



Asymmetric hydrogenation of aromatic ketones by chiral (1*S*,2*S*)-DPEN-Ru(II)Cl₂(TPP)₂ encapsulated in SBA-16

Jianhong Liu^{a,b,c}, Binbin Fan^a, Dong Liang^a, Xiufeng Shi^a, Ruifeng Li^{a,*}, Hua Chen^{c,*}

^a Key Laboratory of Coal Science and Technology, Ministry of Education, Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China

^b College of Chemistry and Chemical Engineering, Shanxi Datong University, Datong 037009, China

^c Key Laboratory of Green Chemistry and Technology, Ministry of Education, The Institute of Homogeneous Catalysis, College of Chemistry, Sichuan University, Chengdu 610064, China

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ABSTRACT

Chiral complex (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ (DPEN = 1,2-diphenylethylenediamine; TPP = triphenylphosphine) was successfully encapsulated in the mesoporous cage of SBA-16 modified with phenyltrimethoxysilane. This was verified by ICP, powder XRD, N₂ adsorption, FTIR, DRS and TEM analysis. The encapsulated chiral Ru complex gave high catalytic activity and excellent enantioselectivity like its homogeneous counterpart in asymmetric hydrogenation of various aromatic ketones. The encapsulated complex also showed high stability and could be recycled without significant loss of activity and enantioselectivity.

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1. Introduction

Homogeneous chiral ruthenium-based catalysts have shown distinguished catalytic properties in asymmetric hydrogenation of prochiral ketones to optically active chiral alcohols [1–5]. However, the difficulties in recovery and recycling of the catalysts limit their reuse [6,7]. Therefore, there has been an increasing demand for the preparation of heterogeneous catalysts. Many methods have been used to develop these heterogeneous chiral ruthenium-based hydrogenation catalysts [8]; the two methods most studied may be impregnation of a Ru–phosphine–diamine complex onto polymer and immobilization of the metal modified by a chiral ligand onto an inorganic support. The former type of catalyst exhibits good enantioselectivity for asymmetric hydrogenation of acetophenone, but the preparation of catalyst is rigorous. The latter type of catalyst can be easily prepared, but its enantioselectivity for the asymmetric hydrogenation of acetophenone is not high. In addition, the two types of catalysts are not highly stable and lose much of their activity after several recycles, so development of simple methods to prepare highly efficient heterogeneous asym-

metric hydrogenation catalysts are very desirable [6–8]. Recently, we reported the encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ in the supercage of zeolite Y. The prepared catalyst shows high activity and stability in the hydrogenation of acetophenone; however, its *ee* value (61%) is a little lower than that of its homogeneous counterpart (75%). The lower *ee* is may be because the encapsulated chiral Ru complex was slightly distorted, resulting from the space constraints of the supercage of zeolite Y [9]. Compared with microporous zeolite Y, mesoporous silica SBA-16 as support material for chiral catalysts due to its high surface area and its large, tunable pore diameter [10]. SBA-16 is a highly ordered porous silica with large mesopores arranged in body centered cubic (bcc) *Im3m* symmetry [11–13]. Its large cages can accommodate metal complexes of large molecular size, whereas the smaller pore entrances may prevent leaching of the metal complex confined in the mesoporous cages [14]. Li and coworkers [15,16] entrapped a chiral Co(Salen) complex in the mesoporous cages of SBA-16 through the “ship-in-a-bottle” method. The encapsulated chiral Co(Salen) complex showed good enantioselectivity as high as the homogeneous counterpart in the hydrolytic kinetic resolution (HKR) of a terminal epoxide. However, to our best knowledge, encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ in the mesoporous cage of SBA-16 has not been reported. Here, we report the preparation of SBA-16 encapsulated Ru complex (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ and its catalytic performance in asymmetric hydrogenation of acetophenone.

* Corresponding authors. Tel./fax: +86 351 601012 (R.F. Li), Tel./fax: +86 28 85412904 (H. Chen).

