



Chiral salen Mn(III) immobilized on sulfoalkyl modified ZPS-IPPA as an effective catalyst for asymmetric epoxidation of unfunctionalized olefins

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ABSTRACT

Sulfoalkyl modified zirconium poly (styrene-isopropenyl phosphonate)-phosphate (ZPS-IPPA), with special structures of new type of organic–inorganic hybrid material were designed and synthesized for immobilization of the chiral salen Mn(III) Jacobsen's homogenous catalyst by axial coordination. All the heterogeneous chiral salen Mn(III) catalysts with different linkage lengths obtained exhibited great catalytic activity and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins. The influence of the linkage lengths on the catalytic performance was investigated. What's more, the catalysts were easily separated from the reaction systems and could be reused for several times without significant loss of catalytic activity.

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Chiral salen metal complexes such as Jacobsen's homogenous catalyst have been studied widely for their excellent catalytic activity in asymmetric epoxidation (AE) of unfunctionalized olefins under homogeneous conditions [1–4]. However, the separation of such homogeneous catalysts from the reaction systems remains troublesome. Heterogeneous systems offer the advantages of catalyst separation and reusability, but a leaching of the complex is an important factor to be taken into account. In previous works, different supports have been used for the preparation of heterogeneous salen Mn(III) catalysts, such as polymeric resins [5], clays [6], zeolites [7,8], or mesostructured MCM-41 silica materials [9,10]. Unfortunately, despite their excellent performance in easy separation, the heterogeneous catalysts often suffer from decreased catalytic efficiency, which is likely due to the leaching of salen Mn(III) complexes during reaction and/or the inaccessibility of the reagents to the catalytic centers [11]. Therefore, a new type and effective heterogeneous chiral salen Mn(III) catalysts is urgently needed for asymmetric epoxidation of various unfunctionalized olefins.

Recently, we have reported a series of organic–inorganic hybrid material as a new type of catalyst supports, include zirconium oligostyrenylphosphonate-phosphate (ZSPP) [12–16], zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZSP-PVPA) [17,18], and zirconium poly (styrene-isopropenyl phosphonate)-phosphate (ZPS-IPPA) [19,20]. The features of these organic–inorganic hybrids

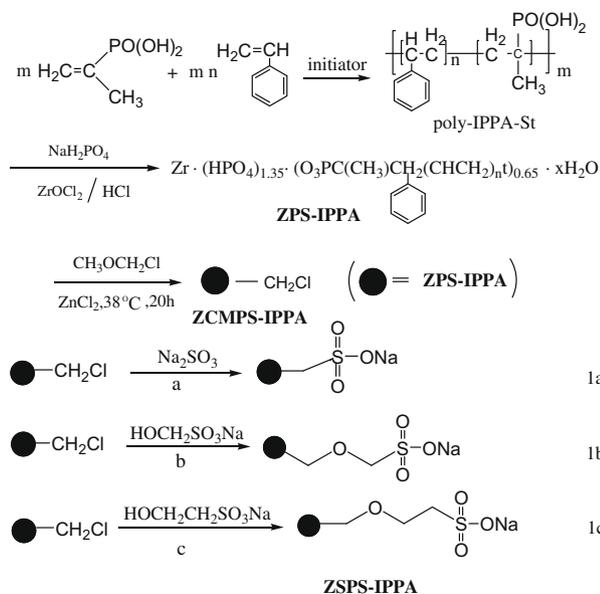
supports are different from either common polystyrene or pure zirconium phosphates. They are consisted of polystyrene parts that are hydrophobic, the zirconium phosphonate parts that are hydrophilic and their self-assembled layered structure with nanometer scale. Thus, a great number of polystyrene segments combined with layered zirconium phosphonate-phosphate will lead to form different caves, holes, porous, micropores, channels and secondary channels with various size and shape which will result to excellent catalytic performance.

In this paper, ZPS-IPPA [20] was transformed into sulfoalkyl modified ZPS-IPPA 1a–1c. A series of new type of chiral salen Mn(III) heterogeneous catalyst 3a–3c with different linkage lengths were obtained by anchoring of chiral salen Mn(III) complexes axially coordinating onto 1a–1c. The resulted heterogeneous chiral salen Mn(III) catalysts were characterized by IR, UV-vis, SEM and TEM. The catalytic performance of the title catalysts for asymmetric epoxidation of unfunctionalized olefins was investigated. The influence of the different linkage lengths on the catalysts performance was compared and discussed.

