

Effect of linkers on the performance of ZnPS-BrPPAS supported chiral Mn(III) salen for the epoxidation of unfunctionalized olefins



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ABSTRACT

Novel layered chiral salen Mn(III) catalysts anchored on ZnPS-BrPPAS display superior dispositions in the epoxidations (yield, up to >99%; ee, up to >99%). The catalysts could be recovered and reused up to nine times. Noticeably, the morphology indicates schistose structure or spheric particle owing to different linkers. In addition, the reversal configurations of epoxides are also taken on.

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1. Introduction

During the past decade, several methods of controlling the product specificity during epoxidation of unfunctionalized olefins have been developed [1–3]. One of the most important is the Jacobsen-Katsuki epoxidation [4–6]. In these reactions, high enantiomeric excesses could be achieved, leading to several experimental studies to elucidate the reaction mechanisms and to discover the origin of the remarkable selectivity [7–14]. Despite these advantages, the large-scale application of these metal complexes is highly hampered by the impossibility to remove the catalyst from the reaction solution at the end of the reaction and to reuse it. To overcome these drawbacks, the complexes could be anchored onto solid supports such as carbon materials, mesoporous silicas, clay materials and organic polymers [15–22].

Recently our group has developed a new method for the synthesis of heterogeneous chiral salen Mn(III) with ZPS-PVPA, ZSPP, ZPS-IPPA, ZnPS-PVPA, AISPP, AIPS-PVPA, CaPS-PVPA as the supports. The supported catalysts indicate superior dispositions in the asymmetric epoxidations of unfunctional olefins and could be recycled for several times without significant loss of the activity as well as could be employed in the large-scale reactions with

superior catalytic disposition being maintained at the same level [23–32].

Herein we report the synthesis of new chiral salen Mn(III) complexes immobilized onto novel type of organic-inorganic hybrid material ZnPS-BrPPAS (Scheme 1). The catalytic abilities of the supported catalysts, and the effects of the linkers which contribute to the morphology and the configurations of enantiomers are systematically investigated in details.

