Rapid Communication

Novel organic polymer–inorganic hybrid material zinc poly (styrene-phenylvinylphosphonate)-phosphate prepared with a simple method

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ABSTRACT

A novel type of organic polymer–inorganic hybrid material layered crystalline zinc poly(styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPP) was synthesized under mild conditions in the absence of any template. And the ZnPS-PVPP were characterized by FT-IR, diffusion reflection UV–vis, AAS, N_2 volumetric adsorption, SEM, TEM and TG. Notably, this method was entirely different from the traditional means used for preparing other zinc phosphonate. Moreover, it could be deduced that ZnPS-PVPP possessed the potential applications for catalyst supports. In the initial catalytic tests, the catalysts immobilized onto ZnPS-PVPP showed comparable or higher activity and enantioselectivity with that of catalysts reported by our group in the asymmetric epoxidation of unfunctional olefins.

1. Introduction

Metal phosphonate chemistry has attracted considerable attention in recent years because of their versatile framework topologies as well as their potential applications in the areas of catalysis, ion exchange, photochemistry and materials chemistry [1,2]. The layered phosphonates attract special interests due to their unique properties, such as their high thermal stability and versatility of organic functional groups that could be introduced [3]. Originally, work in this area was focused on group IV metal phosphonates [4]. Consequently, research in the zirconium phosphates and zirconium phosphonates field is active, which have involved many aspects such as intercalation chemistry [5,6] and proton conductivity [7].

In the previous works, our groups have reported a series of organic–inorganic hybrid zirconium phosphonate–phosphates $Zr(HPO_4)_{2-x}(O_3P–G)_x \cdot nH_2O$ ($x=0–2$, G is organic groups) as various kinds of catalysts or catalyst supports, such as zirconium [N-(phosphonomethyl)iminodiacetic acid-phosphate] $Zr(HPO_4)$ $[O_3PCH_2N(CH_2COOH)_2] \cdot nH_2O$. Subsequently, in order to modulate for the immobilization of homogeneous chiral Salen Mn (III), our group have spent many efforts on these in the last decades such as the synthesis of zirconium oligostyrenylphosphonate–phosphate (ZSPP) and zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA),

which all could be modified by diamine, polyamine, sulfoalkyl or diphenoxyl and used for immobilization of chiral salen Mn(III) complexes through axial coordination. The immobilized catalysts effectively catalyzed epoxidation of styrene and α-methylstyrene (ee, 50–78% and 86 to >99%) with m-CPBA or NaClO. These results were significantly better than those achieved with the homogeneous catalyst under the same reaction conditions (ee, 47% and 65%). At the same time, the immobilized catalysts could be reused at least ten times without significant loss of activity and enantioselectivity [8,9].

Furthermore, as far as we are aware, few attempts have previously been made in organic–inorganic hybrid zinc phosphonate–phosphate as catalyst supports, even less on organic polymer–inorganic hybrid zinc phosphonate–phosphate applied for the immobilization of chiral salen Mn (III). In this work, ZnPS-PVPP 1–7 were prepared (shown in Scheme 1) from the copolymer of styrene-phenylvinylphosphonic acid with zinc acetate dihydrate and sodium dihydrogen phosphate treated with different ratios of phosphate and phosphonate. Delightedly, the immobilized catalyst on ZnPS-PVPP showed comparative activity and enantioselectivity with that of catalysts on ZSPP or ZPS-PVPA in the primary tests.

The question as to whether or not layered and crystalline zinc phosphonate–phosphates hybrid materials could also be synthesized without addition of template is examined here. Unexpectedly, layered and crystalline ZnPS-PVPP 1–7 were obtained in the terms of 66 °C and THF-water as solvent in the absence of any template. The main advantage in the synthesis of ZnPS-PVPP 1–7 lies in that this method is simple, cost-effective and environmentally friendly. Moreover, the strategy is obviously different from

that traditional tactics, which are usually taken the direct reaction of phosphonic acid with metal source by the hydrothermal method, or by heating to reflux appropriate solutions, or by making metal salts contact with molten phosphonic acid.