As shown in Scheme 1, ZPS-IPPA was synthesized and characterized according to the method reported early in [20]. Then $\text{CH}_3\text{OCH}_2\text{Cl}$, ZnCl_2 and ZPS-IPPA were mixed, stirred at 45 °C for 8 h. After cooling, a small amount of water and methanol was added into the mixture, filtered, washed with methanol and acetone and dried in vacuo to obtain chloromethyl zirconium poly (styrene-isopropenyl phosphonate)-phosphate (ZCMPS-IPPA). ZCMPS-IPPA, pre-swelled by distilled water for 3 h, was mixed with sulfating or sulfoalkylating reagents SO_3Na_2 (a), $\text{HOCH}_2\text{SO}_3\text{Na}$

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Scheme 1. Synthesis of the support.

(b) and $\text{HOCH}_2\text{CH}_2\text{SO}_3\text{Na}$ (c) and stirred at 80°C for 24 h. The obtained sulfoalkyl modified ZPS-IPPA (ZSPS-IPPA) were abbreviated as 1a, 1b, 1c in turn. The title chiral salen Mn(III) heterogeneous catalysts 3a–3c were obtained by stirring a suspension of ZSPS-IPPA 1a–1c in a tetrahydrofuran solution containing of Jacobsen's homogenous catalyst. The immobilization of Jacobsen's chiral salen Mn(III) onto supports 1a–1c was carried out successfully in basic condition, yielded the heterogeneous catalysts with a value of 0.54–0.62 mmol/g based on Mn, measured by atomic absorption spectroscopy (Scheme 2).

Comparing IR spectra of ZPS-IPPA with heterogeneous catalyst 3c in Fig. 1, the stretching vibration of phosphonic acid group at 1026 cm^{-1} for ZPS-IPPA is obviously weakened in the IR spectra of title catalyst 3c due to the electronic structure changes for the host–guest interaction. The strong absorption peak of 709 cm^{-1} in IR spectrum of ZCMPS-IPPA (Fig. 1) was ascribed to the stretching vibration of C–Cl bond, which indicated that chloromethyl group had been introduced into the benzene ring of ZPS-IPPA. The new band at 519 cm^{-1} of title catalyst is associated with Mn–N bond. Briefly, in the IR spectra, the band at 1625 cm^{-1} region is assigned to $\nu(\text{C}=\text{N})$ for salen complex in the title catalyst 3c, which means the immobilization of chiral salen Mn(III) complex is successful.

In the DR UV–vis spectra (Fig. 2), the blue shift from 435 nm for chiral salen Mn(III) complex to 424 nm for the title catalyst 3c can

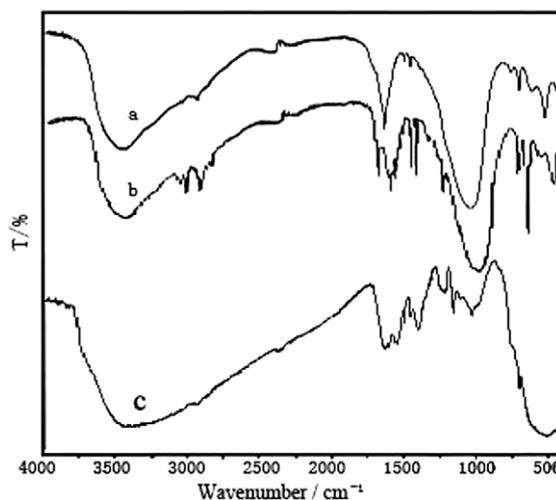
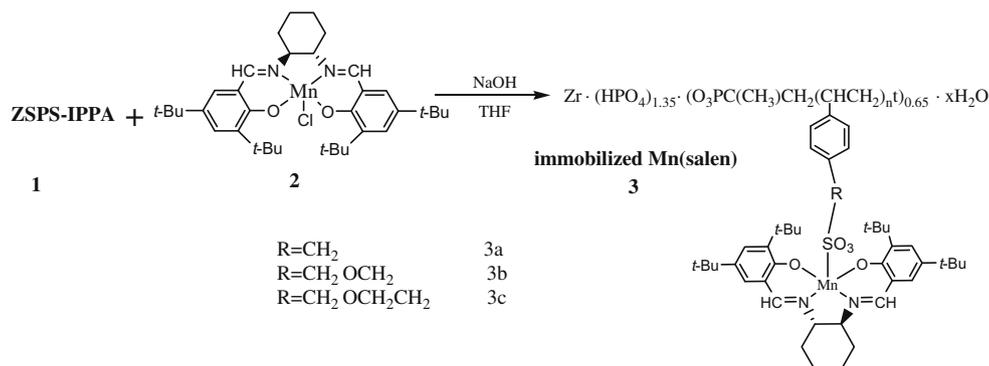


Fig. 1. IR spectra of (a) ZPS-IPPA, (b) ZCMPS-IPPA, (c) immobilized catalyst 3c.

