Asymmetric transfer hydrogenation using recoverable ruthenium catalyst immobilized into magnetic mesoporous silica

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ABSTRACT

Ru-TsDPEN (TsDPEN = N-(p-toluenesulfonyl)-1,2-diphenylethylenediamine) derived catalyst was firstly immobilized in the magnetic siliceous mesocellular foam material. This heterogeneous catalyst afforded high catalytic activities and ee values in the asymmetric transfer hydrogenation of imine in HCOOH–Et_3N system and aromatic ketones in aqueous HCOONa. Furthermore, this heterogeneous catalyst showed an excellent durability and can be reused conveniently by external magnet for at least nine times without noticeable loss of ee values.

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1. Introduction

Asymmetric transfer hydrogenation (ATH) has received considerable attentions due to its high performance, operational simplicity and the easy availability of reductants. Among the various chiral catalysts reported, the most notable is the ruthenium catalyst Ru-TsDPEN (TsDPEN = N-(p-toluenesulfonyl)-1,2-diphenylethylenediamine) developed by Noyori, Ikariya and co-workers [1–3]. This catalyst and related variants have been applied to a wide range of prochiral ketones and imines, affording good to excellent enantioselectivities in 2-propanol, HCOOH–Et_3N mixture and aqueous HCOONa systems [4,5]. Although ATH based on metal complexes has been found to be reliable, the current emphasises for chemical transformations from environmental and economical concerns require high efficiency, low cost, easy separation and the production of minimum waste. Thus heterogeneous catalysts, especially catalysts supported on insoluble matrices, are preferable and can afford clean transformations from laboratory to large-scale operations due to the easy separation and recycling of catalysts through filtration. Several catalysts supported on insoluble supports have been reported for ATH [6–10]. However, in those cases recovery of heterogenized catalysts through filtration or centrifuge is troublesome because the ruthenium hydride species is air-sensitive and potentially liable to decomposition during handling process. In this regard, there is a need to find new methods and strategies in order to overcome this limitation.

Magnetic nanoparticles, owing to their easy separation and location in the presence of an external magnet, have been extensively applied in various biological fields, such as magnetic resonance imaging, drug delivery, biomolecular sensors and bioseparation [11,12]. Magnetic separation provides a convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. This approach may potentially overcome the negative effect caused by air during recovery of catalyst and can increase the durability of the catalysts. Recent reports have shown that magnetic nanoparticles can be used as the supports for catalysts and can facilitate their separation from the reaction media [13–20]. However, the low surface area and easy aggregation of magnetic nanoparticles cumber their practical applications as the supports of catalysts. To overcome these drawbacks, magnetic nanoparticles have been introduced into various mesoporous silica [21–26], which as the supports for the immobilization of chiral catalysts have been widely demonstrated due to their high surface areas, well-defined pore sizes and easy modification by silylation [27]. These types of magnetic nanoparticle-based materials, combining the advantages of both mesoporous silicas and magnetic nanoparticles, are potentially ideal supports for the immobilization of catalyst. Few examples have been reported of chiral catalysts that are immobilized in magnetic mesoporous silica [28]. In this study, we report our efforts to immobilize the Ru-TsDPEN catalyst in a magnetic siliceous mesocellular foam, affording high

catalytic activities and good enantioselectivities in the ATH of imine in HCOOH–Et$_3$N system and aromatic ketones in aqueous HCOONa. Furthermore, this heterogeneous catalyst shows an excellent durability and can be reused conveniently by external magnet for at least nine times with reasonable loss of catalytic activity.

2. Experimental

2.1. Instruments and materials

Nitrogen sorption isotherms were measured at 77 K on an ASAP 2000 system in the static measurement mode. The sample was degassed at 393 K for 6 h prior to the measurement. The pore diameters of the cage and window were calculated from the adsorption and desorption branches of the isotherm using the Barrett–Joyner–Halenda method. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 3400 powder diffraction system using Cu KR radiation over the range $10° < 2\theta < 80°$. Infrared spectra were recorded on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer.

Spherical siliceous mesocellular foam (Foam) was synthesized according to the method described by Ying and co-workers [29]. Magnetic particles were introduced into the Foam by modified methods according to the literature procedure [30], and the resulting magnetic material was denoted as Foam(M). TsDPEN-derived ligand **1** was synthesized according to literature [7].

