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Immobilized chiral Mn (III) salen-containing onium salt onto ZnPS-PVPA for asymmetric epoxidation of unfunctionalized olefins

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ABSTRACT

A series of chiral Mn (III) salen are anchored on ZnPS-PVPA modified by onium salt and characterized. In the asymmetric epoxidation of unfunctionalized olefins with *m*-CPBA and $NaIO_4$ as oxidants, the supported catalysts demonstrate higher catalytic activities than those of the corresponding homogeneous chiral Mn (III) salen catalyst under the same conditions both for experimental scale and for large-scale reactions. Moreover, the catalysts are stable could be recycled nine times without significant loss of activity, which are provided with the potentiality for application in industry.

Metal–salen complexes have attracted significant attention in research areas ranging from catalysis to development of electrochemical sensors and single-molecule magnets [1]. Chiral metal–salen complexes are used as asymmetric catalysts in a variety of oxidation reactions [2]. Among several previously reported catalytic systems, chiral Mn (III)–salen complexes have attracted tremendous attention in recent years in asymmetric epoxidation of alkenes owing to their availability and wide usefulness. Consequently, the design of novel chiral catalysts constitutes an important strategy in asymmetric catalysis [3]. To enhance atom efficiency and develop environmentally friendly technology, many efforts have been devoted to investigate chiral salen complexes in the asymmetric catalysis [4], and an important strategy is the recycle of the salen metal complexes due to the high cost of chiral salen ligands. Therefore, the immobilizations of salen catalysts on polymer, organic or inorganic, and ionic liquids have been developed [5]. In these recycling systems, it is presumed that increasing the molecular weight of the catalysts would make it easier to recycle the catalysts. Additionally, increasing catalytically active metal centers of the catalysts could enhance the catalytic activities and catalyst recovery [6]. Many attempts have been made to use ionic liquids in asymmetric epoxidation of alkenes because ionic liquids as green reaction media can improve the separation, activity, and recycling of the catalysts [7].

Over the last decades, our groups have made efforts to a series of organic–inorganic hybrid zirconium phosphonate-phosphates $Zr(H\ PO_4)_{2-x}(O_3P\text{–}G)_x\bullet nH_2O$ ($x = 0\text{–}2$, G is organic groups), such as zirconium sulfophenylphosphonate-phosphate $Zr(HPO_4)_{2-x}(O_3PC_6H_4SO_3H)_x\bullet H_2O$, and zirconium [N, N di (phosphono methyl) iminodiacetic acid] $Zr\ [(O_3PCH_2)_2\ N\ (CH_2COOH)]\bullet nH_2O$ [8–11]. In addition, we have also focused on the immobilization of homogeneous chiral salen Mn (III) complexes, such as chiral salen Mn (III) catalysts supported on zirconium oligo-styrenylphosphonate-phosphate (ZSPP) and zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA). It is noteworthy that the heterogeneous catalysts show higher performance than that of the homogeneous chiral catalyst in asymmetric epoxidation of unfunctionalized olefins [12–15].

Whereas, few investigations are focused on organic polymer–inorganic hybrid zinc phosphonate-phosphate used for the immobilization of chiral salen Mn (III). In addition, some of the heterogeneous catalysts have proved to be successful in the epoxidation of olefins, which prompts us to pursue a new functional group to bind chiral salen Mn (III) onto zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA) to produce a recyclable asymmetric epoxidation catalyst. Herein, to carry out successful heterogeneous asymmetric epoxidation, not only the design of supported catalysts but also the selection of appropriate oxidation conditions is very important. Inspired by the above pioneering studies and our early work in asymmetric reactions with salen Mn (III), we initiate a study to synthesize a new type of stable, reusable catalysts immobilized on ZnPS-PVPA modified by onium salt (Scheme 1).

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All the catalysts (5a–d) and chiral salen Mn (III)Cl have shown the same band at 1638 cm^{-1} (Fig. S1), attributed to the vibration of the imine group. The azomethene(C = N) stretching vibration band of chiral salen Mn (III)Cl appears at 1613 cm^{-1} (5 in Fig. S1); while for the supported catalysts this band is also observed at the vicinity of 1617 cm^{-1}. The band around 3408 cm^{-1} is observed for the catalysts, assigned to the stretching vibration of N – H groups. The stretching vibration at 1030 cm^{-1}, which is assigned to characteristic vibrations of the phosphonic acid group in the support, is obviously weakened due to the electronic structure changes for the host–guest interaction. In addition, the band close to 757 cm^{-1} is ascribed to the vibration of imidazole ring in the samples of 5a and 5b; the band at the hand of 1279 cm^{-1} is put down to the vibration of triazole ring in the samples of 5c and 5d.

The spectra of (5a–d) have displayed features similar to those of chiral salen Mn (III)Cl on the basis of UV–vis observation (Fig. S2). The band at 335 nm could be attributed to the charge transfer transition of salen ligand. The band at 433 nm is due to the ligand-to-metal charge transfer transition, and the band at 510 nm is assigned to the d-d transition of the salen Mn (III) complex.

