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A new heterogeneous chiral (salen)manganese(III) system for enantioselective epoxidation of non-functionalized olefins

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This communication describes the design and application of a novel catalytic epoxidation system derived from the initial immobilization of a homogeneous sulfonato (salen)Mn(III) complex on two solid carriers (silica gel and siliceous earth) and subsequent dispersion of the supported manganese complexes into ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄) for recycling. The performance of chiral (salen)Mn(III) system in enantioselective epoxidation of olefins was investigated systematically. Even higher enantioselectivity than that of the homogeneous counterpart was obtained with similar catalytic activity. In particular, the best catalytic result is that the combination of the silica gel-supported (salen)Mn(III) catalyst and BMImPF₆ affords 97–100% ee for epoxidation of α -methylstyrene, and high ee values were retained even after three cycles. Copyright (C) 2010 John Wiley & Sons, Ltd.

Keywords: enantioselective epoxidation; heterogeneous; (salen)manganese(III); ionic liquid; olefins

Introduction

Chiral epoxides are versatile building blocks in the synthesis of various pharmaceutical products, so the design and preparation of effective catalysts for asymmetric epoxidation of alkenes have become an important challenge for chemists.^[1-5] In this field, Sharpless and co-workers developed a catalytic system which showed high ee for the epoxidation of functionalized alkenes.^[6] Also, in the case of unfunctionalized alkenes, Jacobsen^[7–9] and Katsuki^[10-12] developed several highly effective epoxidation catalysts baced on some chiral (salen)Mn(III) [salen = N,N'bis(salicylidene)ethylenediaminato] complexes. Owing to convenient preparation and the high reactivity and enantioselectivity of (salen)Mn(III) complexes, there have been many efforts to expand on the homogeneous (salen)Mn(III) system, including special homogeneous catalysts,^[13–16] grafting onto silica,^[17–19] MCM-41,^[20,21] MCM-48^[22] and im-41,^[23] ionic liquid media^[24,25] and others^[26] (Fig. 1). In contrast to the homogeneous catalysts, the immobilization of catalysts on heterogeneous supports allowed easy separation and thus facilitated their reuse, but the leaching of catalysts from the carriers was also noteworthy.

Owing to the limitations of solid-supported catalysts, and to develop an easily recovered catalytic system, reaction media were redesigned. For example, Pozzi^[27] ran catalytic epoxidation reactions in fluorous biphase systems (FBS) by modifying the salen ligand by incorporating a perfluorinated alkyl chain. This improved the solubility of the catalyst in the FBS solvent, and high enantioselectivities were obtained in the epoxidation of indene (ee value 92%). Another important attempt was the application of ionic liquids. Song^[23] investigated the epoxidation of five unfunctionalized alkenes with Jacobsen's catalyst in a mixed solvent of BMImPF₆ with CH₂Cl₂, affording a practical recycling procedure for the epoxidation of 2,2-dimethylchromene with good enantioselectivity, but the catalytic yields decreased gradually owing to inevitable human factors in the experiment. Smith^[24] disclosed the catalytic characteristics of Katsuki's catalyst combined with BMImPF₆ and BMImBF₄ (Fig. 2). Although 100% ee value was achieved in the first cycle of epoxidation of 1,2dihydronaphthalene, recycling issues still existed. Subsequently, the leaching of homogeneous (salen)Mn(III) complexes from ionic liquids into *n*-hexane seemed to be unavoidable.

Herein, we decided to pay more attention to the recovery and recycling of (salen)Mn(III) catalysts in ionic liquids. In the aspect of selecting manganese catalysts, besides Jacobsen's catalyst, we speculated that silica-supported (salen)Mn(III) complexes derived from sulfonation of the 5,5'-positions on the salen ring should also be effective catalysts when being used in conjunction with ionic liquids.^[28] Furthermore, the resulting silica-supported catalysts dispersed in ionic liquid were completely insoluble in *n*-hexane, so the final extraction of products and the recovery and recycling of catalyst should become more convenient. Finally, in view of the economy of catalytic reactions, some commercially available co-catalysts might be applied to replace expensive donor

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Figure 1. Structure of supported-(salen)Mn compounds.



