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Acidic functionalized ionic liquids as catalyst for the isomerization of α-pinene to camphene

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Abstract An acidic functionalized ionic liquids (ILs) $[HSO_3\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ was synthesized and used to catalyze the isomerization of α-pinene in a homogeneous system. The optimum conditions for isomerization were obtained as follows: n(α-pinene):n(ILs) = 9:1, reaction temperature 140 °C, and reaction time 4 h, α-pinene 0.04 mol. Under the optimal conditions, the conversion of α-pinene was 97.6 % and the selectivity for camphene could reach 64.8 %. In addition, the catalyst could be easily separated by centrifugation after the isomerization completely finished. When the ILs were repeatedly used for four times, the conversion of α-pinene and the selectivity for camphene were still excellent, indicating the superb recycle ability of the acidic functionalized ILs catalyst.

Keywords Acidic functionalized ionic liquids · Catalyst · α-Pinene · Isomerization

Introduction

The isomerization of α-pinene can produce camphene, which is an intermediate in the synthesis of camphor and widely used in fragrances and the pharmaceuticals industry. In the isomerization of α-pinene, as catalysts, aqueous mineral acids are playing important roles. However, these aqueous mineral acids have many inevitable shortcomings, such as serious corrosion of equipment, complicated

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separation procedures, environmental pollution, non-recyclability, and so forth. In order to solve these problems, as the primary object, solid acids, such as PW/SBA-15 (SBA-15 supported $H_3PW_{12}O_{40}$), $AlCl_3/\gamma{-}Al_2O_3$ and $AlCl_3/SiO_2$, MSU-$S_{(BEA)}$, have become more and more significant in the catalysts field during the last 10 years. Yao et al. [1] reported that, in the catalysis process of α-pinene, the reaction conditions of PW/SBA-15 (SBA-15 supported $H_3PW_{12}O_{40}$) were listed: reaction temperature 130 °C, w(PW/SBA-15):w(α-pinene) = 2 %, and reaction time 2 h. Based on these conditions, the conversion of α-pinene was 94.5 % and the selectivity for camphene was 48.5 %. After $AlCl_3$ was immobilized on γ-Al_2O_3, the $AlCl_3/\gamma{-}Al_2O_3$ catalyst had high activity leading to the conversion concerning α-pinene of 95.5 % and the selectivity of 40.6 % for camphene. When $AlCl_3$ was immobilized on SiO_2, the $AlCl_3/SiO_2$ catalyst gave only 28.5 % selectivity for camphene and 98.4 % conversion of α-pinene [2]. When MSU-$S_{(BEA)}$ was used as catalyst (molar ratio of Si/Al is 67), the conversion of α-pinene was 97.0 % and the selectivity was just 48.0 % for camphene [3]. Burcu et al. [4] reported the isomerizaton of α-pinene over $H_3PW_{12}O_{40}$ catalysts was supported on natural zeolite, the selectivity for camphene was about 40.0 %, and the conversion of α-pinene was 99.4 %. SO_4^{2-}/ZrO_2 catalyzed the isomerization of α-pinene, the conversion of α-pinene was 96.4 %, and the selectivity of camphene was 49.7 % [5]. Thus, although solid acidic catalysts could avoid the shortcomings of mineral acids, they also had some drawbacks, such as low selectivity for camphene, heterogeneous reaction.

According to the above analysis, the present catalytic systems have a tedious post processing for the mass transfer between interphase and low selectivity for camphene, and cannot provide efficient and green technology for the isomerization of α-pinene. Therefore, it has become a vital aspect for promoting the isomerization of α-pinene to avoid the shortcomings of the present technology to synthesize one kind of perfect catalyst and further to design a novel catalytic system. In recent years, as environmentally friendly catalysts, Brønsted and Lewis acidic ILs have received much attention from researchers, which showed excellent selectivity and yield in several organic reactions, such as esterification [6–9], carbonylation [10, 11], polymerization [12, 13] by Friedel–Crafts [14–19], Beckmann [20, 21], and Diels–Alder [22]. In our laboratory, studies about the catalysts in the isomerization of α-pinene by both traditional catalysts and Brønsted and Lewis acidic functionalized ionic liquids catalysts have been performed at the same time. Compared with traditional catalysts, our results indicated that acidic functionalized ILs catalysts exhibited many outstanding advantages, such as simplicity, efficiency, and easy product isolation.