2.2. The preparation of organic–inorganic hybrid ligand TsDPEN/F(M)

Foam (M) (3 g) was heated at 100 °C in vacuum for 3 h, and then dry toluene (25 mL) and ligand **1** (0.5 g) were added. The reaction mixture was refluxed for 24 h in stirring. The residua were collected by an external magnet, and washed carefully using methanol and CH$_2$Cl$_2$ to give hybrid ligand TsDPEN/F(M). The nitrogen elemental analysis shows that the ligand **1** loading is 0.19 mmol/g.

2.3. Typical procedure for ATH of imine using Ru-TsDPEN/F(M) catalyst

TsDPEM/F(M) (40 mg, containing 7.5 μmol ligand **1**) and [RuCl$_2$(p-cymene)]$_2$ (1.5 mg, 2.5 μmol) were stirred in dry CH$_2$Cl$_2$ (2 mL) for 1 h under argon at room temperature. Then imine **2** (0.1 g, 0.5 mmol), formic acid (0.065 mL, 1.72 mmol) and varying amounts of triethylamine (0.097–0.252 mL, 0.70–1.83 mmol) were added. The reaction was stirred at 40 °C and monitored by TLC. After the completion of the reaction, catalyst was collected by an external magnet and the solution was removed by syringe. The catalyst was then washed with CH$_2$Cl$_2$ (2 mL × 2) and the solvent was removed. A new reaction could be conducted by adding substrate, triethylamine and formic acid to the recovered catalyst. The product was isolated by silica gel column and the ee value was determined by HPLC with Chiralcel OD-H column on Agilent 1100 Series.

2.4. Typical procedure for aqueous ATH of aromatic ketones using Ru-TsDPEN/F(M) catalyst

TsDPEN/F(M) (40 mg, containing 7.5 μmol ligand **1**) and [RuCl$_2$(p-cymene)]$_2$ (1.5 mg, 2.5 μmol) were stirred in degassed H$_2$O (1 mL) for 1 h under argon at 40 °C. Ketone (0.5 mmol), CTAB (72 mg, 0.2 mmol) and HCOONa (0.17 g, 2.5 mmol) were added and the mixture was stirred at 40 °C and monitored by GC. After the completion of the reaction, the catalyst was collected by an external magnet and the solution was removed by syringe. The catalyst was then washed with Et$_2$O (2 mL) and H$_2$O (2 mL × 2) in turn and the solution was removed. A new reaction could be conducted by adding substrate, CTAB and HCOONa to the recovered catalyst. The product was passed quickly through a short silica gel column and the conversion and ee value were determined by an Agilent 6890N
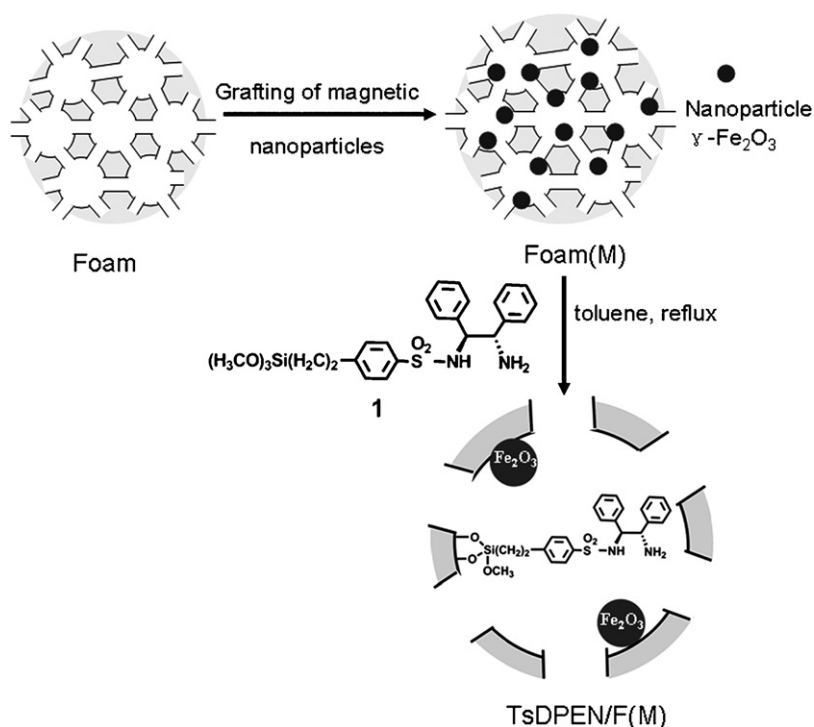
Scheme 1. Schematic description of preparation of hybrid ligand TsDPEN/F(M).
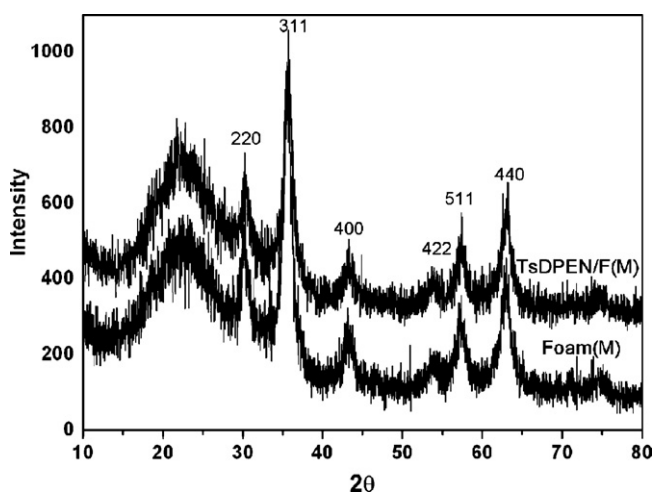
Fig. 1. X-ray diffraction (XRD) pattern of Foam(M) and hybrid ligand TsDPEN/F(M).