Figure 2. Structure of ionic liquid BMImBF₄ and BMImPF₆.

ligands such as PPyNO (4-phenylpyridine *N*-oxide) and PPPyNO [4-(3-phenylpropyl)pyridine *N*-oxide]. If possible, the epoxidation reaction performed in the absence of a co-catalyst would be a convenient approach.

In this work, Jacobsen's catalyst {[(R,R)-N,N'-bis(3,5-di-tertbutylsalicylidene)-1,2-cyclo-hexanediaminato(2-)]manganese(III)chloride)}, together with two silica-supported (salen)Mn(III) catalysts, was employed in the enantioselective epoxidation of unfunctionalized olefins when BMImBF₄ and BMImPF₆ were both used as reaction media for recycling. The two silica-supported (salen)Mn(III) catalysts were derived from immobilizating (salen)Mn(III) complex with two sulfonyl groups onto siliceous earth and silica gel (100–200 mesh), respectively. Hydrous NaClO was selected as terminal oxidant, and NH₄OAc as co-catalyst. Recycling experiments were performed for comparison. The immediate goals of this work were to assess: (1) the recycling capabilities of BMImBF₄ and BMImPF₆ for (salen)Mn(III) catalyzed asymmetric epoxidation of unfunctionalized alkenes; (2) the exact role of NH₄OAc as an epoxidation co-catalyst; and (3) the catalytic abilities of silica-supported (salen)Mn(III) catalysts used with ionic liquids.

Experimental

Materials and Instruments

All chemicals of reagent grade were purchased from Alfa Aesar and used without further purification. Jacobsen's catalyst^[29] and sulfonato-(salen)Mn(III) complex $\mathbf{3}^{[19]}$ were synthesized according to the literature procedure. Siliceous earth (specific surface area 20–70 m² g⁻¹) and column chromatography-grade silica gel (100–200 mesh; specific surface area 300–400 m² g⁻¹) were soaked in hydrochloric acid (6 mol l⁻¹) for 4 h, then washed until chloride ions had been cleared away, and dried at 150 °C for 2 h



Figure 3. Route for preparation of chiral sulfonato-Salen-Mn() complex immobilized on silica supports. Carrier 1, siliceous earth; carrier 2, silica gel.

in a vacuum oven. Two ionic liquids, BMImBF₄ and BMImPF₆, were prepared according to the reported method.^[30] FT-IR spectra were recorded as KBr pellets with a resolution of 4 cm⁻¹ and 32 scans in the range of 400–4000 cm⁻¹ using an Avatar 330 Thermo Nicolet spectrophotometer.

The ultraviolet-visible light (UV-vis) spectra were recorded on a UV-vis Cary 50 spectrophotometer. The sample solution in dichloromethane was poured into a 1 cm quartz cell for UV-vis adsorption with dichloromethane as the reference. The maximum absorption wavelength of epoxides was 254 nm by UV-vis detection.

The M_n element content was measured by the atomic absorption spectroscopy (AAS) on a WFX-1E2 type spectrometer. A standard curve method was used to test samples using Mn(OAc)₂ as a standard. Experimental conditions were: light source, Mn

hollow cathode lamps; lamp current, 2 mA; wavelength, 279.5 nm; passband, 0.2 nm; air pressure, 0.3 MPa.

Three standard racemic epoxide samples including styrene oxide, α -methylstyrene oxide and indene oxide were obtained by the epoxidation of three alkenes catalyzed by a non-chiral (salen)Mn(III) complex {[N,N'-bis(3,5-di-*tert*-butylsalicylidene)-ethylenediaminato(2-)]manganese(III) chloride} when hydrous NaClO (Na₂HPO₄ buffered, pH = 11.3) was used as terminal oxidant in the presence of NH₄OAc as co-catalyst. The ee value and product analysis were determined using a LC-10AT VP Shimadzu HPLC with UV detector (254 nm) using a Chiracel OD-H capillary column with 2-propanol–hexane as eluting agent.

Synthesis of Sulfonato-(salen)Mn(III) Complex 3 (Fig. 3)

The synthetic procedure was carried out according to the reported method.^[19] With tert-butyl salicylaldehyde as the



 \bigcirc =BMIm⁺ \bigcirc =BF⁻₄ or PF⁻₆ - =solid carriers

Figure 4. The catalytic system includes the initial immobilization of sulfonato- Salen-Mn(III) complex on two silica-supports and the subsequent dispersion of supported catalysts into ionic liquid.