2. Experimental

2.1. Synthesis of styrene-phenylvinylphosphonic acid copolymer (PS-PVPA)

1-Phenylvinyl phosphonic acid (PVPA) was synthesized according to literature [10] and its structures were confirmed by ^1H NMR, ^{31}P NMR and FT-IR. ^1H NMR (CDCl$_3$): 6.06 (d, 1H), 6.23 (d, 1H), 7.26–7.33 (m, 3H), 7.48 (m, 2H). ^{31}P NMR (CD$_3$OD): 15.9. IR (KBr): 2710, 2240, 1500, 1200, 1040, 950, 780, 720, 700 cm^{-1}.

1-Phenylvinylphosphonic acid (4 g, 21.7 mmol), styrene (20 mL, 173.9 mmol), ethyl acetate (150 mL) and benzoyl peroxide (BPO, 1.0 g, 4.7 mmol) were used for preparation of PS-PVPA
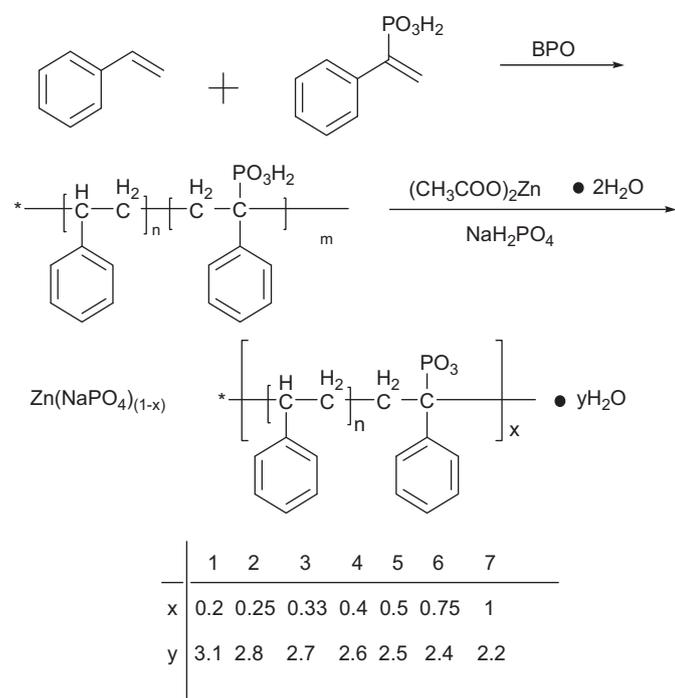
copolymer as literature [8] yield 7.52 g. GPC: Mn=38,608, $m=38$, $n=8$, Mw/Mn=2.

