Catalysis Letters, Vol. 116, Nos. 1–2, July 2007 (© 2007)
DOI: 10.1007/s10562-007-9094-9

Catalytic performance of chiral rhodium complex with water-soluble sulfonated (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl for enantioseletive hydrogenation in ionic liquid biphasic system

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Received 18 March 2007; accepted 19 March 2007

Asymmetric hydrogenation of dimethyl itaconate by the chiral rhodium complex ligated with water-soluble sulfonated (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (labeled as (*R*)-BINAPS) was performed in ionic liquid-isopropanol biphasic catalytic system. A moderate enantiomeric excess (ee) of 64% and initial turnover frequency ($\mathrm{TOF_{max}}$) as high as 1234 $\mathrm{h^{-1}}$ could be obtained at 303 K and 2.0 MPa when the molar ration of substrate to rhodium was set at 1000. Application of imidazolium ionic liquid [bmim]$\mathrm{BF_4}$ (bmim = 1-butyl-3-methyl imidazolium cation) made it possible to reuse the catalyst several times, showing rather good stability in the catalyst performance. According to the ICP-OES analyses, the total extraction of rhodium species by the reactants from the ionic liquid phase was about 3.24 wt% after the catalyst for four runs, which was about three times lower than that of total loss of phosphorous species. The slight decreases in the ee value and $\mathrm{TOF_{max}}$ during the catalyst reuse could be recovered essentially to the pristine levels by replenishing certain amount of the fresh ligand into the used catalyst.

KEY WORDS: rhodium; ionic liquid; biphasic catalysis; water-soluble complex; enantioselective hydrogenation.

1. Introduction

Due to their environmentally benign and easy to prepare and modify to impart desirable characteristics, ionic liquids have been explored as increasing interesting alternatives to traditional volatile organic solvents as reaction media in the past more than decade. The features of ionic liquids particularly make them ideal solvents for the synthesis of high-value chiral organic compounds *via* catalytic processes. In fact, ionic liquids are ideal solvents for asymmetric catalytic syntheses and biocatalytic reactions such as enzymatic syntheses with high enantioslelctivity, facilitating the catalyst recovery and recycling from the reaction products [1–5]. In ideal scenarios, not only high enantioselectivity can be obtained but also both ionic liquids and asymmetric catalysts can be recycled and reused.

High activity and enantioselectivity have been achieved for the asymmetric hydrogenation of olefins by using Rh, Ir and Ru complexes of chiral phosphine, phosphite or their hybrid ligands. Along with the design of chiral ligands, another significant challenge in metal catalysis is recycling of the catalyst since these metals and ligands are usually expensive and air-sensitive. Over the last few years, a number of publications have reported the selective hydrogenation reactions performed in ionic liquids [6–11]. The first metal-catalyzed enantioselective hydrogenation reaction in ionic liquids were reported by Chauvin and his co-workers in 1995 [6]. They showed that the α-acetamidocinnamic acid was hydrogenated to (*S*)-phenylalanine with 64% ee by [Rh(COD)((−)-DIOP)]$\mathrm{PF_6}$ (COD = cycloocta-1,5-diene) in a biphasic [bmim]$\mathrm{SbF_6}$–isopropanol system. After that, Dupont and his co-workers studied the hydrogenation of atropic acid in [bmim]$\mathrm{BF_4}$ with alcohol cosolvents using BINAP-type catalysts [7]. The ee values obtained in these systems were similar to those obtained in homogeneous organic media. The catalytic ionic solution was reusable, showing that the ee values varied from 84% at the first run to 67% at the fourth run. As for the asymmetric hydrogenation of (Z)-α-acetamidocinnamic acid and related compounds, several groups performed a more detail study in ionic liquid biphasic system with the chiral Rh complexes such as [Rh(I)-EtDuPhos] [8], [Rh-MeDuPhos] [9], [Rh(COD)(DIPAMP)$\mathrm{BF_4}$ [10] and so on. Immobilization of the chiral Rh complex [Rh-MeDuPhos] in [bmim]$\mathrm{PF_6}$ afforded 94∼96% ee during the catalyst recycling [9]. Recently, Jessop and coworkers reported the hydrogenation of tiglic acid catalyzed by a BINAP-type complex in [bmim]$\mathrm{PF_6}$-$\mathrm{H_2O}$ system [11]. The product was extracted from the ionic liquid catalytic solution by supercritical $\mathrm{CO_2}$. Up to 99% conversion and 90% ee were obtained.