Figure 5. The enantioselective epoxidation of styrene, α -methylstyrene and indene.

starting material, complex **1** was obtained through aldehyde protection, sulfonation and deprotection. Couping with the (1*R*,2*R*) 1,2-diaminocyclohexane-L-tartarate, complex **2** was successfully converted into complex **3** with Mn(Ac)₂ and LiCl in methanol.

Synthesis of Siliceous Earth-supported (salen)Mn(III) Catalyst 1 (Fig. 3)

A 500 mg aliquot of sulfonato-(salen)Mn(III) complex **3** was suspended in 100 ml of acetonitrile and sonicated for 1 h at room temperature. Activated siliceous earth (3.0 g) was added and the resulting mixture was further refluxed at 100 °C for 24 h. The siliceous earth-supported catalyst was obtained by centrifugation and washed several times with acetonitrile until the color of the supernatant solution disappeared. The brown solid (catalyst 1) was dried at room temperature. The Mn content in catalyst 1 was found to be 4.02×10^{-5} mol g⁻¹ by AAS. FT-IR (KBr): v = 1627, 1570, 1109, 558, 419 cm⁻¹.

Synthesis of Silica Gel-supported (salen)Mn(III) Catalyst 2 (Fig. 3)

The synthetic procedure of catalyst **2** was identical to that of catalyst **1** as described above, and obtained a dark brown soild. The Mn content in catalyst **2** was found to be $1.71 \times 10^{-4} \text{ mol g}^{-1}$ by AAS. FT-IR (KBr): v = 3446, 1636, 1576, 1101, 520, 467 cm⁻¹.

Catalytic Experiments (Figs 4 and 5)

Enantioselective epoxidation reactions were performed according to the established procedure as follows.^[15] A solution of Na₂HPO₄ (0.05 mol l⁻¹, 4 ml) was added to a pre-cooled (0 °C) solution of aqueous NaClO (0.58 mol l⁻¹, 10 ml, 5.8 mmol), adjusting the pH value to 11.3. Subsequently, the solution obtained was divided into five equal portions, then gradually added to another solution containing alkene (2 mmol), catalyst (the molarity of Mn was 0.2 mmol) and co-catalyst (0.4 mmol) with vigorous stirring and five reaction media (from I to V: for medium I, the volume of CH_2Cl_2 was 10 ml; for media II and III, the volume ratio of ionic liquid and CH_2Cl_2 was 3 vs 10 ml; for media IV and V, the volume of ionic

liquid was 10 ml). Moreover, when the media IV and V were used, the mixture of catalyst and ionic liquid was stirred vigorously for one day before use. All catalysts could be easily dispersed into ionic liquids with magnetic stirring at 0 °C and monitored by TLC. After the reaction was over, the two extraction approaches were used based on the reaction medium: (1) for media I, II and III, the reaction mixture was diluted with CH₂Cl₂ (30 ml), and the organic layer was separated, washed with water and brine, dried over anhydrous MgSO₄, then filtered. If medium I was loaded, after removal of the solvent under reduced pressure, the epoxides were obtained by flash chromatography (SiO₂, petroleum ether-CH₂Cl₂, 2:1, v/v). Otherwise, if media II and III were loaded, the volatiles were evaporated under reduced pressure and the residue was stirred with *n*-hexane (60 ml). After concentration of the upper n-hexane phase under reduced pressure, the residue was purified by flash chromatography (SiO₂, petroleum ether-CH₂Cl₂, 2:1, v/v), to afford the epoxides. The brown ionic liquid phase (the lower phase) containing the catalyst was reused. (2) For media IV and V, 60 ml of n-hexane was directly added to the reaction mixture, then a tri-phase system was formed: organic phase (nhexane phase, upper layer), water phase (middle layer) and ionic liquid phase (the bottom). The n-hexane phase was separated and concentrated under reduced pressure, then the residue was purified by flash chromatography (SiO₂, petroleum ether-CH₂Cl₂, 2:1, v/v), to afford the epoxides. On the other hand, the ionic liquid including catalyst was also separated for recycling.