E-mail addresses: rfli@tyut.edu.cn (R. Li), scuhchen@163.com (H. Chen).

2. Experimental

2.1. Reagents and materials

Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) was obtained from Aldrich. Phenyltrimethoxysilane (98%) was purchased from Sigma. (1*S*,2*S*)-DPEN (1,2-diphenyl-1,2-ethylenediamine) was purchased from Chengdu Likai Chrial Tech Co. Ltd. Tetracetylorthosilicate (TEOS), TPP (triphenylphosphine) and acetophenone were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group. The other solvents were distilled and dried prior to use.

2.2. Synthesis of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂

The Ru complex (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ was synthesized through the reaction of RuCl₂(TPP)₃ and (1*S*,2*S*)-DPEN in dichloromethane under N₂ atmosphere [17]. RuCl₂(TPP)₃ was synthesized according to a reported method [18].

2.3. Synthesis of SBA-16

Mesoporous cage-like material SBA-16 was synthesized according to a modified method [19].

2.4. Modification of SBA-16

1.0 g of SBA-16 (evacuated at 150 °C for 6 h under vacuum) was added to 1 mL of dry toluene, followed by addition of 0.2 mL of dry Et₃N and 20 mmol of phenyltrimethoxysilane. After refluxing at 110 °C for 24 h under Ar atmosphere, the solid was filtered, thoroughly washed with toluene and Soxhlet extracted with dried methanol. The resultant solid was denoted as Ph-SBA-16.

2.5. Encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ in the mesoporous cage of Ph-SBA-16

1.0 g of Ph-SBA-16 and 0.0958 g (0.1 mmol) of RuCl₂(TPP)₃ were mixed together, and kept at 150 °C for 24 h under vacuum. After cooling to ambient temperature, 0.0318 g of (1*S*,2*S*)-DPEN (0.15 mmole) and 2 mL of 2-propanol were added. The mixture was refluxed for 24 h under Ar atmosphere. After the solvent was removed under vacuum, the solid was washed with ether to remove free TPP [20] and then extracted in a Soxhlet apparatus with degassed mixture of dichloromethane and 2-propanol (1:1 v:v). The obtained sample was denoted as *S,S*-Ru-Ph-SBA-16. The Ru content of the prepared *S,S*-Ru-Ph-SBA-16 was 0.5 wt%. For comparison, an encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ in the mesoporous cage of unmodified SBA-16 was also carried out according to a similar method, the prepared sample was denoted as *S,S*-Ru-SBA-16.

2.6. Catalytic reaction

The catalyst, KOH, substrate and 2-propanol were added to a 60 mL stainless steel autoclave with a magnetic stirrer. The autoclave was purged with hydrogen five times, then hydrogen was introduced to 3.0 MPa. The mixture was stirred at 25 °C for 5 h. After the pressure of the hydrogen was released, the mixture was thoroughly separated by centrifugation and the resultant liquid mixture was further purified through a short silica gel column. The conversion and enantioselectivity were analyzed on GC-960 with a FID detector and β-DEXTM 120 capillary column (30 m × 0.25 mm, 0.15 μm film). The *ee* value was calculated from the equation: $ee = \frac{C_{(R)} - C_{(S)}}{C_{(R)} + C_{(S)}} \times 100\%$.

2.7. Characterization

ICP (Inductively Coupled Plasma, IRIS Adv) was used to measure the Ru content. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 Diffractometer with Cu Kα radiation. Nitrogen adsorption isotherms were measured at −196 °C on a Quantachrome Autosorb analyzer. Before the measurement, the sample was evacuated at 80 °C for 6 h. The BET surface area was calculated from desorption branch, while the pore volume was estimated at relative pressure of 0.99. The pore size was evaluated from desorption branch with Barret–Joyner–Halenda (BJH) method. FTIR spectra were collected on a Fourier transform infrared spectrometer (Nicolet Nexus 470) by using conventional KBr pellet method. Diffuse reflectance UV–vis spectra (DRS) were recorded on a Varian Australia Pty Ltd Cary-300 spectrophotometer with an integration sphere. TEM micrographs were taken on a JEM-1200 transmission electron microscope at an acceleration voltage of 100 kV.

