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PEG-400-H_2O as a green and recyclable medium for asymmetric hydrogenations of aromatic ketones catalyzed by $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS

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ABSTRACT

PEG-400-H_2O was found to be a green and recyclable reaction medium for asymmetric hydrogenations of aromatic ketones catalyzed by a ruthenium achiral monophosphine complex $RuCl_2(TPPTS)_2$ [TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$] modified by (*S*,*S*)-DPENDS [disodium salt of sulfonated (*S*,*S*)-1,2-diphenyl-1,2-ethylene-diamine]. The acetophenone product was obtained with 86.3% ee under the optimized conditions. The resulting products can be easily separated from the catalyst by extraction with *n*-hexane. The catalyst immobilized in PEG-400-H_2O not only exhibits excellent activity and enantioselectivity, but also can be recycled and reused several times without a loss of activity or enantioselectivity.

1. Introduction

Asymmetric hydrogenation is a useful method for the synthesis of enantiomerically pure compounds. Homogeneous catalysts show distinguished catalytic properties in asymmetric hydrogenations of simple ketones,[1–4] but these catalysts are very expensive and difficult to reuse.[5]

Ionic liquids have attracted a great deal of interest because of their capability to immobilize homogeneous catalysts and to offer an interesting approach to solve the aforementioned problems.[6] In recent years, ionic liquids for the asymmetric hydrogenation of prochiral olefins, ketones, imines, and β-ketoesters have been reported,[7–13] and the results indicate that the organic products can be easily extracted by less polar organic solvents; furthermore the ionic liquids containing homogeneous asymmetric hydrogenation catalysts could be reused several times without a significant loss of catalytic activity or enantioselectivity. However, ionic liquids have the disadvantages of their high price and tedious preparation.

Recently, liquid PEGs have attracted increasing interest as novel solvents for organic reactions due to their benign characteristics.[14,15] In particular, PEGs are inexpensive and have low toxicity. However, PEGs have rarely been reported as reaction media for asymmetric hydrogenations.[16–22] Furthermore, organic solvents are usually added as the co-solvent of PEGs to enhance the solubility of the homogeneous catalysts in catalyst systems (see Figs. 1 and 2).

We are interested in the asymmetric hydrogenation of prochiral ketones in biphasic systems.[23–27] It was reported that PEG-400-H_2O can be used as a green and recyclable reaction medium for the asymmetric hydrogenation of aromatic ketones catalyzed by $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS (Fig. 1) catalyst under mild reaction conditions (Fig. 2). Meanwhile, the resulting products can be easily separated from the catalyst by extraction with *n*-hexane. The catalyst in a PEG-400-H_2O medium not only exhibits excellent reactivities and enantioselectivities, but also simplifies its recycling and reuse.

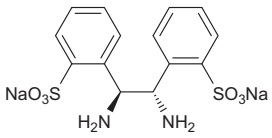

Figure 1. (*S*,*S*)-DPENDS.

2. Results and discussion

2.1. The effect of the solvent and temperature on the asymmetric hydrogenation of acetophenone

In order to determine whether the asymmetric hydrogenation could proceed in PEG-400, we chose acetophenone as a model substrate and investigated the influence of addition of solvent on the reaction. As shown in Table 1, lower catalytic activity and enantioselectivity were observed in pure PEG-400 (Table 1, entry 1). Furthermore, much lower activity and enantioselectivity were obtained when hexane was added to PEG-400 as the co-solvent (Table 1, entry 2). However, the activity and enantioselectivity

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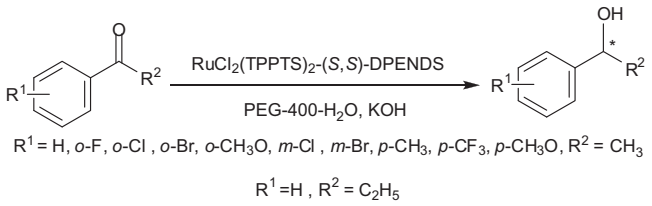

Figure 2. Asymmetric hydrogenation of aromatic ketones.

