(1*S*,2*S*)-1,2-二苯基乙二胺修饰 Ir/SiO₂ 催化苯乙酮及其衍生物不对称加氢

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摘要: 不添加任何稳定剂, 在碱性条件下制备了 5%Ir/SiO₂ 催化剂, 并用于催化苯乙酮的不对称加氢反应中, 详细考察了碱和手性修饰剂种类、氢气压力、反应温度、(1*S*,2*S*)-1,2-二苯基乙二胺 ((1*S*,2*S*)-DPEN) 浓度对反应的影响。在优化反应条件下, 5%Ir/SiO₂ 催化剂表现出较好的反应活性和对映选择性。其中, 苯乙酮不对称加氢反应的对映选择性达 70%。该催化剂不需要任何稳定剂, 制备方法简单, 催化性能稳定, 通过简单的离心分离即可循环使用。

关键词: 铱; 苯乙酮; 多相不对称加氢; (1*S*,2*S*)-1,2-二苯基乙二胺; 对映选择性

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(1*S*,2*S*)-Diphenylethylenediamine Modified Ir/SiO₂ Catalyst for Asymmetric Hydrogenation of Acetophenone and Its Derivatives

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Abstract: An efficient and highly dispersed 5%Ir/SiO₂ catalyst for the asymmetric hydrogenation of acetophenone and its derivatives were prepared under basic conditions without the use of any stabilizer. The effects of different reaction parameters, namely, catalyst preparation, base used, chiral modifier, and concentration of (1*S*,2*S*)-diphenylethylenediamine ((1*S*,2*S*)-DPEN), were evaluated. Under optimum conditions with 5%Ir/SiO₂ modified by (1*S*,2*S*)-DPEN, a high ee value of 70.0% was obtained for the asymmetric hydrogenation of acetophenone. It is noteworthy that this highest ee value was obtained with a supported metal catalyst without any stabilizer. The catalyst preparation is simple and there was no loss of enantioselectivity when the catalyst was reused several times.

Key words: iridium; acetophenone; heterogeneous asymmetric hydrogenation; (1*S*,2*S*)-diphenylethylenediamine; enantioselectivity

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Catalytic hydrogenation is widely used in both research and industry [1–3] because hydrogen is clean and easily available at very low cost. Heterogeneous asymmetric hydrogenation has operational and economical advantages such as facilitating the separation of the catalyst from the reaction medium, and easy recovery and reuse of the expen-

sive and toxic chiral compounds [4]. Therefore, the development of heterogeneous chiral catalysts has attracted much attention in recent years [5–9]. However, due to the high substrate specificity of these catalysts and the difficulties in understanding and designing the reactions, there have been just three established systems reported so far [10]. Numer-

ous efforts have been made for the chiral modification of supported metal catalysts for asymmetric hydrogenation. One approach is by simply adding a chiral modifier to the reaction mixture or depositing it onto the catalyst surface in a pretreatment step before the reaction. Vargas et al. [11,12] successfully used cinchona modified Pt/Al₂O₃ in the asymmetric hydrogenation of activated aromatic ketones. However, there are few successful heterogeneous catalyst examples for the asymmetric hydrogenation of simple aromatic ketones and their derivatives, which is one of the most fundamental subject in modern synthetic chemistry [13–16]. Recently, our group used (1*S*,2*S*)-diphenylethylenediamine ((1*S*,2*S*)-DPEN) modified Ir/HAP(hydroxyapatite) in the asymmetric hydrogenation of acetophenone and its derivatives, and obtained 63.7% ee value for (*R*)-phenylethanol [17]. Marzaletti et al. [18] have reported a cinchonidine modified Ir/SiO₂ catalyst for the asymmetric hydrogenation of acetophenone that gave 60.2% ee value for (*R*)-phenylethanol but they had to use a larger amount of cinchonidine and catalyst.

