Contents lists available at SciVerse ScienceDirect

Catalysis Communications



journal homepage: www.elsevier.com/locate/catcom

Short Communication

Structure-control in assembly of nanosheets: Novel chiral catalysts for the asymmetric epoxidation of α -methylstyrene without axial base

Chenhui Hu^a, Lihong Zhang^a, Junfeng Zhang^a, Liyuan Cheng^a, Zheng Zhai^a, Meng Li^b, Jing Chen^b, Wenhua Hou^{a,*}

^a Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China ^b Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, PR China

ARTICLE INFO

Article history: Received 17 May 2012 Received in revised form 20 August 2012 Accepted 25 August 2012 Available online 30 August 2012

Keywords: Chiral salen Mn(III) complex α -Zr(HPO₄)₂ Nanosheets α -Methylstyrene Epoxidation

ABSTRACT

Heterogeneous chiral catalysts with different structure, surface character and location of active species were assembled by salen Mn(III) complex and α -Zr(HPO₄)₂ nanosheets. The bumpy edge-accumulated surfaces of nanosheets lead the catalyst to have a high ee value without axial base in the asymmetric epoxidation of α -methylstyrene.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The heterogenization of chiral salen Mn(III) complexes (CSM) has attracted particular attention and many types of salen Mn(III) catalysts have been designed and supported on various carriers [1]. Nevertheless, the resulted heterogeneous catalysts have often shown a decrease in activity and enantioselectivity. Recently, the ionic salen Mn(III) complexes provide a new way for their heterogenization on inorganic carriers via a simple ion exchange reaction. Layered inorganic materials such as anionic clays and cationic Zn–Al layered double hydroxides were used to incorporate salen complexes [2,3]. Unfortunately, these layered inorganic materials all suffer a relatively lower ion exchange capacity. By comparison, layered α -Zr(HPO₄)₂·H₂O (α -ZrP), which is famous for its huge ion-exchange capacity (600 mmol/100 g), ease of dimensional and surface functionality control, and facile process of intercalation/exfoliation, has been proved to be an extremely efficient support [4].

Nanosheets, a novel class of advanced nanomaterials which can be obtained by the exfoliation of layered compounds, exhibit extraordinary physicochemical properties and are often used as modules of various nanomaterials [5]. The resulted nanosheets have two large basal planes ($\sim\mu$ m) and thin edges (~1 nm) that may result in two distinct atomic environments (Fig. 1A) [6]. Besides, the exfoliated nanosheets can be restacked in two different modes. One is orderly-stacked layered structure along *z* axis with bumpy surface (Fig. 1B). The other is a rather

disorderly piled-up structure in which the basal plane is relatively large and smooth (Fig. 1C). These two different surfaces could provide different environments for guest molecules.

In the work, α -ZrP nanosheets (ZrPNS) were obtained by exfoliating α -ZrP with tetrabutylammonium hydroxide (TBAOH) [6b], and could be further edge-modified with α -naphtyl phosphonic acid (α -NPA), resulting in another version of ZrPNS noted as ZrPNS-edge (Fig. 1D). The cationic CSM, namely Jacobsen's catalyst [7], was prepared and heterogenized with ZrPNS and ZrPNS-edge respectively through self-assembly. Two heterogeneous chiral catalysts with different structure, surface character and location of CSM were prepared by controlling the loading amount of CSM. The resulted heterogeneous chiral catalysts were evaluated in the asymmetric epoxidation of α -methylstyrene. A detailed characterization and discussion about the different catalytic behaviors was provided.

2. Experimental

2.1. Catalyst preparation

 α -ZrP was prepared by HF approach, as described by Xu et al. [8]. The uniform and stable translucent colloidal suspension of α -ZrP nanosheets (ZrPNS) was prepared by first adding 4.96×10^{-3} mol of TBAOH to 6.64×10^{-3} mol of α -ZrP in 1000 mL of deionized water and then the resulted solution was stirred for 72 h at ambient temperature [6b], followed by centrifugation at 9000 rpm.

Another version of nanosheets was prepared as follows: 8.4×10^{-4} mol of TBAOH was first added into 4.64×10^{-4} mol of



^{*} Corresponding author. Tel.: +86 25 83686001; fax: +86 25 83317761. *E-mail address*: whou@nju.edu.cn (W. Hou).