2.2. Preparation of zinc poly(styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPP)

PS-PVPA (1.0 g, 1 mmol) was dissolved in 100 mL THF at room temperature for 30 min. Sodium dihydrogen phosphate (0.62 g, 4 mmol) in 4 mL of deionized water was added and then zinc acetate (1.1 g, 5 mmol) in 5 mL of deionized water was added dropwise and kept on stirring. Consequently, the temperature was raised to 66 °C step by step. The reaction mixture was kept at 66 °C for 72 h and then laid for another 18 h at room temperature. After Et$_3$N (0.68 g, 6.7 mmol) was added and stirred for 30 min, the solvent was evaporated under reduced pressure. The ivory yellow solid zinc poly (styrene-phenylvinylphosphonate)-phosphate 1 was filtered, washed with deionized water and dried at 60 °C for 24 h in vacuum. Ivory yellow ZnPS-PVPP 2–7 were prepared according to the same procedure. IR (KBr):ν_{max}/cm^{-1} 3059, 3028, 2923 (CH), 1686, 1493, 1453, 756, 698 ($-C_6H_5$), 1027 (P$=$O). ZnPS-PVPP 3: Found: C, 58.08; H, 4.97. Calc. for C$_{72}$H$_{73}$O$_{11}$P$_3$Na$_2$Zn$_3$: C, 59.71; H, 5.04%.
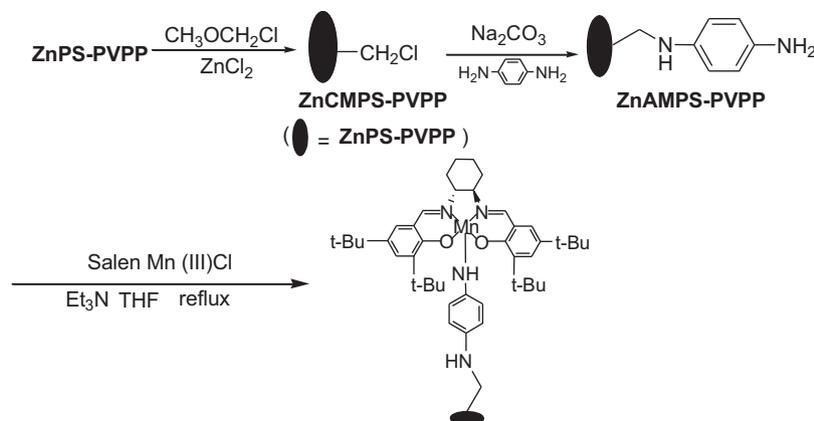
2.3. Synthesis of the supported catalyst (Scheme 2)

2.3.1. Synthesis of chloromethyl-zinc poly(styrene-phenylvinylphosphonate)-phosphate (ZnCMPS-PVPP)

Chloromethyl methyl ether (9.3 mL), anhydrous zinc chloride (3.32 g, 24.34 mmol) and ZnPS-PVPP (5.0 g, 3.4 mmol) were mixed in 40 mL chloroform and stirred at 40 °C for 10 h. After cooling down, sodium carbonate saturated solution was added to neutralize the mixture, and the solvent was evaporated. The product was filtered, washed with deionized water and dried in vacuo to obtain ZnCMPS-PVPP (5.84 g, 90.1%). IR (KBr): ν_{max}/cm^{-1} 3026, 2925 (CH), 2341(O$=$P–OH), 1650, 1542, 1510, 1493 ($-C_6H_5$), 1267 (P$=$O), 700 (C–Cl) cm^{-1}. Found: C, 51.16; H, 4.09%. Calc. for C$_{80}$H$_{81}$O$_{11}$P$_3$Cl$_8$Na$_2$Zn$_3$: C, 52.31; H, 4.41%.

2.3.2. Synthesis of arylaminomethyl-zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnAMPS-PVPP)

Proportional amount of aryldiamine p-phenylenediamine was blended with ZnAMPS-PVPP (1 g), Na$_2$CO$_3$ (1.06 g, 0.01 mol), CuI (0.2 g, 1 mmol) and alcohol 50 mL, and the mixture was stirred and kept at 70 °C for 12 h. Subsequently, the mixture was neutralized and the solvent was vaporized. Then, the product was filtered, washed and dried in vacuo. Reaction yield always

Scheme 1. Synthesis of ZnPS-PVPP 1–7.

	1	2	3	4	5	6	7
x	0.2	0.25	0.33	0.4	0.5	0.75	1
y	3.1	2.8	2.7	2.6	2.5	2.4	2.2

Scheme 2. Synthesis of the supported catalyst.

exceeded 90%. Found: C, 61.15; H, 5.02; N, 9.05. Calc. for $C_{128}H_{137}N_{16}O_{11}P_3Na_2Zn_3$: C, 63.81; H, 5.69; N, 9.31%.

