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Enantioselective epoxidation of unfunctionalized olefins catalyzed by chiral salen Mn(III) catalyst immobilized on zirconium oligostyrenylphosphonate-phosphate

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ABSTRACT

A general method for the covalent attachment of chiral salen Mn(III) complex to zirconium oligostyrenylphosphonate-phosphate has been used. The immobilized chiral salen Mn(III) catalyst shows higher chiral induction (ee, 60–70%) compared with the corresponding homogeneous catalyst (ee, 54%) for asymmetric epoxidation of α-methylstyrene with NaClO as oxidant, while the heterogeneous catalyst exhibits relatively low ee values for asymmetric epoxidation of indene. Interestingly, the ee values for the immobilized catalyst with NaClO as oxidant are higher than those for the same catalyst with m-chloroperbenzoic acid as oxidant. This stands in contrast to the literatures reported. The heterogeneous catalyst can be recycled nine times, while the activity will decrease after use in reactions.

1. Introduction

Enantioselective epoxidation of unfunctional olefins is of great importance in synthesis of fine chemicals, pharmaceuticals and biological chemicals and their intermediates. Chiral salen Mn(III) complexes are excellent catalysts for asymmetric catalytic epoxidation of unfunctionalized alkenes [1–3]. Compared with the homogeneous catalysts, the potential benefits of heterogeneous catalytic systems have the inherent advantages, including facilitation of catalyst separation from reagents and reaction products, simplification of methods for catalysts recovery and recycle, purifying products, better handling properties and the possible adaptation of the immobilized catalyst to continuous-flow processes [4]. Therefore, immobilization of chiral metal (salen) complexes onto various kinds of supports has received great attention in recent years [5,6]. Chiral metal (salen) homogeneous catalysts have been immobilized into mesoporous molecular sieves [7–9], mesoporous silica [10,11], zeolite Y [12,13], macroporous Dowex MSCl resin [14] and Wangs resin [15]. However, the development of practical solid supports-immobilized asymmetric catalysts has proven highly challenging, and immobilization often results in heterogeneous chiral catalysts with lower enantioselectivities or efficiencies than homogeneous counterparts [16].

Recent years, zirconium phosphate–phosphonate hybrid materials have been extensively explored which were types of layered multi-functional materials with about tens to hundreds of surface area, high thermal stability, acid stability, base and chemical stability. And these materials could be used as adsorbents, ion-exchangers, catalysts and catalyst supports [17–20].

In previous work we have explored the preparation of oligostyrenylphosphonous acid (OSPUA) using benzoyl peroxide (BPO) as initiator and brought forward the reaction mechanism according to mass spectral data [21]. Then zirconium oligostyrenylphosphonate-phosphate (ZSPP) and corresponding derivatives were further synthesized [22]. The frameworks of ZSPP can be easily designed and assembled to generate pores or channels of various sizes and shapes by appropriate modification of the polystyrene part. Recently, we have successfully anchored polyamines molybdenum (VI) complexes onto chloromethyl-zirconium oligostyrenylphosphonate-phosphate (ZCMSPP) [23]. Meanwhile, chiral salen Mn(III) complexes axially immobilized on ZCMSPP via diamines have been explored in our group [24]. While a method for the covalent attachment of chiral salen Mn(III) complex to ZSPP was rarely reported.

Herein, a general method for the covalent attachment of chiral salen Mn(III) complex to zirconium oligopolstyrenylphosphonate-phosphate has been used. The heterogeneous salen Mn(III) catalyst shows comparable or even higher enantioselectivities than homogeneous salen Mn(III) catalysts for the asymmetric epoxidation of various unfunctionalized olefins, while the heterogeneous catalyst exhibits relatively low ee values for asymmetric epoxidation of indene. More interestingly, the ee values for the immobilized chiral catalyst are higher in NaClO oxidative system than those for the

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same catalyt in m-chloroperbenzoic acid oxidative system. This stands in contrast to the literatures reported [24–26]. The heterogeneous salen Mn(III) catalyst is relatively stable and can be recycled nine times in the asymmetric epoxidation of α-methylstyrene. The excellent catalytic effect is caused by the special structure of ZSPP.

2. Experimental

2.1. Material and instruments

(1R, 2R)-1,2-diaminocyclohexane, 2,4-dihydroxybenzaldehyde, styrene, indene, α-methylstyrene, n-nonane, 4-phenylpyridine N-oxide (4-PPNO), N-methylmorpholine N-oxide (NMO) and m-CPBA were supplied by Alfa Aesar.