Results and Discussion

Infrared Analysis of Two Silica-supported Sulfonato-(salen)Mn(III) Catalysts

There are two kinds hydroxyl groups on the silica surface. The sharp peak around 3740 cm⁻¹ is a free hydroxyl which has no relationship with adsorbed water and adjacent hydroxyl groups. The broad peak at about 3600 cm^{-1} is a surface hydroxyl group, which has relationship with hydrogen bond and adsorbed water.^[31] In order to avoid the interference of physically adsorbed water with the hydroxyl peak on silica surface, dry silica should be activated for 2 h at 250 °C in a muffle furnace.^[32] The infrared spectroscopy of activated silica gel and silica gel-supported (salen)Mn(III) catalyst was determined. The free sulfonato-(salen)Mn(III) complex 3 exhibited FT-IR bands at 1024 and 1120 cm⁻¹ associated with the symmetric and anti-symmetric stretching modes of the SO_3^- moiety, together with other bands at 1636 cm⁻¹ (CH=N), 1560 cm⁻¹ (C–O), 520 cm⁻¹ (Mn–O) and 467 cm⁻¹ (Mn–N). The IR spectrum of Fig. 6 shows that the sharp peak around 3740 cm^{-1} was reduced and the top tipped away, while the characteristic absorption peaks of catalyst are also shown, indicating that sulfonato-(salen)Mn(III) complex 3 is linked to the silica surface through the reaction with free hydroxyl.

Ionic Liquids Facilitated Epoxidations Freshly Catalyzed by Jacobsen's Catalyst

In this section, the (*R*,*R*)-Jacobsen's catalyst was employed in the asymmetric epoxidations of styrene (A), α -methylstyrene (B) and indene (C) when NaClO was used as a terminal oxidant and NH₄OAc was used as a co-catalyst under five prepared reaction media at 0 °C. Enantioselective epoxidation reactions were performed according to the established procedure.^[15] The results of epoxidations are summarized in Table 1. All reactions



Figure 6. The IR spectrum of silica gel-supported (salen)Mn(III) catalyst.

Table 1.	Enantioselective epoxidat	ion of unfunctionaliz	ed olefins catalyzed by	Jacobsen's catalyst u	nder different medium ^a	
Entry ^b	Alkene ^c	Media ^d	Time ^e (h)	ee ^f (%)	Yield ^g (%)	Configuration ^h
1	А	I	6.0	27	92	R
2		II	2.0	92	68	R
3		III	2.0	65	77	R
4		IV	2.0	64	45	R
5		V	2.0	88	99	R
6	В	I	6.0	76	64	R
7		II	2.0	83	86	R
8		III	2.0	87	65	R
9		IV	2.0	89	73	R
10		V	2.0	91	70	R
11	С	I	6.0	79	94	1 <i>R</i> ,2 <i>S</i>
12		II	2.0	82	77	1 <i>R</i> ,2 <i>S</i>
13		III	2.0	91	50	1 <i>R</i> ,2 <i>S</i>
14		IV	2.0	89	81	1 <i>R</i> ,2 <i>S</i>
15		V	2.0	95	82	1 <i>R</i> ,2 <i>S</i>

^a Reaction conditions: substrate, 2 mmol; catalyst, 0.2 mmol, 10 mol%; co-catalyst, 0.4 mmol, 20 mol%; NaClO, 5.8 mmol.

^b All entries in this article Are numbered consecutively in spite of the table numbers.

^c A, styrene; B, α-methylstyrene; C, indene.

^d Five reaction media: (I) CH₂Cl₂-H₂O; (II) BMImBF₄-CH₂Cl₂-H₂O; (III) BMImPF₆-CH₂Cl₂-H₂O; (IV) BMImBF₄-H₂O; (V) BMImPF₆-H₂O.

^e Monitored by TLC every other half an hour.

^f Determined by HPLC over a chiral OD-H column after comparing the retention times with those of three racemic epoxide samples.

^g Yield of the isolated epoxide.

^h Absolute configurations of major enantiomers which were determined by comparison with the literature values: for styrene oxide and α -methylstyrene oxide^[34]; for indene oxide, see Palucki *et al.*^[35]

proceeded smoothly, and good yields (entry 5, 99% of ee; entry 11, 94% of ee) were reached.