2.3.3. Synthesis grafting chiral salen Mn(III) catalyst onto ZnAMPS-PVPP

Chiral salen Mn(III) (4 mmol) in 10 mL of THF was added dropwise to the solution of ZnAMPS-PVPP (0.5 g) pre-swelled in THF for 30 min and Et_3N (5 mmol) and was stirred for 10 h under reflux. Then the solution was neutralized and the solvent was removed. The dark brown powder was obtained by filtration and washed with CH_2Cl_2 and water until no Mn could be detected by AAS. The amount of Mn (salen) anchored onto ZnPS-PVPP is 0.72 mmol/g ascertained by AAS based on Mn element. Found: C, 69.15; H, 7.01; N, 2.91%. Calc. for $C_{416}H_{545}N_{32}O_{27}P_3Na_2Zn_3Mn_8$: C, 71.65; H, 7.82; N, 3.22%.

2.4. Chemical analysis

In a white porcelain crucible, a sample of 50 mg ZnPS-PVPP 3 was put in it and was heated up to 700 °C for 5 h in Muffle furnace. Due to the high temperature, ZnPS-PVPP 3 decomposed. Then 20 mL of hydrochloric acid (1:1) was added to the porcelain crucible and was heated to boiling for 30 m on the electric furnace. In the resulting solution, the sodium content was determined by AAS.

2.5. Asymmetric epoxidation

The activity of the prepared catalysts were tested for the epoxidation of unfunctionalized olefins in CH_2Cl_2 at -40 °C for 5 h using m-CPBA/NMO as oxidant and with 5 mol% of the catalysts. After reaction, Na_2CO_3 (4 mL, 1.0 M) was added to quench the reaction.

3. Results and discussion

Na content of ZnPS-PVPP 3. The sodium content in ZnPS-PVPP **3** was 1.7%, which was 0.2% lower than that of theoretical values; this can probably be attributed to the surface-bound or intercalated water leading to the augment of the molecular weight.

FT-IR spectra (Fig. S1 in supporting Information) were in good agreement with the expected chemical structure of the organic moieties. In particular the formation of ZnPS-PVPP was confirmed by prominent bands at 1145, 1089, and 986 cm^{-1}, which were attributed to R-PO$_3^{2-}$ phosphonate stretching vibrations, and by the adsorptions at 1201, 1144, and 1077 cm^{-1}, which were due to the phosphonate and phosphate stretching vibrations. The FT-IR spectra confirmed that ZnPS-PVPP were prepared successfully. Meanwhile, shown in Fig. S1, the most informative evidence confirmed the anchoring of the chiral salen–Mn–Cl to the aryl-diamine modified ZnPS-PVPP. The azomethene(C═N) stretching band of salen–Mn–Cl appeared at 1612 cm^{-1} (9 in Fig. S1). While for the supported catalyst, this band was also observed at the vicinity of 1613 cm^{-1}. The heterogenous catalyst and salen–Mn–Cl had shown the same band at 1638 cm^{-1} attributed to the vibration of imine group. The stretching vibration at 1030 cm^{-1}, which was assigned to characteristic vibrations of the phosphonic acid group in ZnPS-PVPP was obviously weakened due to the electronic structure changes for the host–guest interaction. Moreover, an additional band around 3408 cm^{-1} was observed for the catalyst, which was assigned to the stretching vibration of N–H groups.

From the TG curves (Fig. S2), it could be inferred that the sharp weight loss was 54.58% with the decomposition of the appended organic fragments in the temperature range of 200–600 °C.

Moreover, the melting point of the samples increased with the ratio of phosphate in the samples. While for the catalyst, the organic moieties decomposed in the scope of 200–850 °C. The total weight loss was found to be 69.32%. Obviously, catalyst still kept high stability lower than 200 °C. Generally, organic reactions of heterogeneous catalysis were carried out below 200 °C, so both the products and the catalyst had enough thermal stability to be applied in heterogeneous catalytic reactions.

