



Chiral Ru complex immobilized on mesoporous materials by ionic liquids as heterogeneous catalysts for hydrogenation of aromatic ketones

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ABSTRACT

Four kinds of mesoporous material-supported ionic liquid phase catalysts containing chiral Ru complex were synthesized using mesoporous MCM-41, MCM-48, SBA-15 and amorphous SiO₂, respectively. The results of N₂ sorption and XRD indicated the successful immobilization of chiral Ru complex inside the channels of the mesoporous materials. These immobilized catalysts were evaluated in the asymmetric hydrogenation of aromatic ketones and the reaction conditions were optimized. Comparable catalytic activities and enantioselectivities to those of nonimmobilized counterpart were obtained. Moreover, all the four catalysts were stable and could be easily recovered for reuse for at least four times without obvious decrease in conversions and ee values. Especially, the SiO₂-based catalyst still preserved high activity and enantioselectivity in the fifth run. The comparison experiments indicated that the two kinds of ionic liquids in the heterogeneous catalyst were beneficial to the enhancement of the stability of active species.

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1. Introduction

Ionic liquids have received considerable attention as attractive mediums in the catalytic processes over the last decade [1,2]. Many organic reactions have been reported to proceed in ionic liquids or biphasic ionic liquid systems [3,4]. Although immobilization of homogeneous catalysts in biphasic reaction systems allowed effective separation of products and catalysts, a considerable amount of ionic liquid is always required in such system. In view of economic and possible toxicological concerns, it is desirable to minimize the amount of ionic liquid in a potential process while at the same time allowing a facile recovery of the catalyst. A relatively new approach fulfilling such a demand has recently been reported by using supported ionic liquid phases to immobilize homogeneous catalysts [5–10]. As described by Mehnert et al. [5,6], the concept of supported ionic liquid catalysis involves the covalent attachment of a monolayer of ionic liquid and the adsorption of multiple layers of free ionic liquid on the surface of a support material. The catalytic reaction is carried out in the multiple layers where the homogeneous catalyst is dissolved. The immobilized catalyst thus combines the advantages of ionic liquid phases with those of solid supports, and the amount of utilized ionic liquid is significantly reduced. Some studies have successfully used this con-

cept in various catalytic processes, such as olefin hydroformylation [5,11–13], hydrogenation [14–17], Heck reaction [18], hydroamination [19,20], carbonylation [21], and epoxidation [22].

Asymmetric hydrogenation of prochiral ketones is one of the most important methods for the synthesis of enantiomerically pure secondary alcohols, which are valuable building blocks and intermediates for the manufacture of pharmaceuticals and advanced materials [23]. The chiral RuCl₂(diphosphine)(1,2-diamine) complexes, of which the most attractive is Noyori's catalyst [RuCl₂((R)-BINAP)((R,R)-DPEN)] (BINAP = 2,2'-bis-(diarylphosphino)-1,1'-binaphthyl; DPEN = 1,2-diphenylethylenediamine), combined with a base and isopropanol, have proved to be highly efficient for the asymmetric homogeneous hydrogenation of simple ketones [23–29]. However, the high cost of the noble metal and chiral ligand, as well as the difficulties in the separation of the products from the reaction system and the recovery of the catalysts often hinder their practical applications. Thus the immobilization of such homogeneous catalysts has attracted much attention in the last decade due to easy catalyst separation and recovery [30–33]. Unfortunately, in most cases the heterogeneous chiral catalysts always provide lower activities and/or enantioselectivities as compared to those observed for their homogeneous counterparts [33–37].

Herein we employed the supported ionic liquid phase as carrier media to immobilize chiral ruthenium complex composed of a chiral diamine and an achiral monophosphine, with the aim to develop a cheaper, more active, enantioselective and recy-

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able heterogeneous catalyst for asymmetric hydrogenation of prochiral ketones. A few researches have successfully applied the concept of supported ionic liquid catalysis in asymmetric catalytic systems [38]. The organocatalyst *L*-proline was immobilized in a SiO₂-supported ionic liquid phase, and comparable yields and enantiomeric excess (ee) values with respect to the homogeneous catalysis were obtained in aldol reactions between acetone and aromatic aldehydes [39,40]. Dooos and Jacobs [41] immobilized a dimeric Cr(salen) catalyst in ionic liquids onto the surface of SiO₂, and the resulting material showed better reactivity and selectivity for asymmetric ring-opening reactions of epoxides than the Cr(salen) complex immobilized by impregnation. An MCM-48 supported ionic liquid phase catalyst containing chiral Mn(salen) complex was previously reported by our group [22], and the catalytic system exhibited comparable activity and higher enantioselectivity for the asymmetric epoxidation of olefins than the homogeneous counterpart. In the present work, the chiral ruthenium complex containing a cheap achiral monophosphine [RuCl₂(PPh₃)₂(S,S-DPEN)] was prepared and immobilized in the ionic liquid [bmim][BF₄] (bmim = 1-butyl-3-methylimidazolium), which was confined on the surface of imidazolium-based ionic liquid modified mesoporous silicates, including MCM-48, MCM-41, SBA-15, and amorphous SiO₂. The obtained materials were employed as efficient catalysts for the asymmetric hydrogenation of aromatic ketones, and the effects of various reaction conditions on the catalytic performance were studied in detail. It was found that all of these immobilized catalysts exhibited comparable catalytic activity and enantioselectivity to those of homogeneous counterpart, and they could be recycled at least four times with no obvious decrease in catalytic performance.