GC equipped with HP 19091G-B213 (30 m × 0.32 mm × 0.25 μm) column.

3. Results and discussion

Siliceous mesocellular foam is selected as parent support because of its large surface area, cage-like mesopore (20–50 nm) connected by large window (9–26 nm), as well as the large total pore volume [29], which are suitable to accommodate both bulky catalyst and magnetic nanoparticles comfortably, and facilitate the diffusion of substrates. As described in Scheme 1, magnetic nanoparticles were grafted onto the pore surface of the Foam. Subsequentially, the Foam(M) was modified with TsDPEN-derived ligand **1**. The results of the wide-angle X-ray powder diffraction (XRD) pattern of both Foam(M) and hybrid ligand TsDPEN/F(M) are shown in Fig. 1. Several typical peaks for γ-Fe$_2$O$_3$ are observed, and the large peak widths are attributed to the formation of nano-sized particles [31]. The average size of the magnetic nanoparticles is calculated to be about 6 nm by Debye–Scherrer equation using the (3 1 1) peak, and there is no obvious change after the subsequent surface modification. The transmission electron microscopy results also reveal that the Foam has a three-dimensional connected structure and the magnetic nanoparticles are uniformly dispersed over the Foam. Textural properties of the synthesized samples were detected by the N$_2$ sorption experiment. As can be seen in Fig. 2, the Foam shows IV type adsorption isotherm, which is typical of mesoporous materials. It exhibits a high BET surface area of 628 m^2/g, high pore volume of 2.31 cm^3/g, large pore size of 36.2 nm and window size of 18.1 nm (Table 1). After nanoparticles encapsulation, the resulting Foam(M) still exhibits a high BET surface area (377 m^2/g), high pore volume (1.72 cm^3/g), large pore size (32.9 nm) and window size (17.2 nm), although being reduced to some extent compared to those of the parent Foam. Moreover, the N$_2$ sorption isotherm of Foam(M) is of typical type of IV pattern (Fig. 2), which is similar to the parent Foam. This result indicates that the pore structure of the Foam(M) remains unplugged after the grafting of

Table 1
Texture parameters of the Foam, Foam(M) and hybrid ligand TsDPEN/F(M).

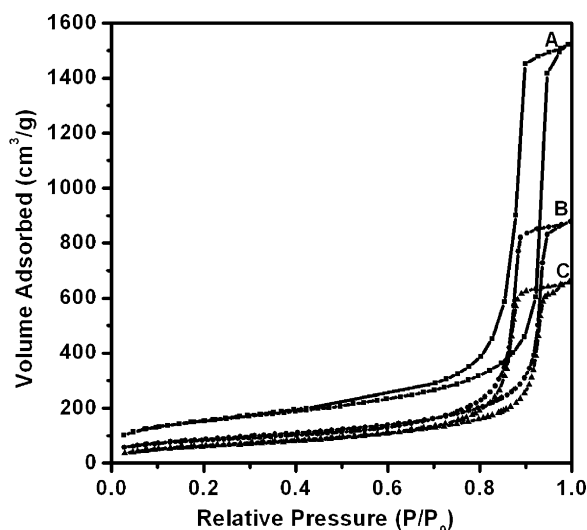| Materials	Pore size (nm)	Window size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)
Foam	36.2	18.1	628	2.31
Foam(M)	32.9	17.2	377	1.72
TsDPEN/F(M)	29.7	16.1	304	1.61