As described in Fig. S3, the XRD patterns of ZnPS-PVPP displayed a broad 001 peak (the lowest-angle diffraction peak in the pattern), accompanied with other peaks at higher-order 00n peaks at larger angles and lower intensities such as at 38.04°. Therefore, it could be deduced that ZnPS-PVPP 1–7 were in crystalline states and all could be applied as mesoporous materials. Shown in Fig. S3, the parts of inorganic phosphate in ZnPS-PVPP 1–6 contributed to the similarity of XRD patterns of samples 1–6 at the vicinity of 24.8° to that of $Zn_3(PO_4)_2$. Furthermore, XRD patterns of ZnPS-PVPP 1–6 close to 20° and 37.92° were nearly identical to that of ZnPS-PVPP 7. They were originated in the sections of zinc poly(styrene-phenylvinylphosphonate) in ZnPS-PVPP samples 1–6. Therefore, conclusion could be obtained that ZnPS-PVPP 1–6 were not the mixture of zinc polystyrene-phenylvinylphosphonate and zinc inorganic phosphate but the zinc poly(styrenephenylvinylphosphonate)-phosphate hybrid materials. Simultaneously, the interlayer distances of ZnPS-PVPP 1–7 were almost 11 Å broader than that of $Zn_3(PO_4)_2$. It could be inferred that the styrene-phenylvinylphosphonic acid copolymer chain introduced in ZnPS-PVPP made the zinc layer stretched and became broader (Fig. 1). The exact structure of it should be affirmed in the future.

The surface area of ZnPS-PVPP 3 (Fig. 2), measured by the BET nitrogen adsorption method (Micromeritics Gemini) after removal of the surfactant, reached 4.9 m^2 g^{-1} with a pore size of 3.5 nm and a pore volume of 1.3×10^{-2} mL g^{-1}. On the other hand, the size of solvated Mn (salen)Cl complex was estimated to be 2.05–1.61 nm by MM2 based on the minimized energy [11]. Herein, ZnPS-PVPP 3 could provide enough room to accommodate the solvated chiral Mn (III) salen complex as well as that the local environment inside the mesopores and pore size of the support did affect the enantioselectivity of the epoxidation reaction. It was the crucial property that ZnPS-PVPP could be used as catalyst supports. Furthermore, the frameworks of ZnPS-PVPP could be easily designed and assembled to generate pores or channels of various sizes and shapes by appropriate modification of the styrene-phenylvinylphosphonic acid copolymer chain (Fig. 3). Maybe the excellent catalytic effect be induced by the special structures of ZnPS-PVPP.

The morphology of the surface of ZnPS-PVPP (Fig. 4), obtained from SEM measurement, indicated that there were regular neat
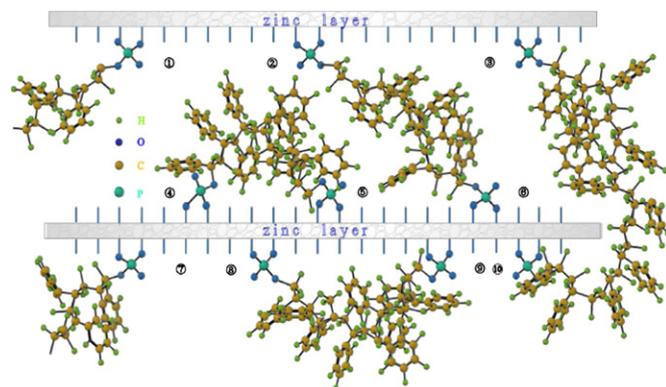