Although the enantioselectivity for the hydrogenation of acetophenone was improved by using supported ruthenium as catalyst, air and moisture sensitive phosphine must be added as a stabilizer to have high activity and enantioselectivity [19–23]. There were much trouble and drawbacks due to the instability of phosphine, e.g., the inconvenience of preventing the oxygenation of phosphine, the decline of enantioselectivity and difficult recycle of the catalyst. We have previous reported a cinchonidine and L-proline stabilized Ir for the hydrogenation of acetophenone that gave good enantioselectivity [24,25]. The heterogeneous asymmetric hydrogenation of simple aromatic ketones catalyzed by supported metal catalysts modified by chiral reagents is a highly challenging task, esp. the finding of a catalyst that does not need a stabilizer. In this paper, we describe the asymmetric hydrogenation of acetophenone and its derivatives by (1*S*,2*S*)-DPEN modified Ir/SiO₂ as catalyst. Acetophenone and its derivatives were hydrogenated with good enantioselectivity.

1 Experiment

1.1 Preparation of catalyst

H₂IrCl₆·6H₂O (0.14 g) and an excess of LiOH were dissolved in a mixture of EtOH and distilled water (*V*(EtOH)/*V*(H₂O) = 10/1), to which SiO₂ (1 g) was added. After stirring for 1 h at room temperature in the autoclave, hydrogen was introduced and pressurized to 3.0 MPa and the reaction mixture was stirred at 373 K for another 5 h. After the mixture was cooled to room temperature, the solid was filtered and washed with ethanol. Then, the solid was

dried under vacuum at 323 K for 1 h to give the Ir/SiO₂ catalyst. The iridium content of all catalysts was 5 wt%, which was determined by inductively coupled plasma (ICP) analysis.

1.2 Asymmetric hydrogenation of acetophenone

The hydrogenation was performed in a 60 ml stainless autoclave with a magnetic stirrer. A typical procedure for the asymmetric hydrogenation of acetophenone is as follows. The catalyst, chiral modifier (Acros, >98%), base, MeOH, and acetophenone (Acros, >99%) were added to the autoclave, followed by purging with hydrogen three times. Hydrogen was introduced to the desired pressure. The mixture was stirred at the reaction temperature for a given time. After the reaction, the pressure was released, and the products were separated and sent for analysis by a GC with a FID detector and a β-DEXTM120 capillary column (30 m × 0.25 mm, 0.25 μm film). The enantiomeric excess (ee value) was calculated from the equation: ee = (*S* – *R*)/(*S* + *R*).

1.3 Characterization of catalyst

The morphology of catalyst was examined with a transmission electron microscope (TEM, JEM-1200) at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos XAM800 in the constant pass energy mode and with non-monochromatic Mg K_α X-ray radiation (*hν* = 1253.6 eV).

2 Results and discussion

2.1 Influence of the base used and catalyst characterization

Since H₂IrCl₆ is acidic, the effect of the base used in the catalyst preparation to get a high performance catalyst was studied. As shown in Table 1, the catalysts prepared in the presence of a base were distinctly superior to that prepared

Table 1 Effect of different bases on the catalyst performance

Base	<i>n</i> (base): <i>n</i> (Ir)	Conversion (%)	ee (%)	Configuration
No	0	5.0	30.0	<i>R</i>
LiOH	18:1	99.4	62.4	<i>R</i>
Li ₂ CO ₃	18:1	43.5	55.2	<i>R</i>
NaOH	9:1	67.0	50.4	<i>R</i>
KOH	9:1	38.4	47.9	<i>R</i>
N(Et) ₃	25:1	73.9	59.1	<i>R</i>

Reaction conditions: *n*(acetophenone):*n*(Ir) = 163:1, acetophenone 0.85 mmol, LiOH 0.35 mol/L, (1*S*,2*S*)-DPEN 5.2 × 10^{−3} mol/L, MeOH 2 ml, *p*(H₂) = 2.0 MPa, 323 K, 3 h.

with no base. The catalyst prepared in the presence of LiOH showed the best activity and enantioselectivity for the asymmetric hydrogenation of acetophenone. In addition, the weak bases Li_2CO_3 and $\text{N}(\text{Et})_3$ added in the preparation of catalyst were more helpful than the strong bases NaOH and KOH. It was determined by ICP analysis that there was no alkali metal cation in the catalyst. Thus the basicity, rather than the alkali metal cation, was the key factor that determined the performance of the catalyst. Figures 1(a) and (b) are the TEM images of the catalyst prepared in the presence of LiOH and in the absence of a base, respectively. Comparing Fig. 1(a) with Fig. 1(b), it can be seen that the Ir particles were well dispersed on SiO_2 in the preparation with the presence of LiOH, and the particle size of Ir was about 2 nm. A high dispersion and nanoparticles result in a large Ir surface area and good catalytic performance [26].

