

## 有机-无机杂化载体-聚(苯乙烯-苯乙烯基膦酸)-磷酸氢锆- 在烯烃环氧化反应中的应用

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**摘要:** 有机聚合物-无机杂化载体-聚(苯乙烯-苯乙烯基膦酸)-磷酸氢锆-轴向固载手性 Salen Mn(III) 催化剂, 将其应用于非官能烯烃的多相不对称环氧化反应。结果表明: 在没有昂贵轴向添加剂参与下, 产率与对映选择性均急剧增加。以间氯过氧苯甲酸 (*m*-CPBA) 为氧化剂催化氧化  $\alpha$ -methylstyrene, 转化率从 25.0% 上升到 98.8%; 对映选择性从 5.3% 提高到 67.3%。催化剂在循环使用 5 次以后, 催化活性无明显改变。

**关键词:** 苯氧基修饰聚(苯乙烯基-苯乙烯基膦酸)-磷酸氢锆; 手性 Jacobsen 催化剂; 非功能化烯烃; 不对称非均相环氧化

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## Organic-Inorganic Hybrid Support-Zirconium Poly (Styrene-Phenylvinylphosphonate)- Phosphate: Application for Heterogeneous Olefin Epoxidation

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**Abstract:** The chiral Mn(III) salen catalyst axially immobilized onto an organic-inorganic hybrid support-phenoxy modified zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA) can afford dramatically increased conversion and ee (Enantiomeric excess) value in the absence of expensive O-coordinating axial bases for the asymmetric epoxidation. Especially for the epoxidation of  $\alpha$ -methylstyrene in the *m*-chloroperbenzoic acid (*m*-CPBA) oxidant system (conv.%: from 25.0% to 98.8%; ee%: from 5.3% to 67.3%). Moreover, the as-synthesized catalyst is relatively stable and can be recycled at least five times without significant loss of activity and enantioselectivity.

**Key words:** phenoxy modified zirconium poly (styrene-phenylvinylphosphonate)-phosphate; chiral Jacobsen's homogeneous catalyst; unfunctionalized olefins; asymmetric heterogeneous epoxidation

## 0 Introduction

The chiral Mn(III) salen complexes have proven to be extremely efficient homogeneous counterpart for asymmetric epoxidation of unfunctionalized olefins<sup>[1-2]</sup>, 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<sup>[3]</sup>. However, separation of such homogeneous catalysts from the reaction mixture and reuse are still problematic. Moreover, it suffers deactivation in

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homogeneous phase by formation of dimeric  $\mu$ -oxo Mn (IV) species, which are inactive in the alkenes epoxidation<sup>[4]</sup>. Consequently, heterogenization of homogeneous Mn (III) salen complexes has become an important strategy for obtaining supported catalysts that retain the active catalytic sites of a homogeneous analogue while providing advantages of easy separation and recycling of the catalyst<sup>[5-6]</sup>. Several papers<sup>[7-8]</sup> have recently reported the heterogenization of chiral salen transition metal complexes to solid supports, including mesoporous molecular sieves, mesoporous silica and Wangs resin. However, in most cases, these heterogeneous catalysts have tended to have inferior catalytic properties compared to their homogeneous counterparts. Besides, almost all the asymmetric epoxidation reactions<sup>[9-11]</sup> catalyzed by heterogeneous Mn (III) salen complexes are in need of excess and expensive additives as axial bases that makes it insignificant for industry application.

