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An effective approach for the immobilization of chiral Mn(III) salen complexes through a supported ionic liquid phase

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Abstract—An effective method based on supported ionic liquid system was employed to immobilize chiral Mn(III) salen complexes. The prepared heterogeneous catalysts exhibited excellent activity and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins. Especially, in the epoxidation of α-methylstyrene, both the conversion and ee value could exceed 99%. Furthermore, the immobilized catalysts were stable and could be recycled three times without loss of activities.

1. Introduction

The asymmetric epoxidation of unfunctionalized olefins is an important reaction to synthesize a variety of valuable chiral compounds, which are widely applied in the synthesis of pharmaceuticals and agrochemicals. To date, the chiral Mn(III) salen complexes have been demonstrated to be very effective catalysts for the enantioselective epoxidation of unfunctionalized olefins. In consideration of the advantages of the heterogeneous catalysis system, for example, easy catalyst/product separation and simple catalyst recycling, many researchers have been devoting to the studies of heterogenization of chiral Mn(III) salen complexes.[1–4] In most cases, the heterogenized chiral Mn(III) salen complexes would lead to lower enantioselectivity than their homogeneous counterparts; only a few documented work have reported higher ee value, however, lower activity is always obtained in this situation.[5–10]

Recently, room temperature ionic liquids (RTIL) have attracted noticeable attention as important solvent in the synthesis and catalysis owing to their strong solvent power for many organic and inorganic substances.[11,12] It was reported by Song and Roh[13] that the chiral Mn(III) salen epoxidation catalyst immobilized in ionic liquid [bmim][PF_6] ($[bmim]^+$ = 1-butyl-3-methylimidazolium cation) offered comparable enantioselectivity as well as increased activity in the asymmetric epoxidation of olefins than that obtained without the employment of ionic liquid. Here, we employed the supported ionic liquid system as carrier media to immobilize chiral Mn(III) salen complexes. Mehnert[14,15] has described the concept of supported ionic liquid catalysis, which involves the treatment of a monolayer of covalently attached ionic liquid on the surface of a support material with additional adsorbed ionic liquid. These layers serve as the reaction phase in which the homogeneous catalyst is dissolved. The supported ionic liquid catalyst combines the advantages of ionic liquids and heterogeneous supports. Active species in the ionic liquid phase acts like a homogeneous catalyst. Several studies[14–20] have successfully confined various ionic liquid phases to the surface of different supports and applied them in some catalytic processes. In the present work, we have prepared chiral Mn(III) salen complexes immobilized on the imidazolium-based ionic liquid modified mesoporous silicate MCM-48, and [bmim][PF_6] was used as the additional adsorbed ionic liquid. The obtained catalyst was employed as an efficient catalyst for the asymmetric epoxidation of unfunctionalized olefins. It is expected that high activity and enantioselectivity can be obtained from these immobilized catalysts due to the solution property of ionic liquid phase and the topological structure of MCM-48.

2. Results and discussion

1-Methyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride was prepared by the reaction of 1-methylimidazole

Keywords: Supported ionic liquid phase; Mn(III) salen; Asymmetric epoxidation; Unfunctionalized olefin.