Fig. 1. TEM image of 5%Ir/SiO₂. (a) 5%Ir/SiO₂ prepared in the presence of LiOH; (b) 5%Ir/SiO₂ prepared in the absence of a base.

The XPS analysis showed that the Ir^0 signal ($4f_{7/2}$ binding energies at 60.7 eV) from 5%Ir/SiO₂ prepared with the presence of LiOH (Fig. 2(a)) was larger than that from the catalyst prepared without any base (Fig. 2(b)). This indicated that the metal prepared under basic condition can be reduced more easily.

Furthermore, the base was also very important in the asymmetric hydrogenation reaction. As shown in Table 2, the use of LiOH gave the best enantioselectivity among the bases used. When a weak organic base $\text{N}(\text{Et})_3$ was added to

Fig. 2. XPS profile for 5%Ir/SiO₂. (a) 5%Ir/SiO₂ prepared in the presence of LiOH; (b) 5%Ir/SiO₂ prepared in the absence of a base.

Table 2 Effect of base on the asymmetric hydrogenation of acetophenone

Base	Concentration (mol/L)	Conversion (%)	ee (%)	Configuration
No	0.00	47.3	39.1	<i>R</i>
LiOH	0.35	99.4	62.4	<i>R</i>
Li_2CO_3	0.18	70.7	59.6	<i>R</i>
NaOH	0.15	98.9	57.3	<i>R</i>
KOH	0.15	98.4	55.9	<i>R</i>
$\text{N}(\text{Et})_3$	0.35	59.6	41.4	<i>R</i>

Reaction conditions were the same as those in Table 1 except base.

the catalytic system, the conversion and ee value were only 59.6% and 41.4%, respectively. In the presence of strong inorganic bases such as NaOH or KOH, the conversion was improved but with a loss in the ee value. Interestingly, the enantioselectivity in the presence of the weaker inorganic base Li_2CO_3 was inferior to that with LiOH. These observations suggest that it was not only the basicity that affected reaction activity and enantioselectivity, but the alkali metal cation also played an important role in the reaction enantioselectivity. This is in agreement with previous results [27–30] that a strong base can attack the proton on the nitrogen atom of (1*S*,2*S*)-DPEN and form a negative nitrogen atom in (1*S*,2*S*)-DPEN that was coordinated to iridium. The negative nitrogen atom induced the heterolytic splitting of

the dihydrogen coordinated to the metal center. In addition, the alkali metal cation was π -bonded to the aryl groups in (1*S*,2*S*)-DPEN, thus, the alkali metal cation radius has to be suitable for the specific bonding site [31]. In our system, Li⁺ was the most suitable alkali metal cation, which was why LiOH and Li₂CO₃ gave better ee values with Ir as the active metal.

2.2 Influence of chiral modifier

The effect of different modifiers on the asymmetric hydrogenation of acetophenone was examined. The results are summarized in Table 3. (1*S*,2*S*)-DPEN was the best, with which the conversion of acetophenone and enantioselectivity to (*R*)-phenyl ethanol were increased to 99.4% and 62.4%, respectively. The chiral diamines containing a bulkier group were unfavorable for the reaction. For example, in the presence of (1*S*,2*S*)-TsDPEN ((1*S*,2*S*)-*N*-*p*-methylphenyl-sulfonyl-1,2-diphenyl-1,2-ethanediamine) [32] or (1*R*,2*R*)-DMTFM-DPEN ((1*R*,2*R*)-(+)-*N,N*-dimethyl-1,2-bis[3-(trifluoromethyl)phenyl]-1,2-ethanediamine)], both conversion and ee value were lower than those with (1*S*,2*S*)-DPEN. In addition, (1*R*,2*R*)-DACH ((1*R*,2*R*)-(-)-1,2-diaminocyclohexane) with the rigid cyclohexyl structure gave low conversion and ee value. Compared with chiral diamines, when chiral modifiers with only an amino or no amino (i.e. cinchonidine, L-proline, and L-tartaric acid) were used, the reaction activity and enantioselectivity were clearly decreased. The data indicate that the 1,2-diamine structure was important for high activity and enantioselectivity. This may be because the coordination ability of the nitrogen atom was stronger than that of the oxygen atom [33] so that the chelating ring formed by 1,2-diamine with iridium was more stable. This would explain why the activity and enantioselectivity were very poor even in the presence of a large amount of L-tartaric acid.