Table 1
Effect of the addition of the solvent on the asymmetric hydrogenation[a]

Entry	Solvent (v/v)	Conversion (%)	ee[b] (%)
1	PEG-400	22.9	70.1
2	PEG-400/hexane = 2/1	7.9	67.5
3	PEG-400/*i*-PrOH = 2/1	60.6	78.9
4	PEG-400/H_2O = 2/1	100	82.1
5	PEG-400/H_2O = 1/1	100	75.0
6	PEG-400/H_2O = 1/2	100	67.5
7	H_2O	68.3	57.7

[a] Reaction conditions: acetophenone: 0.85 mmol; Ru/acetophenone/(*S*,*S*)-DPENDS = 1:224:6; $V_{solvent}$: 0.75 ml; KOH: 20 mg; P_{H2}: 5.0 MPa; *T*: 30 °C; *t*: 3 h.
[b] Configuration: (*R*).

increased when using *i*-PrOH as the co-solvent (Table 1, entry 3). This might be due to the significant co-solvent effect of the alcohol.[28,29]

Literature data indicated that water affects the reaction when ILs are used as the solvent.[30–34] In addition, PEG400-H_2O has been used as a reaction medium for the asymmetric transfer hydrogenations of simple ketones catalyzed by Ru-TsDPEN, and the remarkable effect of H_2O on the reactivity was observed.[35] Therefore, in view of the beneficial effect of water, and to improve the performance of $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS catalyst in PEG-400, we added water to evaluate its effect on the asymmetric hydrogenation of aromatic ketones. The results indicate that the addition of appropriate amounts of water can increase the ee value, and also enhance both the solubility of the catalyst and the concentration of H_2 in PEG-400. However, increasing the amount of water further, resulted in lower enantioselectivity.

The data listed in Table 2 indicate that the enantioselectivity increases as temperature decreases and 86.3% ee was obtained at 5 °C (Table 2, entry 1).

Table 2
The effect of temperature on the asymmetric hydrogenation of acetophenone[a]

Entry	Temperature (°C)	Conversion (%)	ee[b] (%)
1	5	10.5	86.3
2	20	87.3	83.3
3	30	100	82.1
4	45	100	79.2

[a] $V_{PEG-400}$:V_{H2O} = 2:1, other reaction conditions were the same as those in Table 1.
[b] Configuration: (*R*).

2.2. The effect of different ruthenium precatalysts on the asymmetric hydrogenation of acetophenone

As can be seen in Table 3, the asymmetric hydrogenation of acetophenone catalyzed by different ruthenium precatalysts was investigated in PEG-400.

The results indicate that the influence of different ruthenium catalyst precursors on the activity and selectivity is significant. Among the three catalyst precursors, $RuCl_2(TPPTS)_2$ was the most efficient catalyst: the conversion and ee value of the products can reach up to 100% and 82.1%, respectively (Table 3, entry 1).

Table 3
Effect of different ruthenium complex on asymmetric hydrogenation[a]

Entry	Ruthenium complex	Conversion (%)	ee[b] (%)
1	$[RuCl_2(TPPTS)_2]_2$	100	82.1
2	$RuCl_2$(COD)-2TPPTS	54.5	73.3
3	$RuCl_3$-2TPPTS	20.6	73.9

[a] $V_{PEG-400}$:V_{H2O} = 2:1, other reaction conditions were the same as those in Table 1 except for precatalysts.
[b] Configuration: (*R*).

With regard to $RuCl_2$(COD), low activity was observed because COD would be exchanged with TPPTS to form an active catalyst (Table 3, entry 2). In the case of $RuCl_3$ as a catalyst precursor (Table 3, entry 3), there was a longer induction period because the three-valent ruthenium was reduced to a low oxidation state and then coordinated with TPPTS, while TPPTS was partially oxidized to OTPPTS.[36] Hence, the activity was very low. Furthermore, a lower enantioselectivity obtained was due to the oxidation of TPPTS.

