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Catalytic asymmetric epoxidation of unfunctionalized olefins using a series novel type of layered crystalline organic polymer–inorganic hybrid zinc phosphonate–phosphate immobilized aryldiamine modified chiral salen Mn(III) complex

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ABSTRACT

In this report we demonstrate the suitability of layered crystalline organic polymer–inorganic hybrid material ZnPS–PVPA with different content of the organic group and different inorganic phosphate as catalyst supports for asymmetric catalysis. A series of the chiral salen Mn(III) complex immobilized onto ZnPS–PVPA modified by aryldiamine were synthesized and characterized by FT-IR, diffusion reflection UV–vis, AAS, N_2 volumetric adsorption, SEM, TEM, XRD and TG. The supported catalysts displayed superior catalytic activities in the asymmetric epoxidation of α-methylstyrene and indene with m-CPBA and $NaIO_4$ as oxidants, compared with the corresponding homogeneous catalyst (*ee*, >99% vs 54% and >99% vs 65%). And the heterogeneous catalysts are relatively stable and can be recycled nine times in the asymmetric epoxidation of α-methylstyrene. These results revealed that the special structure of ZnPS–PVPA played vital impacts on the conversion and enantioselectivity. Furthermore, this novel type of catalyst can also be validly used in large-scale reactions with superior catalytic disposition being maintained at the same level, which possessed the potentiality for application in industry.

1. Introduction

Owing to the great importance of the chiral compounds in the manufacture of drugs, vitamins, fragrances, and optical material, the preparation of chiral building blocks has attracted special attention. Epoxides of unfunctionalized olefins are very important intermediates in the manufacture of drugs, vitamins, fragrances, and optical materials, because they can be readily transferred into various compounds *via* regioselective ring opening or functional transfer reactions [1–5]. Just as this, asymmetric epoxidation (AE) has become a useful preparative method in organic synthesis. Chiral Mn (salen) complexes developed by Jacobsen, Katsuki and coworkers are effective catalysts for AE of olefins with high levels of enantioselectivity [6–8]. However, a major limitation of Jacobsen's catalyst is that it cannot be recycled due to the decomposition of the catalyst and the formation of inactive dimeric μ-oxo manganese(IV) species [9] in homogeneous phase. The anchoring of the Mn(III) salen complexes onto supports has been found to increase the catalyst stability since the generation of the dimeric μ-oxo manganese(IV) species can be avoided. Many efforts have been focused on the covalent binding of manganese(III) salen complexes to organic polymer [10] and inorganic supports such as MCM-41 [11], zeolites [12] and clays [13]. The trend to develop reusable salen–metal complexes with high efficiency and catalytic stability is increasing from the environmental concerns together with economic considerations. Accordingly, methodologies for the heterogenization of homogeneous salen–metal complexes have emerged. Among them, heterogenization of salen–metal complexes into/onto inorganic or inorganic–organic hybrid supports is one of the promising strategies. For these supported salen–metal complexes, the host–guest interaction can be mechanical, physical, or chemical [14,15].

In the last decades, our groups have reported a series of organic–inorganic hybrid zirconium phosphonate–phosphates $Zr(HPO_4)_{2-x}(O_3P\text{–}G)_x{\cdot}nH_2O$ ($x = 0\text{–}2$, G is organic groups) as various kinds of catalysts or catalyst supports, such as solid acid catalysts zirconium sulfophenyl phosphonate–phosphate Zr $(HPO_4)_{2-x}(O_3PC_6H_4SO_3H)_x{\cdot}nH_2O$, and zirconium [*N*, *N* di (phosphono-methyl)iminodiacetic acid] $Zr[(O_3PCH_2)_2N(CH_2COOH)]{\cdot}nH_2O$ and their palladium complexes as catalysts in hydrogenation [16–19]. Apart from these facts, we have also focused on the immobilization of

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homogeneous chiral salen Mn(III) complexes, such as the supported chiral salen Mn(III) catalysts on modified zirconium oligostyrenylphosphonate–phosphate (ZSPP) and zirconium poly(styrene-phenylvinylphosphonate)-phosphate (ZPS–PVPA). It was noteworthy that the heterogeneous catalysts showed higher enantioselectivity than that of the homogeneous chiral catalyst and superior reusability in asymmetric epoxidation of unfunctionalized olefins under the same conditions [20–23].

Whereas, few investigations were explored in the organic–inorganic hybrid zinc phosphonate–phosphate as catalyst supports, even less in organic polymer–inorganic hybrid zinc phosphonate–phosphate used for the immobilization of chiral salen Mn(III). Moreover, some of the heterogeneous catalysts have proved to be successful in the epoxidation of olefins, which encouraged us to pursue a new functional group to bind chiral salen Mn(III) onto ZnPS–PVPA to produce a recyclable asymmetric epoxidation catalyst. Herein, it is still of academic interest and commercial importance to develop efficient and reusable catalyst for the epoxidation of non-functionalized olefins. In view of this, we documented that a series of new type of layered crystalline organic polymer–inorganic hybrid materials ZnPS–PVPA and aryldiamine modified ZnPS–PVPA applied to immobilize the chiral salen Mn(III) complexes through axial coordination. And we also reported the immobilized catalysts were stable, recoverable, reusable catalysts with superior enantioselectivity, and can be used in large-scale reactions with the enantioselectivity being maintained at the same level. In addition, the question as to whether or not various proportions of organic phosphonate to inorganic phosphate, various inorganic phosphate and different linkages contributed to the catalytic activities and enantioselectivities were also examined here.