2. Experimental

2.1. General

3-Chloropropyltriethoxysilane (95%), Pluronic P123 (EO₂₀-PO₇₀-EO₂₀, 30 wt% PEG) and 1-methylimidazole (≥99%) were purchased from Aldrich. (1*S*,2*S*)-(+)-1,2-Diphenylethylenediamine (S,S-DPEN, ≥97%, ≥99% ee) was obtained by Likai Chiral Tech. Co. Ltd. in Chengdu. Acetophenone (99%) was provided by Kermel Chemical Reagent Co. Ltd. in Tianjin. *o*-Chloroacetophenone (>99%) and *o*-fluoroacetophenone (>98.5%) were purchased from Jintan Kingun Chemical Factory. Tris(triphenylphosphine)ruthenium(II) chloride [RuCl₂(PPh₃)₃] (≥99.9%) was supplied by Shaanxi Kaida Chemical Engineering Co. Ltd. Cetyltrimethylammonium bromide (CTAB, 99%), tetraethyl orthosilicate (TEOS, AR), 1-chlorobutane (>99%) and NaBF₄ (AR) were provided by Jiangtian Chemical Technology Co. Ltd. in Tianjin. The hydrogen gas used in the hydrogenation experiments was of 99.99% purity and was supplied by Tianjin Skarn Gas Co., Ltd. The highly ordered siliceous mesoporous materials MCM-41 and MCM-48 were synthesized according to the literature method [42], using CTAB as template and TEOS as silica source. The purely siliceous SBA-15 was synthesized using a triblock organic copolymer Pluronic P123 as template and TEOS as silica source [43]. Amorphous SiO₂ was purchased from YuMinYuan silica-gel reagent factory. All of the solvents used in the present work were dried over 4A molecular sieves before use.

¹H and ¹³C{¹H} NMR spectra were obtained on a Varian Mercury Vx-300 spectrometer, 300 MHz for ¹H and 75 MHz for ¹³C, respectively. The elemental analysis of C, H and N was performed on a PerkinElmer 240C analyzer. XRD patterns were recorded on a Rigaku D/max-2500 diffractometer with Cu Kα radiation at 40 kV and 100 mA. FT-IR spectra were carried out on a Bruker Vector 22 spectrometer using KBr pellets. N₂ adsorption-desorption analysis was done at 77 K on a Micromeritics TriStar 3000 appa-

ratus. The specific surface areas were determined by the BET (Brunauer-Emmett-Teller) equation using adsorption data in the relative pressure range from 0.05 to 0.2, and the pore size distributions were estimated using the BJH (Barret-Joyner-Halenda) model. The content of Ru leaching in the reaction solution was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an ICP-9000(N+M) spectrometer (TJA Co.). Diffuse-reflectance UV-vis (DR UV-vis) spectra were obtained on a Jasco V-570 UV-vis spectrophotometer in the range of 220–800 nm. The products of hydrogenation reaction were determined by gas chromatography (GC) on a Rock GC7800 gas chromatograph equipped with a flame ionization detector and a chiral capillary column (BETA-DEX 325, 30 m × 0.25 mm × 0.25 μm), using ultrapure nitrogen as a carrier gas. The injection and detector temperatures were set at 523 K and 513 K, respectively, and the column temperature was programmed in the range of 373–393 K (10 min hold at 373 K, 1 K/min from 373 K to 393 K). The injection volume was 0.2 μL using a split ratio of 1:50.

2.2. Synthesis of ionic liquids

2.2.1. Synthesis of ionic liquid [bmim][BF₄]

1-Methylimidazole (4.0 mL, 50 mmol) and 1-chlorobutane (5.2 mL, 50 mmol) were stirred in air at 343 K for 24 h [44]. The reaction mixture was cooled to room temperature and then repeatedly washed with ethyl acetate (3 × 20 mL). The residual ethyl acetate was evaporated at 313 K under reduced pressure, and the residue was dried under vacuum at 323 K to give [bmim]Cl as a white crystalline solid. ¹H NMR (CDCl₃, 300 MHz, Me₄Si): δ (ppm) 0.93–0.98 (t, 3H, CH₂CH₃), 1.34–1.42 (m, 2H, CH₂CH₃), 1.84–1.94 (m, 2H, CH₂CH₂CH₂), 4.12 (s, 3H, NCH₃), 4.31–4.36 (t, 2H, NCH₂), 7.41 (s, 1H, NCH), 7.54 (s, 1H, NCH), 10.49 (s, 1H, NCHN).

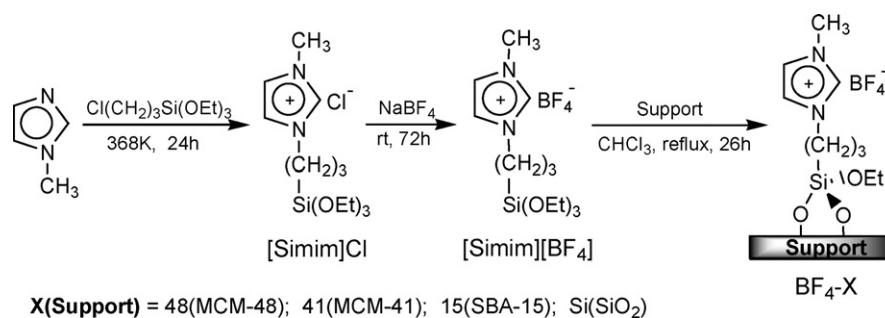
To a solution of [bmim]Cl (7.0 g, 40 mmol) in acetone (50 mL) was added NaBF₄ (5.1 g, 46 mmol) [45]. The resulting mixture was vigorously stirred at room temperature for 72 h and then filtrated. The filtrate was evaporated at 303 K under reduced pressure to remove acetone, and dried at 313 K under vacuum to give [bmim][BF₄] as a clear, pale yellow liquid, which was stored in a vacuum desiccator before use. ¹H NMR (CDCl₃, 300 MHz, Me₄Si): δ (ppm) 0.93–0.98 (t, 3H, CH₂CH₃), 1.25–1.41 (m, 2H, CH₂CH₃), 1.72–1.91 (m, 2H, CH₂CH₂CH₂), 3.96 (s, 3H, NCH₃), 4.16–4.21 (t, 2H, NCH₂), 7.28 (s, 1H, NCH), 7.32 (s, 1H, NCH), 8.83 (s, 1H, NCHN).