Therefore, in this work, a new kind of stable Brønsted–Lewis acidic functionalized ILs $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ was synthesized, characterized, and used in the isomerization of α-pinene. The catalyst showed excellent reuse performance and a superior catalytic activity in the homogeneous reaction and could readily separate after the complete isomerization. The results revealed that Brønsted–Lewis acidic functionalized ILs catalyzing the isomerization of α-pinene, the technology was efficient and environmentally-friendly.

Experimental

Chemicals and instruments

The α-Pinene (99.8 %), deionized water, 1,3-propane sultone (99.7 %, Wuhan Fengfan Chemicals Co. Ltd., China), and other chemicals (analytic purity) such as hydrochloric acid, triethylamine, zinc chloride, anhydrous magnesium sulfate, sodium chloride, and sodium carbonate were all purchased from Aldrich. All materials were directly used without further purification.

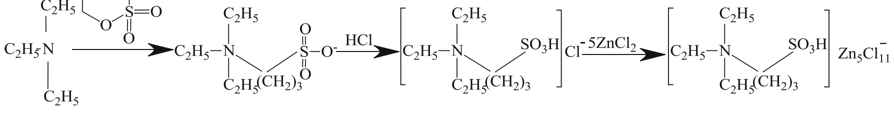
Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 510P FT-IR spectrometer in the range of 4500–400 cm^{-1}. The NMR spectra were taken on a Bruker AV500 Fourier-transform spectrometer with reference to $SiMe_4$ using solvent dimethyl sulphoxide (DMSO) containing a 5 % sample.

Preparation of catalysts

Synthesis of [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ILs

Firstly, under vigorous stirring, 12.2 g (0.1 mol) 1,3-propanesultone was dissolved in 50 mL ethyl acetate, then 10.1 g (0.1 mol) triethylamine was dropped slowly into the solution at 50 °C. The mixture was subsequently stirred for 2 h, and the resultant mixture was filtered to get a white precipitate, which was washed with 30 mL ethyl acetate for three times and dried at 100 °C for 2 h to get 20.6 g white powder NET_3-PS and the yield was 92.4 %. Secondly, 11.15 g (0.05 mol) NET_3-PS was dissolved in 15 mL water, and 4.9 g (0.05 mol) hydrochloric acid was slowly dropped into the solution at room temperature (RT). After dropping, the mixture was stirred at RT for 30 min, heated in an oil bath at about 90 °C for 2 h, and the water under reduced pressure at 90 °C. We got 12.6 g of a white viscous liquid [HO_3S-$(CH_2)_3$-NEt_3]Cl at RT. Finally, under the protection of nitrogen, [HO_3S-$(CH_2)_3$-NEt_3]Cl reacting with various amounts of $ZnCl_2$ at 60 °C for 2 h to get a viscous liquid of [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ at RT. The reaction formula of [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) is shown in Scheme 1.

[HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$: IR (KBr): $v = 3351$, 2989, 1622, 1486, 1458, 1228, 1151, 1043, 952, 816, 794, 735, 694, 600, 518 cm^{-1}; ^1H NMR (500 MHz, D_2O): $\delta = 1.15$ (*t*, 2H), 1.92 (*m*, 2H), 2.81 (*q*, 3H), 3.16 (*t*, 2H), 4.67 (*t*, 1H), 2.85 (*t*, $J = 7.5$ Hz, 2H), 2.25 (m, 2H); ^{13}C NMR (500 MHz, D_2O): $\delta = 6.75$, 17.28, 47.73, 52.12, 54.23.



Scheme 1 Synthesis of ILs [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$). X: the molar fraction of $ZnCl_2$