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1011-372X/07/0700–0070/0

The water-soluble Rh complexes formed with sulfonated phosphines showed excellent activities and selectivities particularly in the biphasic hydroformylation of olefins composed of carbon chain less than six. The excellent water-solubility of the phosphines, which is absolutely essential for the aqueous biphasic method, was achieved by the introduction of sodium sulfonate groups. Very recently, we have carried out the sulfonation of (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*i.e.*, (*R*)-BINAP) with 50 wt% oleum by referring to the reaction conditions in literature [12–14]. The resultant water-soluble ligand (*R*)-BINAP-nSO$_3$Na(n = 3~4) (labeled as (*R*)-BINAPS) was obtained with purity up to 95% according to ^{31}P-NMR. We have reported the biphasic catalytic performances and recycling abilities of the water-soluble complexes of Rh−(*R*)-BINAPS for the asymmetric hydroformylation and Ru−(*R*)-BINAPS for the asymmetric hydrogenation in ionic liquids such as [bmim]BF$_4$ and [bmim]PF$_6$, respectively [13,14]. The water-soluble phosphine ligand and complexes showed low solubility in those ionic liquids at room temperature. After the reaction, however, a red to brown homogeneous solution containing the ionic liquid and the water-soluble complex could be obtained, which stayed at the lower phase (ionic liquid phase) immiscible with the up-phase of organic reactants. The phase separation was easy and there was no formation of emulsions.

Herein the water-soluble Rh-complex [Rh(COD)((*R*)-BINPAPS)]BF$_4$ **1** was chosen as a chiral catalyst for the biphasic asymmetric hydrogenation of dimethyl itaconate by using ionic liquids as solvent and isopropanol as cosolvent. Experiments were carried out at different temperatures and hydrogenation pressures. The reusability of the catalyst in consecutive cycles associated with the leachings of Rh and phosphine derivatives has also been investigated.

2. Experimental

2.1. Materials

1-Butyl-3-methyl-imidazolium tetrafluoroborate [bmim]BF$_4$ and 1-butyl-3-methyl-imidazolium hexafluorophospate [bmim]PF$_6$ were synthesized using the procedures reported in the previous literature [15–20] and were vacuum-treated before each use. Dimethyl itaconate and (*R*)-BINAP were purchased from Aldrich and used as-received without further purification.

The preparation of the water-soluble chiral ligand (*R*)-BINAPS has been described elsewhere [12–14]. The spectra data of the product are as follows: ^{31}P{^{1}H}-NMR(D$_2$O): −13.8 ppm (the ^{31}P{^{1}H}-NMR(CDCl$_3$) of (*R*)-BINAP appeared at −15.5 ppm); ^{1}H-NMR(D$_2$O): 6.69–6.85(m, 4H), 6.98–7.25(m, 18H), 7.54–7.61 (d, 2H), 7.83–7.85 (d, 2H), 8.66–8.68 (d, 2H); Elemental analysis: S/P : Na/P : C/Na ≈ 1.9 : 1.9 : 12. After carefully optimizing the reaction condition, the water-soluble (*R*)-BINAPS are generally achieved with the purities up to 95% (^{31}P{^{1}H}-NMR) containing less than 5% impurity of oxidized phosphorus (V) species. Our studies on NMR and elemental analysis, along with the results in literature, indicated that the formula of (*R*)-BINAPS would be (*R*)-BINAP-nSO$_3$Na (n = 3~4) as illustrated in scheme 1.

