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SHORT COMMUNICATION

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Enantioselective hydrogenation of α-ketoesters catalyzed by cinchona alkaloid stabilized Rh nanoparticles in ionic liquid

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Abstract

The heterogeneous enantioselective hydrogenation of α-ketoesters catalyzed by rhodium nanoparticles (Rh NPs) in ionic liquid was studied with the stabilization and modification of cinchona alkaloids. TEM characterization showed that well-dispersed Rh NPs of about 1.96 nm were obtained in ionic liquid. The results showed that cinchona alkaloids not only had good enantiodifferentiating ability but also accelerated the catalytic reaction. Under the optimum reaction conditions, the enantiomeric excess in ethyl benzoylformate hydrogenation could reach as high as 60.9%.

KEYWORDS

cinchona alkaloid, enantioselective hydrogenation, ionic liquid, rhodium, α-ketoester

1 | INTRODUCTION

Asymmetric catalysis has been the most challenging and interesting topic in the synthesis of pharmaceuticals, agrochemicals, and fragrance/perfumes over the past few decades.[1,2] The heterogeneous catalysis plays an important and crucial role in many chemical processes because of its inherent practical advantages associated with ease of separation and handling.[3,4] Recently, the heterogeneous enantioselective catalysis has become a fast-growing and interesting field.[5,6] For the enantioselective hydrogenation of α-ketoesters, the best explored cinchonidine modified supported metal Pt catalyst achieved enantiomeric excess (ee) values exceeding 95% under optimum reaction conditions.[7-9] Replacing Pt with other transition metals (eg, Ru, Rh, Pd, and Ir) results in lower enantioselectivity.[10-12] It is worth mentioning that Chen et al[13-15] reported polyvinylpyrrolidone and cinchona-stabilized Rh in the asymmetric hydrogenation of α-ketoesters, in which moderate to good enantioselectivities were obtained.

Ionic liquids have been employed as useful media for the preparation of transition-metal nanoparticles of various sizes and shapes.[16,17] So far, ionic liquid-stabilized metal nanoparticles have been used as catalysts mainly in the hydrogenation of alkenes or arenes.[18-20] We

previously reported the use of ionic liquid-stabilized ruthenium nanoparticles to catalyze the tunable chemoselective hydrogenation of aromatic ketones and quinolines.[21-24] However, the research on the use of Rh nanoparticles for enantioselective hydrogenation in ionic liquids was quite limited by now.[25] In this paper, Rh NPs, with diameter about 1.96 nm, were prepared in imidazolium-based ionic liquids by simple H_2 reduction of $RhCl_3{\cdot}3H_2O$. With the stabilization and modification of cinchona alkaloids, Rh NPs exhibited moderate to good activity and enantioselectivity in the asymmetric hydrogenation of α-ketoesters.

2 | MATERIALS AND METHODS

2.1 | Materials

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. Various substrates and other reagents were analytical grade. The purity of hydrogen was over 99.99%. Products were analyzed by GC instrument with an FID detector and Chrompack Chirasil-DEX column (25 m × 0.25 mm). Products were confirmed by GC-MS and NMR. The TEM analyses were performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer.

2.2 | Synthesis of Rh NPs and Ni NPs

In a typical experiment, $RhCl_3{\cdot}3H_2O$ (0.014 mmol) and cinchonidine (0.028 mmol) were well dispersed in $BMIMBF_4$ (1 mL) (BMIM = 1-butyl-2,3-dimethylimidazolium), and the reaction mixture was placed in a 20-mL stainless-steel high pressure reactor. After stirring the mixture at room temperature under an atmosphere of argon for 30 minutes, a constant pressure of H_2(g) (4 MPa) was admitted to the system and the content was stirred for 1 hour at 60°C. The reactor was cooled to ambient temperature and carefully vented. A dark solution was obtained. The Rh NPs embedded in $BMIMBF_4$ were employed for hydrogenation studies (see below). Isolation of the Rh NPs for TEM and XPS analysis was achieved by dissolving the mixture in acetone (5 mL), centrifuging (5000 rpm for 10 min), washing with acetone (3 × 5 mL), and drying under vacuum. Ni NPs catalyst was prepared according to previous work with cinchonidine as the stabilizer and $NaBH_4$ as the reducing agent. [24]