Synthesis of [mim][XCl] ILs

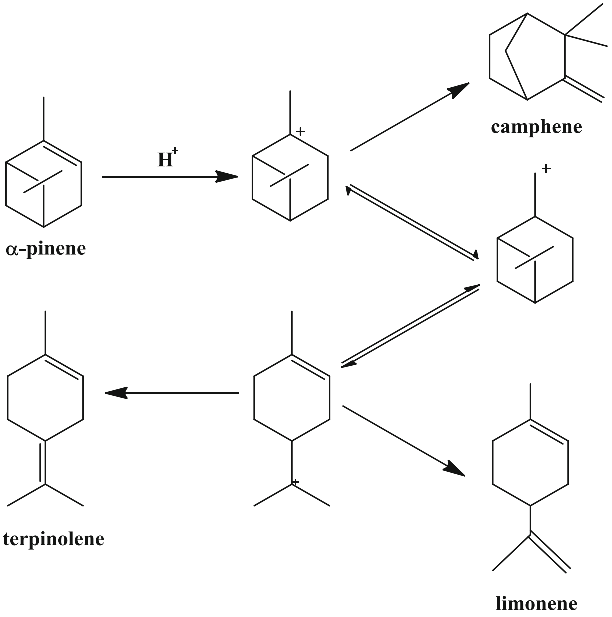
The [mim][XCl] ILs was prepared as follows:

Firstly, N-methylimidazole was reacted with equal-mole hydrochloric acid at 50 °C for 5 h to get [mim]Cl. After the reaction finished, the mixture was washed three times with ethyl acetate and dried under reduced pressure at 90 °C for 4 h.

Secondly, Lewis acidic ILs were synthesized through the reactions between the above products and different metal chlorides, including $AlCl_3$, $FeCl_3$, $ZnCl_2$, $TiCl_4$ and $SnCl_4$, until these two materials completely mixed at 60 °C under the protection of nitrogen.

Isomerization of α-pinene

The formula on isomerization of α-pinene is shown in Scheme 2. The reactions were achieved in a glass reactor provided with a magnetic stirrer, sampling port, temperature bath, and condenser. Then 0.04 mol α-pinene was loaded into the reactor, stirred, and warmed to the desired temperature. Once the desired temperature was attained, the catalyst was loaded into the reactor. Then, the solvent system became a homogeneous phase. The reaction products were analyzed by gas chromatography by taking samples at 120, 180, 240, 300, and 360 min after adding the catalyst, respectively. When the reaction finished, the products cooled to RT at the end of the reaction. When the temperature fell down to RT, the catalyst can separate by centrifugation from the reaction system and easily be recovered.



Scheme 2 The isomerization of α-pinene

Reaction liquid was washed to neutrality with a Na_2CO_3 solution and a saturated NaCl solution, then immediately analyzed with a GC17 Shimadzu gas chromatograph equipped with a FID and a capillary DB1 column (60 m in length). The reaction products were identified by comparing the retention times of terpene standards or using their Kovats index with confirmation by mass spectroscopy. The compounds present in the samples were identified in a Thermofinigan GC Top 8000/Voyager MS Gas chromatograph/mass spectrometer system. The column used was an All Tech AT-5 capillary column 30 m in length and 0.25 mm in internal diameter. The temperatures of the injector and the transference line were maintained constant at 260 °C. The initial temperature of the furnace was maintained at 80 °C for 2 min. Then it was increased at the rate of 4 °C/min up to 160 °C, and kept for 2 min. Finally, the temperature was raised at a rate of 10 °C/min up to 250 °C, maintained for 2 min.

Results and discussion

Effect of different catalysts on the isomerization of α-pinene

The catalytic performance of different catalysts on the isomerization of α-pinene is given in Table 1. First of all, we tested a blank in the experiment and the conversion of α-pinene was 4.9 % and the selectivity for camphene was 15.4 % (Entry 1). When $ZnCl_2$ was chosen as the catalyst, the conversion of α-pinene was 94.6 %, and the selectivity for camphene was 50.4 % (Entry 2). But it was found that $ZnCl_2$ had some drawbacks limiting its further application, for example, its equipment

Table 1 Effect of the types of catalysts on the results of the reaction

Entry	Catalyst	Components of product (%)			C (%)	S (%)
		camphene	limonene	terpinolene		
1	No catalyst	1.23	1.31	1.91	4.9	15.4
2	$ZnCl_2$	47.67	18.02	14.51	94.6	50.4
3	[mimH]$ZnCl_3$	7.73	10.46	21.56	85.0	9.1
4	[mimH]$FeCl_4$	4.97	10.02	17.56	84.3	5.9
5	[mimH]$SnCl_5$	2.66	11.76	11.21	98.7	2.7
6	[mimH]$AlCl_4$	2.26	10.63	14.56	90.5	2.5
7	$[HSO_3(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2(x = 0.83)$	27.92	10.31	10.25	98.3	28.4
8	$[HSO_3(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2(x = 0.50)$	15.85	8.31	10.25	43.2	36.7
9	$[HSO_3(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2(x = 0.67)$	21.85	11.05	15.61	66.4	32.9
10	$[HSO_3(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2(x = 0.80)$	24.22	9.05	9.43	80.2	30.2
11	$[HSO_3(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2(x = 0.86)$	21.07	11.22	12.31	98.9	21.3