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with (3-chloropropyl)trimethoxysilane. The resulting chloride was treated with potassium hexafluorophosphate in acetone for 3 days to give the corresponding ionic liquid **1**. Parent silica MCM-48 materials were synthesized in autoclaves at 383 K for 72 h according to a procedure outlined earlier.[21,22] A gel (molar) composition of 1TEOS/0.46CTAB/0.41NaOH/52.95H_2O was used. The template was removed by calcination at 823 K in air for 5 h. Pretreated mesoporous silicate MCM-48 (dried under vacuum and heated to 393 K overnight, 3.00 g) was stirred with a chloroform solution (50 mL) of ionic liquid **1** (2.16 g, 5 mmol) under refluxing for 26 h to prepare ionic liquid-anchored MCM-48 material (**1**-MCM-48). FT-IR spectrum of **1**-MCM-48 revealed specific IR adsorption characteristics of ionic liquid **1**, which was reflected in: ν(C–H) at 3171 and 3122 cm^{-1}, ν(C=C) at 1578 and 1461 cm^{-1}, δ(C–H) at 1168 cm^{-1}, $\rho_s(-CH_2-CH_2-CH_2-)$ at 1467 cm^{-1}, and ν(P–F) at 840 cm^{-1}. Elemental analysis of **1**-MCM-48 indicated that 0.68 mmol of ionic liquid fragments per gram of **1**-MCM-48 existed. Next, **1**-MCM-48 (1.00 g) was treated with ionic liquid [bmim][PF_6] (300 mg) and an acetone solution of chiral Mn(III) salen pre-catalyst **a** or **b** (Fig. 1, the two (*S*,*S*)-Mn(III) salen chlorides were synthesized according to the literature method,[23,24] 0.30 mmol). After the volatile components were removed under reduced pressure, brown powder was obtained. The prepared catalysts were designated as [bmim][PF_6]/**1**-MCM-48 **a** and [bmim][PF_6]/**1**-MCM-48 **b**. The structure of the catalysts is showen in Figure 1, the ionic liquid phase [bmim][PF_6] containing the chiral Mn(III) salen complexes was immobilized on the surface of the modified support material **1**-MCM-48. The XRD patterns of the two catalysts confirmed that the mesoporous structure of the support still retained good periodicity after the immobilization. The amount of Mn(III) salen in the prepared catalysts was 0.2 mmol g^{-1}, based on Mn as determined by the ICP-AES.

The synthesized heterogeneous catalysts were evaluated in the epoxidation of unfunctionalized olefins with *m*-CPBA/NMO (*m*-chloroperoxybenzoic acid/*N*-methylmorpholine *N*-oxide) as oxidant in CH_2Cl_2 at 273 K for 2 h. The following substrates were employed: styrene, α-methylstyrene, 1-phenylcyclohexene, and indene. Conversions and enantiomeric excess values were determined by gas chromatography with a chiral β-cyclodextrin capillary column. For comparison, the chiral Mn(III) salen pre-catalysts **a** and **b** were also investigated under the reaction conditions mentioned above. The results are listed in Table 1.

As shown in Table 1, the homogeneous catalyst **a** gave high conversion in the epoxidation of α-methylstyrene; however, the ee value was not very high (entry 5). Compared with the homogeneous catalyst, the supported ionic liquid catalyst [bmim][PF_6]/**1**-MCM-48 **a** exhibited notably higher enantioselectivity and comparable catalytic activity in the α-methylstyrene epoxidation: the enantiomeric excess was increased from 50% to >99% (entries 5 and 6), and the conversion of α-methylstyrene reached 99% (entry 6). Both the obtained conversion and ee value were significantly higher than those reported in the literatures related to inorganic supports.[5,7,8,10] Besides the smaller olefin substrates, the heterogenized Mn(III) salen catalysts also showed satisfactory catalytic activity and enantioselectivity for relatively bulkier olefins such as 1-phenylcyclohexene and indene. The epoxidation of 1-phenylcyclohexene by [bmim][PF_6]/**1**-MCM-48 **a** provided a higher ee value of 92% compared with its homogeneous ee of 86%, and comparable substrate conversion was obtained. Similar results were also achieved by [bmim][PF_6]/**1**-MCM-48 **b** with an ee value of 83% (entry 10). It is noteworthy that such remarkably enhanced ee values were obtained with no obvious decrease in olefins conversion. This may be due to the combination of solution chemistry (ionic liquid) and the spatial effect originated from the heterogeneous carrier media MCM-48, which possesses well defined pore size and 3-D topological structure. Recently, it was reported[25] that Mn(III) salen complexes immobilized on MCM-48 via multi-step grafting presented a