Zirconium phosphates and zirconium phosphonates are types of layered multi-functional materials with high thermal, acidic, basic and chemical stability<sup>[12]</sup>. However, the organic-inorganic hybrid zirconium phosphate-phosphonates  $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{PR})_x$  ( $x=0-2$ , R is organic polymer group) are rarely reported, especially in the application of catalyst support for homogeneous chiral Mn (III) salen catalyst in heterogeneous catalysis. Organic polymer-inorganic hybrids materials constitute a new class of compounds in the exploratory research area of advanced materials design. They are expected to possess both the advantages of organic polymer such as light weight, flexibility, and inorganic materials such as high strength, heat stability and ordered structural feature. Our research has, for many years, been concerned with metal phosphonate chemistry for catalysts and catalyst supports<sup>[13-19]</sup>. Recently, we have reported the chiral Mn(III) salen complex axially immobilized on diamine or sulfuric groups modified ZSPP<sup>[14-15]</sup>、ZPS-PVPA<sup>[18-19]</sup>、ZPS-IPPA<sup>[16]</sup> and their catalytic epoxidation of styrene, with high conversion, enantioselectivity and reusability. It needs cancerigenic chloro-methylether when the benzene rings of support are chloro-methylated. While,

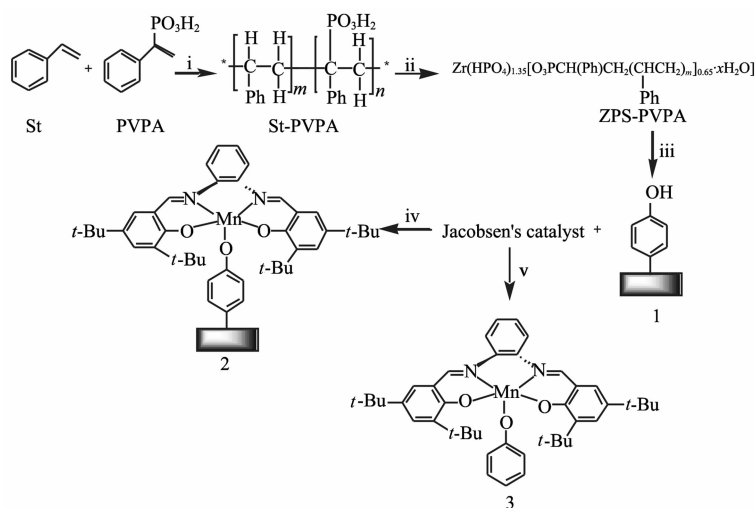
excess and expensive additives as axial bases are still required to improve the catalytic activity of immobilized catalysts. In this work, the chiral Mn(III) salen complexes is axially immobilized onto organic-inorganic hybrid support-zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA) by phenoxy group, which is also a promising method for the heterogenization of Schiff base complexes<sup>[20]</sup>.

## 1 Experimental

### 1.1 Materials and methods

(1S, 2S)-(-)-1,2-diaminocyclohexane,  $\alpha$ -methylstyrene, indene, n-nonane, N-methylmorpholine N-oxide (NMO), 4-Phenylpyridine-N-oxide (PPNO) and *m*-chloroperbenzoic acid (*m*-CPBA) were purchased from Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers.

FTIR spectra were recorded using KBr pellets on a Bruker RFS100/S spectrophotometer (USA). Diffuse reflectance UV-Vis spectra of the solid samples were recorded using a spectro-photometer with an integrating sphere using  $\text{BaSO}_4$  as standard. Scanning electron microscopy (SEM) analysis was performed on a KYKY-EM 3200 (KYKY, China) microscopy. Transmission electron microscopy (TEM) analysis was performed on a TECNAI10 (PHILIPS, Holland) apparatus. AFM was recorded on the instrument of NanoScope Quadrex (veeco USA).  $\text{N}_2$  adsorption-desorption analysis was carried out at 77 K on an Autosorb-1 apparatus (Quantachrome). The surface areas were determined by BET equation and the pore diameters were estimated according to the BJH model. The Mn content of the catalysts was determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy (AAS). The conversions (using n-nonane as the internal standard) and the ee values were analyzed by gas chromatography (GC) using a Shimadzu GC 2010 (Japan) instrument equipped with a chiral column (HP19091G-B213, 30 m $\times$ 0.32 mm $\times$ 0.25  $\mu\text{m}$ ) and FID detector, injector 230  $^\circ\text{C}$ , detector 230  $^\circ\text{C}$ . The column temperature for indene,  $\alpha$ -methylstyrene was in the range of 80~180  $^\circ\text{C}$ .