Fig. 2. Nitrogen adsorption–desorption isotherms of (A) Foam, (B) Foam(M) and (C) hybrid ligand TsDPEN/F(M).

magnetic nanoparticles. The pore size, pore volume and BET surface area are further decreased as the surface is grafted by ligand **1** (Table 1), indicating that the organic ligand **1** has been grafted on the inner surface of the Foam(M). Comparing the IR spectra of Foam(M) and TsDPEN/F(M) (Fig. 3), the latter displays some new bands at 3062, 3029, 2925, 1494, 1454, 765 and 698 cm^{-1}. The bands at 3062 and 3029 cm^{-1} are assigned to the C—H stretching vibrations of phenyl group. The bands at 1492 and 1454 cm^{-1} are attributed to the C=C vibration of phenyl group. The band at 2925 cm^{-1} is assigned to the alkyl chain C—H stretching vibration. The bands at 765 and 698 cm^{-1} are assigned to the breathing vibration of phenyl ring. All these results further confirm a successful grafting of ligand **1** in Foam(M).

In this investigation, we choose as the model reaction the asymmetric reduction of substituted dihydroisoquinoline **2**, because its product has a potentially important physiological activity [3]. We set to examine the reduction of imine **2** with HCOOH–Et$_3$N azeotrope (molar ratio 2.5/1, pH 3.1) as hydrogen donor, as reported initially Noyori and co-workers [3]. The precatalyst was generated in situ by stirring [RuCl$_2$(*p*-cymene)]$_2$ with organic–inorganic
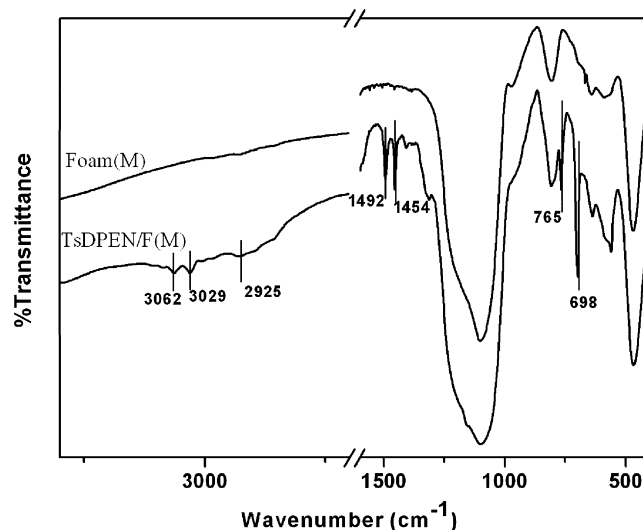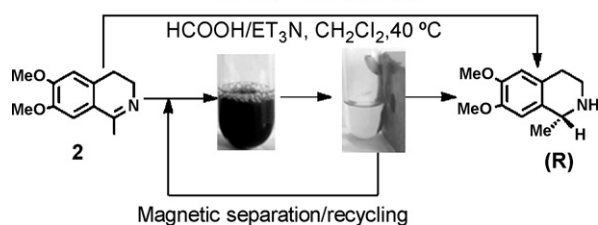

Fig. 3. FT-IR spectra of the Foam(M) and hybrid ligand TsDPEN/F(M).

Table 2
ATH of imine **2** using magnetically recoverable catalyst Ru-TsDPEN/F(M)

Entry	pH[a]	Time (h)	Yield (%)[b]	Ee (%)[c]
1	3.1/4.0	1.5[d]	98	94
2	3.1/4.0	1[d,e]	97	95
3	3.1/4.0	4[f]	98	94
4	3.7/4.7	1.5	98	94
5	4.0/7.9	1.5	99	94
6	4.9/10.4	2.5	98	94
7	–	12[g]	15	89

[a] The former figure was the pH value of HCOOH–Et$_3$N mixture and the latter was the initial solution pH value after adding substrate **2**.

[b] Isolated yield.

[c] Determined by HPLC analysis (Chiralpak OD-H).

[d] HCOOH–Et$_3$N azeotrope (0.18 mL) used.