3. Results and discussion

The XRD patterns of Ph-SBA-16 and *S,S*-Ru-Ph-SBA-16 are shown in Fig. 1. Both samples exhibit a similar XRD pattern to SBA-16, in which the two diffraction (1 1 0) and (2 0 0) peaks are characteristics of mesoporous materials with the cubic *Im3m* structure. This shows that silylation with phenyltrimethoxysilane and following encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ complexes do not have strong influence on the structure of SBA-16. This was further confirmed by the TEM image (not shown) of *S,S*-Ru-Ph-SBA-16 for cubic *Im3m* structure [21].

The nitrogen adsorption–desorption isotherms of SBA-16, Ph-SBA-16 as well as *S,S*-Ru-Ph-SBA-16 (Fig. 2) all exhibit type IV isotherm patterns with typical H2 hysteresis loop [20], indicating that the cage-like structure of SBA-16 was maintained after silylation with phenyltrimethoxysilane and encapsulation of chiral Ru complex. From the structural parameters listed in Table 1, a decrease in BET surface area, pore volume and pore size is observed for Ph-SBA-16 and a further decrease is observed for *S,S*-Ru-Ph-SBA-16. These changes demonstrate that the phenyl group was grafted on the surface of SBA-16 after silylation with phenyltrimethoxysilane and that the chiral Ru complex was encapsulated in the mesoporous cage of SBA-16 [13].

As shown in Fig. 3A, Ph-SBA-16 exhibits additional bands at 1440, 704 and 746 cm^{−1} as compared with SBA-16. The bands at 1440 cm^{−1} can be attributed to the C=C stretching vibration of the phenyl group. The bands at 704 and 746 cm^{−1} are assigned to the bend vibration of the phenyl group. These results further confirm successful grafting of phenyl groups in SBA-16 by silylation. Fig. 3B is the FTIR spectra of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂, SBA-16 and *S,S*-Ru-Ph-SBA-16. The FTIR spectrum of *S,S*-Ru-Ph-SBA-16

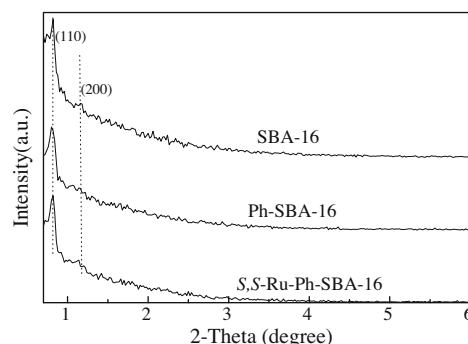


Fig. 1. XRD patterns of SBA-16, Ph-SBA-16 and *S,S*-Ru-Ph-SBA-16.

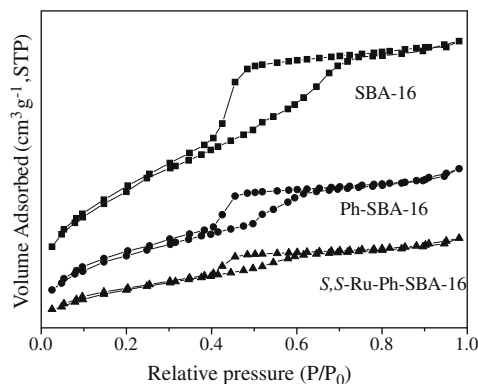


Fig. 2. N₂ sorption isotherms of SBA-16, Ph-SBA-16 and S,S-Ru-Ph-SBA-16.

Table 1

Structural parameters of SBA-16, Ph-SBA-16 and S,S-Ru-Ph-SBA-16.