To further study the effect of the modifier on the asym-

Table 3 Effect of chiral modifier on the asymmetric hydrogenation of acetophenone

Modifier	<i>n</i> (modifier): <i>n</i> (Ir)	Conversion (%)	ee (%)	Configuration
(1 <i>S</i> ,2 <i>S</i>)-DPEN	2:1	99.4	62.4	<i>R</i>
(1 <i>R</i> ,2 <i>R</i>)-DPEN	2:1	100	56.8	<i>S</i>
(1 <i>R</i> ,2 <i>R</i>)- DMTFM-DPEN	2:1	56.3	54.5	<i>S</i>
(1 <i>R</i> ,2 <i>R</i>)-DACH	2:1	57.5	52.7	<i>S</i>
(1 <i>S</i> ,2 <i>S</i>)-TsDPEN	2:1	51.2	40.4	<i>R</i>
Cinchonidine	2:1	42.8	36.8	<i>R</i>
L-proline	15:1	51.7	22.2	<i>R</i>
L-tartaric acid	10:1	28.1	6.8	<i>R</i>

Reaction conditions were the same as those in Table 1 except chiral modifier.

metric hydrogenation of acetophenone, the effect of (1*S*,2*S*)-DPEN concentration was investigated (Table 4). In the absence of (1*S*,2*S*)-DPEN, the reaction almost did not proceed. When the (1*S*,2*S*)-DPEN concentration was just 1.3×10^{-3} mol/L, corresponding to a (1*S*,2*S*)-DPEN/Ir molar ratio of 0.5, 60.0% ee value was achieved with 64.1% conversion. On further increasing the (1*S*,2*S*)-DPEN concentration from 2.6×10^{-3} to 9.1×10^{-3} mol/L (the molar ratio of (1*S*,2*S*)-DPEN/Ir was increased from 1:1 to 4:1), the conversion was increased from 64.1% to 100% while ee value was slightly increased. This demonstrated that the active species was formed through the coordination of (1*S*,2*S*)-DPEN to Ir on the surface of the support, and this was a key factor for high conversion and ee value. Our result is in good agreement with the catalysis with PPh₃ and diamine modified Ru/ γ -Al₂O₃ [34]. With a decreased (1*S*,2*S*)-DPEN concentration, only few metal centers were coordinated with (1*S*,2*S*)-DPEN on the support surface, and so the catalytic activity was poor. In this system, the active species formed on the support surface was the most when the (1*S*,2*S*)-DPEN concentration was 2.6×10^{-3} mol/L, since further increasing the (1*S*,2*S*)-DPEN concentration did not improve the activity. In the hydrogenation of acetophenone catalyzed by cinchonidine modified Pt/ γ -Al₂O₃, a similar result was observed [35].

Table 4 Effect of (1*S*,2*S*)-DPEN concentration on the asymmetric hydrogenation of acetophenone

<i>c</i> ((1 <i>S</i> ,2 <i>S</i>)-DPEN) (10^{-3} mol/L)	<i>n</i> ((1 <i>S</i> ,2 <i>S</i>)-DPEN): <i>n</i> (Ir)	Conversion (%)	ee (%)	Configuration
0.0	0	2.9	0	—
1.3	0.5:1	64.1	60.0	<i>R</i>
2.6	1:1	98.1	61.6	<i>R</i>
5.2	2:1	99.4	62.4	<i>R</i>
7.8	3:1	99.8	62.6	<i>R</i>
9.1	4:1	100.0	63.4	<i>R</i>

Reaction conditions were the same as those in Table 1 except (1*S*,2*S*)-DPEN concentration.

