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(*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3—An efficient heterogeneous catalyst for enantioselective hydrogenation of acetophenone

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Abstract

An efficient enantioselective catalyst of 5 wt.% Ru/γ-Al_2O_3 modified with *R*,*R*-1,2-diphenylethylene-diamine ((*R*,*R*)-DPEN) for the hydrogenation of a non-activated aromatic ketone of acetophenone has been investigated, a relatively high enantiomeric excess (ee) of 60.5% was obtained at both the conversion and selectivity larger than 99%, it was about three times higher than the ee values reported up to now for acetophenone hydrogenation with the supported transition metal catalysts modified by chiral reagents. The influences of some reaction parameters such as phosphine ligand, substrate/catalyst/modifier molar ratios, base, solvent, pressure and reaction temperature have been discussed. The chiral modifier of (*R*,*R*)-DPEN was very important in controlling the enantioselectivity through adsorption competing with other substrates on the surface of active metal species. The phosphine ligand and base were also important and indispensable in the present reaction.

Keywords: Enantioselective hydrogenation; Heterogeneous; Acetophenone; (*R*,*R*)-DPEN; Ru/γ-Al_2O_3

1. Introduction

Enantioselective hydrogenation is a core technology in the production of enantiopure compounds, particularly in the field of pharmaceuticals, flavors, fragrances, and agrochemicals [1]. The chiral metal complexes as efficient catalysts were widely investigated, but they are usually expensive and difficult to separate and recover, therefore the immobilization of homogeneous chiral catalysts and preparation of heterogeneous chiral catalysts have been paid more attention recently. Various strategies have been applied to design heterogeneous chiral catalysts [2–9], the adsorption of chiral modifiers onto the active metal surface of supported catalysts was found to be particularly effective for enantioselective hydrogenation. It was reported that the nickel catalysts modified with tartrate/NaBr were effective for the hydrogenation of β-functionalized and unfunctionalized aliphatic ketones [2,10,11], and the platinum catalysts modified with cinchona alkaloids were efficient for the hydrogenation of α-functionalized ketones [12–15]. But, the Ni-tartaric acid system was limited in the hydrogenation of aliphatic ketones [16–19] and the Pt-cinchona alkaloid system was limited in the hydrogenation of activated ketones [13,20,21]. As far as non-activated aromatic ketones are concerned, the enantioselectivity is still low [22–25], for example, in the enantioselective hydrogenation of acetophenone, an enantioselectivity of 22% ee was reported over *S*-proline-modified Pd/C catalyst [22], 20% ee was reported over cinchona-modified Pt/C catalyst [23] and 24% ee was obtained over chiral organotin modified Pt- and Rh-based catalysts [24,25]. Thus, the investigation in the asymmetric hydrogenation of non-activated aromatic ketones with supported metal catalysts is still a challenge. In the present work, the enantioselective hydrogenation of acetophenone, a non-activated aromatic ketone, has been studied with (*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3 catalyst. Some reaction parameters were examined and the results indicated that the acetophenone could be

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hydrogenated to 1-phenylethanol selectively with a high enantioselectivity.

2. Experimental

5-wt.% Ru/γ-Al_2O_3, 5-wt.% Ru/C catalysts were purchased from WAKO and used as received, 1-wt.% Ru/SiO_2 was prepared as described in the literature [26]. All the substrates of trisodium tris(*m*-sulfonatophenyl)-phosphine (TPPTS) purchased from Fluca; *R*,*R*-1,2-diphenylethylene-diamine ((*R*,*R*)-DPEN), acetophenone, $KOC(CH_3)_3$, triphenylphosphine (TPP), tris(4-fluorophenyl)-phosphine and tri-*o*-tolyl-phosphine from Aldrich; KOH, triethylamine (Et_3N) and all the solvents from Beijing Chemical Reagent Plant, are of analytical grade and used without further purification. Gases of N_2 (99.9%) and H_2 (99.999%) were used as delivered.