Reaction conditions: Entry 1: α-pinene 5.44 g. Entry 2: α-pinene 5.44 g, w($ZnCl_2$):w(α-pinene) = 3:100, reaction temperature 140 °C, and reaction time 10 h. Enter (3–11): α-pinene 0.04 mol, *n*(α-pinene):*n*(catalyst) = 1:1, reaction temperature 140 °C, and reaction time 4 h

C conversion of α-pinene, *S* selectivity for camphene

corrosion, tedious work-up procedures, environmental problems, and also it cannot be reused. Then, we chose $[ZnCl_3]^-$ as the anion to design and synthesize $[mimH][ZnCl_3]$ ILs as a Lewis acid, and investigated the catalytic efficiency, but the conversion of α-pinene was 85.0 % and the selectivity for camphene was only 9.1 % (Entry 3). At the same time, when the $[SnCl_5]^-$ and $[AlCl_4]^-$ were as the anions, the conversion of α-pinene was excellent . Nevertheless, the selectivity for camphene was just 2.5 % (Entry 5–6).

Therefore, to get new catalysts that are of excellent catalytic activity and selectivity for camphene, Bronsted-Lewis acidic functionalized ILs $[HSO_3\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ was designed and synthesized. As shown in Table 1, when the molar fraction of $ZnCl_2$ was 0.83, the conversion of α-pinene was 98.3 % and the selectivity for camphene was 28.4 % (Entry 7). When the Bronsted acid was introduced to the ILs, compared with the Entries (3–6), the conversion of α-pinene had great growth, and the selectivity for camphene was better . With the increase of the molar fraction of $ZnCl_2$, the conversion of α-pinene correspondingly improved, but the selectivity for camphene oppositely decreased. For example, when the molar fraction of $ZnCl_2$ was 0.50, the conversion of α-pinene was 43.2 % (Entry 8), which was lower compared with that of 0.86 of the molar fraction of $ZnCl_2$ (98.9 %, Entry 11), and the selectivity for camphene was 36.7 % (Entry 8), which was higher than that of 0.86 of the molar fraction of $ZnCl_2$ (21.3 %, Entry 11), respectively. This may be ascribed to the different acidity of ILs by the molar fraction of $ZnCl_2$. To characterize the Lewis acidity of the prepared catalyst, acetonitrile, a weak Lewis base, was used as the probe for FTIR analysis. It was reported that acetonitrile had two characteristic absorption peaks around 2290 and 2250 cm^{-1}, and if the reactive group of CN reacted with Lewis acid, thus, it would be a new absorption peak at 2200–2400 cm^{-1} [23]. As shown in Fig. 1, the characteristic absorption peaks of acetonitrile/$[HSO_3\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.5$) were nearly the same as that of acetonitrile, indicating that $[HSO_3\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.5$) was not of

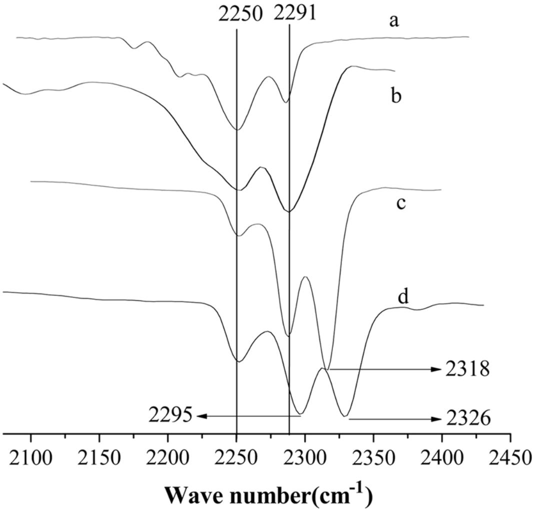


Fig. 1 FT-IR spectra of ILs using acetonitrile as probe. **a** Pure acetonitrile; **b** Acetonitrile/$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.5$); **c** Acetonitrile/$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.8$); **d** Acetonitrile/$[HO_3S\text{-}(CH_2)_3\text{-}mim]Cl\text{-}ZnCl_2$ ($x = 0.83$). Acetonitrile is 1/2 in volume in the samples of (**b**–**d**)