^{1566-7367/\$ –} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.catcom.2012.08.028



Fig. 1. The schematic structure of (A) a single α -ZrP nanosheet, (B) bumpy edge-accumulated surface of orderly-restacked nanosheets along z axis, (C) smooth basal plane in disorderly piled-up structure, (D) the edge modification of α -ZrP nanosheet with α -naphthyl group.

 α -ZrP in 100 mL of deionized water at room temperature and then 4.8×10^{-4} mol of α -NPA was added and stirred for 2 h to allow the exchange of phosphates. After that, the suspended colloid was restacked with 0.1 mol/L HCl, washed with deionized water and dried at 333 K. The resulted solid was exfoliated with TBAOH again, followed by centrifugation at 9000 rpm to obtain the colloidal suspension of ZrPNS-edge.

Two catalysts were prepared by using two versions of nanosheets and changing the loading amount of CSM. Concretely, ZrPNS (2 mg/mL) was combined with 8.92×10^{-6} mol of CSM to obtain catalyst noted as CSM/ZrPNS. ZrPNS-edge (1.7 mg/mL) was mixed with 2.52×10^{-5} mol of CSM and the resulted catalyst was noted as CSM/ZrPNS-edge. (Figure S1 in Supporting Information).

2.2. Catalyst characterization

XRD patterns were obtained on a Philips X'Pert X-ray diffractometer with monochromatized Cu K α radiation. FT-IR spectra were recorded on a Nicolet 6700 spectrometer with a resolution of 2 cm⁻¹ and 64 scans in the range of 400–4000 cm⁻¹. The size distribution and morphology were analyzed by transmission electron microscopy (TEM JEOL JEM-200CX, operated at an accelerating voltage of 200 kV) and scanning electron microscopy (SEM JEOL JEM-6300F). The BET surface area was measured at 77 K by using a Micromeritics ASAP 3020 volumetric adsorption analyzer and the pore-size distributions were obtained using the BJH model. The manganese content in catalysts was determined by atomic absorption spectroscopy (AAS) using a Varia AA240Duo spectrometer. Elemental analyzer. UV–vis reflectance spectroscopic measurements were performed on a Shimadzu UV-3600 spectrophotometer by dispersing sample on BaSO₄.

2.3. Catalyst test

Enantioselective epoxidation reactions were performed in 5 mL of CH_2Cl_2 at 273 K using heterogeneous and homogeneous catalysts (0.01 mmol, based on Mn element) with α -methylstyrene as substrate (0.5 mmol), toluene (40 µL) as the internal standard, N-methylmorpholine-N-oxide (NMO) as an axial base, and *m*-chloroperoxybenzoic acid (*m*-CPBA, 1 mmol, added in five equal portions) as an oxidant.

After reaction, the heterogeneous catalysts were separated by centrifugation, and the filtrate was washed with 5 mL of 1 mol/L NaOH and 5 mL of brine, and then dried over anhydrous Na₂SO₄. For the homogeneous catalyst, the solvent was removed and the product was separated and collected by a short column of silica gel. Conversions and ee values were determined by GC using the internal standard method with a chiral β -cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m×0.25 mm×0.25 µm).

3. Results and discussion

Because α -ZrP can be easily hydrolyzed with TBAOH at edges, an addition of the appropriate amount of α -naphthyl phosphonic acid (α -NPA) to the suspension of ZrPNS enables the edge-modification of nanosheets with organic groups. XRD, IR, UV, SEM and elemental analyses results confirmed that the organic groups were successfully anchored at the edges of ZrPNS (Figure S2 in Supporting Information).

The XRD patterns of the resulted catalysts are shown in Fig. 2 (inset: photos of catalysts). The as-prepared α -ZrP exhibits all characteristic reflections which are well matched with literature [6a], indicating a highly ordered lamellar structure. By comparison, CSM/ZrPNS exhibits a new diffraction peak at 2θ = 6.4° (d_{002} = 13.8 Å)



Fig. 2. XRD patterns of (A) α-ZrP, (B) CSM/ZrPNS, and (C) CSM/ZrPNS-edge.

and a large decrease of peak intensity. Considering the size of salen Mn(III) (20.5 Å×16.1 Å) [9], the thickness of α -ZrP layer (ca. 10 Å) and the diameter of TBA⁺ ions (ca.10 Å) [6a], it can be suggested that the exchange of cationic CSM with TBA⁺ ions mainly occurs at the edges of ZrPNS where there is a relatively higher electron density due to the partial hydrolysis of HPO₄^{2–}, and the remained TBA⁺ ions are resided between nanosheets through a single-layer arrangement [6b]. For CSM/ZrPNS-edge, the characteristic (002) diffraction peak is no longer observed. Since the edges of nanosheets are modified by naphthyl groups, CSM can only be loaded on the basal planes of nanosheets to replace TBA⁺ ions and resulting in an irregularly stacking of ZrPNS-edge.