2.2.2. Synthesis of ionic liquid

1-methyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate ([Simim][BF₄])

The ionic liquid [Simim][BF₄] was obtained through the synthesis sequence given in Scheme 1 [37]. 1-Methylimidazole (3.0 mL, 38 mmol) was reacted with 3-chloropropyltriethoxysilane (9.1 mL, 38 mmol) at 368 K under nitrogen atmosphere for 24 h. The reaction mixture was cooled to room temperature and then washed completely with diethyl ether. After dried under vacuum at 303 K, a slight yellow viscous liquid 1-methyl-3-(3-triethoxysilylpropyl)-imidazolium chloride ([Simim]Cl) was obtained. ¹H NMR (CDCl₃, 300 MHz, Me₄Si): δ (ppm) 0.59–0.65 (t, 2H, SiCH₂), 1.20–1.25 (t, 9H, CH₂CH₃), 1.97–2.07 (m, 2H, CH₂CH₂CH₂), 3.79–3.86 (q, 6H, CH₂CH₃), 4.13 (s, 3H, NCH₃), 4.32–4.37 (t, 2H, NCH₂), 7.26 (s, 2H, NCH), 11.01 (s, 1H, NCHN).

To a solution of [Simim]Cl (9.7 g, 30 mmol) in acetone (40 mL), NaBF₄ (3.8 g, 35 mmol) was added slowly. The resulting mixture was vigorously stirred at room temperature for 72 h and then filtrated. The liquid phase was evaporated at 303 K under reduced pressure to remove acetone, and dried under vacuum at 313 K to give [Simim][BF₄] as a yellow viscous liquid, which was stored in a vacuum desiccator before use. ¹H NMR (CDCl₃, 300 MHz, Me₄Si): δ (ppm) 0.56–0.62 (t, 2H, SiCH₂), 1.20–1.25 (t, 9H, CH₂CH₃), 1.95–2.05



Scheme 1. The synthesis of ionic liquid modified supports BF₄-X.

(m, 2H, CH₂CH₂CH₂), 3.79–3.86 (q, 6H, CH₂CH₃), 3.95 (s, 3H, NCH₃), 4.17–4.22 (t, 2H, NCH₂), 7.28 (s, 2H, NCH), 8.61 (s, 1H, NCHN).

2.3. Synthesis of immobilized chiral Ru catalysts

2.3.1. Synthesis of chiral Ru complex **C1**

The complex RuCl₂(PPh₃)₂(S,S-DPEN) **C1** was synthesized [46] by refluxing RuCl₂(PPh₃)₃ (0.5 g, 0.52 mmol) with S,S-DPEN (0.11 g, 0.52 mmol) in CH₂Cl₂ (30 mL) under nitrogen atmosphere for 5 h and then stirring at room temperature for 15 h (Scheme 2). ¹H NMR (CDCl₃, 300 MHz, Me₄Si): δ (ppm) 3.35 (m, 2H, NHH), 3.71 (m, 2H, NHH), 4.29 (m, 2H, CH), 6.82–7.54 (m, 40H, 6-H). ¹³C{¹H} NMR (CDCl₃, 75 MHz, Me₄Si): δ (ppm) 63.5, 127.1, 127.6, 128.0, 128.7, 129.2, 134.9, 136.1, 139.6.

2.3.2. Synthesis of ionic liquid modified supports (BF₄-X)

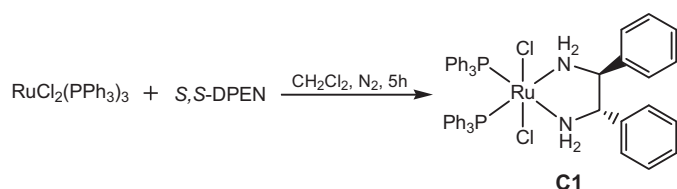
The pretreated mesoporous material (3.0 g, dried under vacuum and heated to 393 K overnight) was suspended in chloroform (50 mL), and then ionic liquid [Simim][BF₄] (1.5 g, 4.0 mmol) was added. The resulting mixture was refluxed under vigorous stirring for 26 h, and then the white solid BF₄-X (Scheme 1, X = 48, 41, 15 and Si while MCM-48, MCM-41, SBA-15 and SiO₂ was used as support material, respectively) was obtained by filtration, washed orderly with chloroform, acetone and diethyl ether, and Soxhlet-extracted with dichloromethane for 20 h. The nitrogen contents of BF₄-X determined by elemental analysis are shown in Table 1.

2.3.3. Heterogenization of chiral Ru complex **C1**

Chiral Ru complex **C1** (0.55 mmol) and ionic liquid [bmim][BF₄] (2.2 mmol) were dissolved in acetone (50 mL), and to the solution BF₄-X (1.5 g) was added. The resulting mixture was stirred at room temperature for 3 h, and then evaporated under reduced pressure to remove the volatile components. The obtained heterogeneous catalysts were denoted as BF₄-X/**C1**, and their structures are shown in Fig. 1.

2.4. Asymmetric hydrogenation of aromatic ketone

The heterogeneous catalysts BF₄-X/**C1** (0.01 mmol, 0.5 mol%), KOH (0.011 g, 0.2 mmol), isopropanol (10 mL) and ketone (2 mmol)



Scheme 2. The synthesis of chiral Ru complex **C1**.

Table 1

Physico-chemical properties of BF₄-X, BF₄-X/**C1** and the parent mesoporous supports.