In practice, when the epoxidation was over, different phases were separated in the five reaction media after magnetic stirring was discontinued. For media **I**, **II** and **III**, a biphasic system formed, with a water phase (upper layer) and dichloromethane phase (the bottom, containing the ionic liquid or not). However, with media **IV** and **V**, a tri-phase system formed, with an organic phase (upper layer), water phase (middle layer) and ionic liquid phase (bottom). For all alkenes, reaction acceleration was achieved only in the case

of ionic liquids (from media **II** to**V**) existing, and it seemed that improving yields were obtained with a larger proportion of ionic liquid (entry 5 vs entry 3; entry 10 vs entry 8; entry 14 vs entry 12; entry 15 vs entry 13).

Owing to the different miscibilities of both BMImBF₄ and BMImPF₆ with water (BMImBF₄ is soluble in water at \geq 6 °C ^[25] and BMImPF₆ is completely insoluble in water), the water phases of reaction media containing BMImBF₄ (media II and IV) turned slightly yellow compared with other reaction media (media I, III and V). It is interesting to note that reaction media play an

Table 2.	Enantioselective	epoxidation of u	nfunctionalized olefins	catalyzed by Jacobse	n's catalyst with the id	onic liquids as reaction	n media ^a		
			ee (%) [yield (%), time (h)]						
Entry	Alkene	Media	Cycle fresh ^b	Cycle 1	Cycle 2	Cycle 3	Cycle 4		
16	А	II	92 (68, 2.0)	65 (55, 2.0)	65 (60, 2.0)	33 (35, 3.0)	29 (16, 3.0)		
17		III	65 (77, 2.0)	55 (42, 2.0)	31 (29, 2.0)	81 (70, 2.0)	41 (30, 2.5)		
18		IV	64 (45, 2.0)	59 (49, 2.0)	59 (30, 2.0)	55 (24, 2.5)	52 (46, 2.5)		
19		V	88 (99, 2.0)	89 (52, 2.0)	72 (43, 2.0)	74 (19, 2.0)	74 (15, 2.0)		
20	В	П	83 (86, 2.0)	80 (39, 2.0)	62 (58, 2.0)	55 (34, 2.5)	55 (40, 2.5)		
21		III	87 (65, 2.0)	79 (32, 2.0)	73 (20, 2.0)	79 (56, 2.0)	79 (15, 3.0)		
22		IV	89 (73, 2.0)	80 (66, 2.0)	79 (71, 2.0)	70 (44, 2.0)	67 (30, 2.0)		
23		V	91 (70, 2.0)	91 (72, 2.0)	89 (65, 2.0)	89 (69, 2.0)	90 (42, 2.0)		
24	С	П	82 (77, 2.0)	70 (56, 2.0)	81 (38, 2.0)	85 (20, 2.0)	77 (21, 3.0)		
25		III	91 (50, 2.0)	91 (31, 2.0)	91 (33, 2.0)	83 (38, 2.0)	71 (44, 2.0)		
26		IV	89 (81, 2.0)	87 (75, 2.0)	83 (72, 2.0)	80 (70, 2.0)	79 (71, 2.0)		
27		V	95 (82, 2.0)	89 (95, 2.0)	87 (88, 2.0)	87 (80, 2.0)	85 (75, 2.0)		

^a Reaction conditions, together with other indexes were almost identical to their counterparts in Table 1. Entries 16–27 were 12 respective recycling experiments of four cycles. The absolute configurations of major enantiomers of styrene oxide, α -methylstyrene oxide and indene oxide were *R*, *R* and 1*R*,2*S*, respectively.

^b The fresh cycles of entries 16–27 were consecutive copies of entries 2–5, 7–10 and 12–15 for the convenience of comparison.