2.3 | General procedure for the enantioselective hydrogenation of α-ketoesters

In stainless steel autoclave, previously prepared Rh(0) catalyst was charged with the appropriate modifier, cosolvent and substrate, and then the autoclave was sealed and purged with pure hydrogen several times. After the reactants were heated to predetermined temperature, the reaction timing began. After completion of the reaction and cooling to ambient temperature, the products were isolated by high speed centrifugation or liquid-liquid extraction and analyzed by gas chromatography.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization of Rh NPs

The synthesis of Rh NPs was achieved through the H_2 reduction of $RhCl_3{\cdot}3H_2O$ in $BMIMBF_4$ (BMIM = 1-butyl-2,3-dimethylimidazolium) in the presence of 2.0 equivalent of cinchona alkaloids, which afforded a dark suspension. For comparison, we also synthesized Rh NPs without any additional stabilizer. A black powder could be separated from the black suspension by the addition of acetone followed by centrifugation (5000 rpm for 10 min). Washed three times with acetone and dried under reduced pressure, the isolated powder was analyzed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS).

TEM analysis was used to characterize the obtained Rh NPs and determine the average diameter (Figure 1). The TEM image of cinchonidine stabilized Rh NPs exhibited a regular spherical shape and a narrow size distribution with an average diameter of 1.96 nm.

The XPS analysis of the cinchonidine stabilized Rh NPs was employed to elucidate the nature of the stabilizing layer of the nanoparticles. XPS analysis of Rh NPs stabilized by cinchonidine showed the presence of rhodium, boron, nitrogen, and oxygen, which signified the presence of the $BMIMBF_4$ and cinchonidine in the ligand sphere of the Rh NPs. The binding energies for Rh, 307.1 eV and 311.7 eV (Figure 2), which indicated the Rh NPs were composed of Rh(0).[26] In comparison with the previous report of laser-induced synthesis of Rh(0) in ionic liquid,[27] herein, cinchona alkaloid stabilized Rh(0) NPs in the presence of ionic liquid protective layer exhibited no obvious electron transfer. In short, the TEM and XPS results indicated that the rhodium (III) species was completely reduced