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å) ^a	Content of N (mmol/g)
MCM-41	822	0.77	28.8	–
BF ₄ -41	669	0.46	26.3	1.41
BF ₄ -41/ C1	372	0.31	18.8	–
MCM-48	1188	0.96	26.4	–
BF ₄ -48	969	0.67	24.5	1.21
BF ₄ -48/ C1	459	0.23	20.1	–
SBA-15	813	1.11	62.3	–
BF ₄ -15	413	0.60	60.0	1.23
BF ₄ -15/ C1	232	0.42	59.2	–
SiO ₂	347	0.93	86.0	–
BF ₄ -Si	276	0.71	82.5	1.08
BF ₄ -Si/ C1	74	0.28	80.8	–

^a The most probable pore diameter.

were added to a 30 mL stainless steel autoclave with a magnetic stirrer. The mixture was stirred at room temperature for 0.5 h, followed by a purge with hydrogen for three times. Then hydrogen was introduced to the desired hydrogen pressure. After the reaction was completed, hydrogen was carefully released. The solid catalyst was recovered by filtration, washed thoroughly with isopropanol, and dried for reuse. The conversions and ee values were determined by gas chromatography with a chiral BETA-DEX 325 capillary column.

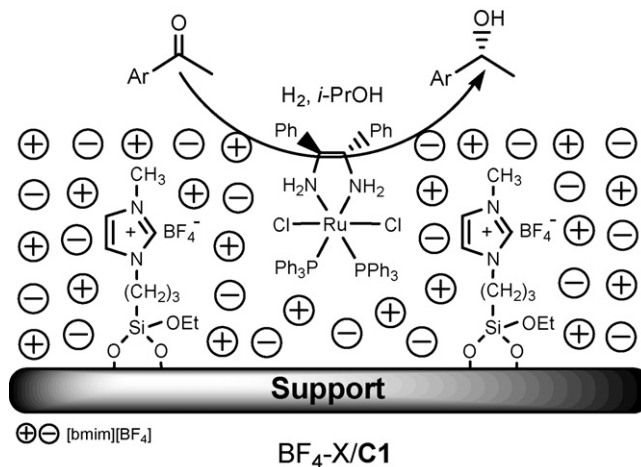


Fig. 1. Supported ionic liquid phase catalyst BF₄-X/**C1** for asymmetric hydrogenation of aromatic ketone.

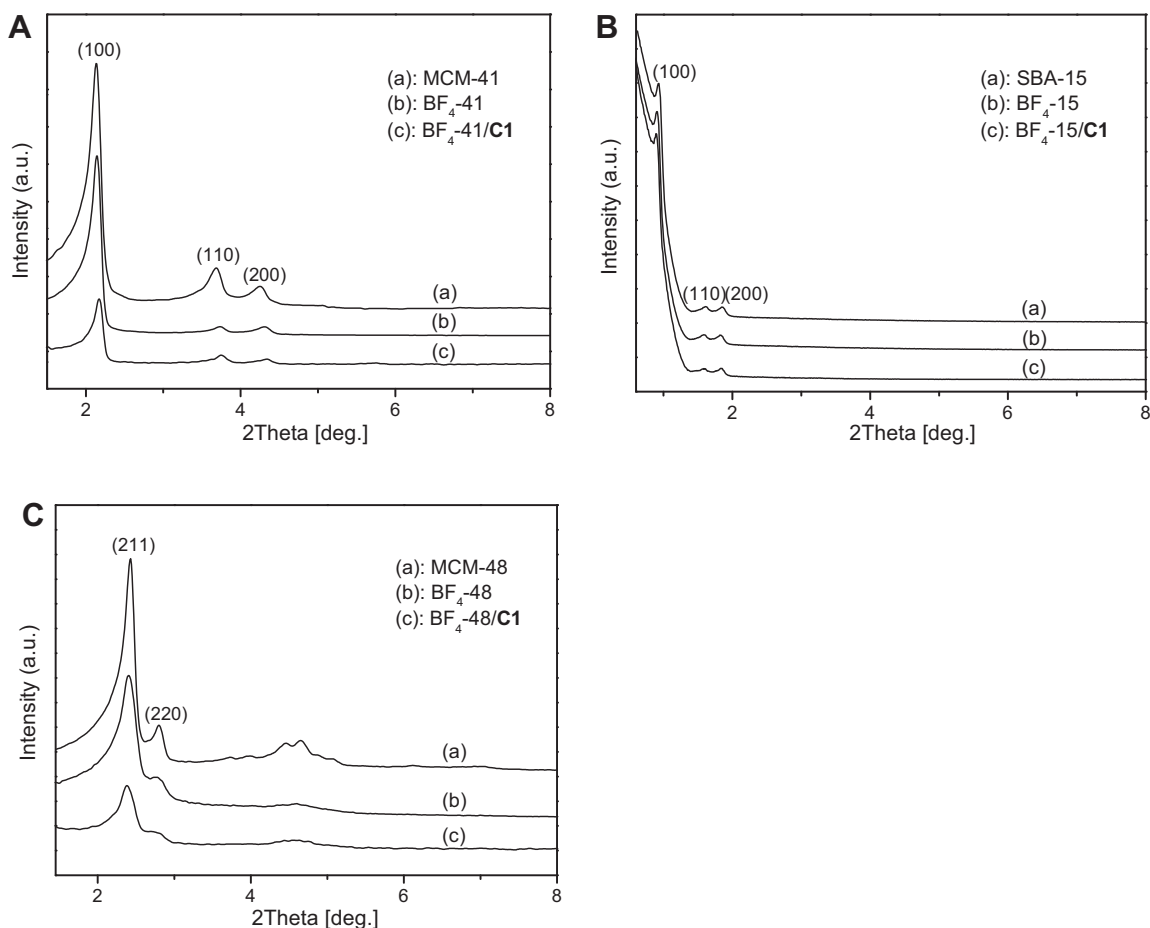


Fig. 2. Powder XRD patterns of parent support, $\text{BF}_4\text{-X}$ and $\text{BF}_4\text{-X/C1}$: (A) $X=41$, (B) $X=15$, and (C) $X=48$.

