

Constraining asymmetric organometallic catalysts within mesoporous supports ZnPS–BrPPAS boosts their enantioselectivity



Jing Huang^{a,c,*}, Li Yuan^a, Jiali Cai^b

^a Research Center for Advanced Computation, Xihua University, College of Science, Xihua University, Chengdu 610039, PR China

^b College of Rongchang, Southwest University, Chongqing 402460, PR China

^c Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, PR China

ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form 22 June 2015

Accepted 9 October 2015

Available online 22 October 2015

Keywords:

Chiral Mn(III) salen

Organic–inorganic hybrid material

Unfunctionalized olefins

Heterogeneous catalyst

Asymmetric epoxidation

ABSTRACT

Novel layered heterogeneous chiral salen Mn(III) catalysts are synthesized with organic–inorganic hybrid material ZnPS–BrPPAS as the support and employed in the asymmetric epoxidations of unfunctionalized olefins. Characterizations indicate that the different linkers could contribute to the morphology varying from schistose structure to spheric particle. The catalysts manifest superior catalytic dispositions (yield, up to >99%; ee, up to >99%) in the epoxidations of olefins such as α -methylstyrene and indene. Moreover, the catalysts could be recovered and reused up to nine times with retention of catalytic dispositions. In addition, the reversal configurations of epoxides are observed with respect to 6-cyano-2,2-dimethylchromene and 6-nitro-2,2-dimethylchromene.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The transformation of alkenes to corresponding epoxides is both an important industrial technology and a useful synthetic method for a wide range of products including pharmaceuticals and agrochemicals. Chiral Mn(III) salen complexes (Jacobsen's catalyst) have demonstrated very high activity and selectivity for the enantioselective epoxidation of unfunctionalized olefins under homogeneous condition [1–3]. However, such catalysts are not easily recovered for reuse or recycle in homogeneous catalytic systems. Therefore, the heterogenization of chiral Mn(III) salen complexes have received great attention in the last decades due to efficient product purification and easy catalyst recovery [4–15]. Recently, considerable studies have also concentrated on the investigation of inorganic–organic hybrid materials as active heterogeneous catalysts/supports [16,17]. These kinds of materials have the advantage of possessing a broad and non-uniform distribution of pore size, the distribution of functional organic groups or/and catalytic active centers within their framework. Accordingly, the heterogeneous catalysis systems are possessed, not only with high reactivities and enantioselectivities but also easy catalyst/product separation and

simple catalyst recycling. Our research has, for many years, been concerned with metal phosphonate chemistry for catalysts and catalyst supports. Our group have reported the preparation of a series of organic polymer–inorganic hybrid such as ZSPP, ZPS-IPPA, ZPS-PVPA, ZnPS-PVPA and their applications as catalyst supports in immobilizing chiral salen Mn(III) [18–22]. In most cases, these supported chiral Mn(III) salen catalysts indicate comparable or even higher activity and enantioselectivity, compared with the homogeneous counterparts for asymmetric epoxidation. Furthermore, the immobilized catalyst could be reused at least nine times without significant loss of activity.

Mesoporous materials have become attractive materials due to their potential applications as promising materials, such as catalysis, separation, material recognition and hydrogen storage materials. To date, many mesoporous materials have been designed. MCM-41 and SBA-15 are the most frequently used mesoporous materials for the immobilization of homogeneous chiral catalysts. In our group, the layered crystalline ZnPS-PVPA are prepared in mild and facile conditions in water-THF media at 66 °C, entirely apart from the traditional methods. Owing to the layered mesoporous structure, ZnPS-PVPA could be employed as the catalyst supports, enabling one to take advantage of the site isolation effect and the cooperation effect, and bridging the gap between heterogeneous catalysts and homogeneous catalysts [23–28].

However, the effects of organic linkers on the catalytic performance of mesoporous material-supported chiral Mn(III) salen

* Corresponding author at: Research Center for Advanced Computation, Xihua University, College of Science, Xihua University, Chengdu 610039, PR China.

E-mail addresses: hj41012@163.com, 394454290@qq.com (J. Huang).

complex have seldom been systemically investigated for the asymmetric epoxidation. Herein, this prompts us to design a novel type of organic–inorganic hybrid material ZnPS–BrPPAS applied in the immobilization of chiral salen Mn(III). The catalytic performance of the supported catalysts, and the effects of the linkers on the morphology and the catalytic activities are systemically discussed in details.