The reaction was performed in a 50 ml stainless autoclave reactor with a magnetic stirrer. A definite quantity of the catalyst, (*R*,*R*)-DPEN, TPP, $KOC(CH_3)_3$ and solvent were placed into the reactor, then 0.85 mmol of the acetophenone was introduced under nitrogen atmosphere and the reaction was carried out with continuous stirring at the desired temperature and hydrogen pressure. After reaction, selected samples were centrifuged and analyzed by gas chromatograph equipped with FID detector (Shimadzu GC-2010) with a chiral capillary column (β-DEX Trade Mark 120, 30 m × 0.25 m × 0.25 μm), and the products were identified by GC/MS. The enantiomeric excess was determined as ee (%) = $100 \times |R - S|/(R + S)$, the reproducibility of ee was within ±0.5%. The filtrate was collected and analyzed by GFAAS (PE AA800) for the leaching of Ru from supported catalyst.

3. Results and discussion

The enantioselective hydrogenation of acetophenone, a non-activated aromatic ketone without electron-withdrawing functional groups in the aromatic ring or a functional group at α-position, was selected as the target reaction for investigating the catalytic performance of (*R*,*R*)-DPEN-modified supported ruthenium catalysts. The activity of several catalysts of Ru supported on different supports like γ-Al_2O_3, C and SiO_2 have been compared, Ru/γ-Al_2O_3 was more effective than Ru/C and Ru/SiO_2 catalysts for the acetophenone hydrogenation, the difference in activity of supports may be attributed to the interactions among support, metal, and substrates [27,28]. In this work, the (*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3 catalyst was selected for the following studies.

3.1. Phosphine ligand

Several phosphine ligands have been firstly checked as a promoter for acetophenone hydrogenation with Ru/γ-Al_2O_3 catalyst as shown in Table 1. The results indicated that the ee was only 6.5% in the absence of phosphine, and it was still lower when TPPTS, tris(4-fluorophenyl)-phosphine or tri-*o*-tolylphosphine was used, however, a higher ee of 54.3% was obtained at a conversion of 99.4% in the case of using TPP,

Table 1
The conversion and enantioselectivity of acetonphenone hydrogenation with Ru/γ-Al_2O_3 catalyst in the presence of different phosphine ligands

Phosphine ligand	Conversion (%)	ee (%)
–	99.3	6.5
TPPTS[a]	6.4	6.5
Tris(4-fluorophenyl)-phosphine	71.6	4.3
Tri-*o*-tolyl-phosphine	100	3.7
TPP	99.4	54.2

Reaction conditions: acetophenone/Ru/DPEN/phosphine ligang = 420/1/4/4; acetophenone: 0.85 mmol; [$KOC(CH_3)_3$]: 0.18 mol/l; *i*-PrOH: 2.0 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.
[a] Solvent: ethylene glycol 2.0 ml.

and the concentration of TPP presented a large effect on the enantioselectivity. The concentration of TPP was changed with varying mole ratio of TPP/Ru at a constant concentration of acetophenone/Ru/DPEN = 420/1/4, the results in Fig. 1 showed that a maximum ee presented at TPP/Ru = 4 and the conversion of acetophenone was larger than 99%. It is worth noting that phenylethanol was formed as an isolated product with a selectivity of 100% under all the reaction conditions. These results suggested that phosphine ligands had a marked effect on the conversion and enantioselectivity, which may be attribute to its influence on the formation of chiral micro-circumstance through the interaction with chiral modifier. Ru(II) complexes containing achiral monodentate phosphine ligands and a chiral reagent of 1,2-diphenylethylenediamine have been employed successfully in the enantioselective hydrogenation of ketones, with which a higher enantioselectivity was reported, and it was interpreted by the synergistic effect of the phosphine and diamine ligands [29,30].

3.2. Molar ratios of chiral modifier/substrate/catalyst

Varying the molar ratio of chiral modifier of *R*,*R*-1,2-diphenylethylene-diamine (DPEN) to the reactant of acetophenone (DPEN/substrate) showed a marked impact as illustrated in Fig. 2. The conversion and ee increased with increasing of the molar ratio of modifier/substrate at the con-

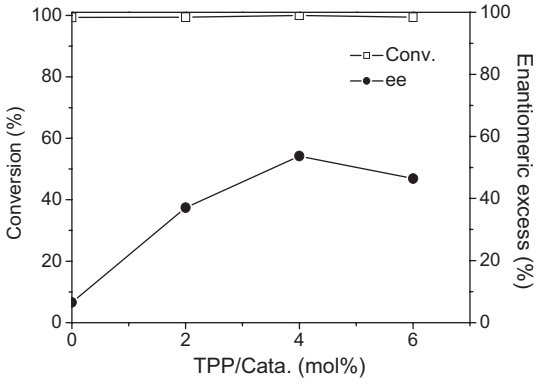

Fig. 1. Effect of the concentration of triphenylphosphine on the enantioselective hydrogenation of acetophenone. Reaction conditions: acetophenone/Ru/DPEN = 420/1/4; acetophenone: 0.85 mmol; [$KOC(CH_3)_3$]: 0.18 mol/l; *i*-PrOH: 2 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.