Reagents: (i) BPO, EtPOAc, reflux, 24 h; (ii)  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4$ , THF, 70 °C, 24 h; (iii)  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ , EtOH, 50 °C 20 h; (iv)  $\text{Mn}(\text{salen})\text{Cl}$ , NaOH, THF, reflux, 24 h; (v) PhONa,  $\text{Mn}(\text{salen})\text{Cl}$ , EtOH, 80 °C, 3 h

Scheme 1 Synthetic route for the heterogeneous catalysts

## 1.2 Preparation of ZPS-PVPA

The synthesis and characterization of ZPS-PVPA have been reported early by our group<sup>[18]</sup>.

## 1.3 Preparation of ZHPS-PVPA (1)

ZPS-PVPA (6.00 g, 8.55 mmol) was added to ethanol (80.0 mL) containing concentrated sulfuric acid (3.44 g, 35.0 mmol) and catalyst  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (132 mg, 0.488 mmol) and this suspension was stirred for 30 min at 50 °C. Then  $\text{H}_2\text{O}_2$  (13.2 mL) was added to the mixture and the mixture was stirred for an additional 20 h. The solid was filtrated and washed with ethanol and deionized water until neutrality to give ZHPS-PVPA. Yield: 86.5%.

## 1.4 Preparation of ZHPS-PVPA - [Mn(III) salen complex] (2)

A mixture of  $\text{Mn}(\text{salen})\text{Cl}$  (2.73 g, 4.30 mmol), ZHPS-PVPA (0.50 g) and sodium hydroxide (0.150 g, 3.75 mmol) was added to tetrahydrofuran (80.0 mL) and the suspension was stirred for 20 h under reflux. The mixture was then filtrated, washed thoroughly with ethanol  $\text{CH}_2\text{Cl}_2$  and demonized water, respectively, to produce (2) as dark brown powder and dried in vacuo. The heterogeneous chiral Mn(III) salen complex catalyst was thoroughly washed by ethanol and  $\text{CH}_2\text{Cl}_2$  until no peaks could be detected from the UV-Vis spectra of the filtrate (with  $\text{CH}_2\text{Cl}_2$  as reference). The amount of salen Mn(III) complex was  $0.38 \text{ mmol} \cdot \text{g}^{-1}$  determined by AAS

based on the Mn element. Yield: 90.0%.

## 1.5 Preparation of homogeneous chiral Jacobsens catalyst

Chiral Jacobsens catalyst was synthesized according to the standard literature procedures<sup>[1]</sup>.

## 1.6 Preparation of homogeneous chiral Mn(salen) OPh complexes (3)

Mn(III) salenCl (1.56 g, 2.56 mmol) and PhONa (0.359 g, 3.09 mmol, and 1.2 equiv.) were added ethanol (60.0 mL), and the mixture was refluxed for 5 h at 80 °C. (Scheme 1). After cooling to room temperature, ethanol was removed.  $\text{CH}_2\text{Cl}_2$  was added, and the organic phase was washed with distilled water, then washed with saturated NaCl solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removing  $\text{CH}_2\text{Cl}_2$  gives brown-dark solid Mn(III) salenOPh complexes, yield: 80.0%.

## 1.7 Asymmetric epoxidation of unfunctionalized olefins

The method was according to the reference<sup>[18]</sup>.

# 2 Results and discussion

## 2.1 Characterization

The immobilized catalyst 2 was characterized by FTIR, DR UV-Vis, AAS, SEM, and TEM. FTIR spectra and the DR UV-Vis spectra of catalyst 2 match well with the expected chemical structure of the chiral Mn(III) salen complex. The presence of the characteristic imine