The complexes of [Rh(COD)((*R*)-BINAPS)]BF$_4$ **1** and [Rh(COD)((*R*)-BINAP)]BF$_4$ **2** were prepared by referring to the procedure in literature [21], using [Rh(COD)Cl]$_2$ and Rh(COD)$_2$BF$_4$ as precursors. [22,23]. The structures were confirmed by the studies of FTIR and NMR. The resonance signals of ^{31}P{^{1}H}-NMR for **1** appeared at 39.3 ppm (D$_2$O) and **2** at 41.2 ppm (CDCl$_3$), respectively.

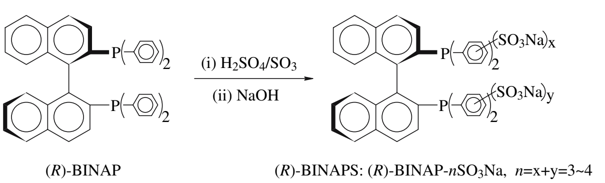
2.2. Spectroscopy

IR spectra were measured on a Nicolet 740 FTIR spectrometer with a resolution of 4cm^{-1}. NMR spectroscopy was recorded on a Brucker AVANCE 400 MHz spectrometer. ^{31}P(^{1}H)-NMR spectra were recorded at 202 MHz at room temperature in CDCl$_3$ for organic-soluble compounds and in D$_2$O for water-soluble ones. The chemical shift was referenced to 85% H$_3$PO$_4$. ^{1}H-NMR spectra were referenced to SiMe$_4$ for organic-soluble compounds and DSS for water-soluble ones.

The contents of phosphorus and Rh in the organic phase were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) on a Thermo Elemental IRIS Intrepid II XSP after each reaction. The samples were treated by evaporation to remove organics and then with 5 mL of aqua regia at 363 K for 5–10 min, followed by heating at 363 K for 5–10 min. The resultant solutions were diluted with water to 25 mL for the measurements.

2.3. Reaction procedure

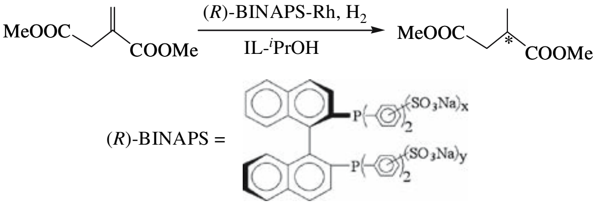
To exclude air, a 60 mL stainless steel autoclave equipped with a magnetic stirrer was charged with solutions containing the Rh complex, the substrate (dimethyl itaconate), ionic liquid and oxygen-free isopropanol cosolvent. After filling in the liquids the autoclave was purged with hydrogen three times and heated up to the desired temperature. Hydrogen was added to adjust the pressure. After the reaction, the



(*R*)-BINAP (*R*)-BINAPS: (*R*)-BINAP-nSO$_3$Na, n=x+y=3~4

Scheme 1. Synthesis of water-soluble chiral ligand (*R*)-BINAPS.

reactor was cooled to 273 K and decompressed. Finally, the organic phase (up layer, containing reactants and cosolvent) and the catalyst phase (lower layer, containing ionic liquid and complexes) were separated by decantation in the case of biphasic system. The catalyst phase was reused directly for the next reaction, if necessary, without any further treatments. The organic phase, after drying, was taken for GC analysis (FID, hydrogen as carrier gas). A 30 m $\times$ 0.25 mm $\times$ 0.25 μm capillary with a Supelco β-Dex-225 was used for the separation and quantitative analysis of the sample components including the chiral products. The products were verified using authentic samples. The reaction conversions were calculated with the corrected area normalization method. The reaction rates and turnover frequencies (TOF_{max}) were calculated from the initial reaction rates. Those were obtained from a least-squares fit of the slopes of the plots of the initial linear decrease in hydrogen pressure versus reaction time. Since these plots were always practically linear up to 70–90% conversion, the determination of initial rates was straightforward.