[e] Ru-TsDPEN used.

[f] S/C = 250.

[g] Reaction was performed in H$_2$O (1.5 mL) with HCOONa (5 equivalent) and CTAB (0.2 mmol).

hybrid ligand TsDPEN/F(M) in CH$_2$Cl$_2$ at room temperature for 1 h. To our delight, following the addition HCOOH–Et$_3$N azeotrope (0.18 mL) and imine **2** with a substrate/catalyst (S/C) ratio of 100, the reaction furnished a 98% yield and 94% ee in 1.5 h reaction time (Table 2, entry 1). A comparison was made with the catalyst Ru-TsDPEN under the identical conditions, delivering a 97% yield and 95% ee in 1 h (Table 2, entry 2). At a higher S/C ratio of 250, the catalyst Ru-TsDPEN/F(M) still worked well and gave a 98% yield in 4 h (Table 2, entry 3). When we tried to reuse the Ru-TsDPEN/F(M) with HCOOH–Et$_3$N azeotrope as reductant, it was found that free Fe^{3+} was determined in the reaction mixture with aqueous phenol. Though the pH value of solution is *ca.* 4.0 at the beginning of the reaction after the addition of basic imine **2** [32], the nanoparticles γ-Fe$_2$O$_3$ are at the risk of acid corrosion in many reuses.

To address this issue, we tried to carry out the reaction at a higher pH value by adjusting the molar ratio HCOOH/Et$_3$N; the volume of formic acid remained constant at 0.067 mL, however. At enhanced pH values of HCOOH–Et$_3$N of 3.7 (molar ratio 1.6/1) and 4.0 (molar ratio 1.4/1), the initial solution pH values after adding imine **2** were increased to 4.7 and 7.9 respectively; the catalyst Ru-TsDPEN/F(M) exhibited the almost same activities and ees compared with that in HCOOH–Et$_3$N azeotrope, affording complete conversions and 94% ee in 1.5 h (Table 2, entry 4.5). Further increase the pH value of HCOOH–Et$_3$N mixture to 4.9 (molar ratio 1.1/1.0), the solution pH value was enhanced sharply to 10.4. Concomitantly, the reaction time was prolonged to 2.5 h, without little compromise on enatioselectivity (Table 2, entry 6). This result suggests that imine **2** may be not protonated at a high pH value and coordinate competitively to the metal center, which possibly impedes the generation of ruthenium hydride species. Recently, Deng et al. demonstrated that imine **2** can be reduced efficiently in aqueous HCOONa in the presence of surfactants [33]. The catalyst Ru-TsDPEN/F(M) afforded a low yield of 15% and 89% ee in aqueous HCOONa system in 12 h, partly owing to the low solubility of imine **2** in water (Table 2, entry 7).

Based on the results above, attempts were made to recycle the catalyst Ru-TsDPEN/F(M) using imine **2** as substrate with HCOOH–Et$_3$N mixture (pH 4.0), where the initial solution pH value

Table 3
Conversions and ees (%) against number of runs in the ATH of imine **2** using catalyst Ru-TsDPEN/F(M).

Recycle runs[a]	1	2	3	4	5	6	7	8	9
Conversion (%)[b]	99	99	99	99	99	99	99	99	99
Ee (%)[c]	94	94	94	94	93	93	91	91	90

[a] Reactions were performed at 40 °C within 1.5–7 h, using imine **2** (0.5 mmol), HCOOH–Et$_3$N mixture (molar ratio 1.4/1, pH 4.0) and a S/C ratio of 100 in 2 mL of CH$_2$Cl$_2$.

[b] Determined by TLC and ^{1}H NMR.

[c] Determined by HPLC analysis (Chiralpak OD-H).

is 7.9. The catalyst was collected by a magnetic bar and the solution phase was removed by syringe. A demonstration of excellent recycling of the catalyst is shown in Table 3. The Ru-TsDPEN/F(M) catalyst can be reused consecutively for at least nine times with ee ranging from 94% to 90%. Toward the end of recycles, the reaction time was prolonged from initial 1.5–7 h. The decrease in catalytic activity is mainly due to catalyst loss caused by mechanical stirring. The ICP analysis showed that total 11 mol% ruthenium leached from catalyst after nine runs. Furthermore, the slight decrease in ee also implies that catalyst was decomposed partly in the consecutive reuses. It is indispensable to exclude water from current system; it was observed that red magnetic nanoparticles were eroded easily and fell off from the inner wall of foam material in the presence of water.