band at  $1\,630\text{ cm}^{-1}$  in the FTIR spectra and the broad bands at near 250, 320 and 420 nm in the diffusion reflection UV-Vis spectra confirms the successful anchoring of the chiral homogeneous Jacobsens catalyst axially coordinated onto ZPS-PVPA by phenoxy group. The amount of chiral Mn(III) salen complex is  $0.36\text{ mmol}\cdot\text{g}^{-1}$  as determined by AAS based on the Mn element. XPS spectrum **2** gives further evidence for the successful immobilization based on the fact that the characteristic peak at 641.2 eV of  $\text{Mn}2p_{3/2}$  is clear. The SEM (Fig.1) and TEM (Fig.2) images indicate that the diameter of the particles of the heterogeneous catalyst **2** is in submicron region. Actually for the micro-crystals of amorphous zirconium phosphonate, the layer structure follows the arrangement of “order in short range, but disorder in long distance”, thus the possible structure of the title catalyst is deduced as shown in the inset of Fig.3.

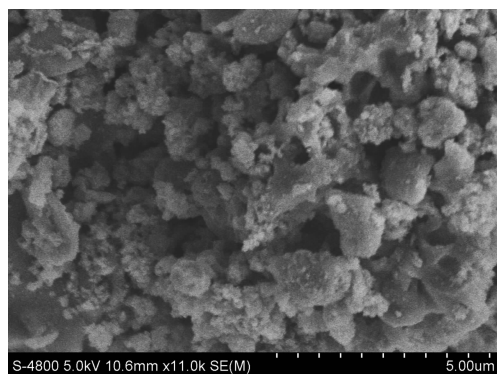


Fig.1 SEM photograph of heterogeneous catalyst **2**

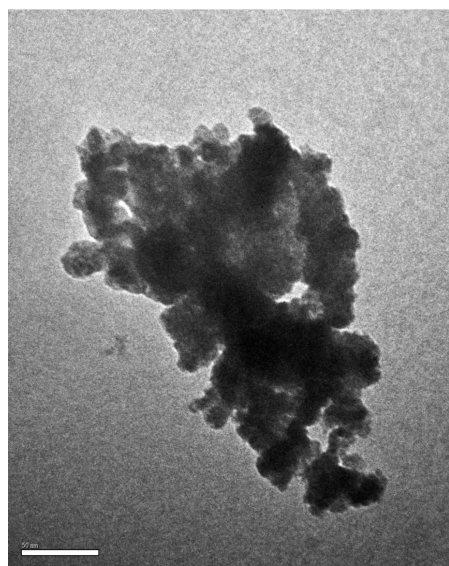


Fig.2 TEM photograph of heterogeneous catalyst **2**

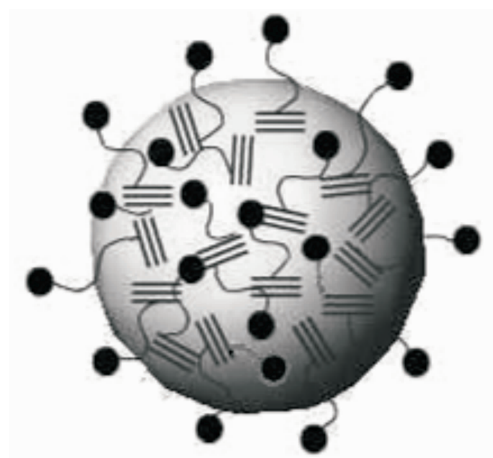
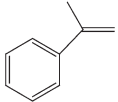
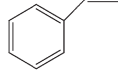
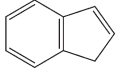