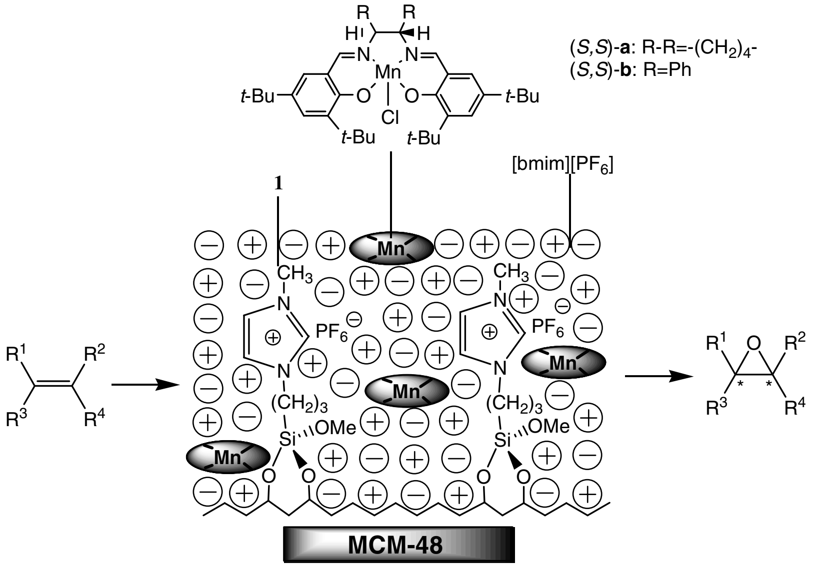

Figure 1. The asymmetric epoxidation of olefins over the chiral Mn(III) salen complexes immobilized on ionic liquid modified MCM-48.

Table 1. Asymmetric catalytic epoxidation of unfunctionalized olefins[a]

Entry	Substrate	Catalyst	Conv. (%)[b]	ee (%)[c]
1	Styrene	**a**	>99	48(*S*)
2	Styrene	[bmim][PF_6]/**1**-MCM-48 **a**	50	41(*S*)
3	Styrene	**b**	89	64(*S*)
4	Styrene	[bmim][PF_6]/**1**-MCM-48 **b**	52	48(*S*)
5	α-Methylstyrene	**a**	>99	50(*S*)
6	α-Methylstyrene	[bmim][PF_6]/**1**-MCM-48 **a**	99	>99(*S*)
7	1-Phenylcyclohexene	**a**	96	86(1*R*,2*R*)
8	1-Phenylcyclohexene	[bmim][PF_6]/**1**-MCM-48 **a**	95	92(1*R*,2*R*)
9	1-Phenylcyclohexene	**b**	82	78(1*R*,2*R*)
10	1-Phenylcyclohexene	[bmim][PF_6]/**1**-MCM-48 **b**	83	83(1*R*,2*R*)
11	Indene	**b**	97	88(1*S*,2*R*)
12	Indene	[bmim][PF_6]/**1**-MCM-48 **b**	97	87(1*S*,2*R*)

[a] Reaction conditions: reaction temperature 273 K, reaction time 2 h, solvent: CH_2Cl_2, oxidant: *m*-CPBA/NMO, substrate/catalyst/*m*-CPBA/NMO = 1:0.01:2:5.

[b] Conv.% determined by GC with chiral column using toluene as internal standard.

[c] Ee% determined by GC with RESTEK RT-BetaDEXse chiral column.

Table 2. The recycling studies of immobilized catalysts [bmim][PF_6]/**1**-MCM-48 **a** and [bmim][PF_6]/**1**-MCM-48 **b** in the epoxidation of 1-phenylcyclohexene[a]

Recycling number	Catalyst	Conv. (%)	ee (%)
1st	[bmim][PF_6]/**1**-MCM-48 **a**	95	92(1*R*,2*R*)
	[bmim][PF_6]/**1**-MCM-48 **b**	83	83(1*R*,2*R*)
2nd	[bmim][PF_6]/**1**-MCM-48 **a**	93	90(1*R*,2*R*)
	[bmim][PF_6]/**1**-MCM-48 **b**	80	81(1*R*,2*R*)
3rd	[bmim][PF_6]/**1**-MCM-48 **a**	93	91(1*R*,2*R*)
	[bmim][PF_6]/**1**-MCM-48 **b**	82	83(1*R*,2*R*)

[a] Reactions were performed in CH_2Cl_2 at 273 K for 2 h with *m*-CPBA/NMO as oxidant and in the presence of 1 mol % of the catalysts.

high ee value of 99% for the epoxidation of α-methylstyrene due to the restrain of free rotation of the intermediate by the topological structure of MCM-48, but the conversion was much lower (only 34%).