2.3 Influence of hydrogen pressure

The influence of hydrogen pressure on reaction activity and enantioselectivity is shown in Fig. 3. At 2.0 MPa pressure, the conversion and enantioselectivity were 99.4% and 62.4%, respectively. The conversion and ee value increased initially with the increase of hydrogen pressure, and then they decreased gradually for pressure above 2.0 MPa. The effect of hydrogen pressure on the hydrogenation reaction demonstrated that competitive adsorption between the substrates (H₂ and acetophenone) and (1*S*,2*S*)-DPEN on the Ir surface exist. A low pressure resulted in low hydrogen concentration at the Ir center, and was unfavorable for activity

Fig. 3. Effect of pressure on the asymmetric hydrogenation of acetophenone. Reaction conditions were the same as those in Table 1 except for the H_2 pressure.

and enantioselectivity [36]. When the pressure was moderately increased, the Ir centers were completely occupied by H_2 and (1*S*,2*S*)-DPEN, and so excellent catalytic activity and selectivity were obtained. However, as the pressure was further increased, too much H_2 adsorbed on the catalyst surface led to the desorption of (1*S*,2*S*)-DPEN and resulted in low conversion and ee value.

2.4 Influence of temperature

Figure 4 shows the effect of temperature on the asymmetric hydrogenation of acetophenone. With the increase of temperature from 283 to 333 K, the conversion increased dramatically from 50% to 100%. The best ee value was 70.0% obtained at 293 K. With further increasing or lowering of the reaction temperature, the enantioselectivity decreased. A similar result was also reported in the literature [19,37,38]. It may be that H_2 was not efficiently activated on the Ir surface at a low temperature, which diminished the

Fig. 4. Effect of temperature on the asymmetric hydrogenation of acetophenone. Reaction conditions were the same as those in Table 1 except the temperature.

catalytic activity and enantioselectivity. However, the energy difference between the transition states of the two enantiomers would become smaller with increasing temperature, resulting in decreased ee value.

2.5 Asymmetric hydrogenation of acetophenone and its derivatives

Acetophenone and its derivatives were hydrogenated with the (1*S*,2*S*)-DPEN modified 5%Ir/SiO₂ catalyst. The results are summarized in Table 5. The catalyst gave high enantioselectivities except with 2'-methoxyacetophenone. In particular, 84.0% ee value was obtained for the asymmetric hydrogenation of 2'-(trifluoromethyl)acetophenone. Obviously, the electronic and steric effects markedly affect the reaction activity and enantioselectivity.

Table 5 Asymmetric hydrogenation of acetophenone and its derivatives

Substrate	Conversion (%)	ee (%)	Configuration
Acetophenone	75.6	70.0	<i>R</i>
Propioacetophenone	85.6	67.4	<i>R</i>
Isobutyacetophenone ^a	74.2	70.9	<i>R</i>
2'-Fluoroacetophenone	66.8	64.6	<i>R</i>
2'-Chloroacetophenone	70.8	70.9	<i>R</i>
2'-Bromoacetophenone	74.7	70.0	<i>R</i>
2'-(Trifluoromethyl)acetophenone ^a	55.0	84.0	<i>R</i>
2'-Methoxyacetophenone ^a	77.1	40.9	<i>R</i>

Reaction conditions were the same as those in Table 1 except that the temperature was 293 K. ^aReaction time was 12 h.

2.6 Recycling of the catalyst

To explore the stability of the catalyst, recycling of the catalyst was investigated. After the first run, the reaction mixture was centrifuged, and the catalyst was separated from the liquid mixture by centrifugation. The catalyst was washed three times with MeOH and then reintroduced into the reactor with MeOH and fresh acetophenone, (1*S*,2*S*)-DPEN and LiOH for the recycle run. The catalyst could be reused six times without significant loss of enantioselectivity. However, (1*S*,2*S*)-DPEN must be added in each run because it was soluble in the organic solution and remained in the solution after reaction. To avoid this, we added (1*S*,2*S*)-DPEN in the process of catalyst preparation to get the 5%Ir-(1*S*,2*S*)-DPEN/SiO₂ catalyst, which exhibited good stability in the recycling without (1*S*,2*S*)-DPEN being added. As shown in Fig. 5, the 5%Ir-(1*S*,2*S*)-DPEN/SiO₂ catalyst could be reused four times and the ee values was maintained in the range from 55.8% to 57.6%. These ee values were lower than that obtained with (1*S*,2*S*)-DPEN