Fig.3 Possible structure of the heterogeneous catalyst **2**

## 2.2 Catalytic activities

The catalytic activity of chiral heterogeneous catalyst **2** was explored for the asymmetric epoxidation of simple unfunctionalized olefins using  $\text{NaClO}/\text{PPNO}$  or  $m\text{-CPBA}/\text{NMO}$  as an oxidant system in the presence of 5 mol% of the catalyst (based on Mn), Jacobsens catalyst and corresponding homogenous chiral Mn(salen) OPh were also examined for comparison purposes. The results are summarized in Table 1. The racemic samples of the epoxides were independently prepared by the epoxidation of corresponding alkenes with  $m\text{-CPBA}$  in  $\text{CHCl}_3$  [19]. All reactions proceed smoothly. When it comes to the Mn(Salen) OPh, the classic Jacobsens catalyst affords somewhat higher ee values at the equal conversions; this proves that the counter-anion plays a little role in reaction to some degree. When  $\alpha$ -methylstyrene is used as substrate with catalyst **2**, there is a significantly higher enantioselectivity than that observed for their corresponding homogeneous counterpart, and the increase in ee values is mainly attributed to the unique spatial environment constituted by the axial rigid bulky group and the microenvironment effect of ZPS-PVPA immobilized chiral Mn(III) salen complex, which results from the various caves, holes, porous and channels with different shape and size existed in the ZPS-PVPA supports and accommodated immobilization of chiral Mn(III) salen catalytic active sites, and the balance adjustment between the hydrophobic of polystyrene parts and the hydrophilic of phosphate parts. And these features of

**Table 1** Asymmetric epoxidation of alkenes catalyzed by catalyst **2** with NaClO<sup>a</sup> or *m*-CPBA<sup>b</sup> as oxidants

Entry	Substrate	Catalyst	Oxidant	Time / h	Temp / °C	Conv. / % <sup>c</sup>	ee / % <sup>d</sup>
1		Jaco	NaClO/PPNO	6	20	99.9	54.0 <sup>e</sup>
2		<b>3</b>	NaClO/PPNO	6	20	99.5	52.3 <sup>e</sup>
3		<b>2</b>	NaClO/PPNO	24	20	98.9	66.2 <sup>e</sup>
4		<b>2</b>	NaClO	24	20	95.5	73.9 <sup>e</sup>
5		<b>2</b>	NaClO	24	0	87.6	74.2 <sup>e</sup>
6		Jaco	<i>m</i> -CPBA/NMO	1	0	99.8	52.0 <sup>e</sup>
7		<b>3</b>	<i>m</i> -CPBA/NMO	1	0	99.8	49.8 <sup>e</sup>
8		<b>2</b>	<i>m</i> -CPBA/NMO	2	0	25.0	5.3 <sup>e</sup>
9		<b>2</b>	<i>m</i> -CPBA	2	0	98.8	67.3 <sup>e</sup>
10		<b>2</b>	<i>m</i> -CPBA	4	-78	65.5	68.2 <sup>e</sup>
11		Jaco	NaClO/PPNO	6	20	99.9	38.5 <sup>f</sup>
12		<b>2</b>	NaClO/PPNO	24	20	70.4	4.9 <sup>f</sup>
13		<b>2</b>	NaClO	24	20	66.4	25.8 <sup>f</sup>
14		Jaco	<i>m</i> -CPBA/NMO	1	0	99.9	47.0 <sup>f</sup>
15		<b>2</b>	<i>m</i> -CPBA/NMO	2	0	32.8	11.6 <sup>f</sup>
16		<b>2</b>	<i>m</i> -CPBA	2	0	87.3	12.9 <sup>f</sup>
17		<b>2</b>	<i>m</i> -CPBA	4	-78	85.3	23.4 <sup>f</sup>
18		Jaco	NaClO/PPNO	6	20	98.8	65.0 <sup>g</sup>
19		<b>2</b>	NaClO/PPNO	24	20	76.2	56.6 <sup>g</sup>
20		<b>2</b>	NaClO	24	20	63.1	77.8 <sup>g</sup>
21		Jaco	<i>m</i> -CPBA/NMO	1	0	99.9	65.0 <sup>g</sup>
22		<b>2</b>	<i>m</i> -CPBA/NMO	2	0	49.9	23.5 <sup>g</sup>
23		<b>2</b>	<i>m</i> -CPBA	2	0	98.7	56.6 <sup>g</sup>
24		<b>2</b>	<i>m</i> -CPBA	4	-78	92.3	78.8 <sup>g</sup>