important role in chiral induction under the present reaction conditions. Chiral outputs were obtained as shown in Table 1. The epoxidation in pure $BMImPF_6$ (media **V**) afforded higher ee values than pure $BMImBF_4$ (media IV) (entry 5 vs entry 4; entry 10 vs entry 9; entry 15 vs entry 14) and BMImPF₆-CH₂Cl₂-H₂O (media III) (entry 5 vs entry 3; entry 10 vs entry 8; entry 15 vs entry 13). These preliminary results clearly indicated that the reaction media was important in the aspect of improving enantioselectivity. Pure ionic liquids appeared to be better than ionic liquid-CH₂Cl₂ mixed systems, and BMImPF₆ seemed to be better than BMImBF₄ in terms of chiral induction. Taking into account the structures of Jacobsen's catalyst and the two ionic liquids, we speculated that an anion exchange process between CI^- and PF_6^- (or between Cl⁻ and BF₄⁻) might occur during the reaction which probably affected the enantioselectivities.^[33] Since BF₄⁻ is water-soluble,^[25] the anion exchange process between Cl⁻ and BF₄⁻ would be weakened during epoxidation; therefore the BMImBF₄ afforded lower enantioselectivities.

Ionic Liquids Recycled Epoxidations Catalyzed by Jacobsen's Catalyst

Since the initial catalytic studies indicated that ionic liquids had a notable effect on both the reaction yields and enantioselectivity, it was significant that BMImBF₄ and BMImPF₆ as mobile carriers enhanced the recycling of Jacobsen's catalyst. To further appreciate the recycling potentials of two ionic liquids and to optimize the reaction conditions, the recycling experiments were carried out using pure ionic liquid media (**IV** and **V**) and mixed CH_2Cl_2 -ionic liquid media (**II** and **III**). Subsequently, NH₄OAc or none was selected as co-catalyst as the reference for industrial application. The general conditions for recycling are similar to those described in the section on catalytic experiments except for the reloaded NH₄OAc before every cycle, because NH₄OAc was completely insoluble in both CH₂Cl₂ and ionic liquids and thus its consumption in each cycle was inevitable.

The results of recycling experiments are summarized in Table 2. In general, all catalytic reactions were completed within 3 h. Similar to the first catalytic results, the epoxidation reactions in pure ionic liquid media (**IV** and **V**) afforded higher ee values and yields than those in ionic liquid– CH_2CI_2 mixed media (**II** and **III**). Furthermore, in the recycling reaction, the performance of BMImPF₆ was better than that of BMImBF₄. For example, the best recycling result came from recycled epoxidations of α methylstyrene in the pure BMImPF₆, ee values varying from 91 to 89% (entry 23) without bringing low yields. Besides that entry, under the same reaction condition (medium **V**), acceptable yields of 75–95% were obtained associated with ee values of 85–95% in the case of indene epoxidations (entry 27).

From the standpoint of economy, we next investigated the exact role of NH₄OAc as co-catalyst. Although replacement of PPyNO or PPPyNO with NH₄OAc had been reported,^[36] the exact interaction of NH₄OAc with (salen)Mn(III) units dispersed in ionic liquid has not been clear until now. Since the pure ionic liquid medium was outstanding as a recycling carrier, the epoxidations under pure ionic liquid environments (media **IV** and **V**) in the absence of NH₄OAc should be worthy from the point of economy and manipulation.

The catalytic results were collected in Table 3. Overall, all reactions proceeded smoothly and acceptable yields were obtained within 3 h. Compared with the data in Table 2, in the absence of NH₄OAc, however, the ionic liquids recycling experiments for all substrates afforded much poorer ee values than their corresponding reactions loaded with NH₄OAc as co-catalyst in all ionic liquids (entry 28 vs entry 18; entry 29 vs entry 19; entry 30 vs entry 22; entry 31 vs entry 23; entry 32 vs entry 26; entry 33 vs entry 27). This suggested that NH₄OAc as a co-catalyst played an important role in the control of enantioselectivity even using ionic liquid as recycling medium. Nevertheless, in the absence of NH₄OAc, ee values derived from BMImPF₆-facilitated reactions were generally higher than those of BMImBF₄-facilitated reactions when α -methylstyrene and indene were selected as substrates, but the variation of enantioselectivity was opposite in the case of styrene. Interestingly, an ee value of 91% was achieved in the second reuse of Jacobsen's catalyst using medium V in the asymmetric epoxidation of α -methylstyrene (entry 31), but the overall control of chiral induction was still unsatisfactory.