As can be seen in Fig. 3, individual nanosheets with smooth basal planes can be obtained after exfoliation. In addition, ZrPNS-edge shows a morphology with bumpy edges while ZrPNS flat edges. The resulted catalysts exhibit different morphologies due to the location of CSM and the restacking ways of nanosheets. CSM/ZrPNS exhibits a relatively more ordered layered structure while CSM/ZrPNS-edge presents a rather disordered piled-up structure, being consistent with XRD results.

Furthermore, IR results also confirm the successful loading of CSM on ZrPNS and ZrPNS-edge, respectively (Figures S3). The contents of Mn in two catalysts are determined as 0.30 and 1.25 mmol/g, respectively. Both two heterogeneous catalysts exhibit a characteristic type IV N₂ adsorption-desorption isotherm and a uniform pore diameter (~3.5 nm) (Figure S4). The resulted mesoporous structure can be attributed to the irregular and loosely restacking of nanosheets. Nevertheless, due to the highly disordered arrangement of nanosheets, CSM/ZrPNS-edge has a much higher surface area and pore volume than CSM/ZrPNS (Table 1). The above catalyst characterizations confirm that CSM is successfully immobilized on α -ZrP nanosheets and the two heterogeneous asymmetric catalysts have different structure, surface character and location of CSM.

Table 2 lists the catalytic performance of two chiral catalysts. According to the previous literature, the same total amount of active species (~2 mol% of olefins, based on the Mn content) was used for homogeneous and heterogeneous catalysis to exclude the possibility that the different catalytic performances were caused by the various densities of active species on the support. Interestingly, without NMO, CSM/ZrPNS in which CSM is mainly loaded at the edge of ZrPNS, shows the highest ee value of 78 % at a conversion of 100 % in 6 h (Entry 2). Even when the amount of catalyst is decreased 3 times, an ee value of 31 % is still reached (Entry 3). By comparion, CSM/ZrPNS-edge in which



Fig. 3. TEM images of ZrPNS (A) and ZrPNS-edge (B), and SEM mages of CSM/ZrPNS (C) and CSM/ZrPNS-edge (D).

Table 1

Some physico-chemical properties of α -ZrP and two heterogeneous chiral catalysts.

Sample	Mn loading mmol/g	$\begin{array}{c} S_{BET} \\ m^2/g \end{array}$	Pore volume cm ³ /g	Pore size nm	Microanalysis (%)		
					С	Н	Ν
α-ZrP	/	3.5	0.015	/	/	/	/
CSM/ZrPNS CSM/ZrPNS-edge	0.30 1.25	20.5 91.9	0.043 0.145	3.4 3.6	9.0 11.6	4.0 4.4	0.5 0.2

CSM is mainly loaded on the basal planes of ZrPNS-edge, shows a much lower ee value of 39 % in 9 h (Entry 5), although it has the much higher content of Mn, surface area and pore volume (Table 1). These results suggest that the catalytic performance is closely related with the intrinsic structure of catalyst rather than the loading amount of CSM and the unique surface character of α -ZrP nanosheets is essential to the ee value. The thin and bumpy edge-accumulated surface plays a different role from large and smooth basal plane.

With the addition of NMO, both catalysts afford a surprisingly low conversion, ee value and TOF, especially a greatly decreased ee value for CSM/ZrPNS. It indicates that the costly NMO is unfavorable to the enhancement of catalytic performance, especially enantioselectivity.

Furthermore, to exclude the possibility that the catalytic performances were caused by different fractions of catalyst species leached to the solution, the solvent CH_2Cl_2 was changed to hexane in which CSM is insoluble and the ee value was found to be increased from 78 % to 87 %.

It is generally believed that the ee value is mainly related to the attack of substrate oriented to active intermediate salen Mn(V) = O for asymmetric epoxidation of olefins. As shown in Fig. 4A, Jacobsen et al. believed that there were four different approaches (a, b, c and d) while Hosoya et al. considered that the two benzene rings of salen Mn(V) = O were folded, one up and one down during the reaction, and the substrate got close to salen Mn(V) = O through approach e [10,11]. Recently, Zou et al. reported that the attack oriented might be approach a and the stereo-effect of position 3 and 3' also played an important role [12]. In addition, it was stated that NMO could bring the metal closer to the substrate, leading to the enhancement of enantioselectivity [13].