Samples	BET surface area (m ² /g)	Pore volume (mL/g)	Pore diameter (nm)
SBA-16	830.30	0.703	4.05
Ph-SBA-16	474.17	0.408	3.52
S,S-Ru-Ph-SBA-16	293.28	0.207	3.30

displays bands at 2930, 2860, 1480, 1430, 754 and 698 cm⁻¹; these bands are similar to the neat complex. The bands at 2930, 2860 cm⁻¹ are ascribed to the C–H stretching vibration [22], while the peaks at 1480 and 1430 cm⁻¹ can be ascribed to the C–P vibration of TPP coordinated to the metal [23]. The peaks of 754 and 698 cm⁻¹ can be ascribed to characteristic vibration of phenyl. In the DRS spectra of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ and S,S-Ru-Ph-SBA-16, three bands attributed to intra-ligand transition, ligand to metal charge transfer (CT) and d–d electron transitions [24], are at 206, 262 and 410 nm, respectively (Fig. 4). In contrast, these bands are absent in the spectrum of SBA-16. The FTIR and DRS results gave effective evidences for the successful encapsulation of (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ in the SBA-16.

Catalytic asymmetric hydrogenation of various aromatic ketones over the prepared heterogeneous catalyst S,S-Ru-Ph-SBA-16 was investigated and the results are summarized in Table 2. As indicated in Table 2, S,S-Ru-Ph-SBA-16 shows high catalytic activity in the asymmetric hydrogenation of acetophenone and its derivatives except for 2'-aminoacetophenone and isobutyrophenone;

high enantioselectivity is obtained in the asymmetric hydrogenation of acetophenone, isobutyrophenone, 2'-(trifluoromethyl)acetophenone and 2'-aminoacetophenone. These results are in agreement with those obtained in the hydrogenation of various aromatic ketones with TPPTS stabilized Ru-(1*R*,2*R*)-DPENDS-KOH catalyst [25].

It is known that the solvent and basic additive play significant roles in obtaining a high conversion and *ee* value in the asymmetric catalytic hydrogenation of aromatic ketones [26]. As shown in Table 3, there is a roughly linear correlation between the enantioselectivity and the polarity among the chosen alcohol solvents. With an increase in polarity of solvent, the *ee* value increases and the conversion decreases (Table 3, entries 1–4). *i*-Propanol was found to be the most effective solvent, while lower activity and enantioselectivity were observed for methanol, ethanol, and 95%-ethanol. This was similar to the results of corresponding homogeneous catalysts [1] and some immobilized catalysts [17]. As shown in Table 4, all alkaline additives, typically KOH and (CH₃)₂CHOK enhanced the activity and enantioselectivity [27]. The activity and enantioselectivity also depended on the base concentration. The *ee* value increased with an increase in KOH concentration in the range of 0–2.8 mmol/L, where a maximum *ee* of 74.9% was obtained at 2.8 mmol/L of KOH. Upon further increases in KOH concentration, the *ee* value decreased slightly (Table 4, entries 1–5).

The activity and enantioselectivity for recovered S,S-Ru-Ph-SBA-16 remain almost constant even after the seventh recycling. The small decrease of activity was probably due to the loss of solid cat-

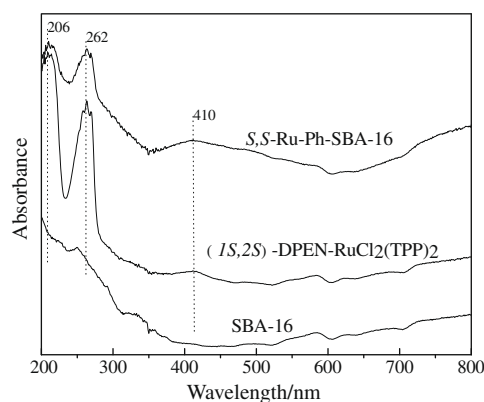


Fig. 4. UV-vis diffuse reflectance spectra of SBA-16, (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ and S,S-Ru-Ph-SBA-16.