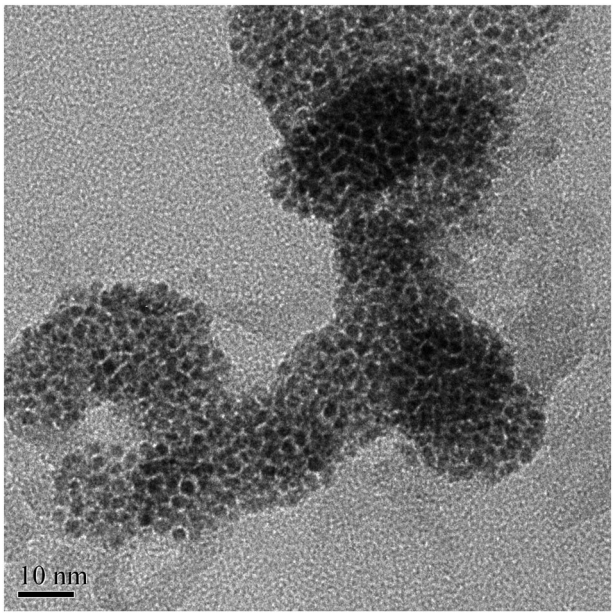


FIGURE 1 TEM image of cinchonidine stabilized Rh NPs prepared in $BMIMBF_4$

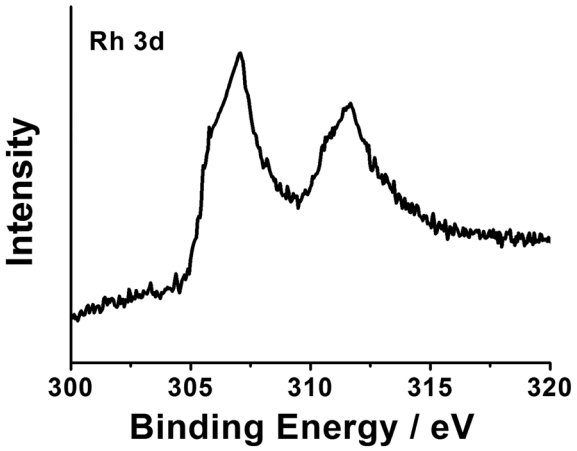


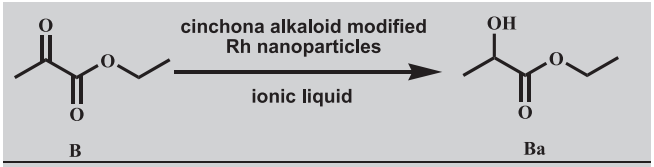
FIGURE 2 XPS spectrum of Rh 3d in cinchonidine stabilized Rh NPs prepared in $BMIMBF_4$

to Rh NPs, and these Rh NPs could be protected by the $BMIMBF_4$ and cinchonidine without any change of valence.

3.2 | Catalytic hydrogenation

Enantioselective hydrogenation was performed in a 20-mL stainless autoclave with a magnetic stirrer bar, by using Rh NPs as a catalyst in the presence of cinchona alkaloids as chiral modifiers. Ethyl pyruvate was selected as the model substrate to explore the catalytic performance of cinchonidine stabilized Rh NPs (Table 1). In the absence of stabilizer, 41.1% conversion and only 2.6% ee were obtained in the ethyl pyruvate asymmetric hydrogenation with Rh NPs in $BMIMBF_4$ (Table 1, entry 1). Further introduction of cinchonidine stabilizer during the preparation of Rh NPs significantly improved the catalytic hydrogenation activity, but the ee was still rather low (Table 1, entry 2). In some previous heterogeneous enantioselective catalysis reports,[28-30] the solvent used often have significant effect on the reactivity and enantioselectivity. To further optimize catalytic activity and enantioselectivity, we attempted to introduce cosolvent into the catalytic system (Table 1, entries 3-8). The introduction of alcohol cosolvent into $BMIMBF_4$ resulted in a significant increase in catalytic activity, but the ee was still fairly low (Table 1, entries 3-5). Toluene and acetic acid are the most commonly used solvents

TABLE 1 Optimization of reaction conditions for the enantioselective hydrogenation of ethyl pyruvate[a]



Entry	Ionic Liquid	Cosolvent	Conversion, %	ee, %	config.[b]
1[c]	$BMIMBF_4$	-	41.1	2.6	*R*
2	$BMIMBF_4$	-	100.0	5.6	*R*
3	$BMIMBF_4$	MeOH	73.0	14.5	*R*
4	$BMIMBF_4$	EtOH	100.0	11.0	*R*
5	$BMIMBF_4$	*i*PrOH	96.4	3.7	*R*
6	$BMIMBF_4$	Toluene	100.0	5.8	*R*
7	$BMIMBF_4$	Acetic acid	12.3	5.8	*R*
8	$BMIMBF_4$	THF	99.5	45.5	*R*
9[d]	$BMIMBF_4$	THF	0.0	0.0	-
10	$BMIMPF_6$	THF	98.8	30.0	*R*
11	$BMIMNTf_2$	THF	99.4	32.9	*R*
12	BMIMAcO	THF	6.5	0.0	-
13[e]	$BMIBF_4$	THF	81.0	36.0	*R*
14[f]	$BPyBF_4$	THF	0.0	0.0	-
15	$BPyPF_6$	THF	0.0	0.0	-

[a]Reaction was carried out at 20°C for 5 h, PH_2: 5.0 MPa, substrate: 0.90 mmol, cinchonidine as the stabilizer, substrate/Rh/modifier = 200:1:5, V ionic liquid: 1 ml, V ionic liquid: V cosolvent = 1:1. Products were analyzed by a GC instrument with an FID detector and β-DEX120 capillary column.