Scheme 2. General method for the asymmetric catalytic hydrogenation of dimethyl itaconate in ionic liquid-isopropanol biphasic system.

3. Results and Discussion

As observed in several cases for the asymmetric hydrogenations in water, the ee value was slightly diminished with the aqueous biphasic system [24,25]. The highest ee value of 79.4% for the asymmetric hydrogenation of dimethyl itaconate in the aqueous biphasic system was reported by Köckritz and coworkers with Ru complexes of phosphorylated BINAP derivatives, where no catalyst recycling ability was available [26]. Recently, robust and reusable heterogeneous asymmetric hydrogenation catalysts with good to excellent performance have been prepared by immobilization of Rh diphosphine complexes using expensive DuPhos [27–29] and JosiPhos [29] as chiral ligands onto Al-MCM-41 and SBA-15 supports. Up to 94% ee and higher than 99% conversion were observed in the case of the hydrogenation of dimethyl itaconate [29].

The potential of the Rh complex **1** with the water-soluble ligand (*R*)-BINAPS for the hydrogenation of dimethyl itaconate has been investigated associated with biphasic catalysis in the media of ionic liquid-iospropanol (scheme 2). A comparison for the hydrogenation of dimethyl itaconate by **1** and **2** in several solvent systems has been listed in table 1. The introduction of water-soluble groups of sodium sulfonates into the phenyl skeletons might disturb slightly the enantioselection step during the catalytic cycle. The conventional aqueous biphasic system by using (*R*)-BINAPS as ligand provided lower TOF_{max} of 226 h^{-1} and lower ee of 49% ee at 2.0 MPa and 303 K (Entry 1). When $[bmim]BF_4$-isopropanol was used as solvent, the highest TOF_{max} of 1234 h^{-1} and 64% ee associated with biphasic catalytic system were obtained under identical conditions (Entry 2), where the catalyst system was consisted of the lower layer of ionic liquid-complex and the upper layer of isopropanol-reactant. The reaction conversions could be obtained as high as 99% using both imidazolium-based ionic liquids at the substrate to Rh (S/C) molar ratio of 1000, but the highest TOF_{max} and ee value were obtained by using the solvent pair of $[bmim]BF_4$-iospropanol whether the catalysts generated either from (*R*)-BINAPS or (*R*)-BINAP (Entries 2 and 7). As compared to the Rh-complex generated from (*R*)-BINAP, the one from the water-soluble (*R*)-BINAPS afforded relatively lower activity and ee value. The

Table 1
The hydrogenation of dimethyl itaconate by **1** and **2** in *different*solvent system[a]

Entry	Catalyst	Solvent system(2 mL/2 mL)	Time (min)	Conversion (%)	ee (%)	TOF_{max}[b](h^{-1})
1	**1**	H_2O-toluene	330	99	49	226
2	**1**	$[bmim]BF_4$–isopropanol	60	99	65	1234
3	**1**	$[bmim]PF_6$–isopropanol	900	99	45	93
4 [c)]	$Rh(COD)_2BF_4$ + (*R*)-BINAPS	$[bmim]BF_4$–isopropanol	60	70	54	1017
5	**2**	$[bmim]BF_4$–toluene	600	100	61	131
6	**2**	$[bmim]BF_4$–isopropanol	40	100	70	1990
7	**2**	$[bmim]PF_6$–isopropanol	480	99	68	180
8 [c)]	$Rh(COD)_2BF_4$ + (*R*)-BINAP	$[bmim]BF_4$–isopropanol	40	85	62	1836

[a] Reaction conditions: Temperature 303 K, P (H_2) = 2.0 MPa, complex = 0.006 mmol (8.0 mg for **1** and 5.5 mg for **2**), substrate to Rh (S/C) = 1000 (molar ratio), ionic liquid/isopropanol = 2.0/2.0 mL; [b] TOF_{max}: Turnover Frequency, moles of product by per mole of ruthenium species per hour (mol-product mol-$Ru^{-1}h^{-1}$, for short, h^{-1}). See Experimental Section for calculation details. [c] Ligand/Rh = 1/1 (molar ratio).

results in table 1 also indicated that the catalyst generated *in-situ* either with (*R*)-BINAPS or (*R*)-BINAP as chiral ligand induced lower conversions and ee values (Entries 4 and 8).