Fig. 5. Recycling of the 5%Ir-(1*S*,2*S*)-DPEN/SiO₂ catalyst. Reaction conditions were the same as those in Table 1 except that no (1*S*,2*S*)-DPEN was added into the solution.

added in situ. The activity decrease was probably due to the loss of 5%Ir-(1*S*,2*S*)-DPEN/SiO₂ in the separation process. The leaching of Ir from 5%Ir/SiO₂ into the solution was determined by ICP, but only 0.1% Ir was detected in the liquid phase after the first hydrogenation of acetophenone.

2.7 Comparison with the other heterogeneous catalyst systems

In the literature, the enantioselectivity in the hydrogenation of acetophenone with supported transition metal catalysts modified with chiral modifiers is still low (Table 6). For example, an ee of 28.8% was obtained over a *S*-proline modified Pd/SBA-15 catalyst [16]. Although ee value could be increased to 60.2% over cinchonidine modified Ir/SiO₂

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

Modifier and catalyst	ee (%)	Reference
<i>S</i> -proline-modified Pd/C ^a	22.5	[14]
<i>S</i> -proline-modified Pd/SBA-15 ^b	28.8	[16]
Cinchona-modified Pt/C ^c	20	[15]
Cinchonidine-modified Pt/Al ₂ O ₃ -SiO ₂ ^d	63	[13]
Cinchonidine-modified Pt/Al ₂ O ₃ ^d	33	[13]
Cinchonidine-modified Ir/SiO ₂ ^e	60.2	[18]
(1 <i>S</i> ,2 <i>S</i>)-DPEN-modified Ir/HAP ^f	63.7	[17]
(1 <i>S</i> ,2 <i>S</i>)-DPEN-modified Ir/SiO ₂	70.0	present work

Reaction conditions: ^a400 mg Pd/C, *S*-proline 5.25 g, 0.05 mol acetophenone, MeOH as solvent, 0.5 MPa, 298 K, 1.2 h; ^b50 mg Pd/SBA-15, *S*-proline 500 mg, 0.86 mmol acetophenone, 3.0 MPa, 288 K, 10 min; ^c80 mg Pt/C, 40 mg cinchonidine, 0.7 mmol acetophenone, isooctane and H₂O as solvent, 0.1 MPa, 298 K, 5 h; ^d42 mg Pt/Al₂O₃-SiO₂(Pt/Al₂O₃), 8 mg cinchonidine, 0.92 mmol acetophenone, toluene as solvent, 9.0 MPa, 293 K, 4 h; ^e100 mg Ir/SiO₂, 5.0 g cinchonidine, 0.58 mol acetophenone, cyclohexane as solvent, 4.0 MPa, 298 K, 6 h; ^f20 mg Ir/HAP, 4.0 mg (1*S*,2*S*)-DPEN, 0.85 mmol acetophenone, MeOH as solvent, 3.0 MPa, 303 K, 3 h.

catalyst, this required a higher cinchonidine concentration [18]. Very recently, Baiker et al. [13] reported cinchonidine modified Pt/Al₂O₃-SiO₂ for the asymmetric hydrogenation of acetophenone with which 63% and 33% ee values were obtained, but with only 2% and 55% conversions, respectively [13]. In our present work with the (1*S*,2*S*)-DPEN modified 5%Ir/SiO₂ catalyst, an excellent ee value of 70.0% was obtained. This is a higher enantioselectivity than any value reported up to now for acetophenone hydrogenation catalyzed by a supported metal catalyst modified by a chiral reagent.

3 Conclusions

A (1*S*,2*S*)-DPEN modified Ir/SiO₂ catalyst showed excellent catalytic activity and enantioselectivity for the asymmetric hydrogenation of acetophenone and its derivatives. The preparation of the catalyst is simple and the catalyst can be reused several times without significant loss of enantioselectivity. The use of a suitable alkali is the key factor for preparing a highly efficient catalyst.

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