Table 3. Enantioselective epoxidation of unfunctionalized olefins catalyzed by Jacobsen's catalyst in the absence of co-catalyst with the ionic liquids as reaction media^a

			ee (%) [yield (%), Time (h)]				
Entry	Alkene	Media	Cycle fresh	Cycle 1	Cycle 2	Cycle 3	Cycle 4
28	А	IV	56 (49, 2.0)	56 (60, 2.0)	55 (42, 2.0)	46 (35, 2.0)	40 (19, 3.0)
29		V	80 (33, 2.0)	69 (58, 2.0)	60 (46, 2.0)	60 (29, 2.0)	55 (25, 2.0)
30	В	IV	70 (41, 2.0)	72 (35, 2.0)	70 (45, 2.0)	71 (47, 2.0)	65 (29, 3.0)
31		V	73 (49, 2.0)	75 (49, 2.0)	91 (48, 2.0)	74 (34, 2.0)	70 (25, 3.0)
32	С	IV	86 (45, 2.0)	83 (34, 2.0)	82 (37, 2.0)	79 (44, 2.0)	78 (46, 2.0)
33		V	74 (69, 2.0)	70 (75, 2.0)	75 (71, 2.0)	79 (68, 2.0)	52 (65, 2.0)

^a Reaction conditions and other indexes were identical to those in Table 2 except for the removal of NH_4OAc .

Table 4. Epoxidations catalyzed by two silica-supported chiral (salen)Mn(III) catalysts with the ionic liquids as reaction media^a

				ee (%) [yield (%), time (h)]				
Entry	Catalyst	Alkene	Media	Cycle fresh	Cycle 1	Cycle 2	Cycle 3	Cycle 4
34	1	А	I	76 (94, 2.0)	76 (89, 2.0)	74 (82, 2.0)	72 (79, 2.0)	77 (70, 2.0)
35			V	95 (95, 2.0)	80 (90, 2.0)	86 (88, 2.0)	77 (72, 2.0)	79 (70, 2.0)
36		В	I	71 (47, 2.0)	68 (100, 2.0)	65 (88, 2.0)	66 (85, 2.0)	67 (56, 2.5)
37			V	95 (81, 2.0)	81 (94, 2.0)	72 (90, 2.0)	75 (87, 2.0)	84 (83, 2.0)
38		С	I	79 (100, 2.0)	92 (97, 2.0)	93 (92, 2.0)	94 (90, 2.0)	93 (92, 2.0)
39			V	86 (100, 2.0)	83 (92, 2.0)	86 (94, 2.0)	79 (88, 2.0)	78 (90, 2.0)
40	2	Α	I	96 (75, 2.0)	86 (65, 2.0)	85 (64, 2.0)	85 (59, 2.0)	82 (62, 2.5)
41			V	100 (87, 2.0)	96 (80, 2.0)	96 (75, 2.0)	92 (74, 2.0)	95 (60, 2.0)
42		В	I	95 (75, 2.0)	89 (80, 2.0)	84 (96, 2.0)	80 (72, 2.0)	85 (55, 3.0)
43			V	100 (63, 2.0)	100 (64, 2.0)	100 (64, 2.0)	97 (71, 2.0)	97 (64, 2.0)
44		С	I	83 (97, 2.0)	63 (95, 2.0)	74 (90, 2.0)	82 (72, 2.0)	88 (70, 2.0)
45			V	89 (92, 2.0)	90 (90, 2.0)	86 (88, 2.0)	93 (86, 2.0)	94 (87, 2.0)

^a Reaction conditions, together with other indexes were identical to their counterparts in Table 1. Entries 34–45 were 12 respective recycling experiments of four cycles. The absolute configurations of major enantiomers of styrene oxide, α -methylstyrene oxide and indene oxide were *R*, *R* and 1*R*,2*S*, respectively.

As for the extraction of epoxide products, *n*-hexane was used to wash the ionic liquid layer containing (salen)Mn(III) complex. Although dispersed in the ionic liquid, the (salen)Mn(III) complex was dissolved slightly in *n*-hexane based on the FT-IR analysis of the crude epoxide products. Not surprisingly, the linkage of (salen)Mn(III) complex with ionic liquid was not strong enough to prevent the catalyst leaching into *n*-hexane. Since a small amount of catalyst was lost from ionic liquid to *n*-hexane, the reduction amount of catalyst led to the yield decrement during the whole recycling experiments. Therefore, we had to investigate optimized approaches to overcome the dissolution of (salen)Mn(III) complex into *n*-hexane without losing chiral induction.