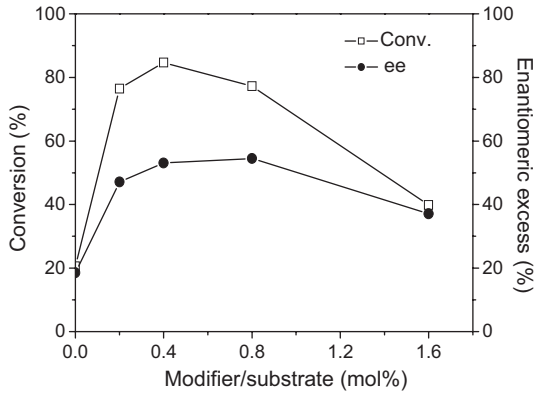

Fig. 2. Influence of modifier/substrate molar ratio on the enantioselective hydrogenation of acetophenone. Reaction conditions: acetophenone/Ru/TPP = 1000/1/4; acetophenone: 0.85 mmol; [$KOC(CH_3)_3$]: 0.18 mol/l; *i*-PrOH: 2 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.

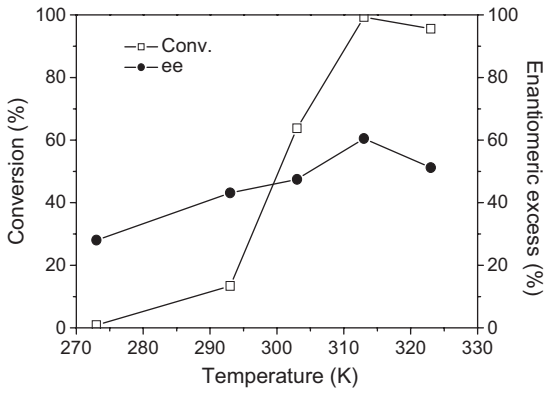

Fig. 3. Effect of temperature on the enantioselective hydrogenation of acetophenone. Reaction conditions: acetophenone/Ru/DPEN/TPP = 1000/1/4/4; [$KOC(CH_3)_3$]: 0.124 mol/l; acetophenone: 0.85 mmol; *i*-PrOH: 2.0 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.

stant concentration ratio of TPP and catalyst. The highest conversion and ee were achieved at a DPEN/substrate ratio of 0.4 mol%. With further increase in the concentration of DPEN, the conversion decreased drastically, while the ee changed very slightly. Which is similar to the literature for the hydrogenation of 3, 5-bis(trifluoromethyl)acetophenone with Pt/Al_2O_3 catalyst modified by cinchonidine (CD) [21]. It was easy to understand that the ee increased naturally with increasing chiral modifier of DPEN, but the excessive amount of DPEN would prohibit the adsorption of substrates on the surface of metal catalyst, thus lowered the reaction conversion. The nature of the active sites on supported catalysts modified with chiral reagents is still a concerning topic of ongoing debate and investigation.

It suggested that the metal catalyst particles are not perfectly symmetric structures, they may contain the defects which are chiral, but in which the amount of left- and right-handed sites is equal, and such catalysts are racemic and do not yield enantiomeric excess in the absence of additional chiral modifier [31]. A chiral modifier may interact differently with chiral metal sites of opposite handedness resulting in one enantiomer of the site can be selectively poisoned, leaving the other enantiomer preferentially exposed and accessible for the reactant. If this chiral site is catalytically active, enantiomeric excess will be induced, which may be suitable to the present $Ru/\gamma\text{-}Al_2O_3$-DPEN-TPP system. From the results in Table 2, an increase in the amount of catalyst at constant ratio of Ru/DPEN gave out the same ee values (entries 1 and 2) and an increase in conversion. However, at constant ratio of substrate/DPEN the increase in the amount of metal catalyst led to a decrease of ee (entries 1 and 3), similar to the increase of Ru/DPEN. Therefore, it was not the ratio of substrate/DPEN but the ratio of Ru/DPEN was crucial for enantioselectivity, namely the interaction and/or the adsorption of DPEN (chiral modifier) on the metal cites played an important role in the present catalytic system. While, it is worth indicating that 18.5% ee was achieved even in the absence of chiral modifier in the present hydrogenation.