2. Experiment

2.1. Materials and instruments

(1R,2R)-(–)-1,2-Diaminocyclohexane, 2,4-dihydroxybenzaldehyde, indene, α -methylstyrene, *n*-nonane, 4-phenylpyridine Noxide (4-PPNO) and sodium hypochlorite were supplied by Alfa Aesar, $[\text{Br}(\text{CH}_2)_3\text{P}(\text{O})(\text{OEt})_2]$ and $[\text{Br}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2]$ were prepared according to the procedures by the literature [29], Chiral Jacobsen's catalyst [30], 6-cyano-2,2-dimethylchromene and 6-nitro-2,2-dimethylchromene [31] 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 radiation and internal silicon powder standard with all samples. Scanning electron microscope (SEM) analyses were performed on KYKYEM3200 (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 Chiralcel column (OD).

2.2. Synthesis of the catalysts (Scheme 1)

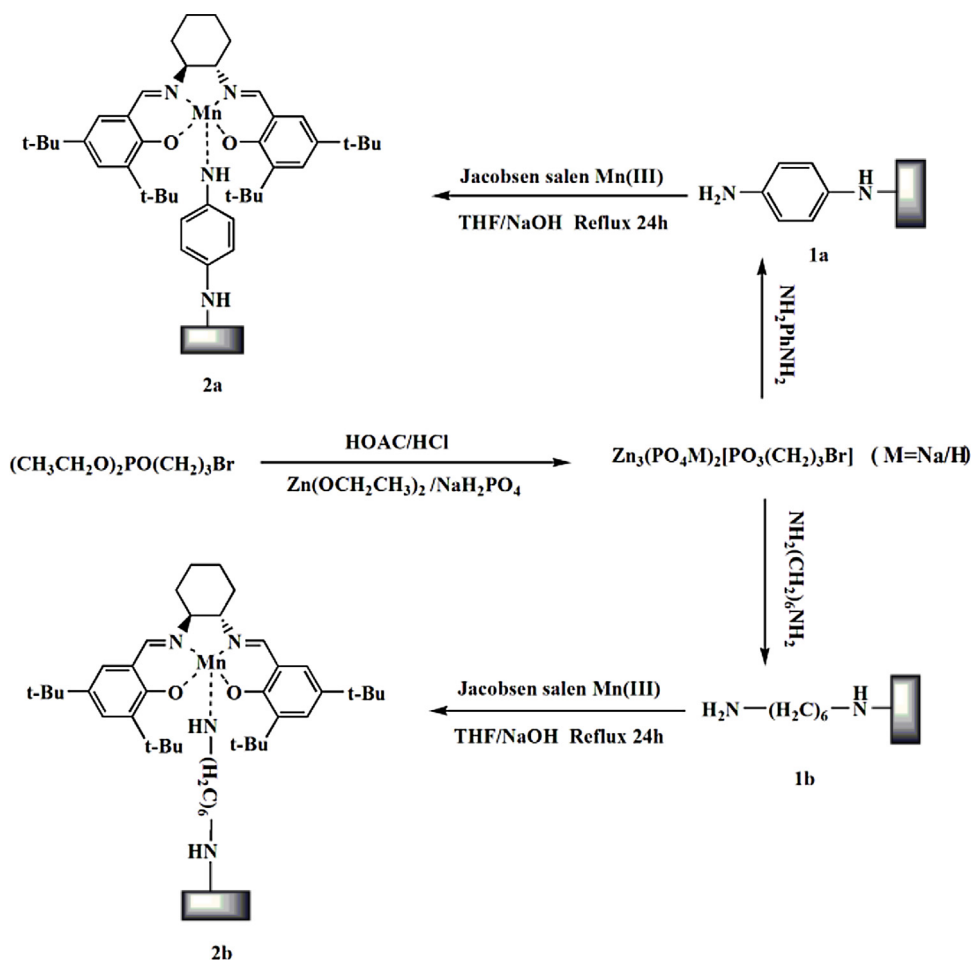
2.2.1. Preparation of the hybrid zinc

3-bromopropylphosphonatephosphate (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 the mixture was 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. Synthesis of diamine-modified ZnPS–BrPPAS (1a–b)

The appropriate amount of diamine (such as 1,6-hexamethylenediamine, *p*-phenylenediamine) was mixed with ZnPS–BrPPAS (3.16 g, 0.50 mmol), Et_3N (0.1 g, 1.0 mmol) and CH_3CN



Scheme 1. Synthetic route for the supported catalysts.

Download English Version:

<https://daneshyari.com/en/article/64719>

Download Persian Version:

<https://daneshyari.com/article/64719>

[Daneshyari.com](https://daneshyari.com)