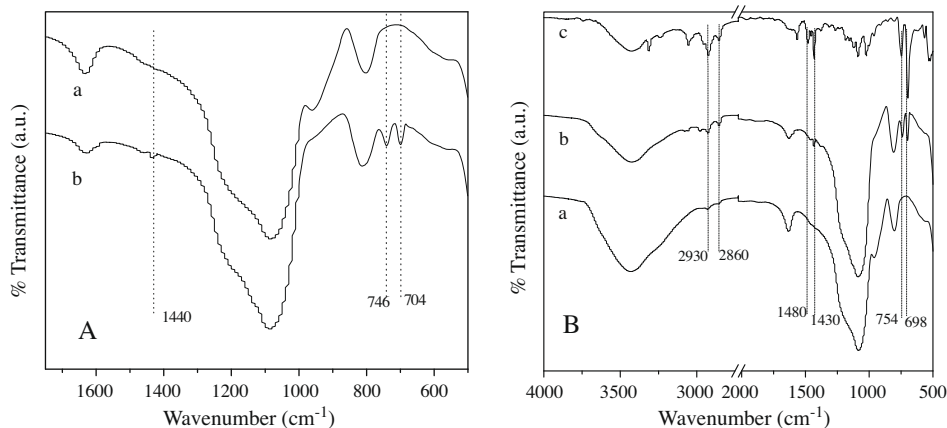


Fig. 3. FTIR spectra A (a) SBA-16, (b) Ph-SBA-16; B (a) SBA-16, (b) S,S-Ru-Ph-SBA-16, (c) (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂.

Table 2Asymmetric hydrogenation of acetophenone and its derivatives over *S,S*-Ru-Ph-SBA-16.

Entry	Substrates	Conversion (%)	ee (%)	Configuration
1	Acetophenone	100.0	74.9	(<i>R</i>)
2	Isobutyrophenone	60.0	75.0	(<i>R</i>)
3	2'-Fluoroacetophenone	95.7	49.3	(<i>R</i>)
4	2'-Chloroacetophenone	94.0	65.5	(<i>R</i>)
5	2'-Bromoacetophenone	96.4	63.4	(<i>R</i>)
6	1-(3-Bromo-phenyl)-etganone	97.5	57.8	(<i>R</i>)
7	2'-Aminoacetophenone	43.0	76.1	(<i>R</i>)
8	2'-	98.7	78.6	(<i>R</i>)
9 ^a	(trifluoromethyl)acetophenone	100.0	75.0	(<i>R</i>)

Reaction conditions: aromatic ketone: 0.85 mmol; *S,S*-Ru-Ph-SBA-16: 25 mg; KOH-2-propanol ($C_{\text{KOH}} = 2.8 \text{ mmol.L}^{-1}$): 2.0 mL; hydrogen pressure: 3.0 MPa; temperature: 25 °C; reaction time: 5 h.

^a The homogeneous (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ was used in the asymmetric hydrogenation of acetophenone.

Table 3Effect of the solvents on the asymmetric hydrogenation of acetophenone over *S,S*-Ru-Ph-SBA-16.

Entry	Solvent	Conversion (%)	ee (%)	Configuration
1	CH ₃ OH	100	72.5	(<i>R</i>)
2	EtOH	100	70.2	(<i>R</i>)
3	95% EtOH	90.7	63.0	(<i>R</i>)
4	<i>i</i> -PrOH	100	74.9	(<i>R</i>)

Expect the solvent, the other reaction conditions: acetophenone: 0.85 mmol; *S,S*-Ru-Ph-SBA-16: 25 mg; KOH-solvent ($C_{\text{KOH}} = 2.8 \text{ mmol.L}^{-1}$): 2.0 mL; hydrogen pressure: 3.0 MPa; temperature: 25 °C; reaction time: 5 h.

Table 4Effect of the bases on enantioselective hydrogenation of acetophenone over *S,S*-Ru-Ph-SBA-16.