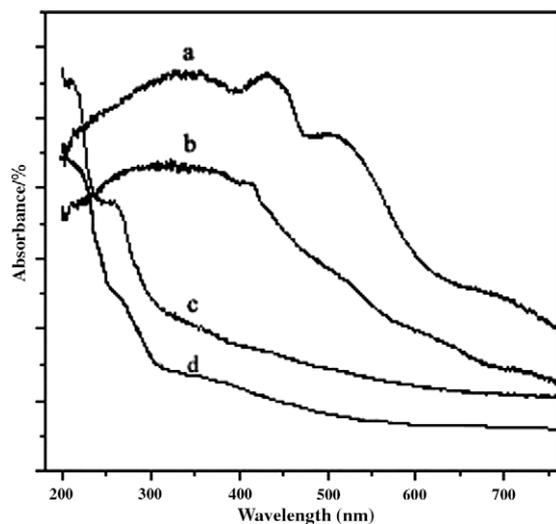


Fig. 2. UV–vis spectra of (a) Salen Mn(III), (b) immobilized catalyst 3c and (c) ZPS-IPPA.

be observed, which is due to ligand-to-metal charge transfer transition, indicating that there existed an interaction between chiral salen Mn(III) complex and the sulfoalkylated modified ZPS-IPPA support, which further confirmed that Jacobsen's chiral salen Mn(III) complex has been anchored onto the support.

In our previous work [20], it is known that in the structure of copolymer PS-IPPA, the main mode of linking is $-(St)_m-IPPA-(St)_n-$ ($6 < m, n < 12$), and a lot number of hydrophobic segments of polystyrene might gather together to form half or part of channels, holes, caves and micropores with different volumes and shapes, which result in preparation of ZPS-IPPA from copolymer PS-IPPA. During the process of synthesis of ZPS-IPPA from copolymer PS-IPPA, almost all the phosphonate in the copolymer PS-IPPA and the phosphate in the solution participate in forming the white colloidal precipitation of ZPS-IPPA. One of the advantageous of the layered zirconium phosphonate-phosphate is all the organic groups are located on the surface of the layers, the interlamellar region and interlayer surface no matter whether they are crystalline semi-crystalline or amorphous, which are resulted from their self-assembled layered structure with nanometer scale. Otherwise, in the ZPS-IPPA precipitation particles, the segments of polystyrene are hydrophobic, while the zirconium phosphonate-phosphate layers are hydrophilic. So the ZPS-IPPA organic-inorganic hybrid support can offer better multiplex micro-environment, which are different from either common polystyrene or pure zirconium phosphates, and the corresponding heterogeneous salen Mn(III) catalysts 3a–3c could provide better asymmetric induce effect and enough space for asymmetric epoxidation of unfunctional olefins, which maybe one of the main factor of the excellent catalytic activities and properties of the title catalysts.

SEM and TEM morphology of the title salen Mn(III) catalyst 3c are shown in Fig. 3, which shown that the structure of heterogeneous catalyst 3c was loose and in the form of aggregates with micro particulates, various caves, holes, porous and channels with different shape and size as mentioned above could be observed clearly. The diameters of these holes, caves, porous and channels are in the scale of 10–40 nm. So the title heterogeneous catalysts posses excellent catalytic performance and reuseability for asymmetric catalytic reaction including asymmetric epoxidation of unfunctional olefins.

The catalytic activity and enantioselectivity of the title catalysts (3a–3c) were explored for the asymmetric epoxidation of unfunctionalized olefins using NaClO/PPNO as an oxidant system in different reactive conditions. The results are summarized in Tables 1–3. The data reported show that all the supported catalysts exhibited excellent catalytic activity, enantioselectivity and could be reused several times without significant loss of its catalytic activity.

From Table 1, the *ee* value is 54% for homogenous Jacobsen's catalyst, after immobilization it increases to 84% for α -methylstyrene, similar results were reported earlier for salen Mn(III) complex immobilized on MCM-41 [21]. It was found that catalyst 3c showed the best catalytic effect among these three new immobilized catalysts. The *ee* values obtained for the reactions catalyzed by the catalysts (3a–3c) increased from 78% to 84% in asymmetric

Table 1Asymmetric epoxidation of α -methylstyrene by heterogeneous catalysts.^a

Entry	Catalyst	Temp. (°C)	Time (h)	Conv. (%)	<i>ee</i> (%) ^b
1	3	20	6	>99.0	54
2	3a	20	24	63.5	78
3	3b	20	24	66.6	79
4	3c	20	24	70.1	84
5	3c	10	24	56.8	88
6	3c	0	24	44.9	94

^a Reactions were performed in CH₂Cl₂ (2 mL) with α -methylstyrene (1.0 mmol), nonane (1.0 mmol), immobilized salen Mn(III) catalyst (3 mol%) and NaClO (pH 11.3, 0.55 M, 3.64 μ mL, PPNO: 0.38 mmol).