2. Experimental

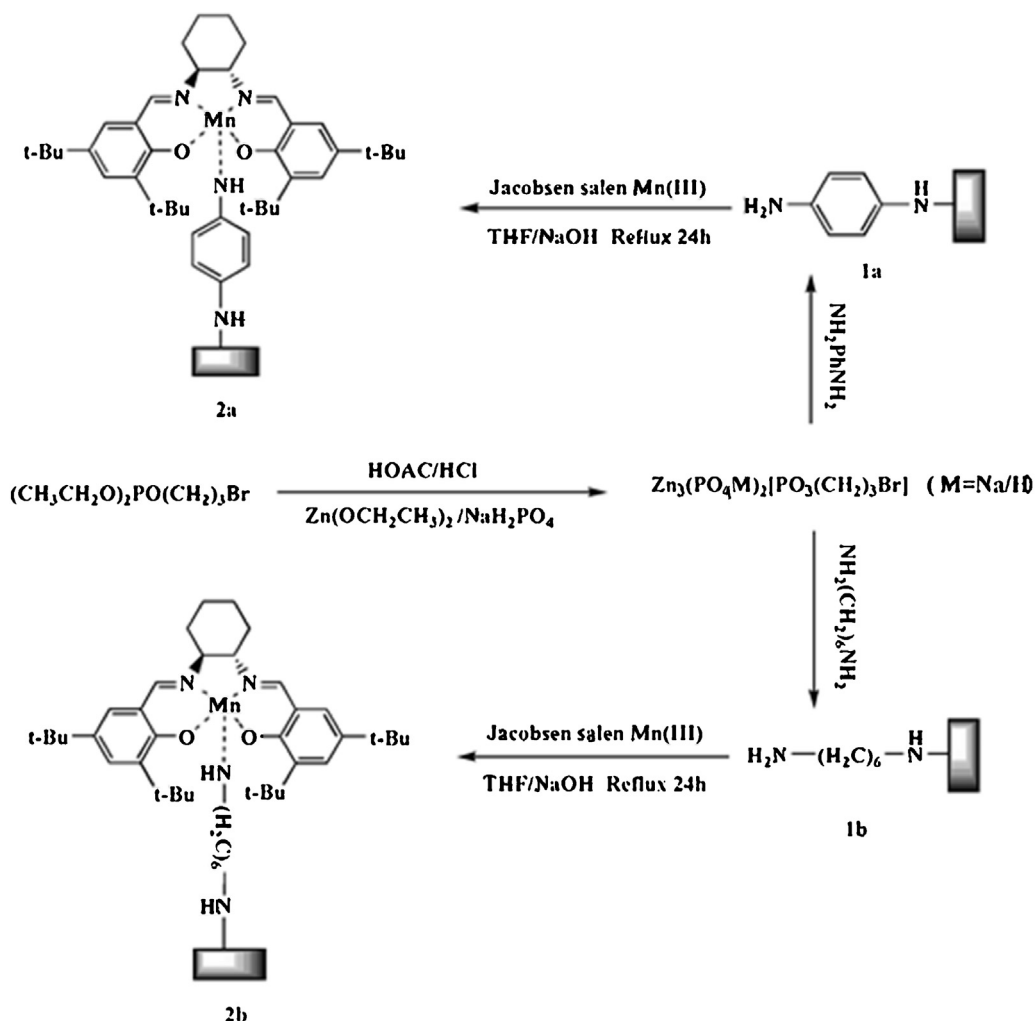
2.1. Materials and instruments

(1*R*,2*R*)-(–)-1,2-Diaminocyclohexane, 2,4-dihydroxybenzaldehyde, indene, α -methylstyrene, *n*-nonane, 4-phenylpyridine *N*-oxide (4-PPNO) and sodium hypochlorite were supplied by Alfa Aesar, [Br(CH₂)₃P(O)(OEt)₂] and [Br(CH₂)₃P(O)(OH)₂] were prepared according to the procedures by the literature [33], Chiral Jacobsen's catalyst [4], 6-cyano-2,2-dimethylchromene and 6-nitro-2,2-dimethylchromene [34] were synthesized according to the literature procedures.

FT-IR spectra were recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA). TG analysis was performed on a SBTQ600 Thermal Analyzer (USA). ¹H NMR was determined by Bruker AV-300. The interlayer spacings were obtained on DX-1000 automated X-ray power diffractometer, using Cu-K α

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Scheme 1. Synthetic route for the supported catalysts.

radiation and internal silicon powder standard with all samples. Scanning electron microscope (SEM) analyses were performed on KYKY-EM3200 (KYKY, China) microscopy. The BET surface areas were determined with the use of N_2 sorption data measured at 77 K (Quantachrome Autosorb⁻¹). The conversion (with *n*-nonane as internal standard) and the ee values of indene and α -methylstyrene were measured on GC with Shimadzu GC2014 (Japan) instrument equipped. For the 2,2-dimethylchromenes epoxides, the ee values were determined on HPLC by using a Chiral cel column (OD).

2.2. Synthesis of the immobilized catalysts

2.2.1. Preparation of the hybrid zinc 3-bromopropylphosphonate-phosphate (ZnPS-BrPPAS)

The mixture of the diethyl 3-bromopropylphosphonate (5 mmol), 8 mL of concentrated hydrochloric acid (36%) and 25 mL of acetic acid was stirred at 80 °C for 24 h, followed by cooling down and evaporating under reduced pressure as well as neutralizing. Sodium dihydrogen phosphate (1.56 g, 10 mmol) in 8 mL of deionized water and zinc acetate (3.29 g, 15 mmol) in 10 mL of deionized water were added while gradually raising the temperature to 66 °C and then retaining for 72 h and laying for another 18 h at room temperature. The white powder zinc phosphonates were obtained by filtering, washing thoroughly

with deionized water and drying in vacuum. Yield: 92.0%. Found: C, 5.65; H, 0.92. Calc. for $\text{C}_3\text{H}_6\text{O}_{11}\text{P}_3\text{BrNa}_2\text{Zn}_3$: C, 5.70; H, 0.95%.

2.2.2. Preparation of diamine-modified ZnPS-BrPPAS (1a-1b)

The appropriate amount of diamine (such as 1,6-hexamethylenediamine, *p*-phenylene-diamine) was mixed with ZnPS-BrPPAS (3.16 g, 0.50 mmol), Et_3N (0.1 g, 1.0 mmol) and CH_3CN (the molar ratio of diamine to bromine element in ZnPS-BrPPAS is 5:1). After the mixture was kept at 80 °C for 24 h under N_2 atmosphere, the resin-like product was filtered and washed with deionized water and CH_3CN to remove superfluous diamine and dried over vacuum. 1a, yield: 74.0%; Found: C, 24.15; H, 2.86; N, 6.24. Calc. for $\text{C}_9\text{H}_{13}\text{O}_{11}\text{P}_3\text{N}_2\text{Na}_2\text{Zn}_3$: C, 24.39; H, 2.94; N, 6.32%. 1b, yield: 70.0%; Found: C, 16.12; H, 3.06; N, 4.13. Calc. for $\text{C}_9\text{H}_{21}\text{O}_{11}\text{P}_3\text{N}_2\text{Na}_2\text{Zn}_3$: C, 16.19; H, 3.15; N, 4.20%.

2.2.3. Synthesis of heterogeneous Mn(III) salen catalysts (2a-2b)

A solution of chiral salen Mn(III) (2.73 g, 4.30 mmol), 1a (0.50 mmol) and an adequate amount of Et_3N in THF was vigorously stirred for 24 h under reflux, followed by cooling down and neutralizing as well as evaporating. The product 2a was collected by filtration and washed thoroughly with CH_2Cl_2 and deionized water, and dried under vacuum. The sample 2b was gained according to the similar procedure. 2a, yield: 84.0%; Found: C, 51.76; H, 6.08; N, 5.27. Calc. for $\text{C}_{45}\text{H}_{64}\text{O}_{11}\text{P}_3\text{N}_4\text{Na}_2\text{Zn}_3\text{Mn}$: C, 51.85;

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