Entry	Base	Concentration (mmol/L ⁻¹)	Conversion (%)	ee (%)	Configuration
1	KOH	0	10.1	31.0	(<i>R</i>)
2	KOH	0.7	48.0	57.2	(<i>R</i>)
3	KOH	1.4	89.2	70.3	(<i>R</i>)
4	KOH	2.8	100	74.9	(<i>R</i>)
5	KOH	4.0	98.0	71.5	(<i>R</i>)
6	LiOH	2.8	83.2	64.2	(<i>R</i>)
7	NaOH	2.8	90.3	71.0	(<i>R</i>)
8	K ₂ CO ₃	2.8	98.0	73.0	(<i>R</i>)
9	(CH ₃) ₂ CHOK	2.8	100	75.5	(<i>R</i>)

Except the bases the other reaction conditions: acetophenone: 0.85 mmol; *S,S*-Ru-Ph-SBA-16: 25 mg; 2-propanol: 2.0 mL; hydrogen pressure: 3.0 MPa; temperature: 25 °C; reaction time: 5 h.

alysts during the recycling process [13]. The ICP analysis showed that no appreciable leaching of Ru was detected in the reaction mixture. These results demonstrate that the chiral Ru complex is encapsulated in the mesoporous cage of SBA-16 and the modified pore entrance can efficiently prevent encapsulated chiral Ru complex from leaching. Silylation of SBA-16 with phenyltrimethoxysilane to tailor the pore entrance is a key factor to preparation of stable and reusable heterogeneous catalyst. As shown in Fig. 5, after recycling *S,S*-Ru-SBA-16 only three times, it had lost nearly all of its activity. The conversion quickly declined from 100% to 14.6%, while the *ee* value slightly decreased from 75% to 68.7%. The loss of the catalytic activity was believed to be mainly due to the leaching of Ru complex, as substantiated by ICP analysis showing Ru was detected in the reaction mixture. One explanation for

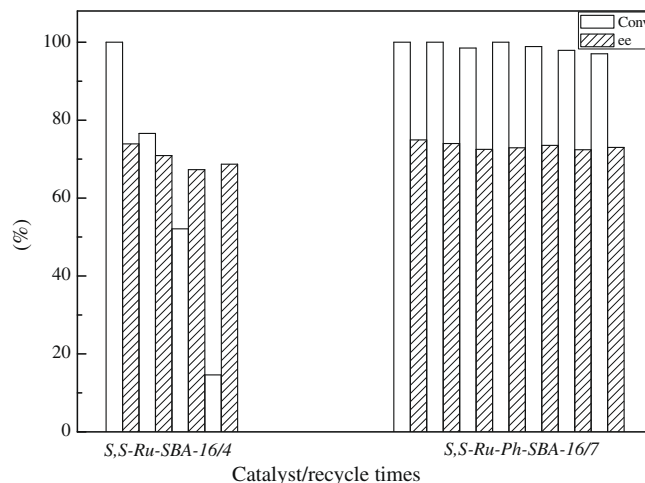


Fig. 5. Recycle of *S,S*-Ru-SBA-16 and *S,S*-Ru-Ph-SBA-16 in asymmetric hydrogenation of acetophenone. (Reaction conditions: acetophenone: 0.85 mmol; catalyst: 25 mg; KOH-2-propanol ($C_{\text{KOH}} = 2.8 \text{ mmol.L}^{-1}$): 2.0 mL; hydrogen pressure: 3.0 MPa; temperature: 25 °C; reaction time: 5 h).

the observed leaching may be that the entrance size of SBA-16 is larger than that of the (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ complex and cannot provide steric limitation for the encapsulated Ru complex.

4. Conclusions

Chiral homogeneous catalyst (1*S*,2*S*)-DPEN-RuCl₂(TPP)₂ can be effectively encapsulated into the mesoporous cage of SBA-16 silylanized with phenyltrimethoxysilane. The prepared *S,S*-Ru-Ph-SBA-16 exhibits 100% conversion with 74.9% *ee* in the asymmetric hydrogenation of acetophenone. The activity and enantioselectivity are as high as corresponding homogeneous counterpart. The *S,S*-Ru-Ph-SBA-16 is stable and can be recycled at least seven times without any significant loss of activity or enantioselectivity.

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