The homogeneous catalyst **b** showed high activity and enantioselectivity for the epoxidation of indene, a ee value of 88% was collected (entry 11). Immobilizing the Mn(III) salen complex **b** on the **1**-MCM-48 with [bmim][PF_6] led to a similar result for indene epoxidation, an ee value of 87% was achieved with no decrease in indene conversion.

The used catalysts [bmim][PF_6]/**1**-MCM-48 **a** and [bmim][PF_6]/**1**-MCM-48 **b** were reused for the epoxidation of 1-phenylcyclohexene and the results are presented in Table 2. The results showed that the activity and enantioselectivity had no obvious decrease for at least 3 runs. At the end of each cycle, dichloromethane was removed under reduced pressure and the residue was stirred with hexane. Then the solid catalyst was filtered, dried and reused. No leaching of ionic liquid and Mn(III) salen complex was observed by NMR and ICP.

3. Conclusions

In summary, the Mn(III) salen complexes were immobilized by imidazolium-based ionic liquid modified MCM-48 for the asymmetric epoxidation of unfunctionalized olefins. These heterogeneous catalysts were stable, recyclable and exhibited comparable activity and remarkably higher enantioselectivity (e.g., >99% and 92% ee for α-methylstyrene and 1-phenylcyclohexene, respectively) than those obtained by the homogeneous counterparts.

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References and notes

1. Bianchini, C.; Barbaro, P. *Top. Catal.* **2002**, *19*, 17–32.
2. Song, C.-E.; Lee, S.-G. *Chem. Rev.* **2002**, *102*, 3495–3524.
3. McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108–122.
4. Li, C. *Catal. Rev.—Sci. Eng.* **2004**, *46*, 419–492.
5. Kim, G.-J.; Shin, J.-H. *Tetrahedron Lett.* **1999**, *40*, 6827–6830.
6. Zhou, X.-G.; Yu, X.-Q.; Huang, J.-S.; Li, S.-G.; Li, L.-S.; Che, C.-M. *Chem. Commun.* **1999**, 1789–1790.
7. Kim, G.-J.; Kim, S.-H. *Catal. Lett.* **1999**, *57*, 139–143.
8. Xiang, S.; Zhang, Y.; Xin, Q.; Li, C. *Chem. Commun.* **2002**, 2696–2697.
9. Kureshy, R. I.; Ahmad, I.; Khan, N. H.; Abdi, S. H. R.; Singh, S.; Pandia, P. H.; Jasra, R. V. *J. Catal.* **2005**, *235*, 28–34.
10. Zhang, H.; Xiang, S.; Li, C. *Chem. Commun.* **2005**, 1209–1211.
11. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
12. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
13. Song, C. E.; Roh, E. J. *Chem. Commun.* **2000**, 837–838.
14. Mehnert, C. P.; Cook, R. A.; Dispenziere, N. C.; Afeworki, M. *J. Am. Chem. Soc.* **2002**, *124*, 12932–12933.
15. Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50–56.
16. Mehnert, C. P.; Mozeleski, E. J.; Cook, R. A. *Chem. Commun.* **2002**, 3010–3011.

17. Riisager, A.; Wasserscheid, P.; Hal, R. van; Fehrmann, R. *J. Catal.* **2003**, *219*, 452–455.
18. Gruttadauria, M.; Riela, S.; Meo, P. L.; D'Anna, F.; Noto, R. *Tetrahedron Lett.* **2004**, *45*, 6113–6116.
19. Breitenlechner, S.; Fleck, M.; Müller, T. E.; Suppan, A. *J. Mol. Catal. A: Chem.* **2004**, *214*, 175–179.
20. Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397–1399.
21. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712.
22. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.
23. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801–2803.
24. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron Lett.* **1990**, *31*, 7345–7348.
25. Yu, K.; Lou, L.-L.; Ding, F.; Wang, S. J.; Wang, Z. L.; Liu, S. X. *Catal. Commun.* **2006**, *7*, 170–172.