<sup>[a]</sup>Reactions were carried out at desired temperature in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) with NaClO aqueous solution (pH value of 11.3, 0.55 mol·L<sup>-1</sup>, 1.37 equiv., 1.25 mL), alkene (0.5 mmol), PPNO (2.5 mmol, if necessary), nonane (internal standard, 0.5 mmol) and immobilized Mn(III) salen complexes (0.025 mmol, 5.0 mol%), based on the Mn element

<sup>[b]</sup>Reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) with *m*-CPBA (1.0 mmol) and NMO (2.5 mmol, if necessary). And nonane (internal standard, 0.5 mmol)

<sup>[c]</sup>Conversion was determined by GC, by integration of product peak against an internal quantitative standard (nonane), correcting for the response factor

<sup>[d]</sup>Determined by GC with a chiral capillary column (HP19091G-B233, 30 m×0.25 mm×0.25 μm)

<sup>[e]</sup>Epoxide configuration *S*<sup>[19]</sup>

<sup>[f]</sup>Epoxide configuration *S*<sup>[19]</sup>

<sup>[g]</sup>Epoxide configuration 1*S*, 2*R*<sup>[19]</sup>

the ZPS-PVPA organic-inorganic hybrids support are different from either common polystyrene or pure inorganic support<sup>[14]</sup>. Furthermore, the catalytic activity and enantioselectivity of catalyst **2** for the relatively hindered alkenes like indene is comparable to the chiral homogenous Jacobsens catalyst. This shows that the catalytic centers located in the caves, holes, porous or channels of ZPS-PVPA are easily accessible for the bulkier substrates too. However, in the case of styrene, enantioselectivity and conversion are both not encouraging.

To our surprise, in the absence of O-coordinating axial additives, all reactions also proceed smoothly. The heterogeneous catalyst **2** even shows higher ee values at the same conversion level compared to the results obtained in the presence of additives. Especially, in *m*-CPBA oxidant system for the epoxidation of  $\alpha$ -methylstyrene (Entry 8 vs Entry 9), the results are more obvious, these observations are not in agreement with lots of earlier reports on the Mn(III) salen complex<sup>[9-11]</sup>. The explanation for this novel behavior may be that the phenoxyl linkers, which have longer and more rigid



than those usually employed linkers to prevent possible chain folding, would allow facile access of the olefin substrate to the metal center. Besides, the axial rigid bulky group actually plays a part in the O-coordinating axial bases that are essential for both catalyst stability and selectivity. In contrast, in the presence of O-coordinating axial bases additive, it may disturb the microenvironment of the heterogeneous catalytic epoxidation. For example, in the NaClO aqueous/organic biphasic system, the layers of ZPS-PVPA are expanded in that the layers are peeled off by polar water molecule and hydroxyl or even partly decompose and more secondary channels are formed, and the original secondary channels are also enlarged, as a result, some of the embed catalytic active sites are exposed in the base reaction solution, the substrates and the reactants could easily diffuse to these catalytic sites through the enlarged secondary channels, even if the O-coordinating axial bases additive PPNO is coordinated to the chiral Mn(III) salen complex, the enlarged secondary channels can overcome the influence that the increasing size of molecular makes the caves, holes, porous, microporous, channels and secondary channels of support too crowd each other to afford better or comparable micro-environment or confinement effect. However, in the *m*-CPBA oxidation system, the nanoparticles of immobilized catalyst gather together, and the structure of the catalyst is rigid and very stable with relatively less secondary channels, and part of the

embed catalytic active sites can not work effectively. When the O-coordinating axial bases additive is added to the chiral Mn(III) salen complex that may not lead to a well-defined molecular geometry about the Mn center. And because of the gathering, the surface area, pore volume, and pore diameter are likely decreasing on immobilization of chiral Mn(III) salen complex onto the parent support ZPS-PVPA. Moreover, the relatively small pore size of the obtained catalysts would increase the diffusion resistance of reactants to the active sites located on the inner surfaces of the support. Thus, this catalyst exhibits dramatically decreased performance. In addition, due to the gathering, the size of the obtained catalysts in pore volume, pore diameter and channel may not be match with substrates, which leads to the decrease in chirality recognition, thus it is impossible to optimize the reactivity and conformation of the complex.