Table 2
The enantioselectivity and conversion of acetophenone hydrogenation with $Ru/\gamma\text{-}Al_2O_3$ catalyst

Entry	Sub./Cata./TPP/DPEN	Conversion (%)	ee (%)
1	420/1/4/4	100	53.6
2	1000/1/4/4	84.7	53.1
3	420/4.2/4/4	100	37.0

Reaction conditions: acetophenone: 0.85 mmol; [$KOC(CH_3)_3$]: 0.18 mol/l; *i*-PrOH: 2 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.

3.3. Temperature

The effect of temperature is shown in Fig. 3. The conversion increased sharply with increasing of temperature from 273 to 313 K, and then decreased slightly at 323 K. Enantioselectivity increased with the increase of temperature from 273 to 313 K, the ee presented a maximum of 60.5% at 313 K, and then decreased to 51.2% at 323K. The same result was also obtained in the literature [3,21,32], but no unambiguous explanation has yet been provided for this effect. A feasible interpretation has been given for asymmetric hydrogenation of ethyl pyruvate with Rh/Al_2O_3 catalyst, that the substrate adsorption mode on rhodium surface changed and the energy difference between transition states of two enantiomers became smaller with increasing temperature [32].

3.4. Pressure

The influence of hydrogen pressure on conversion and enantioselectivity is shown in Fig. 4. Under the lower loading of catalyst ((a) acetophenone/Ru/DPEN/TPP = 1000/1/4/4), both the conversion and ee values increased initially with increasing of the hydrogen pressure, then the conversion reduced but the ee values changed very slightly at the pressures above 5 MPa. Under the higher concentration of catalyst ((b) acetophenone/Ru/DPEN/TPP = 420/1/4/4), both the conversion and ee values increased with hydrogen pressure and then changed less after 4 MPa. It is obviously that high pressure is corresponding to high hydrogen concentration, which may directly influence the adsorption of reactant or modifier and such a competition

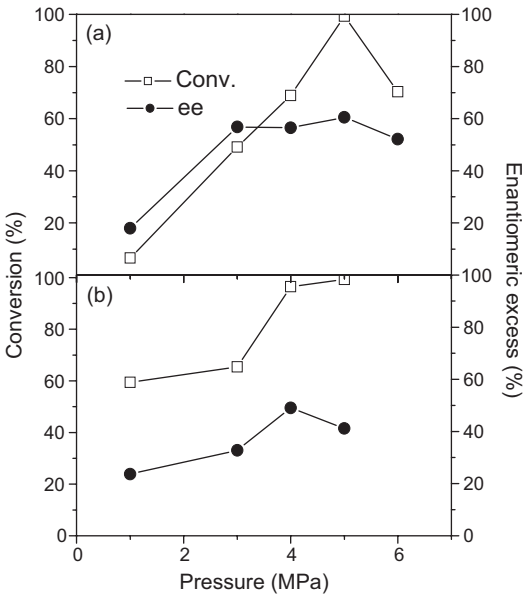

Fig. 4. Effect of hydrogen pressure on the enantioselective hydrogenation of acetophenone. Reaction condition: acetophenone: 0.85 mmol; *i*-PrOH: 2.0 ml; *T*: 313 K; *t*: 16 h. (a) Acetophenone/Ru/DPEN/TPP = 1000/1/4/4; [$KOC(CH_3)_3$]: 0.124 mol/l. (b) Acetophenone/Ru/DPEN/TPP = 420/1/6/6; [$KOC(CH_3)_3$]: 0.18 mol/l.

among them may be more severe under the lower concentration of catalyst.

3.5. Solvent

The effect of different solvents was compared in Table 3. The results showed that protonic solvent was more effective than aprotonic one. *i*-PrOH was most active for the present reaction. The solvent polarity is characterized by the empirical solvent parameter E_T^N [33,34] and the relative permittivity (dielectric constant, ε_T). There is no clear correlation between ee and solvent polarity, but higher ee could be achieved in protonic solvents with H-bond donors. This could be attributed to the molecular interactions among solvent with the reactant, modifier and metal surface.