3. Results and discussion

3.1. Material characterization

The structure information of all the solid materials was studied using powder XRD and N_2 sorption. Fig. 2A and B shows the powder XRD patterns of parent supports MCM-41 and SBA-15, $[\text{Simim}][\text{BF}_4]$ modified supports $\text{BF}_4\text{-41}$ and $\text{BF}_4\text{-15}$, and the heterogeneous catalysts $\text{BF}_4\text{-41/C1}$ and $\text{BF}_4\text{-15/C1}$. On modification with ionic liquid $[\text{Simim}][\text{BF}_4]$, a slight decrease in the relative intensities of the XRD reflections was observed, but the well-resolved (1 1 0) and (2 0 0) reflections for $\text{BF}_4\text{-41}$ and $\text{BF}_4\text{-15}$ indicated that the mesoporous structure of the parent supports remained intact after the modification. Although the intensities of all peaks decreased after the immobilization of chiral Ru complex **C1**, the typical hexagonal structure of the parent supports was maintained. Fig. 2C shows the powder XRD patterns of MCM-48, $\text{BF}_4\text{-48}$ and $\text{BF}_4\text{-48/C1}$. A gradual decrease in the relative intensities of all peaks was observed on $[\text{Simim}][\text{BF}_4]$ modification and complex **C1** immobilization, while the cubic mesostructure of MCM-48 was also preserved in the heterogeneous catalyst $\text{BF}_4\text{-48/C1}$. Thus it can be confirmed from the XRD results that immobilization of ionic liquid $[\text{Simim}][\text{BF}_4]$ and Ru complex **C1** did not destroy the structure of the support materials.

All of the parent supports, $[\text{Simim}][\text{BF}_4]$ modified supports $\text{BF}_4\text{-X}$ and the corresponding heterogeneous catalysts $\text{BF}_4\text{-X/C1}$ were characterized by N_2 sorption. Fig. 3 shows the low-temperature N_2 adsorption–desorption isotherms of these materials. It could be observed that all the samples exhibited type IV isotherms

with well-defined sharp inflections characteristic for capillary condensation within mesopores. This indicated that the mesoporous structures of parent supports were preserved in the modified supports $\text{BF}_4\text{-X}$ and heterogeneous catalysts $\text{BF}_4\text{-X/C1}$. Moreover, after modification with $[\text{Simim}][\text{BF}_4]$ and then immobilization of Ru complex on the parent support, the position of the inflection points gradually shifted to lower value of the relative pressure, indicating that the pore diameters of the material decreased gradually. Table 1 gives the textural parameters of all the samples calculated by N_2 adsorption–desorption isotherms. It could be observed that $\text{BF}_4\text{-X}$ showed decreased BET surface area, pore volume, and pore size compared with the corresponding parent support. This suggests that ionic liquid $[\text{Simim}][\text{BF}_4]$ is mainly located inside the channels of the parent supports. A further decrease in BET surface area, pore volume, and pore size was observed after immobilization of chiral Ru complex **C1** on $\text{BF}_4\text{-X}$, indicating that the complex **C1** lies mainly on the interior surfaces of $\text{BF}_4\text{-X}$.

The composition of the mesoporous material $\text{BF}_4\text{-X}$ was determined by FT-IR. Fig. 4 shows the representative FT-IR spectra in the scan range of $400\text{--}3500\text{ cm}^{-1}$ for MCM-41 and $[\text{Simim}][\text{BF}_4]$ modified MCM-41 ($\text{BF}_4\text{-41}$). In the spectrum of MCM-41, the IR bands presented at around 1080 , 810 , and 460 cm^{-1} were assigned to characteristic vibrations of the Si–O–Si framework, and the band near 1630 cm^{-1} was attributed to the O–H bending vibrations of adsorbed water. Besides these absorptions, the FT-IR spectrum of $\text{BF}_4\text{-41}$ showed the specific absorptions of ionic liquid $[\text{Simim}][\text{BF}_4]$. The IR bands at 3164 and 3120 cm^{-1} were due to C–H stretching vibrations of aromatic imidazole rings, and the bands near 2900 cm^{-1} could be attributed to C–H stretching vibra-