Table 2 lists the molar ratio effect of S/C on the hydrogenation performance of dimethyl itaconate by **1** and **2** in [bmim]BF_4-isopropanol solvent. It was shown that the TOF_{max} increased as the S/C and reached maximum when the S/C at 1000, keeping a similar ee value for a given catalyst. We then used the S/C at 1000 for the following investigations.

The influence of the reaction temperature on the enantioselectivity is shown in figure 1. The TOF_{max} increased slowly at higher reaction temperature. The enantioselectivity decreased gradually at enhanced reaction temperature due to the increment of disorder. The results suggested that the enantioselectivity hydrogenation by the two complexes **1** and **2** might follow the same reaction mechanism in [bmim]BF_4-isopropanol system.

Figure 2 shows the enantioselectivity and TOF_{max} as a function of hydrogen pressure in the hydrogenation of dimethyl itaconate in [bmim]BF_4-isopropanol. Again, the catalytic behaviors of the complexes **1** and **2** in [bmim]BF_4– isopropanol were similar to each other. No significant influence on the ee value was obtained by raising the hydrogenation pressure, in other words, the increase in solubility of hydrogen by enhancing the hydrogen pressure could only result in an increase in TOF_{max} in the present case. We noted that Dupont and co-workers investigated the asymmetric hydrogenation of (Z)-α-acetamidocinnamic acid in ionic liquid-isopropanol system [8], where the catalyst used was (−)-1,2-bis((2*R*,5*R*)-2,5-diethylphospholano)-benzene-(cyclooctadiene)-Rh(I) trifluoromethanesulfonate, and the substrate/catalyst molar ratio (S/C) was 100. In that case the conversion after 24 h reaction time and ee values measured in [bmim]PF_6 under 50 bar pressure were found to be 26% and 81%, respectively, while 73% was the conversion in [bmim]BF_4 in 50 bar pressure, obtaining 93% ee value in 24 h reaction time. They explained the higher enantioselectivity using [bmim]BF_4 as solvent by the better solubility of hydrogen. Our results in table 1 showed that the lower TOF_{max} and ee value was achieved by using [bmim]PF_6 instead of [bmim]BF_4, obtaining a similar dependence on the type of ionic liquids to that of Dupont's group. Conceivably, the results were related to the hydrophobic property of [bmim]PF_6 [18]. However, no beneficial effects on the ee value were obtained by increasing the solubility of hydrogen using higher pressure under the present condition (figure 2). We believed that the coordination between the bidendate phosphine and Rh species was considerably structurally stable in the [bmim]BF_4 even if under the higher hydrogen pressure.

Table 2

The effect of S/C on the hydrogenation of dimethyl itaconate by **1** and **2** in [bmim]BF_4–isopropanol[a]

Entry	Catalyst	S/C (molar rati)	Time (min)	Conversion (%)	ee (%)	TOF_{max} (h^{-1})
9	**1**	300	20	88	65	1070
10	**1**	500	25	81	64	1136
11	**1**	1000	40	84	64	1234
12	**1**	2000	80	79	63	1196
13	**2**	300	15	85	69	1453
14	**2**	500	20	89	70	1717
15	**2**	1000	30	92	70	1990
16	**2**	2000	60	87	69	1957

[a] Reaction conditions: Temperature = 303 K, P (H_2) = 2.0 MPa, others are the same as in table 1.