It was reported that the ee strongly depended on the conversion in the enantioselective hydrogenation of ketones over

Table 3
Results for enantioselective hydrogenation of acetophenone in different solvents

Solvent	E_T^N	ε_T	Conversion (%)	ee (%)
MeOH	0.762	32.6	41.1	53.3
EtOH	0.654	24.6	51.3	55.0
n-PrOH	0.617	20.1	93.6	56.4
n-BuOH	0.602	7.8	92.5	51.5
i-PrOH	0.546	19.92	99.4	54.2
DMF	0.404	36.71	2.3	4.1
EtOAc	0.228	6.02	1.5	45.5
THF	0.207	7.58	0	–
Toluene	0.099	2.38	3.4	4.2

Reaction conditions: acetophenone/Ru/DPEN/TPP = 420/1/4/4; acetophenone: 0.85 mmol; solvent: 2 ml; [$KOC(CH_3)_3$]: 0.18 mol/l; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 16 h.

Table 4
Changes of conversion and entioselectivity with reaction time in different solvents

Solvent	Time (h)	Conversion (%)	ee (%)
EtOH[a]	16	15.6	53.0
	24	27.2	50.9
	32	45.0	51.6
n-PrOH[b]	5	55.3	55.6
	10	76.6	56.9
	16	93.7	56.4
i-PrOH[c]	3	7.36	15.1
	10	54.4	45.5
	16	99.3	60.5

Reaction conditions: acetophenone: 0.85 mmol; *T*: 313 K; P_{H_2}: 5 MPa; solvent: 2 ml.
[a] Acetophenone/Ru/DPEN/TPP = 1000/1/4/4; [$KOC(CH_3)_3$]: 0.124 mol/l.
[b] Acetophenone/Ru/DPEN/TPP = 420/1/4/4; [$KOC(CH_3)_3$]: 0.18 mol/l.
[c] Acetophenone/Ru/DPEN/TPP = 1000/1/4/4; [$KOC(CH_3)_3$]: 0.124 mol/l.

Pt/Al_2O_3 catalyst modified by cinchona alkaloid due to the competing hydrogenation of cinchonidine [14,35,36]. From our results as shown in Table 4, the enantioselectivity increased with increasing of conversion in *i*-PrOH, however, it did not change with conversion in EtOH and *n*-PrOH.

3.6. Base

The results in Table 5 indicate that the reaction proceeds smoothly in the presence of alkaline base such as KOH, $KOC(CH_3)_3$. However, the reaction could not proceed in the absence of base or in the case of using weak base (Et_3N). The effects of concentration of $KOC(CH_3)_3$ are shown in Fig. 5, with increasing of the concentration of $KOC(CH_3)_3$, the conversion increased largely and then decreased quickly; while, the ee reached a maximum value and then changed slightly. Base is important and indispensable in the present hydrogenation, the role of it playing in the reaction has been discussed in several literature, but it is still a research point for the enantioselective hydrogenation of ketones up to now. The enantioselective hydrogenation of ketones using Noyori's *trans*-(bisphosphine)$RuCl_2$(diamine) catalyst provided with an exceptionally high turnover frequency and excellent enantioselectivity for optically active secondary alcohols [37–40]. It was suggested that at least 2 equiv. of alkoxide base are needed to neutralize HCl formed in the catalyst activation, and a hydride complex is responsible for an unconventional transfer of dihydrogen from the hydride on ruthenium and

Table 5
Effect of base on the enantioselective hydrogenation of acetophenone

Base	Conversion (%)	ee (%)
$KOC(CH_3)_3$	40.2	31.8
KOH	15.1	31.1
Et_3N	0	–
–	0	–

Reaction conditions: acetophenone/Ru/DPEN/TPP = 420/1/4/4; acetophenone: 0.85 mmol; [base]: 0.18 mol/l; *i*-PrOH: 2 ml; P_{H_2}: 5 MPa; *T*: 313 K; *t*: 3 h.