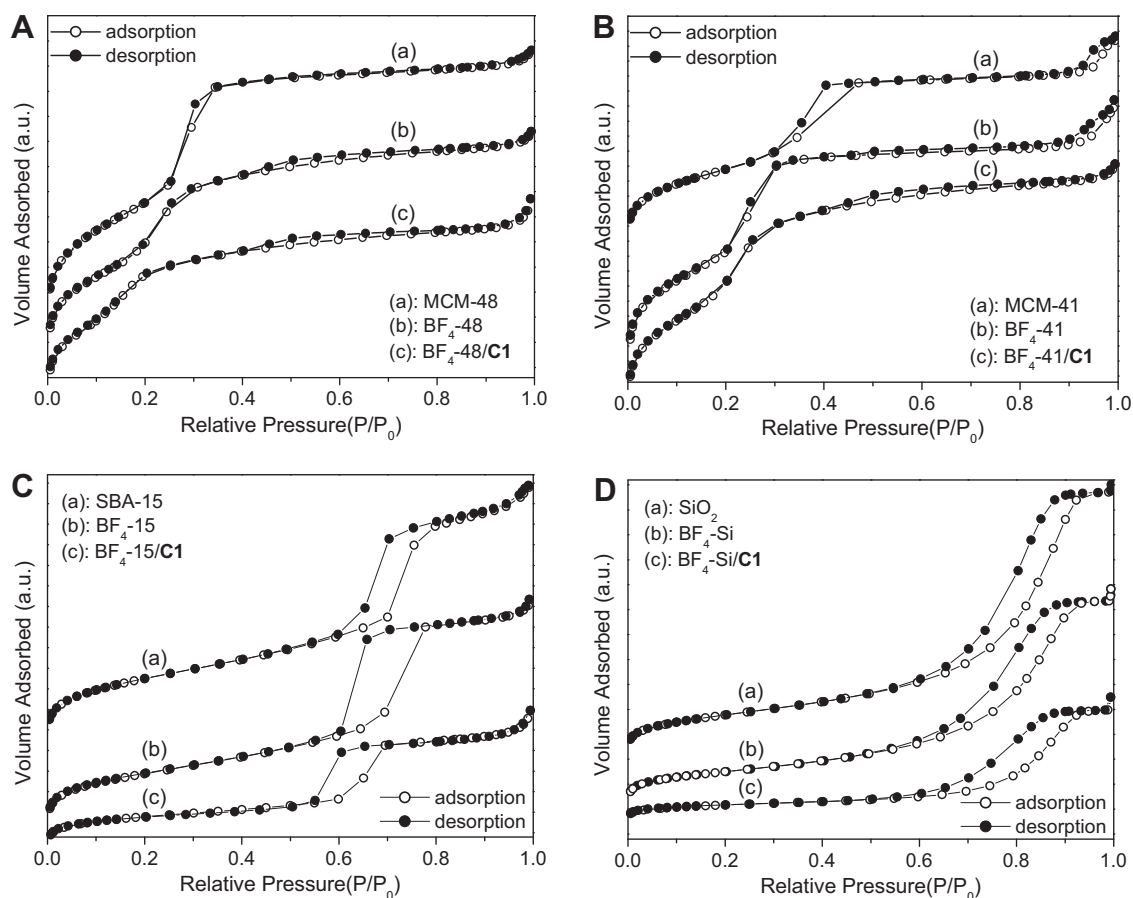


Fig. 3. N_2 adsorption-desorption isotherms of parent support, BF_4 -X and BF_4 -X/C1: (A) X = 48, (B) X = 41, (C) X = 15, and (D) X = Si.

tions of alkyl groups. The IR absorptions at 1574 and 1461 cm^{-1} were assigned to $C=C$ stretching vibrations of imidazole rings and $C-H$ deformation vibrations of alkyl groups, respectively. The band presented at 1169 cm^{-1} could be attributed to $C-H$ in-plane deformation vibrations of imidazole rings, and the absorption assigned to $B-F$ stretching vibrations appeared at around 1055 cm^{-1} , which was overlapped by the $Si-O-Si$ vibrations. The FT-IR spectra con-

firmed the successful modification of the mesoporous support with ionic liquid [Simim][BF_4].

3.2. Catalytic tests

3.2.1. Effects of reaction conditions on the asymmetric hydrogenation reaction

The prepared heterogeneous catalysts BF_4 -X/C1 were evaluated in the asymmetric hydrogenation of aromatic ketones, which produced chiral secondary alcohols via a metal-ligand bifunctional mechanism [23,29]. The effects of reaction temperature, reaction time and hydrogen pressure on the catalytic performance were studied in detail using BF_4 -48/C1 as a model catalyst and acetophenone as a substrate in order to achieve suitable reaction conditions.

As shown in Table 2, the catalytic activity increases significantly with the increasing of reaction temperature, while the enantiose-

Table 2
Influence of reaction temperature on asymmetric hydrogenation of acetophenone.^a

Entry	Temperature (K)	Conv. (%) ^b	ee (%) ^c
1	273	14	80(R)
2	283	66	78(R)
3	293	100	78(R)
4	308	100	76(R)
5	323	100	61(R)

^a Reactions were performed in isopropanol under 3.0 MPa of H_2 for 6 h using BF_4 -48/C1 with acetophenone/Ru/KOH = 1:0.005:0.1.

^b Conversion % determined by GC with chiral column.

^c The ee value of the chiral product was determined by GC with BETA-DEX 325 chiral column and calculated from the expression: $ee (\%) = 100 \times (R - S)/(R + S)$, where R and S are the molar fractions of the respective enantiomers.

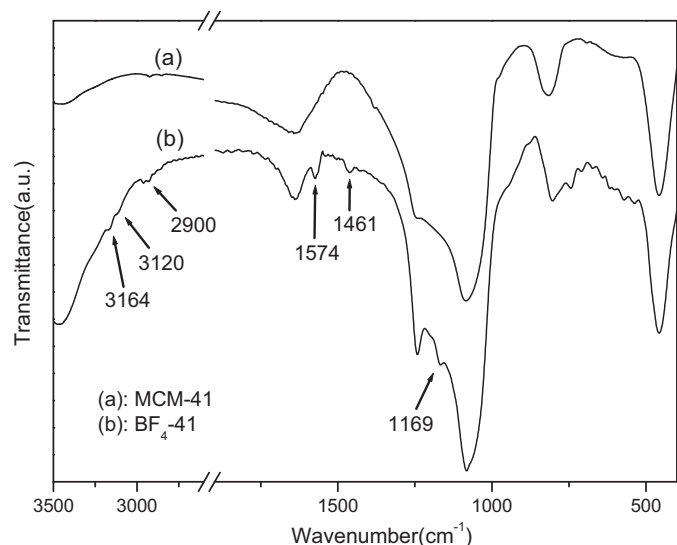


Fig. 4. Representative FT-IR spectra of (a) MCM-41 and (b) BF_4 -41.