Lewis acidity. In the spectra of acetonitrile/[HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.8$) and acetonitrile/[HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$), besides the two peaks mentioned above, new absorption peaks at 2318 and 2326 cm^{-1} appeared. This demonstrated that both [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.8$) and [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) had Lewis acidity. Moreover, the peak of [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) was higher than that of [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.8$), which displayed that the Lewis acidity of [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) was stronger than that of [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.8$). It was found that the conversion of α-pinene could be increased in Lewis acidity [24]. However, the selectivity for camphene decreased to 21.3 %, when the Lewis acidity of ILs was too strong ($x = 0.86$). Therefore, taking account of all considerations, we concluded that the Brønsted–Lewis acidic ILs [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) could give excellent catalytic performance for the isomerization of α-pinene. Next, the process optimization on the isomerization of α-pinene using [HSO_3-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) as catalysts is discussed in detail.

The optimization of reaction conditions

The performance of the catalyst has a great influence on the conversion of α-pinene and the selectivity for camphene in the isomerization of α-pinene. However, the performance of the catalyst will be affected by many factors. Thus, we investigated the related condition parameters affecting the performance of acidic functionalized ILs in the isomerization of α-pinene, including of the amount of catalyst, reaction temperatures, and reaction time.

Effect of the amount of ILs

Table 2 shows the effects of different amounts of catalyst [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$) on the isomerization of α-pinene. With increasing the amount of [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ ($x = 0.83$), the conversion of α-pinene did not obviously change, but the selectivity for camphene apparently increased and then decreased. As we observed from Table 2, when n(α-pinene):n(ILs) was 9:1, the

Table 2 Effect of different amounts of ILs on the results

n(α-pinene):n(ILs)	Components of product (%)			C (%)	S (%)
	Camphene	Limonene	Terpinolene		
11:1	42.22	7.86	7.24	96.4	43.8
10:1	50.97	8.79	8.59	96.9	52.6
9:1	63.24	8.83	11.88	97.6	64.8
8:1	55.07	12.92	20.21	98.7	55.8
7:1	53.43	15.32	21.37	98.4	54.3

Reaction conditions: α-pinene 0.04 mol, reaction temperature 140 °C, reaction time 4 h

C conversion of α-pinene, *S* selectivity for camphene

selectivity for camphene could reach a maximum value of 64.8 %. The result may be explained by the increase of ILs, the superficial area of catalyst became larger, and the activation performance became powerful, so the conversion of α-pinene became increscent. But the strong catalyst activation leads to increasing side effects. Over all considerations, the optimal dosage of catalyst was *n*(α-pinene):*n*(ILs) = 9:1.

Influence of reaction temperatures

The influence of different reaction temperatures on the isomerization of α-pinene was investigated by monitoring the conversion of α-pinene and the selectivity for camphene through varying the reaction temperature (120, 130, 140, 150, 160 °C) (Table 3). From Table 3, with the enhancement of temperature, the conversion of α-pinene dramatically increased, but the selectivity for camphene decreased. When the reaction temperature was 140 °C, the selectivity for camphene could reach 64.8 %. The reason might be that, the higher the temperature, the greater the electron shaking, the conversion of α-pinene increased and reduced the selectivity of the reaction by increasing the number of accessible reaction pathways [25]. Therefore, 140 °C was the optimal reaction temperature.

Optimization of reaction time

We investigated the effect of reaction time (2, 3, 4, 5, 6 h) on the isomerization of α-pinene as shown in Table 4. The conversion of α-pinene increased with the aid of reaction time. However, the selectivity for camphene obviously improved and decreased. At the reaction time of 4 h, the selectivity for camphene could reach 64.8 %, consistent with that of the amount of catalyst (9:1) and the reaction temperature (140 °C). Therefore, the optimal reaction time of 4 h was chosen.

Based on these optimal reaction conditions, with the synthesized catalyst of acidic functionalized ILs $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ for the isomerization of α-pinene, we obtained 97.6 % of the conversion of α-pinene and 64.8 % of the selectivity for camphene, which was better than previous reported [3].