Based on our results, it can be suggested that approach a is the optimum attack oriented and the catalytic performance is mainly associated with the surface character. Concretely, for CSM/ZrPNS, the active center is more accessible to reactants since CSM is mainly exposed at the edges of ZrPNS. Besides, the thin edges of nanosheets may act as the role of NMO and the bumpy edge-accumulated surface will greatly restrict other attack directions, leading to a high conversion, ee value and TOF via approach a (Fig. 4B). When NMO is added, the surroundings of the active center appear too crowded and approach a is greatly obstructed, resulting in a great decrease in conversion, ee value and TOF.

Table 2

Asymmetric epoxidation of α -methylstyrene catalyzed by CSM and two chiral heteregeneous catalysts ^a.

Entry	Catalyst	Add.	t (h)	Con (%)	ee (%) ^b	TOF $(10^{-3} \text{ s}^{-1})^{c}$
1	CSM	NMO	1	100	50	13.89
2	CSM/ZrPNS	-	6	100	78	2.31
3	CSM/ZrPNS ^d	-	6	100	31	6.95
4	CSM/ZrPNS	NMO	6	21	13	0.49
5	CSM/ZrPNS-edge	-	9	100	39	1.55
6	CSM/ZrPNS-edge	NMO	9	22	23	0.34
7	CSM/ZrPNS-edge ^e	NMO	9	100	15	1.02

 a Reaction conditions: α-methylstyrene (0.5 mmol), m-CPBA (1 mmol), catalyst (2 mol%, based on Mn content), NMO (2.5 mmol), CH₂Cl₂ (5 mL). Reaction temperature, 273 K.

^o R-configuration.

^c TOF=[product]/([catalyst]×time).

^d CSM/ZrPNS (0.67 mmol%, 10 mg).

e NMO (0.25 mmol).



Fig. 4. (A) The attack-oriented for substrate to the active intermediate salen Mn(V) = 0, (B) CSM on the thin edge. (C) CSM on the basal plane.

By comparison, for CSM/ZrPNS-edge, CSM is mainly loaded on the basal plane of α -ZrP nanosheets since the edges of nanosheets are modified with organic groups. The large and smooth basal plane of α -ZrP nanosheets could act as the role of NMO, but it may also restrict all attack directions to some extent, resulting in a much lower ee value and TOF (Fig. 4C).

After adding NMO, the active centers are greatly obstructed by both the basal plane and NMO, leading to a decrease in conversion, ee value and TOF. When the amount of NMO is decreased 10 times, the conversion and TOF are greatly increased. Nevertheless, the ee value is decreased (Entry 7). The reason may be that a small amount of NMO is not enough to fundamently change the attack approach. This system is also suitable to other substrates such as styrene.

Table S1 lists the preliminary recycling results of CSM/ZrPNS. When the used catalyst was recycled by the post-treatment and re-used for the second, third and fourth times, the corresponding ee values were 31 %, 35 % and 33 %, respectively, being quite stable although much lower than the original value of 78 %. Owing to the reversible assembly and the exfoliation/flocculation properties of nanosheets, it is expected that CSM and nanosheets in the used catalyst can be reassembled into the original structure by controlling the molar ratio of TBAOH to nanosheets, and thus the ee value might be recovered. The corresponding work is currently under way in our lab.

4. Conclusion

In summary, novel heterogeneous asymmetric catalysts can be assembled by cationic CSM and negatively-charged α -ZrP nanosheets. By controlling the loading amount of CSM and the edge-modification of nanosheets, the structure, surface character and location of CSM can be tuned, giving rise to the distinct performances of the resulted catalysts in the asymmetric epoxidation of α -methylstyrene. The thin edges of nanosheets can be restacked into the bumpy surfaces, providing a new and different chemical environment for CSM other than large basal planes and leading to a high ee value without costly NMO. It may provide a new idea for the design and fabrication of novel heterogeneous chiral catalysts with potential applications.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21073084 and 20773065), Natural Science Foundation of Jiangsu Province (Grant No. BK2011438), and 973 Project (Grant No. 2009CB623504). We aslo thank Prof. Limin Zheng for providing α -naphthyl phosphonic acid.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.08.028.