Table 3
Influence of reaction time on asymmetric hydrogenation of acetophenone.^a

Entry	Time (h)	Conv. (%)	ee (%)
1	1	15	78(R)
2	2	43	76(R)
3	4	82	75(R)
4	6	100	78(R)
5	10	100	77(R)

^a Reaction temperature: 293 K, other conditions were the same as those in Table 2.

lectivity decreases gradually. The conversion of acetophenone and the ee value of the products were 14% and 80% at 273 K, respectively. 100% conversion was obtained when the reaction temperature was increased to 293 K with an ee value of 78%. A further increase in reaction temperature to 323 K led to a much lower ee value of 61%. Considering both catalytic activity and enantioselectivity, the reaction temperature 293 K was suitable over the catalyst for asymmetric hydrogenation of acetophenone.

Table 3 displays the effect of reaction time on the catalytic performance of BF₄-48/C1 for acetophenone hydrogenation. Only 15% conversion was obtained for 1 h; with the increase of reaction time, acetophenone conversion increased gradually while the ee value of the products changed marginally. After 6 h the reaction achieved steady-state, the conversion and ee value reached 100% and 78%, respectively.

The data listed in Table 4 indicated that hydrogen pressure has a great effect on the catalytic activity for asymmetric hydrogenation of acetophenone. The conversion increased from 29% to 100% when hydrogen pressure was increased from 0.5 MPa to 3.0 MPa. No obvious effect of hydrogen pressure on the enantioselectivity was observed. Thus the following reactions in this work were all performed under 3.0 MPa of hydrogen.

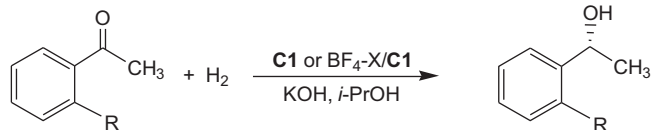
3.2.2. Asymmetric hydrogenation of aromatic ketones with different catalysts

The four immobilized catalysts were evaluated in the asymmetric hydrogenation of acetophenone. For comparison, the chiral Ru pre-catalyst C1 was also investigated under the same reaction conditions. The results are summarized in Table 5. The homogeneous catalyst C1 exhibited 100% conversion and 78% ee, which are comparable to the literature report [47]. It could be observed that all the heterogeneous catalysts showed comparable conversions and ee values to the homogeneous counterpart. The high catalytic activities may be attributed to the homogeneous-like properties of the active species in ionic liquid phase on the mesoporous supports. Among these heterogeneous catalysts, BF₄-48/C1 exhibited a slightly higher ee value of 78% than those obtained for BF₄-41/C1 (72%) and BF₄-15/C1 (72%), which could be due to the better confinement effect of the three-dimensional topological structure of MCM-48 than that of the one-dimensional channel of MCM-41 and SBA-15. The SiO₂-based catalyst BF₄-Si/C1 also provided a rather good enantioselectivity (77% ee) that might be attributed to the complicated channel structure of SiO₂.

Table 4
Influence of H₂ pressure on asymmetric hydrogenation of acetophenone.^a

Entry	H ₂ pressure (MPa)	Conv. (%)	ee (%)
1	0.5	29	73(R)
2	1.0	72	74(R)
3	2.0	99	77(R)
4	3.0	100	78(R)
5	5.0	100	76(R)

^a Reaction temperature: 293 K, reaction time: 6 h, other conditions were the same as those in Table 2.

Table 5
Asymmetric catalytic hydrogenation of aromatic ketones by different catalysts.^a

Entry	Ketone	Catalyst	Conv. (%)	ee (%)
1	R=H	C1	100	78(R)
2	R=H	BF ₄ -48/C1	100	78(R)
3	R=H	BF ₄ -41/C1	100	72(R)
4	R=H	BF ₄ -15/C1	100	72(R)
5	R=H	BF ₄ -Si/C1	100	77(R)
6	R=Cl	C1	99	66(R)
7	R=Cl	BF ₄ -48/C1	99	64(R)
8	R=F	C1	97	45(R)
9	R=F	BF ₄ -48/C1	98	48(R)

^a Reaction temperature: 293 K, reaction time: 6 h, H₂ pressure: 3.0 MPa, other conditions were the same as those in Table 2.

Besides acetophenone, the immobilized catalysts also showed satisfactory catalytic activity and enantioselectivity for other aromatic ketones. As shown in Table 5, BF₄-48/C1 gave comparable conversions and ee values to the homogeneous counterpart for the asymmetric hydrogenation of *o*-chloroacetophenone and *o*-fluoroacetophenone.

3.2.3. Catalyst recycling and stability

To assess the stability and reusability of BF₄-X/C1, recycling experiments were carried out with acetophenone as a substrate over the four heterogeneous catalysts. After each experiment, the catalyst was recovered by filtration, washed thoroughly with isopropanol, dried and then subjected to a new run with fresh reactants under identical hydrogenation conditions. The results are shown in Fig. 5.

It could be found that all the four heterogeneous catalysts showed no obvious decrease in catalytic activity and enantioselectivity for four runs. In the fifth cycle, the SiO₂-based catalyst BF₄-Si/C1 still maintained its catalytic performance with comparable conversion and ee value to the first run, while the other three kinds of catalysts exhibited an obvious decrease in activity. ICP-AES analysis showed no leaching of Ru in the filtrates for each recycle experiment, suggesting that the Ru complex C1 was effectively confined on the surface of mesoporous supports and the loss of activity observed in the three reused catalytic systems was not caused by catalyst leaching. The decrease of catalytic activity might be due to the blockage of some mesopore channels during the recycling experiments, which caused increased diffusional resistance and the inaccessibility of some active species located inside the channels. The higher stability of BF₄-Si/C1 could be attributed to the larger pore size and complicated channel structure in SiO₂ particles, which favors material transmission and makes it possible that the pore channels maintained intact after several runs. After five catalytic runs, the total turnover number (TON) of the immobilized catalyst BF₄-Si/C1 (1000) was much higher than that of the corresponding homogeneous catalyst C1 (200), which could not be recycled after reaction.