With these results in hand, the catalyst Ru-TsDPEN/F(M) was extended to the ATH of aromatic ketones, and the results are summarized in Table 4. With HCOOH–Et$_3$N azeotrope as hydrogen donor in CH$_2$Cl$_2$, acetophenone was reduced completely at S/C ratio of 100 in 9 h, affording 97% ee (Table 4, entry 1). Increasing pH value of HCOOH–Et$_3$N mixture, a somewhat higher activity was observed (Table 4, entry 2), which is partly attributed to the increase of concentration of HCOO$^-$. Recent studies have demonstrated that HCOONa–water system is an excellent medium for the ATH of aromatic ketones. Not only does water accelerate the ATH rates, it enhances the life of the catalyst as well [5,34,35]. When being in aqueous HCOONa, the Ru-TsDPEN/F(M) catalyst afforded an 89% conversion and 93% ee in 10 h (Table 4, entry 3). The reaction was significantly accelerated in the addition of surfactant CTAB and gave a complete conversion in 3 h with remained ee (Table 4,

Table 4
ATH of aromatic ketones using catalyst Ru-TsDPEN/F(M)
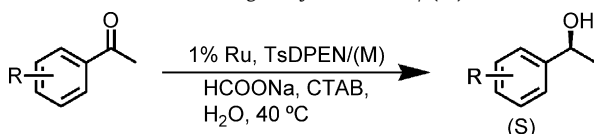
Entry	R	Time (h)	Conversion (%)[a]	Ee (%)[a]
1	H	9[b]	99	97
2	H	6[c]	99	97
3	H	10[d]	89	93
4	H	3	99	93
5	H(2nd)[e]	4	99	93
6	H(4th)	8	99	92
7	4-Cl	3	99	91
8	4-Br	3	99	91
9	3-CF$_3$	2	99	89
10	3-F	2	99	90
11	3-CH$_3$	5	99	91

[a] Determined by GC with equipped with HP 19091G-B213.

[b] HCOOH–Et$_3$N azeotrope (0.18 mL) and CH$_2$Cl$_2$ (1 mL).

[c] HCOOH–Et$_3$N mixture (molar ratio 1.1/1, pH 4.9) and CH$_2$Cl$_2$ (1 mL).

[d] No CTAB.

[e] The second reuse.

entry 4), which is in line with the results of Tu and co-workers [8]. This result indicates that the presence of surfactant improves the diffusion limitation of substrate and facilitates its access to the active sites. The Ru-TsDPEN/F(M) catalyst was recycled at least four times with the maintained ee value, though a prolonged reaction time was needed. The Ru-TsDPEN/F(M) catalyst can also efficiently reduce various substituted acetophenones in water. The substrates with electron-withdrawing groups show higher reaction activities. For instance, 3-fluoroacetopheone was reduced completely only in 2 h with 90% ee (Table 4, entry 10). In contrast, that with electron-donating group provides a low activity (Table 4, entry 11). These observations are agreement with those made with the parent catalyst Ru-TsDPEN [34].

4. Conclusion

We have developed a magnetically recoverable catalyst, which combines the merits of mesoporous silicas and magnetic nanoparticles. This heterogeneous catalyst showed comparable activities and enatioselectivities with the parent catalyst Ru-TsDPEN in ATH of imine and aromatic ketones. The notable feature for current system is the fact that this catalyst can easily recovered from the reaction medium by an external magnet, and this catalyst was reused consecutively for at least nine times without noticeable loss of ee values. This study provides a potential and general approach for the convenient separation and recycle of expensive catalyst, especially for air-sensitive metal complexes.

