiral induction for the asymmetric epoxidation. Furthermore, a few similar results have been reported to give higher ee values

Table 5

Asymmetric epoxidation of alkenes catalyzed by homogeneous and heterogeneous catalysts ($3a \sim 3d$) with NaIO₄ as oxidant systems.^a



^a alkenes (1 mmol), NaIO₄ (2 mmol), homogeneous catalyst **3** and heterogeneous catalysts (0.047 mmol, respectively), *n*-nonane (internal standard, 1 mmol), THF (8 ml), H₂O (4 ml), rt.

^b Conversions were determined by GC, by integration of product peaks against an internal quantitative standard (nonane), correcting for response factors.

 c Determined by GC with chiral capillary columns HP 19091G-B213 (30 m \times 0.32 mm \times 0.25 μm) or HPLC with chiral OD (4.6 mm \times 250 mm) column.

^d Epoxide configuration *R*.

^e Expoxide configuration S.

^f Epoxide configuration 1*S*,2*R*.

than the homogeneous ones for the asymmetric epoxidation and this was attributed to the confinement effect of supports [36]. The support ZnPS-PVPA was regularly layered structure, which still kept good layered structure after the immobilization of salen Mn(III) catalyst and owned larger surface area, various sizes of pores, micropores, and channels as compared with the support. Accordingly, the increase in enantiomeric excess may be attributed to the microenvironment effect and confinement effect differing from either pure polystyrene or inorganic supports, these effects are provided by the layered structure and micropores of ZnPS-PVPA and the balance adjustment between the hydrophobic of polystyrene parts and the hydrophilic of phosphate parts [19].

In addition, the asymmetric epoxidation of the relatively bulkier olefin like indene were also tested by these heterogeneous catalysts. Whereas, the catalytic system showed a lower or comparable catalytic performance (ee: 52-73%, entries 22-25) than that of homogenous catalyst 3 (ee: 61%, entries 21), the reason may be that indene is too large to accommodate into the micropores or between the layers of ZnPS-PVPA. So that indene may merely react with a few active sites on the external surface of the ZnPS-PVPA. These results are different from Zou [20] reported, where the chiral salen Mn(III) catalyst immobilized onto zirconium phosphonate and showed an ee value of 99.5% for the asymmetric epoxidation of indene. The most probable explanation is that the support of zirconium phosphonate is amorphous with bigger nanopore sizes, surface areas, and pore volumes [18] compared to those of the support ZnPS-PVPA. Moreover, there are more chances for the bulkier indene to approach the catalytic active sites in the microporous and channels of the Zou's catalyst. However, in the case of small olefin like styrene and α -methylstyrene, the enantiomeric excess values obtained by the

The recycles of catalyst **3d** in the asymmetric epoxidation of α -methylstyrene.^a

Run	Time (h)	Conv. (%)	ee (%) ^b	Mn leached (%) ^c
1	24	97	>99	0.6
2	24	97	>99	0.3
3	24	96	>99	0
4	24	95	99	0
5	24	95	97	0
6	24	93	97	0
7	24	92	96	0
8	24	90	95	0
9	24	90	93	0
10	24	88	92	0

^a α-methylstyrene (1 mmol), NaIO₄ (2 mmol), catalyst **3d** (0.047 mmol), *n*-nonane (internal standard, 1 mmol), THF (8 ml), H₂O (4 ml), rt. The conversion and the *ee* value were determined by GC with chiral capillary columns HP 19091G-B213 (30 m × 0.32 mm × 0.25 μm).

^b Expoxide configuration *S*.

^c Determined by atomic absorption spectrometry.

Zou's catalyst were not satisfactory. Hence, the different types of supports obviously affected the reaction performance for the heterogeneous asymmetric epoxidation. Further studies concerning the mechanism of this novel behavior for these immobilized catalysts are currently in progress.

3.3. The recycling of the supported chiral salen Mn(III) catalyst

To study the stability and reusability of the supported chiral salen Mn(III) catalysts, we chose catalyst 3d in repeated epoxidation reactions with α -methylstyrene as a model substrate. The catalyst was separated form the reaction mixture after each experiment by simple filtration, washed with water and hexane, dried carefully before using it in the subsequent run. Furthermore, the filtrates were collected for determination of Mn leaching. No manganese was detected in the filtrates after the first two runs by atomic absorption spectrometry. The data in Table 6 indicate only a slightly decrease in activity and enantioselectivity after ten consecutive times (conversion: from 97% to 88%; ee: from excess 99% to 92%). The decrease in the conversion and enantioselectivity for more cycles might be caused by a physical loss during the recovery process and/or by a gradual degradation of catalysts under the epoxidation condition and continuous stirring. Moreover, because channels, pores and cavums with various sizes and shapes of catalysts were partly plugged after several recycle epoxidations, it can induce the decrease of the activity.

3.4. Preparation for large-scale asymmetric epoxidation of α -methylstyrene

We further performed large-scale asymmetric epoxidation reactions with 40 mmol of α -methylstyrene (Table 7). The corresponding catalyst loading as in the experimental scale was used. The large-scale experiments can be facilely carried out using the

Table 7

Large-scale asymmetric epoxidation of α -methylstyrene catalyzed by heterogeneous catalysts (**3a ~ 3d**) with NalO₄ as oxidant systems.^a

Entry	Substrate	Catalyst	Time (h)	Conv. (%)	ee (%) ^b
1		3a	36	85	97
2	\land	3b	36	89	98
3		3c	36	88	98
4		3d	36	90	99

^a α-methylstyrene (40 mmol), NalO₄ (80 mmol), heterogeneous catalysts (1.88 mmol, respectively), *n*-nonane (internal standard, 40 mmol), THF (320 ml), H₂O (160 ml), rt. The conversion and the *ee* value were determined by GC with chiral capillary columns HP 19091G-B213 (30 m × 0.32 mm × 0.25 μm). ^b Exposide configuration *S*.

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same procedure as for the experimental scale reactions. As can be seen from the result, delightfully, the enantioselectivity maintained at the same level for the large-scale reactions.

4. Conclusions

Chiral salen Mn(III) complex has been first immobilized on diphenol-modified layered of ZnPS-PVPA by axial coordination, which was incorporated into the interlayer space of support, and was able to transfer an oxygen atom from NaIO₄ to an olefin substrate exhibiting significant catalytic activity. The obtained excellent conversions and enantioselectivities were mainly attributed to the special structure of the novel layered support ZnPS-PVPA. In summary, we demonstrate that supported chiral salen Mn(III) catalysts are featured by: (i) easy preparation and handling of the catalysts and commercially available of support; (ii) no need of axial additive in the catalytic system; (iii) great conversions and much higher ee values than that observed in the homogeneous phase; (iv) convenient and effective recycles and preferable stability (v) could be efficiently used in large-scale asymmetric epoxidation reactions for the first time, which may carry out the possibility for wide application in organic synthesis as well as in industry of chiral Jacobsen-type catalyst.

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