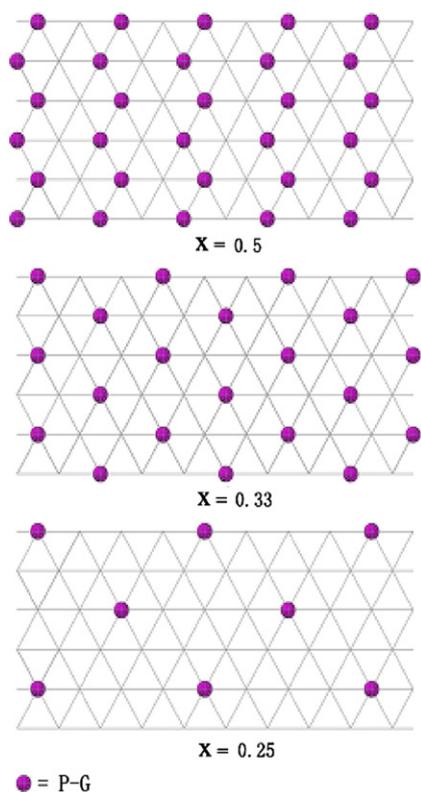**Fig. 1.** Hypothesized layered structure of ZnPS-PVPP **3**.
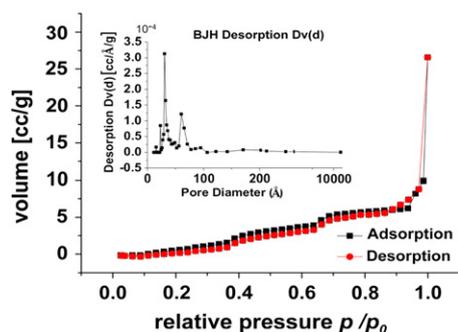
Fig. 2. Cross sections of the x=0.25, 0.33 and 0.5.

Fig. 3. Nitrogen adsorption–desorption isotherm and pore distribution of ZnPS-PVPP **3**.

Fig. 4. (A) SEM image of layered ZnPS-PVPP 3; and (B) TEM images of the layered ZnPS-PVPP **3**.

plate layers, which were mainly aggregation of the parts of zinc inorganic phosphate in ZnPS-PVPP; while the anomalous suborbicular segments were congregation of proportion of zinc poly(styrene-phenylvinylphosphonate) in ZnPS-PVPP. Meanwhile, the supports were various caves, holes, porous and channels with different shape and size were existed in every particles. Some micropores and secondary channels would increase the surface area of the catalyst and provide enough chance for substrates to access to the catalytic active sites. The TEM photography of the ZnPS-PVPP (Fig. 4) displayed that the structure of the support was spheroid, its channels, holes and cavums could be observed clearly, and their sizes were about 70–80 nm, as well as the average diameter of these secondary channels among the layers of the supports were around 50–60 nm. Based on the interlayer spacings of the sample determined by XPRD, it could be deduced that each particle was made up of stacks of 25–30 layers of the sample, leading to few mesopores with the average dimensions of 3.5 nm. So the supports could provide enough space for
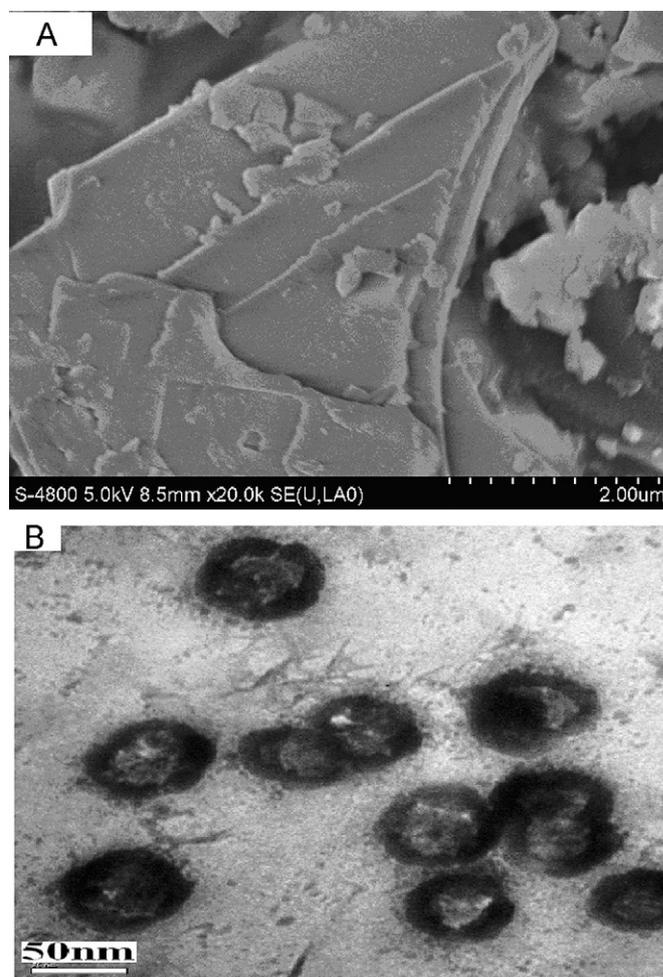
symmetric epoxidation of unfunctionalized olefins, which might induce the excellent catalytic activities and properties of the heterogeneous chiral catalysts.