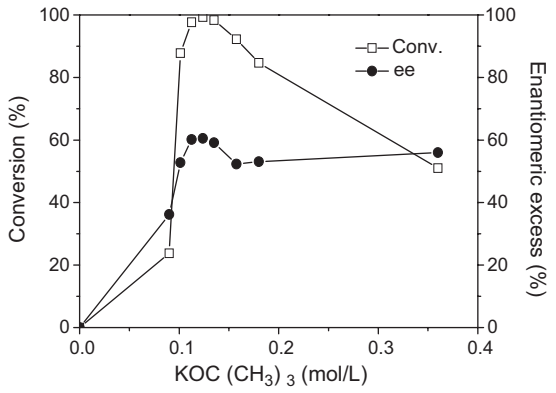

Fig. 5. Effect of the concentration of $KOC(CH_3)_3$ on the enantioselective hydrogenation of acetophenone. Reaction conditions: acetophenone/Ru/DPEN/TPP = 1000/1/4/4; acetophenone: 0.85 mmol; *i*-PrOH: 2.0 ml; *T*: 313 K; P_{H_2}: 5 MPa; *t*: 16 h.

hydrogen on a diamine amino group to ketone to give alcohol product [37].

3.7. The recycling of catalyst

For confirming which phase the reactions occur, is it performed heterogeneously on the surface of the supported catalyst or homogeneously in the reaction solution? The recycling of catalyst and leaching of Ru have been investigated. After the first run, the reaction mixture was centrifuged, and then the catalyst was separated from liquid mixture by decantation. The catalyst was washed three times and then introduced into the reactor with solvent of *i*-PrOH, and fresh acetophenone, (*R*,*R*)-DPEN, TPP, and $KOC(CH_3)_3$ were charged into the reactor again for recycling runs. The catalyst could be reused four times without loss of activity and enantioselectivity under the same reaction conditions. It is worth noting that the modifer and ligand should be added again with substrate together in the recycling because these reagents were left in the solution. By contrast, no reaction occurred when the filtrate liquid phase was mixed with equivalent fresh acetophenone under the same reaction conditions. The leaching of Ru from Ru/γ-Al_2O_3 into solution has been measured by using GFAAS (graphite furnace atomic absorption spectrophotometry), the result shows that only 6 ppm Ru dissolved into the liquid phase at 100% conversion, indicating that the reaction was really carried out heterogeneously on the surface of catalyst, but not homogeneously in the liquid phase. Furthermore, the ee values obtained with the heterogeneous catalyst of Ru/γ-Al_2O_3 changed markedly with the variation of reaction conditions as discussed above. It is absolutely different to the result with homogeneous chiral complexes in *i*-PrOH that the ee did not change with reaction conditions [37].

3.8. Comparison with the other heterogeneous catalytic systems

The enantioselective hydrogenation of acetophenone with supported metal catalysts modified with chiral reagent has been reported in several literature and the results are compared in Table 6. An ee of 22.5% was obtained over *S*-proline-modified Pd/C catalyst [22], and 20% ee over cinchona-modified Pt/C catalyst [23], which is similar to the results obtained over cinchona-modified Pt/Al_2O_3 catalyst [20,21]. It was also reported that chiral organotin modified Pt- and Rh-based catalysts were able to hydrogenate acetophenone to phenylethanol with a selectivity over 97%, but it gave a low ee of 20% [24]. As well as we known, the enantioselectivity of the hydrogenation of acetophenone with supported transition metal catalysts modified with chiral modifiers is still low, with an ee value around 20%. However, in the present work with (*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3 catalyst, the phenylethanol was formed as an isolated product and a higher ee of 60.5% was obtained at the conversion of acetophenone above 99%, it is about three times higher compared with the results reported in the literature up to now for the enantioselective hydrogenation of acetophenone with the supported transition metal catalysts modified with the chiral modifiers.

Table 6
Comparison of the entioselectivity of acetophenone hydrogenation with heterogeneous catalysts modified by chiral reagents

Catalyst	ee (%)	Reference
S-proline-modified Pd/C	22.5	[22]
Cinchona-modified Pt/C	20	[23]
Pt (−)-Men_3SnMe	24	[24]
Cinchonidine-modified Pt/Al_2O_3	17	[20,21]
(*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3	60.5	Present work

4. Conclusions

A new type of enantioselective catalyst of (*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3 has been testified to be an effective heterogeneous catalyst for enantioselective hydrogenation of a non-activated ketone of acetophenone. The results demonstrated that the chiral modifier of (*R*,*R*)-DPEN was very important in controlling the enantioselectivity through competing adsorption to other substrates on the active metal species, and the phosphine ligand and base were also indispensable in the present reaction. Some research topics such as the role of base playing in the reaction and the catalytic mechanism are still faint in the enantioselective hydrogenation of ketones, which is being studied in our further research work.

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