Table 3 Influence of reaction temperatures on the results

Reaction temperature (°C)	Components of product (%)			C (%)	S (%)
	Camphene	Limonene	Terpinolene		
120	15.30	3.17	5.93	22.9	66.8
130	28.07	4.91	14.86	56.7	49.5
140	63.24	8.83	11.88	97.6	64.8
150	46.51	7.43	29.56	97.1	47.9
160	41.06	5.86	26.24	98.7	41.6

Reaction conditions: α-pinene 0.04 mol, *n*(α-pinene):*n*(ILs) = 9:1, reaction time 4 h

C conversion of α-pinene, *S* selectivity for camphene

Table 4 Effect of reaction time on the results

Reaction time (h)	Components of product (%)			C (%)	S (%)
	Camphene	Limonene	Terpinolene		
2	39.24	10.31	8.31	77.1	50.9
3	47.70	3.74	10.54	86.1	55.4
4	63.24	8.83	11.88	97.6	64.8
5	56.66	8.89	17.36	98.2	57.7
6	48.46	9.13	22.14	98.7	49.1

Reaction conditions: α-pinene 0.04 mol, n(α-pinene):n(ILs) = 9:1, reaction temperature 140 °C

C conversion of α-pinene, *S* selectivity for camphene

Table 5 The results of repeated use of $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.83$)

Times	C (%)	S (%)
1	97.6	64.8
2	95.3	62.6
3	94.7	60.3
4	93.2	59.7

Reaction conditions: α-pinene 0.04 mol, n(α-pinene):n(ILs) = 9:1, reaction temperature 140 °C, reaction time 4 h

C conversion of α-pinene, *S* selectivity for camphene

The reusability of the ILs

When the reaction finished and the reaction temperature declined below 40 °C, the ILs became solid in the lower layer and the product was in the top layer, and we obtained the ILs in the low layer after centrifugation, and the ILs could be entirely separated from α-pinene and easily be recovered. The reusability of $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.83$) was investigated (Table 5). It could be seen that the conversion of α-pinene and the selectivity for camphene was almost unchanged after $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.83$) was repeatedly used four times, which indicated that the Brønsted–Lewis acidic functionalized ILs had excellent recyclability in the isomerization of α-pinene. This result was explained in terms of two aspects. First, in the $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ ($x = 0.83$), an alkane sulfonic acid group was catalytically active for the isomerization, which was covalently tethered to the ILs cation, and this group could not be easily lost. Second, the $[ZnCl_3]^-$ anion of the ILs, which was inert and stable in water or Brønsted acid and its activity was also not easily lost, was the site of catalytic activity for the isomerization. At the same time, acid strength was also tested. The FT-IR spectra of ILs using acetonitrile as the probe is shown in Fig. 2. It can be clearly observed the reused (four times) ILs acid strength was nearly unchanged compared with that of the fresh ILs, which indicated that the structure of the reused ILs was retained and the synthesized ILs exhibited superb recycling ability.

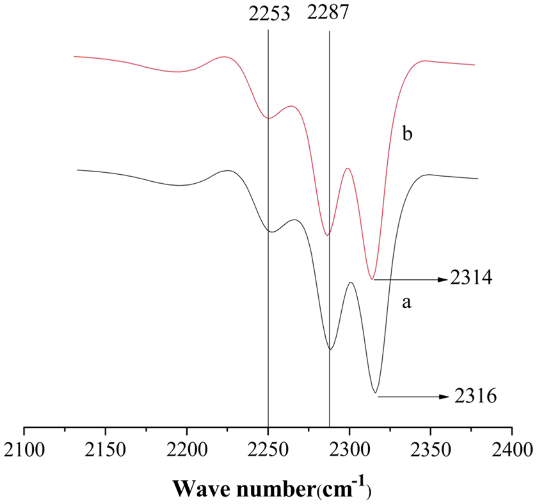


Fig. 2 FT-IR spectra of ILs using acetonitrile as probe (**a** New ILs, **b** Reused ILs for four times)

Conclusions

The Brønsted–Lewis acidic functionalized ILs of [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ was synthesized, characterized, and used in the isomerization of α-pinene. Compared with traditional catalysts, the Brønsted–Lewis functionalized acidic ILs exhibited many outstanding advantages, such as simplicity, efficiency, and easy product isolation. The optimum conditions for isomerization were obtained as follows: n(α-pinene):n(ILs) = 9:1, reaction temperature 140 °C, and reaction time 4 h. Under the optimal conditions, the conversion of α-pinene was 97.6 % and the selectivity for camphene was 64.8 %. The [HO_3S-$(CH_2)_3$-NEt_3]Cl-$ZnCl_2$ catalyst could be recycled up to four times and nearly no loss in activity was observed. Thus, more researches should be done to improve the catalytic performance of the Brønsted–Lewis acidic functionalized ILs.