We applied catalyst **2** in repeated epoxidation reactions with  $\alpha$ -methylstyrene as a model substrate in the *m*-CPBA system. At the end of each cycle, the catalyst was precipitated from the reaction system by adding hexane and subsequently used in next runs without further purification. The filtrate shows no trace of the metal complex on UV-Vis and by AAS after the first run, indicating that the chiral Mn(III) salen complex was strongly bonded on the phenoxyl modified ZPS-PVPA supports. The data in Table 2 show only a slightly decrease in activity and enantioselectivity for

**Table 2** Recycling of immobilized catalyst **2** in the asymmetric epoxidation of  $\alpha$ -methylstyrene with *m*-CPBA as oxidants<sup>a</sup>

Entry	Cycle	Catalyst	Oxidant	Temp / °C	Conv. / (%·h) <sup>b</sup>	ee / % <sup>c</sup>
1	Fresh	<b>2</b>	<i>m</i> -CPBA	0	98.8(2)	67.3 <sup>d</sup>
2	2	<b>2</b>	<i>m</i> -CPBA	0	97.9(2)	65.1 <sup>d</sup>
3	3	<b>2</b>	<i>m</i> -CPBA	0	97.5(2)	63.1 <sup>d</sup>
4	4	<b>2</b>	<i>m</i> -CPBA	0	95.5(2)	62.5 <sup>d</sup>
5	5	<b>2</b>	<i>m</i> -CPBA	0	95.2(2)	62.5 <sup>d</sup>
6	6	<b>2</b>	<i>m</i> -CPBA	0	92.8(2)	60.2 <sup>d</sup>
7	7	<b>2</b>	<i>m</i> -CPBA	0	85.8(3)	58.7 <sup>d</sup>
8	8	<b>2</b>	<i>m</i> -CPBA	0	77.8(3)	58.5 <sup>d</sup>
9	9	<b>2</b>	<i>m</i> -CPBA	0	70.1(4)	54.8 <sup>d</sup>
10	10	<b>2</b>	<i>m</i> -CPBA	0	68.8(4)	54.2 <sup>d</sup>
11	11	<b>2</b>	<i>m</i> -CPBA	0	53.6(5)	52.4 <sup>d</sup>

<sup>[a]</sup>See Table 1; <sup>[b]</sup>See Table 1; <sup>[c]</sup>See Table 1; <sup>[d]</sup>Epoxide configuration S<sup>[19]</sup>

the first five runs (Conv%: from 98.8% to 95.2%; ee%: from 67.3% to 62.5%). Further recycling of heterogeneous catalyst results in poor conversions, however, still higher enantioselectivity than that of homogeneous counterpart was obtained even after ten cycles. The well performance of these heterogeneous catalysts for ee may be mainly due to the support integrating properties of the inorganic and organic components. The microenvironment of ZPS-PVPA for asymmetric epoxidation, are consisted of hydrophobic polystyrene parts, the hydrophilic hybrid zirconium phosphonate parts, and their self-assembled layered structure with nanometer scale. The decrease in the activity for more cycles might be caused by a physical loss during the recovery process and/or by a gradually degradation of catalysts under the epoxidation condition and continuously stirring.

### 3 Conclusions

In conclusion, the title catalyst affords remarkably increase of conversion and ee values in the absence of expensive O-coordinating axial bases for the asymmetric epoxidation of olefins, especially for the epoxidation of  $\alpha$ -methylstyrene (Conv%: from 25.0% to 98.8%; ee%: from 5.3% to 67.3%) in the *m*-CPBA oxidant systems. To the best of our knowledge, there are no reports on the asymmetric epoxidation generating the products in very good conversions and excellent enantioselectivity under mild conditions without using any additives in the heterogeneous chiral Mn(III) salen system, which may overcome the last obstacle for wide application in organic synthesis as well as in industry of chiral Jacobsens catalyst. More detailed studies concerning the mechanism of this novel behavior for these immobilized catalysts are currently in progress.

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