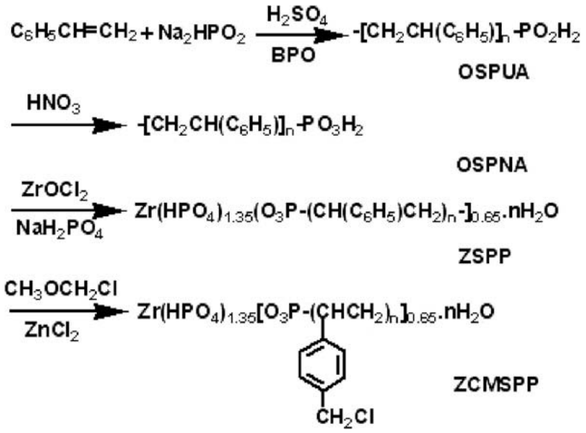
FT-IR spectra were recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA) and diffuse reflectance UV–vis spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using $BaSO_4$ as standard. The Mn content of the catalyst was determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy. X-ray photoelectron spectra (XPS) were performed on a ESCALAB250 apparatus. Scanning electron microscopy (SEM) analyses were performed on KYKY-EM3200 (KYKY, China) microscopy. Transmission electron microscopy (TEM) analysis was recoded on a TECNAI10 (PHILIPS, Holand) apparatus. 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 conversion (with n-nonane as internal standard) and the ee values were analyzed by GC with Shimadzu GC2014 (Japan) instrument equipped using a chiral column (HP19091G-B213, 30 m × 30 m × 0.32 mm × 0.25 μm) and FID detector, injector 230 °C, detector 230 °C. The column temperature for styrene, indene, α-methylstyrene was in the range of 80–180 °C.

2.2. Synthesis of ZCMSPP

The synthesis and characterization of ZCMSPP have been reported early [23] (Scheme 1).

2.3. Synthesis of chiral salen ligand 1

The chiral salen ligand 1 was synthesized according to the literature [27] (Scheme 2).



Scheme 1. Synthesis of the support.

2.4. Attaching chiral salen ligand 1 on the ZCMSPP (Scheme 3)

To a suspension of ZCMSPP (200 mg, 0.50 mmol Cl) that had been pre-swelled in 10 ml of THF for 30 min was added salen 1 (452 mg, 1.0 mmol), NaOH (120 mg, 3 mmol), The yellow suspension was refluxed under the protection of argon (Ar) for 24 h, then filtered and rinsed sequentially with THF, CH_2Cl_2 and finally dried in vacuum to yield 295 mg of the product as yellow beads.

2.5. Synthesis of supported salen Mn(III) complex 3

Manganese inserted into the salen ligand was accomplished by adding a solution of Mn $(OAc)_2 \cdot 4H_2O$ (103.0 mg, 0.42 mmol) in 10 ml 1:1 ethanol/toluene to the supported salen with stirring. The mixture was refluxed for 3 h under the protection of Ar. Then air was bubbled for an additional 2 h, and 26.7 mg of solid LiCl was added. After refluxing for 1 h the bead was filtered and rinsed sequentially with CH_2Cl_2, ethanol, H_2O and finally dried in vacuum to yield brown power 3. The content of the manganese determined by AAS was 0.78–0.82 mmol/g.

2.6. Asymmetric epoxidation

2.6.1. Using NaClO as oxidant [24]

To a solution of alkene (0.5 mmol), n-nonane (internal standard, 89.3 μl, 0.5 mmol), 4-PPNO (42 mg, 0.25 mmol), homogeneous (3 mol%) or heterogeneous salen Mn(III) catalysts (3 mol%), CH_2Cl_2 (4 ml), NaClO aqueous solution(pH 11.3, 0.55 M, 1.37 equiv, 1.25 ml) was added. The mixture was stirred at desired temperature.

2.6.2. Using m-CPBA as oxidant [24]

A solution of alkene (0.5 mmol), NMO (338 mg, 2.5 mmol), n-nonane (internal standard, 89.3 μl, 0.5 mmol), homogeneous (3 mol%) or heterogeneous salen Mn(III) catalysts (3 mol%), CH_2Cl_2 (4 ml) was cooled to the −78 °C. Solid m-CPBA (173 mg, 1 mmol) was added in four portions over 2 min. After reaction, NaOH (4 ml, 1.0 M) was added to quench the reaction.

2.7. The reusability of the catalyst

In a typical recycle experiment, the equal volume of hexane was added to the reaction mixture after the reactions, then the organic phase was separated, and the used black catalyst was washed with hexane and water, and then dried over vacuum at 60 °C to remove the remaining hexane and water. The recovered dried solid catalyst was weighed and reused in the next run. In every run the same ratio of the substrate-to-catalyst and solvent-to-catalyst was kept.

3. Results and discussion

3.1. Spectral analysis

Comparing the IR spectra of the ZCMSPP (Fig. 1a) with the supported chiral salen ligand (Fig. 1b), it is found that the IR bond of the supported chiral salen at 1632 cm^{-1} is assigned to the characteristic stretching vibration of C═N. The IR bonds at 2935, 2862, 1405, 1365 cm^{-1} are due to C–H vibration of alkyl groups. And the IR peaks at 1026 and 1473 cm^{-1} demonstrate the formation of the ether link between salen ligand and ZSPP. Simultaneously, 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. The difference between supported chiral salen and supported salen Mn(III) (Fig. 1c) is also clear. The bonds