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

Table 2Asymmetric epoxidation of different substrates by catalyst 3c, compared with Jacobsen's catalyst.^a

Entry	Substrate	Catalyst	Temp. (°C)	Time (h)	Conv. (%)	<i>ee</i> (%) ^b
1		3	20	6	>99.0	42
2		3c	20	24	57.6	48
3		3	20	6	>99.0	54
4		3c	20	24	70.1	84
5		3	20	6	92	65
6		3c	20	24	74	98

^a Same as in Table 1.

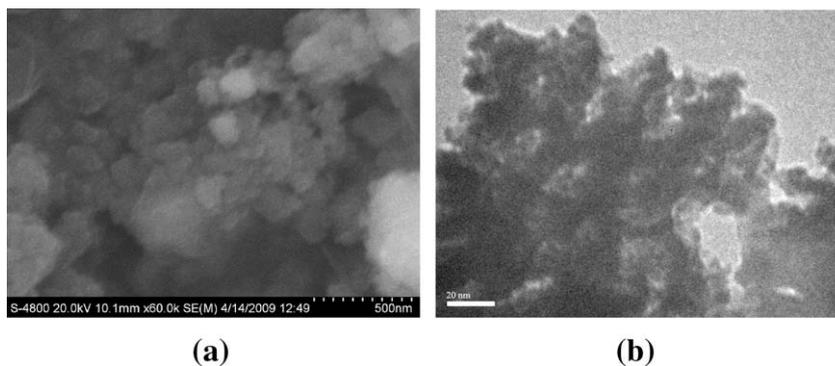
^b Same as in Table 1.

Table 3The recycling of immobilized catalyst in the epoxidation of α -methylstyrene.

Entry	Cycle	Conv. (%)	<i>ee</i> (%)
1	Fresh	70.1	84
2	1	70	81
3	2	60.1	80
4	3	58.7	76
5	4	57.9	79
6	5	55	75
7	6	48	69
8	7	44.1	63
9	8	36.2	59
10	9	32.5	58

Reactions were performed in CH₂Cl₂ at 20 °C for 24 h with NaClO/4-PPNO as oxidant and in the presence of 3% of the catalysts.

epoxidation of α -methylstyrene, which are similar with the results obtained by Zhang and Li [22]. These results were due to the longer

**Fig. 3.** SEM and TEM of immobilized catalyst 3c.

linkage lengths which connected ZPS-IPPA and salen Mn(III) would decrease resistance of heterogeneous catalytic system, and restrain the free rotation of the reaction intermediate. Furthermore, more Mn content of catalyst 3c resulted from also the longest linkage length that can offer more catalytic centers maybe another causation for the better catalytic effect.

Table 1 also summarizes the catalytic performance of the catalyst 3c at different reaction temperatures. A decrease of reaction temperature led to the decrease of the epoxide conversion. However, an increase of enantioselectivity was observed, which was similar to the results reported previously in Ref. [23]. The reason should be due to both an increase in enantiofacial selectivity in the initial C–O bond forming step and suppression of the trans-pathway in the second step at low temperature [24].

Interestingly, this new type of heterogeneous catalysts showed better catalytic activity and enantioselectivity for bulkier olefins such as indene (Table 2).

The reusability of the title catalyst could be one of the most important benefits of these heterogeneous chiral catalysts, for corresponding homogenous chiral catalysts are often expensive to purchase or prepare. Thus, to assess the long-term stability and reusability of the immobilized catalysts, α -methylstyrene was used as a model substrate with NaClO/PPNO under basic system, and recycling experiments were carried out with the catalyst 3c. After each experiment, the catalyst was precipitated from the reaction system by adding hexane and subsequently used without further purification. The recycling results of the title catalyst 3c are listed in Table 3 which indicated within five runs the conversion and the enantioselectivity both decreased slightly.

In conclusion, sulfoalkyl modified ZPS-IPPA, a new type of inorganic–organic hybrid material, was prepared and used as catalyst supports for immobilization of the chiral salen Mn(III) Jacobsen's homogenous catalyst by axial coordination for the first time. The heterogeneous catalysts with different linkage lengths obtained exhibit comparable or even higher enantioselectivities than that of homogeneous catalyst for the asymmetric epoxidation of several unfunctionalized olefins in the presence of NaClO. It was found that the title catalyst with longer linkage lengths performance better catalytic activity and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins. The title catalysts are relatively stable and can be recycled five times in the asymmetric epoxidation of α -methylstyrene with little loss of conversion and enantioselectivity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2009.12.034](https://doi.org/10.1016/j.inoche.2009.12.034).

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