2.3. Influence of the molar ratio of ruthenium to (*S*,*S*)-DPENDS and KOH concentration

As shown in Tables 4 and 5, the influence of (*S*,*S*)-DPENDS and KOH on the asymmetric hydrogenation of acetophenone is very significant. Only 9.9% of the substrate was converted, and no ee value was obtained in the absence of (*S*,*S*)-DPENDS (Table 4, entry 1). The addition of (*S*,*S*)-DPENDS apparently heightened the catalytic activity and enantioselectivity. When the molar ratio of ruthenium to (*S*,*S*)-DPENDS was 1:6, the conversion and ee value could reach up to 100% and 82.1%, respectively (Table 4, entry 3).

Table 4
The effect of the molar ratio of ruthenium to (*S*,*S*)-DPENDS on the asymmetric hydrogenation of acetophenone[a]

Entry	Molar ratio	Conversion (%)	ee[b] (%)
1	No (*S*,*S*)-DPENDS	9.9	
2	1:3	95.1	81.7
3	1:6	100	82.1
4	1:9	100	80.3

[a] $V_{PEG-400}$:V_{H2O} = 2:1, other reaction conditions were the same as those in Table 1 except for concentration of (*S*,*S*)-DPENDS.
[b] Configuration: (*R*).

The importance of a base has been well-established for homogeneous catalysts for the asymmetric hydrogenation of ketones.[1–4] Similar to homogeneous and some heterogeneous reactions,[37–39] a basic additive can be useful to enhance the catalytic properties. The reaction did not proceed in the absence of KOH (Table 5, entry 1). Increasing the KOH concentration, increased the conversion and ee. When the amount of KOH was 5 mg, 100% conversion and 82.1% ee were obtained (Table 5, entry 3). However, increasing the

Table 5
The effect of KOH concentration on the asymmetric hydrogenation of acetophenone[a]

Entry	Concentration (mol/L)	Conversion (%)	ee[b] (%)
1	0	—	—
2	5 mg	42.9	74.9
3	20 mg	100	82.1
4	30 mg	100	81.5

[a] $V_{PEG-400}$:V_{H2O} = 2:1, other reaction conditions were the same as those in Table 1 except for the concentration of KOH.
[b] Configuration: (*R*).

amount of KOH further, resulted in no increase in the conversions and ee values.

The results shown in Tables 4 and 5 indicate that there was a synergistic effect between (*S*,*S*)-DPENDS and KOH. Similar phenomena were observed in our previous work.[23–27,40]

2.4. Asymmetric hydrogenation of different substrates

Various aromatic ketones were hydrogenated with the $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS catalyst in PEG-400 and the results are summarized in Table 6. The data indicate that this novel catalyst shows a good catalytic performance for most aromatic ketones.

The steric bulk, which influences the reactant-modifier interaction, markedly affects the activity. As a result, higher conversions were obtained in the asymmetric hydrogenation of acetophenone and *para*-substituted aromatic ketones than those of other aromatic ketones. Furthermore, electronic effects also have an influence on the conversions. Among *ortho*-substituted aromatic ketones, moderate conversions were achieved for the substrates with electron-withdrawing groups while lower results were obtained for electron-donating substituents. For example, only 10.6% conversion was found for 2′-methoxyacetophenone (Table 6, entry 6), and while no product was detected for 2′-hydroxyacetophenone (Table 6, entry 7), which contributed to the formation of a phenoxy anion in the presence of a base.[41]

The enantioselectivity was affected by both the steric bulk and the electronic nature of the substrate. As shown in Table 6, entries 3–5, the enantioselectivity increased when the electronegativity of the halogen decreased. More than 80% enantioselectivities were achieved for acetophenone, 2′-chloroacetophenone, and 2′-bromoacetophenone. It should be noted that 1-(2′-methoxyphenyl)ethanol had an (*S*)-configuration, which is the same as Baiker's report.[42]