The diffuse reflectance UV–vis spectrum for the ZnPS-PVPP (Fig. S4) showed a strong absorption around 227 nm, which could be assigned to the π–π^* transition of the phenyl groups. There was another strong absorption around 326 nm, which was originated in the involvement of the charge transfer transitions from the O atoms of the phosphate or phosphonate to the empty 4s orbitals of the Zn^{2+} ions. Therefore, it could be deduced that the samples might be applied in the field of shielding UV, such as sunscreen creams. Further investigations were in progress. On the other hand, according to salen–Mn–Cl, the bands at 334 nm could be attributed to the charge transfer transition of salen ligand; the band at 435 nm was due to the ligand-to-metal charge transfer transition; the band at 510 nm was assigned to the d–d transition of Mn(III) salen system. While for the heterogenerous catalysts, all the characteristic bands appeared in their spectra but the immobilized salen Mn(III) catalysts exhibited a blue shift from 334, 435 and 510 nm to 330, 427 and 503 nm, which indicated that an interaction existed between the salen Mn(III) complex and the aryldiamine modified ZnPS-PVPP.

The activity of the prepared catalyst immobilized chiral salen–Mn–Cl onto ZnPS-PVPP was tested for the epoxidation of α-methylstyrene and indene in CH_2Cl_2 at $-20\,^{\circ}C$ for 6 h using m-CPBA/NMO as oxidant and with 5 mol% of the catalyst. The conversion and ee values of the epoxide were determined by GC.

Table 1
Asymmetric epoxidation of α-methylstyrene and indene catalyzed by heterogeneous catalysts with m-CPBA/NMO[a] as oxidant systems.

Entry	Substrate	Catalyst	Time	Con. (%)	Ee (%)
1	α-Methyl styrene	A	6	> 99	> 99
2	Indene	A	6	> 99	> 99
3	Indene	B	6	62	59
4	α-Methyl styrene	B	6	56	18

A=the immobilized chiral salen Mn (III) catalysts on p-phenylenediamine modified ZnPS-PVPP;
B=the immobilized chiral salen Mn (III) catalysts on p-phenylenediamine modified ZPS-IPPA.

[a] Reactions were carried out at –20 °C in CH_2Cl_2 (4 mL) with α-methylstyrene (1 mmol) or indene (1 mmol), n-nonane (internal standard, 1 mmol), NMO (5 mmol), homogeneous (5 mol%) or heterogeneous salen Mn (III) catalysts (5 mol%) and m-CPBA (2 mmol). The conversion and the ee value were determined by GC with chiral capillary columns HP19091G-B213, 30 m × 0.32 mm × 0.25 μm.

The primary results were summarized in Table 1. The activity of catalyst A was significant better than that of catalyst B synthesized by our group before. Further researches were under way.

4. Conclusions

In summary, this work demonstrated that layered crystalline inorganic–organic polymer hybrid materials ZnPS-PVPP could be synthesized under mild conditions and the catalyst immobilized chiral salen Mn (III) onto ZnPS-PVPP showed obviously superior activity and enantioselectivity.

Acknowledgments

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.06.026.

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