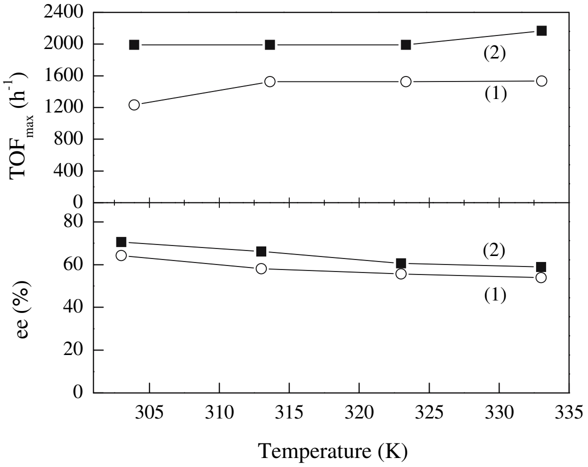


Figure 1. The enantioselectivity and TOF_{max} as a function of temperature in the hydrogenation of dimethyl itaconate in [bmim]BF_4–isopropanol with (1) Rh complex **1** and (2) Rh complex **2** as catalysts. The reaction conditions are the same as in table 1. (a) TOF_{max}; (b) enantioselectivity.

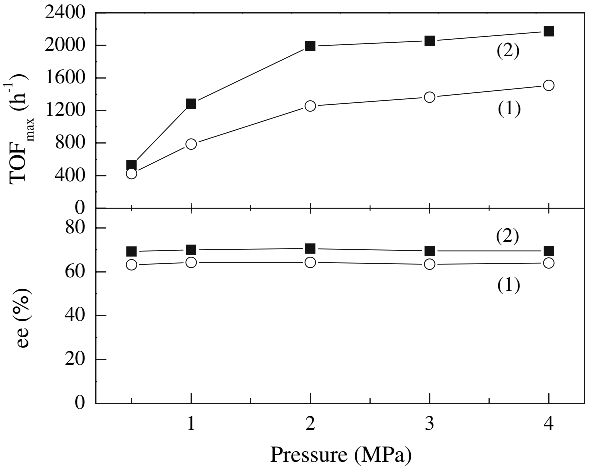


Figure 2. The enantioselectivity and TOF_{max} as a function of hydrogen pressure in the hydrogenation of dimethyl itaconate in [bmim]BF_4–isopropanol with (1) Rh complex **1** and (2) Rh complex **2** as catalysts. The reaction conditions are the same as in table 1. (a) TOF_{max}; (b) enantioselectivity.

Next, the stabilities of the Rh complexes derived from (*R*)-BINAPS and (*R*)-BINAP in [bmim]BF_4–isopropanol have been checked separately by the consecutive recycling runs. The results are illustrated in figure 3. The catalyst based on (*R*)-BINAP showed continuous drops in TOF_{max} and ee value from the first to fourth run (the recyclings from 0 to 3), which was believed in connection with the leachings of Rh and phosphorus species into the organic phase. Contrast to this, the catalyst generated from the (*R*)-BINAPS showed considerable stability in catalytic performance from the first to fourth run at 303 K and 2.0 MPa, affording the TOF_{max} varied from 1234~1190h^{-1} and 64% ee, respectively. However, there existed apparent drops in TOF_{max} and ee value from the fifth run (the fourth recycling) as shown in figure 3. The small decrease in the TOF_{max} and ee value could be owing to the loss of catalyst during decantation and no addition of any fresh catalysts to keep an identical amount of catalyst used. However, other possibilities could not be ruled out, such as the leachings of Rh species (for instance, the formation of carbonyls) and phosphorus species into the organic phase due to the extraction of organics in the process of recycling runs, the degradation of phosphorus species in the course of reaction, the oxidation of phosphorus species due to the air invasion during the decantation and so on.