References

- a) C. Li, Catalysis Reviews Science and Engineering 46 (2004) 419–492;
 b) K. Yu, Z.C. Gu, R.N. Ji, L.L. Lou, F. Ding, C. Zhang, S.X. Liu, Journal of Catalysis 252
 - (2007) 312–320;
 c) P. Mcmorn, GJ. Hutchings, Chemical Society Reviews 33 (2004) 108–122.
- [2] a) S. Bhattacharjee, J.A. Anderson, Chemical Communications 5 (2004) 108–122.
 - b) S. Bhattacharjee, T.J. Dines, J.A. Anderson, Journal of Catalysis 225 (2004) 398–407;
 - R.I. Kureshy, N.H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, R.V. Jasra, Journal of Catalysis 221 (2004) 234–240;
 - d) M. Wu, B. Wang, S.F. Wang, C.G. Xia, W. Sun, Organic Letters 11 (2009) 3622–3625;
 - e) C.E. Song, E.J. Roh, Journal of the Chemical Society, Chemical Communications 10 (2000) 837–838;
 - M.J. Sabater, A. Corma, A. Domenech, V. Forne's, H. Garcia, Chemical Communications 14 (1997) 1285–1286;
 - g) K.B.M. Jannsen, J. Laquire, W. Dehaen, R.F. Parton, I.F.J. Vankelecom, P.A. Jacobs, Tetrahedron-Asymmetry 8 (1997) 3481–3487;
 - h) D.R. Leonord, J.R.L. Smith, Journal of the Chemical Society, Perkin Transactions 2 (1991) 25;
 - I.F.J. Vankelecom, D. Tas, R.F. Parton, V.V.D. Vyver, P.A. Jacobs, Angewandte Chemie International Edition 35 (1996) 1346–1348.
- [3] J.M. Fraile, J.I. García, J. Massam, J.A. Mayoral, Journal of Molecular Catalysis A: Chemical 136 (1998) 47–57.

- [4] a) C.H. Liu, H.X. Wu, Y.J. Yang, L.N. Zhu, Y.L. Teng, Journal of Applied Polymer Science 120 (2010) 1106–1113;
 - b) L. Sun, W.J. Boo, D. Sun, A. Clearfield, H.J. Sue, Chemistry of Materials 19 (2007) 1749–1754.
- [5] a) F. Carn, A. Derré, W. Neri, O. Babot, H. Deleuze, R. Backov, New Journal of Chemistry 29 (2005) 1346–1350;
 - b) Y. Omomo, T. Sasaki, L. Wang, M. Watanabe, Journal of the American Chemical Society 125 (2003) 3568–3575;
 - c) T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, H. Nakazawa, Journal of the American Chemical Society 118 (1996) 8329–8335.
- [6] a) H.N. Kim, S.W. Keller, T.E. Mallouk, J. Schmitt, G. Decher, Chemistry of Materials 9 (1997) 1414–1421;
 - D.M. Kaschak, S.A. Johnson, D.E. Hooks, H.N. Kim, M.D. Ward, T.E. Mallouk, Journal of the American Chemical Society 120 (1998) 10887–10894;
 - c) T.E. Mallouk, J.A. Gavin, Accounts of Chemical Research 31 (1998) 209-218;
 - d) D.M. Kaschak, T.E. Mallouk, Journal of the American Chemical Society 118 (1996) 4222–4223;

- e) G. Alberti, M. Casciola, R. Palombari, Solid State Ionics 61 (1993) 241–244;
 f) G. Cao, H.G. Hong, T.E. Mallouk, Accounts of Chemical Research 25 (1992) 420–427.
- [7] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, Journal of the American Chemical Society 112 (1990) 2801–2803.
- [8] J. Xu, Y. Tang, H. Zhang, Z. Gao, Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 27 (1997) 303–317.
- [9] C. Li, H.D. Zhang, D.M. Jiang, Q.H. Yang, Chemical Communications 6 (2007) 547–558.
 [10] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, Journal of the American Chemical Society 113 (1991) 7063–7064.
- N. Hosoya, A. Hatayama, R. Irie, H. Sasaki, T. Katsuki, Tetrahedron 50 (1994) 4311–4322.
 X.C. Zou, X.K. Fu, Y.D. Li, X.B. Tu, S.D. Fu, Y.F. Luo, X.J. Wu, Advanced Synthesis and
- Catalysis 352 (2010) 163–170. [13] P.G. Cozzi, Chemical Society Review 33 (2004) 410–421.