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References

1. P.Q. Yao, L.H. Zhu, J. Yang, Appl. Mech. Mater. **483**, 134 (2014)
2. Y.H. Wu, F.P. Tian, M. He, T.X. Cai, Chinese J. Catal. **32**, 1138 (2011)
3. J. Wang, W.M. Hua, Y.H. Yue, Z. Gao, Biores. Technol. **101**, 7224 (2010)
4. A. Burcu, G. Gönül, Chem. Eng. J. **168**, 1311 (2011)
5. J.Y. Luo, C.G. Ni, Z.G. Wang, X.N. An, J. Nanjing For. Univ. Nat. Sci. Ed. **28**, 51 (2004)
6. X.X. Duan, G.R. Sun, Z. Sun, J.X. Li, S.T. Wang, X.H. Wang, S.W. Li, Z.J. Jiang, Catal. Commun. **42**, 125 (2013)
7. D.C. Forbes, K.J. Weaver, J. Mol. Catal. A **214**, 129 (2004)
8. H.L. Li, S.T. Yu, F.S. Liu, C.X. Xie, L. Li, Catal. Commun. **8**, 1759 (2007)
9. C.X. Xie, H.L. Li, L. Li, S.T. Yu, F.S. Liu, J. Hazard. Mater. **15**, 1847 (2008)
10. W.J. Zhao, X.Z. Jiang, Catal. Lett. **107**, 123 (2006)

11. T. Li, Y.S. Souma, Q. Xu, Catal. Today **111**, 288 (2006)
12. W.O. Siodłak, K. Dziubek, Appl. Catal. A Gen. **484**, 134 (2014)
13. H.B. Xing, T. Wang, Z.H. Zhou, Y.Y. Dai, Ind. Eng. Chem. Res. **44**, 4147 (2005)
14. J. Joni, M. Haumann, P. Wasserscheid, Adv. Synth. Catal. **351**, 423 (2009)
15. J. Li, Y. Zhou, D. Mao, G.J. Chen, X.C. Wang, X.N. Yang, M. Wang, L.M. Peng, J. Wang, Chem. Eng. J. **254**, 54 (2014)
16. X.L. Shi, H.K. Lin, P.Y. Li, W.Q. Zhang, Chem. Catal. Chem. **6**, 2947 (2014)
17. C. Hardacre, P. Nancarrow, D.W. Rooney, J.M. Thompson, Org. Process Res. Dev. **12**, 1156 (2008)
18. D.H. Yin, C.Z. Li, L. Tao, N.Y. Yu, S. Hua, D.L. Yin, J. Mol. Catal. A **245**, 260 (2006)
19. M.Y. Yoon, J.H. Kim, D.S. Choi, U.S. Shin, J.Y. Lee, C.E. Song, Adv. Synth. Catal. **349**, 1725 (2007)
20. R. Kore, R. Srivastava, J. Mol. Catal. A Chem. **376**, 90 (2013)
21. S. Guo, Z.Y. Du, S.G. Zhang, D.M. Li, Z.P. Li, Y.Q. Deng, Green Chem. **8**, 296 (2006)
22. C.Z. Li, D.H. Yin, B.M. Li, L. Tao, D.L. Yin, Chin. J. Catal. **26**, 194 (2005)
23. S. Liu, C. Xie, S. Yu, F. Liu, Catal. Commun. **9**, 2030 (2008)
24. Y. Liu, S.W. Liu, L. Li, Sci. Technol. Chem. Ind. **5**, 21 (2013)
25. S.W. Liu, L. Zhou, S.T. Yu, C.X. Xie, F.S. Liu, Z.Q. Song, Biomass Bioenerg. **57**, 238 (2013)