Acknowledgements

References

[1] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 7562.
[2] N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 4916.
[3] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 2521.
[4] T. Ikariya, K. Murata, R. Noyori, Org. Biomol. Chem. 4 (2006) 393.
[5] X.F. Wu, J.L. Xiao, Chem. Commun. 24 (2007) 2449.
[6] D.J. Bayston, C.B. Travers, M.E.C. Polywka, Tetrahedron: Asymmetry 9 (1998) 2015.
[7] P.N. Liu, P.M. Gu, F. Wang, Y.Q. Tu, Org. Lett. 6 (2004) 169.
[8] P.N. Liu, J.G. Deng, Y.Q. Tu, S.H. Wang, Chem. Commun. 18 (2004) 2070.
[9] X.H. Huang, J.Y. Ying, Chem. Commun. 18 (2007) 1825.
[10] H.Q. Yang, J. Li, J. Yang, Z.M. Liu, Q.H. Yang, C. Li, Chem. Commun. 10 (2007) 1086.
[11] A.H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 46 (2007) 1222.
[12] Y.W. Jun, J.W. Seo, A. Cheon, Accounts Chem. Res. 41 (2008) 179.
[13] R. Abu-Reziq, H. Alper, D.S. Wang, M.L. Post, J. Am. Chem. Soc. 128 (2006) 5279.
[14] A.G. Hu, G.T. Yee, W.B. Lin, J. Am. Chem. Soc. 127 (2005) 12486.
[15] G. Chouhan, D.S. Wang, H. Alper, Chem. Commun. 45 (2007) 4809.
[16] M. Kawamura, K. Sato, Chem. Commun. 32 (2007) 3404.
[17] S.Z. Luo, X.X. Zheng, H. Xu, X.L. Mi, L. Zhang, J.P. Cheng, Adv. Synth. Catal. 349 (2007) 2431.
[18] C. O' Dalaigh, S.A. Corr, Y. Gun'ko, S.J. Connon, Angew. Chem. Int. Ed. 46 (2007) 4329.
[19] L.M. Rossi, F.P. Silva, L.L.R. Vono, P.K. Kiyohara, E.L. Duarte, R. Itri, R. Landers, G. Machado, Green Chem. 9 (2007) 379.
[20] P.D. Stevens, J.D. Fan, H.M.R. Gardimalla, M. Yen, Y. Gao, Org. Lett. 7 (2005) 2085.
[21] A.F. Gross, M.R. Diehl, K.C. Beverly, E.K. Richman, S.H. Tolbert, J. Phys. Chem. B 107 (2003) 5475.
[22] J. Lee, D. Lee, E. Oh, J. Kim, Y.P. Kim, S. Jin, H.S. Kim, Y. Hwang, J.H. Kwak, J.G. Park, C.H. Shin, J. Kim, T. Hyeon, Angew. Chem. Int. Ed. 44 (2005) 7427.
[23] B. Folch, J. Larionova, Y. Guari, C. Datas, C. Guerin, J. Mater. Chem. 16 (2006) 4435.
[24] R.P. Hodgkins, A. Ahniyaz, K. Parekh, L.M. Belova, L. Bergstrom, Langmuir 23 (2007) 8838.
[25] J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, K. An, Y. Hwang, C.H. Shin, J.G. Park, J. Kim, T. Hyeon, J. Am. Chem. Soc. 128 (2006) 688.
[26] A.B. Bourlinos, A. Simopoulos, N. Boukos, D. Petridis, J. Phys. Chem. B 105 (2001) 7432.
[27] C.E. Song, S.G. Lee, Chem. Rev. 102 (2002) 3495.
[28] D. Lee, J. Lee, H. Lee, S. Jin, T. Hyeon, B.M. Kim, Adv. Synth. Catal. 348 (2006) 41.
[29] Y. Han, S.S. Lee, J.Y. Ying, Chem. Mater. 18 (2006) 643.
[30] Y.M. Zhang, J. Li, D.F. Han, H.D. Zhang, P. Liu, C. Li, Biochem. Biophys. Res. Commun. 365 (2008) 609.
[31] D.K. Yi, S.S. Lee, G.C. Papaefthymiou, J.Y. Ying, Chem. Mater. 18 (2006) 614.
[32] The pH values of HCOOH–Et₃N mixture were determined in 2 mL of H₂O, using 0.067 mL of HCOOH and varying amounts of Et₃N. The initial solution pH values were determined in the presence of catalyst Ru-TsDPEN/F(M) and imine **2** (0.1 g, 0.5 mmol) under identical conditions.
[33] J.S. Wu, F. Wang, Y.P. Ma, X.C. Cui, L.F. Cun, J. Zhu, J.G. Deng, B.L. Yu, Chem. Commun. 16 (2006) 1766.
[34] X.F. Wu, X.G. Li, W. Hems, F. King, J.L. Xiao, Org. Biomol. Chem. 2 (2004) 1818.
[35] X.F. Wu, J.K. Liu, D.D. Tommaso, J.A. Iggo, C.R.A. Catlow, J. Bacsa, J.L. Xiao, Chem. Eur. J. 14 (2008) 7699.