2. Experiment

2.1. Materials and instruments

(1R,2R)-(−)-1, 2-diaminocyclohexane, chloromethyl methyl ether (toxic compound), α-methylstyrene, n-nonane, N-methylmorpholine N-oxide (NMO) and m-chloroperbenzoic acid (m-CPBA) were supplied by Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers. Chiral salen ligand and chiral homogeneous catalyst salen Mn(III) were synthesized according to the standard literature procedures [24], and further identified by analysis and comparison of IR spectra with literature [25].

FT-IR spectra were 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 $BaSO^4$ as standard. ^1H NMR and ^{31}P NMR were performed on AV-300 NMR instrument at ambient temperature at 300 and 121 MHz, respectively. All of the chemical shifts were reported downfield in ppm relative to the hydrogen and phosphorus resonance of TMS and 85% H_3PO_4, respectively. Number- and weight-average molecular weights (Mn and Mw) and polydispersity (Mw/Mn) were estimated by Waters1515 gel permeation chromatograph (GPC; against polystyrene standards) using THF as an eluent (1.0 mL min^{-1}) at 35 °C. X-ray photoelectron spectrum was recorded on ESCALab250 instrument. The interlayer spacings were obtained on DX-1000 automated X-ray power diffractometer, using Cu Kα radiation and internal silicon powder standard with all samples. The patterns were generally measured between 3.00° and 80.00° with a step size of 0.02° min^{-1} and X-ray tube settings of 36 kV and 20 mA. C, H and N elemental analysis was obtained from an EATM 1112 automatic elemental analyzer instrument (Thermo, USA). TG analyses were performed on a SBTQ600 thermal analyzer (USA) with the heating rate of 20 °C min^{-1} from 25 to 1000 °C under flowing N_2 (100 mL min^{-1}). The Mn contents of the catalysts were determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy. SEM were performed on KYKY-EM 3200 (KYKY, China) micrograph. TEM were obtained on a TECNAI10 (PHILIPS, Holland) apparatus. Nitrogen adsorption isotherms were measured at 77 K on a 3H-2000I (Huihaihong, China) volumetric adsorption analyzer with BET method. The racemic epoxides were prepared by epoxidation of the corresponding olefins by 3-chloroperbenzoic acid in CH_2Cl_2 and confirmed by NMR (Bruker AV-300), and the gas chromatography (GC) was calibrated with the samples of n-nonane, olefins and corresponding racemic epoxides. The conversions (with n-nonane as internal standard) and the *ee* values were analyzed by gas chromatography (GC) with a Shimadzu GC2010 (Japan) instrument equipped using a chiral column (HP19 091G-B213, 30 m × 30 m × 0.32 mm × 0.25 μm) and FID detector, injector 230 °C, detector 230 °C. Ultrapure N_2 was the carrier gas (rate 34 mL min^{-1}) with carrier pressure 39.1 kPa and the injection pore temperature was set at 230 °C. The column temperature for indene, α-methylstyrene was programmed in the range of 80–180 °C. The oven temperature program was initially started at 80 °C, held for 3 min; then raised to 150 °C at 7 °C min^{-1} and held for 5 min at 150 °C; raised to 220 °C at 7 °C min^{-1}, and was finally set at 220 °C constant for 3 min. The total run time of the GC program for α-methylstyrene was 30 min. The appearance time of n-nonane, α-methylstyrene, two racemic epoxides was at 5.29, 9.2, 12.9, 13.0 min, respectively. The similar run program was set for indene.

2.2. Synthesis of the support (Scheme 1)

2.2.1. Synthesis of styrene–phenylvinyl phosphonic acid copolymer (PS–PVPA)

1-Phenylvinyl phosphonic acid (PVPA) was synthesized according to literature [26] 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_3OD): 15.9. IR (KBr): 2710, 2240, 1500, 1200, 1040, 950, 780, 720, 700 cm^{-1}.

1-Phenylvinyl phosphonic 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 [22] yield 7.52 g. GPC: Mn = 38,608, $m = 38$, $n = 8$, Mw/Mn = 2.

2.2.2. Synthesis of ZnPS–PVPA

PS–PVPA (1.0 g, 1 mmol), sodium dihydrogen phosphate (0.62 g, 4 mmol), zinc acetate (1.1 g, 5 mmol) and Et_3N (0.68 g, 6.7 mmol) were used for the synthesis of ZnPS–PVPA according to the literature [27]. IR (KBr):ν_{max}/cm^{-1} 3059, 3028, 2923 (CH), 1686, 1493, 1453, 756, 698 ($-C_6H_5$), 1027 (P=O).

2.2.3. Synthesis of chloromethyl-zinc poly(styrene-phenylvinyl-phosphonate)-phosphate (ZnCMPS–PVPA)

Chloromethyl methyl ether (9.3 mL), anhydrous zinc chloride (3.32 g, 24.34 mmol) and 1a (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 under reduced pressure, filtered, washed with deionized water and dried in vacuo to obtain **2a** (5.84 g, 90.1%). 2b–2h were synthesized in compliance with the similar course. 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}.