2.5. Catalyst recycling

Finally, the separation of the products and the recycling of the catalyst were explored for the asymmetric hydrogenation of aromatic ketones in PEG-400-H_2O. The data demonstrate that the chiral alcohol products could be easily separated by extraction with *n*-hexane, while the catalyst and modifiers immobilized in PEG-400 could be recycled and reused several times. As shown in Table 7, although the conversions started to drop from the sixth run, the ee value could still be maintained above 77%. The conversion increased from 76.9% (run 6) to 85.7% (run 7) when 10 mg KOH was added in the seventh run, which further shows the notable effect of base on the catalytic performance. This phenomenon is in agreement with our previous report.[24,27] The loss of ruthenium catalyst was minimal, and was only 0.1% from ICP analysis

Table 7
Recycling and reuse of $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS in PEG-400-H_2O[a]

Run	Conversion (%)	ee[b] (%)
1	100	82.1
2	100	81.1
3	100	80.7
4	100	78.7
5	95.2	77.5
6	76.9	77.7
7[c]	85.7	77.3
8	73.1	77.5

[a] Reaction conditions were the same as those in Table 6.
[b] Configuration: (*R*).
[c] 10 mg of KOH were added in the seventh run.

3. Conclusions

In conclusion, PEG-400-H_2O was found to be a green and recyclable reaction medium. In PEG-400-H_2O, the $RuCl_2(TPPTS)_2$-(*S*,*S*)-DPENDS catalyst was successfully applied to asymmetrically hydrogenate aromatic ketones, with high activity, and good enantioselectivity. The catalyst cannot only be easily separated from the products by extraction with *n*-hexane, but also reused several times without obvious loss of activity or enantioselectivity. Furthermore, we have demonstrated that the addition of appropriate amounts of water can accelerate the reaction and increase the ee value.

4. Experimental

4.1. Materials and methods

Aromatic ketones (>98% Acros) and hydrogen (99.99%) were used as purchased and other reagents were all of analytical grade. TPPTS, $RuCl_2(TPPTS)_2$ and chiral modifier (*S*,*S*)-DPENDS were synthesized according to known methods in our laboratory.[43–46]

4.2. Typical procedure for asymmetric hydrogenation of aromatic ketones

To a 60 mL stainless autoclave with a glass liner and magnetic stirrer were added PEG-400, H_2O, $RuCl_2(TPPTS)_2$, (*S*,*S*)-DPENDS, KOH, and reactant. Hydrogen was introduced to the desired pressure after the reaction mixture had been purged with H_2 five times. The products were extracted by *n*-hexane and analyzed by GC-960 with a FID detector and β-DEX™120 capillary column (30 m × 0.25 mm, 0.25 μm film) at 115 °C. The enantiomeric excess (ee value) was calculated from the equation: ee (%) = 100 × (*R* − *S*)/(*R* + *S*).

Table 6
Asymmetric hydrogenation of different substrates[a]

Entry	Substrates	Conversion (%)	Ee (%)	Configuration
1	Acetophenone	100	82.1	(*R*)
2	Propiophenone	100	81.3	(*R*)
3	2′-Fluoroacetophenone	65.8	61.1	(*R*)
4	2′-Chloroacetophenone	56.7	80.1	(*R*)
5	2′-Bromoacetophenone	64.8	84.3	(*R*)
6	2′-Methoxyacetophenone	10.6	46.9	(*S*)
7	2′-Hydroxyacetophenone	—	—	—
8	3′-Chloroacetophenone	40.1	70.2	(*R*)
9	3′-Bromoacetophenone	45.3	72.5	(*R*)
10	4′-Methylacetophenone	100	78.3	(*R*)
11	4′-Methoxyacetophenone	100	75.6	(*R*)
12	4′-(Trifluoromethyl)acetophenone	100	65.7	(*R*)

[a] Reaction conditions: Substrate: 0.85 mmol; Ru/substrate/(*S*,*S*)-DPENDS = 1:224:6; $V_{solvent}$: 0.75 ml; $V_{PEG-400}$:V_{H2O} = 2:1; KOH: 20 mg; P_{H2}: 5.0 MPa; *T*: 30 °C; *t*: 3 h.

4.3. A typical procedure for catalyst reuse

The reaction mixture was extracted with *n*-hexane under an argon atmosphere. The organic layer was siphoned from the PEG-400 and the residual *n*-hexane was removed by blowing with argon gas before the addition of a new ketone substrate.

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