[b]Determined by sign of rotation.

[c]No stabilizer added in the Rh nanoparticles synthesis.

[d]Cinchonidine stabilized Ni NPS as catalyst.

[e]BMI = 1-butyl-3-dimethylimidazolium.

[f]BPy = 1-butylpyridinium.

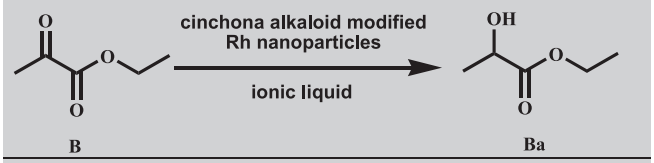
in the previous enantioselective hydrogenation of α-ketoesters.[31] The introduction of toluene and acetic acid as cosolvents did not significantly improve ee (Table 1, entries 6-7). Among the cosolvents tested, the THF cosolvent combing with $BMIMBF_4$ achieved the best catalytic performance (99.5% conversion and 45.5% ee, Table 1, entry 8). Ni nanoparticles were also tested in the ethyl pyruvate enantioselective hydrogenation; however, no catalytic activity was detected (Table 1, entry 9). Additionally, an improvement in catalytic activity and ee was also observed when THF was introduced into the Rh catalyst prepared in $BMIMPF_6$ or $BMIMNTf_2$ (Table 1, entries 10-11). However, the chiral inducing ability of the Rh catalyst was not detected in the solvent BMIMAcO-THF (Table 1, entry 12). More ionic liquids including $BMIBF_4$ (BMI = 1-butyl-3-dimethylimidazolium), $BPyBF_4$ (BPy = 1-butylpyridinium), and $BPyPF_6$ were also tested (Table 1, entries 13-15). In $BMIBF_4$, slightly decrease in catalytic activity and enantioselectivity was observed; unexpectedly, no catalytic activity was detected in $BPyBF_4$ and $BPyPF_6$.

Chiral modifiers are sources of enantioselectivity in most heterogeneous enantioselective catalytic reactions. Appropriate introduction of modifiers into nanometal catalytic systems is one of the most effective ways to promote the performance of heterogeneous enantioselective catalytic systems.[32,33] As shown in Table 2, different cinchona alkaloids modified Rh NPs have significantly different catalytic reactivity and enantioselectivity. When cinchonidine was used as a modifier for the preparation of Rh NPs and as the modifier in the catalytic asymmetric hydrogenation, the enantioselectivity of the catalytic hydrogenation reaction could reach 45.5% (Table 2, entry 1). However, other cinchona alkaloid modifiers (Table 2, entries 2-4) are not conducive to catalytic hydrogenation enantioselectivity. Cinchona alkaloid derivatives including 9-amino(9-deoxy)epicinchonidine and *o*-acetylcinchonidine were also tested as the chiral modifier, and decreased catalytic activity and enantioselectivity was observed (Table 2, entries 5-6). Only cinchonidine gave much higher enantioselectivity compared with the other cinchona alkaloids in the asymmetric reduction should be owing to the high substrate specificity of heterongeneous enantioselective catalysis.[32,33]

Table 3 is some representative examples of the asymmetric hydrogenation of α-ketoesters catalyzed by cinchonidine-stabilized and modified Rh NPs. Catalytic reactivity and enantioselectivity are subtlely affected by substituents in the substrate. At room temperature (Table 3, entries 1-4), the activity of substrates methyl pyruvate A and ethyl pyruvate B was higher than methyl benzoylformate C and ethyl benzoylformate D, the ee values of C (50.7%) and D (53.3%) were higher than those of A (24.5%) and B (45.5%), which should be explained by the influence of the structure of the substrate on the formation of steric hindrance of catalytic heterogeneous enantioselective hydrogenation. The heterogeneous asymmetric hydrogenation reaction temperature is further decreased to 0°C. The ee of the substrate B could reach 55.8%; the ee of C could reach 56.3%; and the ee of D could reach as high as 60.9%.