As described in the TG curves (Fig. S3), the initial weight loss is 4.5% below 180 °C. It is attributed to surface-bound or intercalated water in this stage. In the temperature range of 180–600 °C, the organic moieties decompose, accompanied with 37.48% weight loss. Obviously, catalyst 5b still keeps high stability lower than 180 °C. In general, organic reactions of heterogeneous catalysis are carried out below 180 °C. Therefore, the catalyst 5b has adequate thermal stability to be applied in heterogeneous catalytic reactions.

Based on the desorption isotherm (Fig. 1), the nitrogen adsorption–desorption isotherms are characteristic type V, with a sharp increase in N_2 adsorption at higher P/P_0 values (~0.9) and a distinct hysteresis loop (type H_1). The pore diameters of the particles are mainly distributed between 15 Å and 15 nm, which is in the scope of mesoporous.

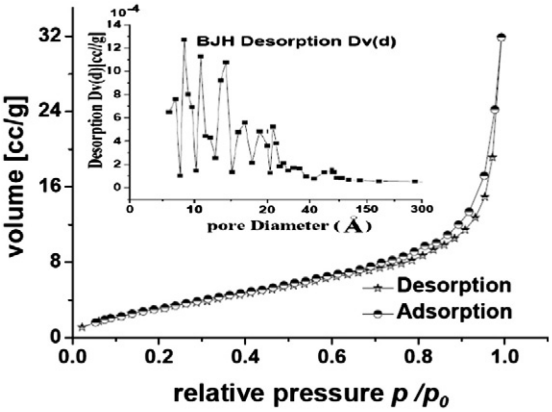
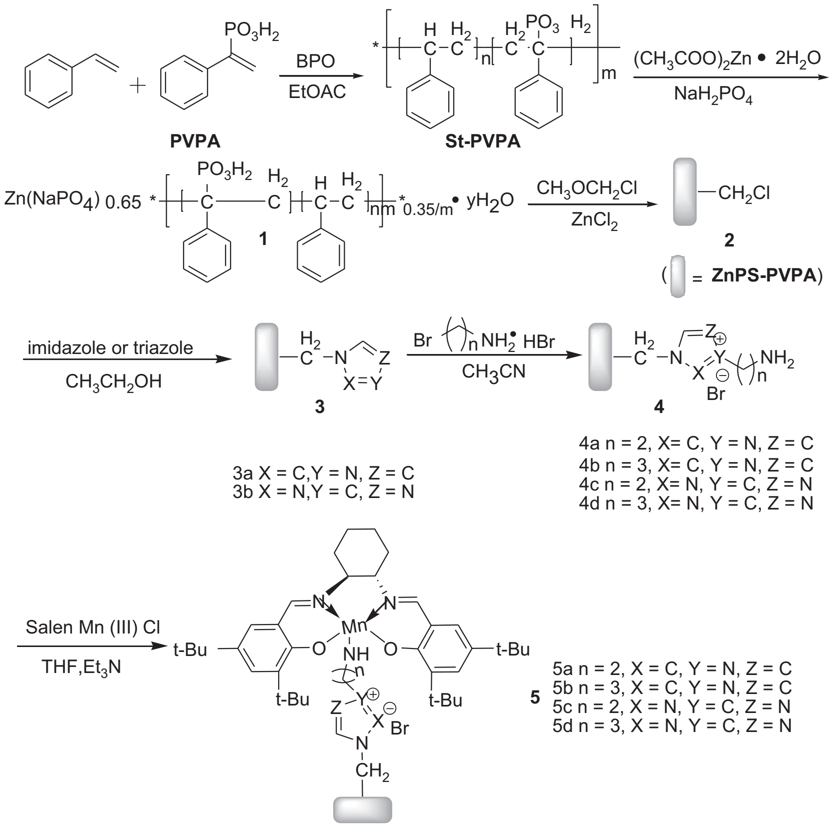


Fig. 1. The nitrogen adsorption–desorption isotherm and pore distribution of the supported catalyst 5a.

The corresponding textural parameters calculated by N_2 adsorption–desorption isotherms are presented in Table 1.

As shown in Table 1, an obvious increase in BET surface area is observed after chloromethylation (1 vs 2, from 4.9 to 36.9), as well as the increase in the pore volume (1 vs 2, from 1.3 to 18.82 × 10^{-2} cm^3/g) and in average pore diameter (1 vs 2, from 3.5 to 10.21 nm). It is due to that the chloromethylation of the support makes the interlayer distance enlarged and the chloromethyl group is relatively small so that BET surface area, pore volume and pore diameter still increase. Inversely, a decrease in BET surface area (2 vs 5a, from 36.9 to 22.6 m^2/g), in pore volume (2 vs 5a, from 18.82 to 5.3 × 10^{-2} cm^3/g) and in average pore diameter (2 vs 5a, from 10.21 to 7.36 nm) is observed upon immobilization of the chiral salen Mn (III)Cl onto 4a. Although the interlayer distance is augmented after the chloromethylation, the steric bulkyl Mn (III) salen complex is



Scheme 1. Synthesis of the supported catalysts.