Ionic Liquids Recycled Epoxidations Catalyzed by Two Silicasupported Chiral (salen)Mn(III) Catalysts

To overcome the (salen)Mn(III) leaching problem, two silicasupported sulfonato-(salen)Mn(III) catalysts were further dispersed in ionic liquids. A series of epoxidation reactions catalyzed by recycled silica-supported catalysts (**1** and **2**) were conducted using CH_2Cl_2 as solvent for the purpose of comparison. Subsequently, in view of the recycling potential of BMImPF₆, and with the same catalyst proportion as for Jacobsen's catalyst at 10 mol%, silica-supported catalysts (**1** and **2**) combined with BMImPF₆ were employed in the recycling epoxidation reactions of styrene, α -methylstyrene and indene in the presence of NH₄OAc as cocatalyst. As shown in Table 4, all recycling reactions whether ionic liquid-facilitated or not finished within 3 h, and afforded generally higher yields compared with the previous results (Table 4 entries vs Table 2 entries). The enhanced recycling capabilities of silica-supported catalysts (1 and 2) might be attributed to the heterogeneity of silica-supported catalysts in *n*-hexane during the extraction procedure.

In the aspect of chiral induction, 79–94% ee values accompanied by high yields were obtained in the recycling epoxidations of indene catalyzed by catalyst 1 (entry 38), meanwhile catalyst 2 afforded a series of ee values of 82–96% in the recycling asymmetric epoxidation of styrene without losing reactivity (entry 40). Moreover, the presence of BMImPF₆ greatly improved the enantioselectivities in the recycling epoxidations (entry 35 vs entry 34; entry 37 vs entry 36; entry 41 vs 40; entry 43 vs 42; entry 45 vs entry 44). In particular, the combination of catalyst 2 with BMImPF₆ afforded 97-100% ee for recycling asymmetric epoxidations of α -methylstyrene, and an ee value of 100% was retained even after three cycles (entry 43). Undoubtedly, this is the most encouraging result achieved in this work. Herein, it was interesting to reconsider the possibility of anion exchanging procedure when (salen)Mn(III) catalyst was dispersed in ionic liquid. In our manipulation, it was found that the color of the mixture containing BMImPF₆

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(media **V**) and catalyst [both homogeneous and heterogeneous (salen)Mn(III)] changed from brown to deep green then to yellow under pre-stirring before catalysis, but the color of the mixture containing BMImBF₄ (media **IV**) and catalyst remained brown during the stirring.Possibly, a kind of (salen)Mn(III)PF₆ type catalyst, which was the product of anion exchanging procedure, could offer better ee values than (salen)Mn(III)Cl type catalyst.

To prove the speculation of an anion exchange process between Cl⁻ and PF₆, the complex of (salen) Mn (III) PF₆ was synthesized and dispersed in BMImPF₆ under stirring, and only the yellow mixing solution was obtained. It was proved that the speculation was right by the experiment. Ionic liquid in our manipulation was only reaction medium without catalytic function. The colored solutions owning to anion exchange between Cl⁻ and PF₆ could catalyze epoxidation, but (salen) Mn (III) complex was separated by centrifugation, while ionic liquid could not do that. It was evident that (salen) Mn (III) PF₆ was the more effective catalyst.

Conclusions

In summary, three goals of this work were achieved to some extent. At first, the recycling potential of BMImBF₄ and BMImPF₆ for the homogeneous or heterogeneous (salen)Mn(III) catalyzed asymmetric epoxidation of unfunctionalized alkenes was revealed in a stepwise manner: accelerated reactions, acceptable ee values and yields were achieved. Secondly, the presence of NH₄OAc played an important role in the improvement of enantioselectivity. At last, the two silica-supported chiral (salen)Mn(III) catalysts used in conjunction with BMImPF₆ afforded not only high yields (92-100%) but also excellent enantioselectivity (97-100%). In fact, this work emphasized an effective approach for amplifying the chiral induction capability and reactivity of Jacobsen-type catalyst. This new approach included the initial immobilization of Jacobsen-type catalyst on silica support through the linkage anchored on the 5,5'-positions of salen ring and the subsequent dispersion of supported catalyst into ionic liquid, which brought about excellent catalytic results.

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