To clarify the role of ionic liquids in the heterogeneous catalyst system, two kinds of catalysts MCM-48/C1 (in which the Ru complex C1 and ionic liquid [bmim][BF₄] were directly adsorbed onto unmodified MCM-48) and BF₄-48'/C1 (in which C1 was immobilized onto [Simim][BF₄] modified MCM-48 without the additional adsorbed ionic liquid [bmim][BF₄]) were synthesized and evaluated in the asymmetric hydrogenation of acetophenone. The unmodified MCM-48 supported catalyst MCM-48/C1 exhibited comparable catalytic performance (100% conversion and 77% ee) to those of

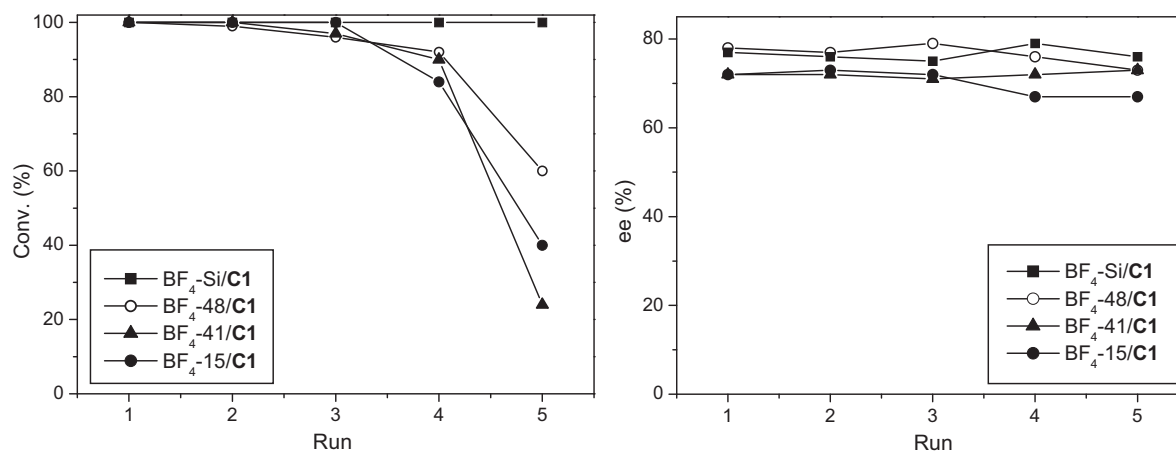


Fig. 5. Conversions (left) and ee values (right) in the repeated experiments of acetophenone hydrogenation over the four immobilized catalysts.

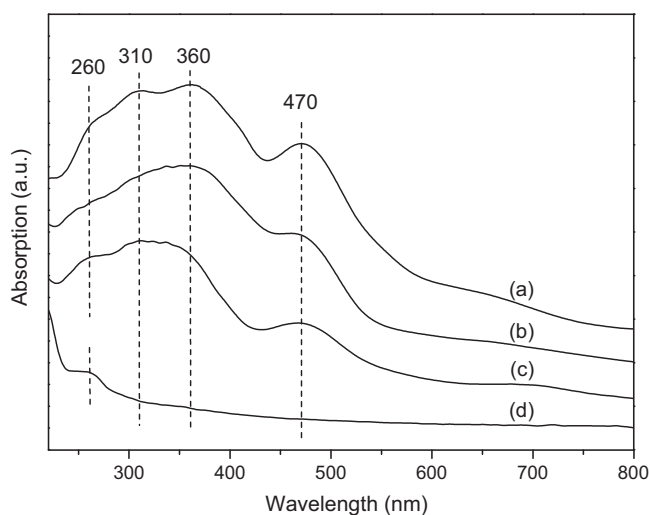


Fig. 6. DR UV-vis spectra of (a) Ru complex C1, (b) fresh catalyst BF₄-Si/C1, (c) used catalyst Re-BF₄-Si/C1, and (d) BF₄-Si.

BF₄-48/C1. However, it gave a much lower conversion (only 8%) when reused for the second time, indicating that the covalently anchored ionic liquid on the surface of mesoporous supports was of benefit to the stability of the heterogeneous catalyst system. Similar results were obtained by the catalyst BF₄-48'/C1, 6% conversion was presented for the second run. Thus it could be concluded that the synergistic interaction between the two kinds of ionic liquids can significantly enhance the stability of heterogeneous catalyst.

The heterogeneous catalyst Re-BF₄-Si/C1, which was recovered after two cycles of acetophenone hydrogenation, was submitted to DR UV-vis analysis. As shown in Fig. 6, the spectrum of Re-BF₄-Si/C1 exhibited features similar to those of Ru complex C1 and fresh catalyst BF₄-Si/C1. The characteristic absorption bands near 260, 310, 360 and 470 nm for Ru complex C1 were all presented in the spectrum of Re-BF₄-Si/C1. This indicated the maintenance of active Ru complex on the recovered catalyst.

4. Conclusions

The chiral Ru complex composed of a chiral diamine and a cheap achiral monophosphine was successfully immobilized in ionic liquids onto the surface of four ionic liquid-modified mesoporous materials, *i.e.*, MCM-41, MCM-48, SBA-15 and amorphous SiO₂. These heterogeneous catalysts were highly active and enantioselective for the asymmetric hydrogenation of aromatic ketones, and comparable conversions and ee values to those of the homogeneous counterpart were obtained. Moreover, all the four catalysts were stable and recyclable, no obvious decrease in catalytic activity and enantioselectivity was observed after four runs. In particular, the SiO₂-supported catalyst showed the best stability, comparable conversion and ee value (100% and 76%, respectively) to the homogeneous catalytic results could be obtained for the fifth run, thus providing a significantly higher TON (1000) than the homogeneous one (200). The comparison experiments showed that both the two kinds of ionic liquids in the catalytic system had great effects on the stability of the heterogeneous catalyst.

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