It is known that the molar ratio of phosphorous/Rh below the saturated level is crucial both for the reaction rate and ee value, owing to the electronic and steric effects. To investigate the losses of phosphorus and Rh from the ionic liquid phase, we have measured the contents of phosphorus and Rh in the organic phase by the ICP-OES after each reaction. Table 3 lists the leaching of Rh and phosphorus from the ionic liquid phase into the organic phase after each catalytic run. Apparently, the extraction of phosphorous species bearing with water-soluble groups of sodium sulfonate by the organic reactant from the [bmim]BF_4 phase was larger than that of Rh species. The total extraction of phosphorous species by the reactants from the ionic liquid phase was about 11.1 wt% (corresponding to the phosphorous species with a neat amount of 1.33 μmol) after the catalyst for four runs (the recyclings from 0 to 3), which was about three times larger than that of total loss of Rh species (totally 3.24 wt%, corresponding to the Rh species with a neat amount of 0.194 μmol). Further calculation revealed that the molar ratio of the total loss of phosphorous over Rh during the four runs was about 6.85, which was obviously larger than that of the stoichiometric molar ratio in **1**. Therefore, we replenished the (*R*)-BINAPS ligand in a calculation amount of phosphorous /Rh = 2 (molar ratio) after the sixth run. The results showed that the TOF_{max} and ee value were increased almost to those with the pristine catalyst (figure 3), indicating that the loss or/and degradation of ligand should be crucial for the drops in activity and ee value although the Rh leaching was not totally depressed.

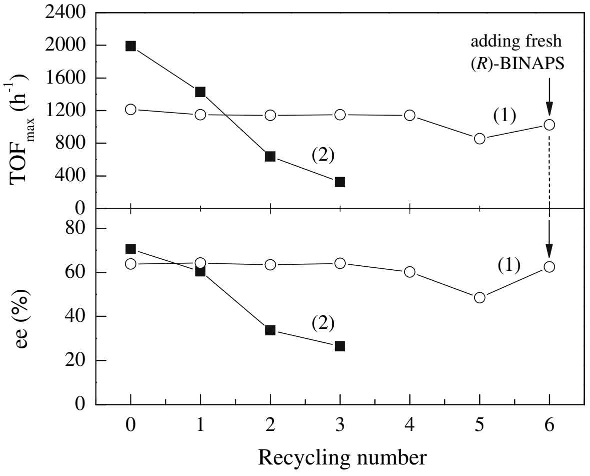


Figure 3. The recycling of Rh complexes **1** and **2** in [bmim]BF_4–isopropanol for the asymmetric hydrogenation of dimethyl itaconate with (1) Rh complex **1** and (2) Rh complex **2** as catalysts. The reaction conditions are the same as in table 1. (a) TOF_{max}; (b) enantioselectivity.

Table 3

The leachings of Rh and phosphorous in the product phase during the catalyst recycling in the hydrogenation of dimethyl itaconate by **1** in [bmim]BF_4–isopropanol[a]

Recycling number	0	1	2	3	4	5
Rh loss (wt%)	0.80	0.81	0.81	0.82	0.83	0.83
Phosphorous loss (wt%)	2.6	2.7	2.8	3.0	44.0	16.3

[a] Reaction conditions are the same as in table 1.

In summary, the asymmetric hydrogenation of dimethyl itaconate could be achieved by water-soluble [Rh(COD)((*R*)-BINAPS)]BF_4 **1** catalyst in ionic liquid-isopropanol biphasic system with enantioselectivity and activity approaching the homogenous catalytic system and superior to the aqueous bipashic one. Investigating the temperature and hydrogen pressure dependences of the asymmetric hydrogenation of dimethyl itaconate, we found that the best enantioselectivity (~64%) could be achieved at 303 K and 2.0 MPa. The catalyst could be reused four cycles without significant changes in the catalytic performance, but further recycling use caused the declines in TOF_{max} and ee value, which were largely due to the loss of phosphorous species besides the leaching of Rh species. Introducing a proper amount of fresh ligand into the used catalyst could recover the catalytic performance close to the original level.

Acknowledgments

The authors gratefully acknowledge the financial supports from the NSFC (Nos: 20021002, 20473065 and 20433030), the Key Project of Fujian Province (No: 2005HZ01–3) and the Research Fund for the Doctoral

Program of Higher Education (No: 20050384011) and the Key Project of Chinese Ministry of Education (NO: 106099).

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