Figure 3 illustrated the recyclability of cinchonidine stabilized Rh NPs in heterogeneous enantioselective hydrogenation of ethyl pyruvate, and it was found

TABLE 2 Effect of different cinchona alkaloid modifiers on enantioselective hydrogenation of ethyl pyruvate[a]



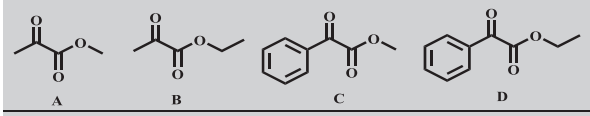
Entry	Modifier	Conversion, %	ee, %	config.
1	Cinchonidine	99.5	45.5	*R*
2	Cinchonine	99.0	4.8	*S*
3	Quinidine	99.4	0.8	*S*
4	Quinine	99.7	6.6	*R*
5[b]	I	63.5	7.8	*R*
6[c]	II	40.5	3.6	*R*

[a]The reaction conditions are the same as in Table 1 (V $BMIMBF_4$: V THF = 1:1).

[b]I = 9-amino(9-deoxy)epicinchonidine.

[c]II = *o*-acetylcinchonidine.

TABLE 3 Enantioselective hydrogenation of α-ketoesters catalyzed by cinchonidine stabilized Rh nanoparticles[a]



Entry	Substrate	*t*, h	T, °C	Conversion, %	ee, %	config.
1	A	5	20	100	24.5	*R*
2	B	5	20	99.3	45.5	*R*
3	C	5	20	75.0	50.7	*R*
4	D	5	20	84.7	53.3	*R*
5	A	10	0	48.5	30.4	*R*
6	B	10	0	45.0	55.8	*R*
7	C	10	0	50.8	56.3	*R*
8	D	10	0	66.5	60.9	*R*

[a]The reaction conditions are the same as in Table 1 (V $BMIMBF_4$: V THF = 1:1).

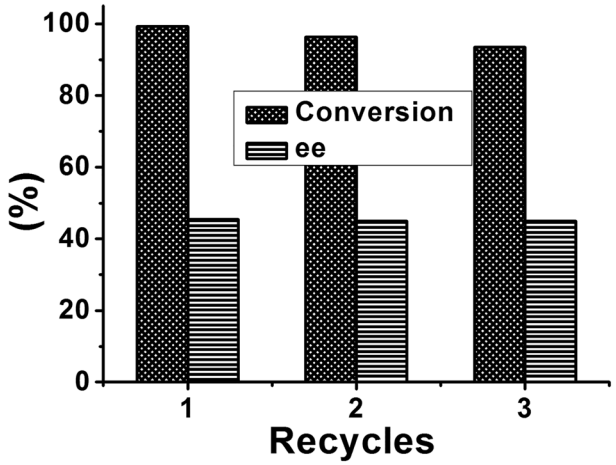


FIGURE 3 Recyclability of cinchonidine stabilized Rh NPs catalyst for enantioselective hydrogenation of ethyl pyruvate. Reaction conditions are the same as in Table 1

that the leaching amount of the catalyst Rh NPs was negligible from ICP-AES analysis in continuous catalytic cycle. The Rh NPs catalyst can be reused by removing the THF cosolvent under reduced pressure at a low temperature and separating the product by diethyl ether extraction. There was no significant decrease in the catalytic activity and enantioselectivity during the three catalytic cycles.

4 | CONCLUSION

In conclusion, Rh NPs having a diameter of about 1.96 nm were prepared in imidazolium-based ionic liquids by convenient H_2 reduction of $RhCl_3{\cdot}3H_2O$. With the stabilization and modification of cinchona alkaloids, Rh NPs exhibited moderate to good activity and up to 60.9% ee in the asymmetric hydrogenation of α-ketoesters. Additional work is currently in progress in this and related areas.

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