新型Brønsted-Lewis酸性离子液体的合成及其在松香二聚反应中的应用

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摘要： 合成、表征了新型 Brønsted-Lewis 酸性离子液体 1-(3-磺酸)-丙基-3-甲基咪唑氯锌酸盐 ([HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$)，并将其用于催化松香二聚反应. 结果表明, [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (ZnCl$_2$摩尔分数 $x > 0.5$) 为 Brønsted 和 Lewis 双酸性，且以 [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ ($x = 0.64$) 的催化性能较佳. 在松香 5.0 g，甲苯15 g，离子液体质量分数 5%，反应温度 110 ^{o}C 和反应时间 4 h 的较佳实验条件下，所得产物聚合松香的软化点为 118 ^{o}C. 此外，该催化剂的使用有利于产物的分离且分离的离子液体催化剂具有良好的重复使用性能.

关键词： Brønsted-Lewis酸性离子液体；松香；二聚反应；催化

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A Brønsted-Lewis Acidic Ionic Liquid: Its Synthesis and Use as the Catalyst in Rosin Dimerization

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Abstract: Brønsted-Lewis acidic ionic liquids 1-(3-sulfonic acid)-propyl-3-methylimidazole chlorozincinates ([HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$) were synthesized and characterized. The characterization results indicated that [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (molar fraction of ZnCl$_2$ $x > 0.5$) had both Brønsted and Lewis acid properties. The catalytic properties of these ionic liquids were investigated using the dimerization of rosin, and it was shown that ionic liquid [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ ($x = 0.64$) was a good catalyst. Under the optimum conditions for polymerization, i.e., rosin 5.0 g, toluene 15 g, the mass fraction of ionic liquid 5%, reaction temperature 110 ^{o}C, and reaction time 4 h, a product with the softening point of 118 ^{o}C was obtained. It was also found that the product was easily separated from the reaction mixture and the ionic liquid catalyst had good reusability.

Key words: Brønsted-Lewis acidic ionic liquid; rosin; dimerization; catalysis

Rosin is a kind of solid resinous mass obtained naturally from pine trees. Rosin mainly contains resin acids (abietic and pimaric) and a small amount of nonacidic components. The abietic resin acids contain neoabietic acid, palustric acid, abietic acid, etc., and the pimaric resin acids include pimaric acid, isopimaric acid, sandarecopimaric acid, etc. Due to the conjugated double bonds and carboxyl group,

resin acids can be easily oxidized by air and crystallized in the process of usage. To solve these problems, rosin is modified to polymerized rosin, which is produced by the dimerization of abietic acids. Polymerized rosin is widely used in paints, varnishes, cosmetics, printing ink, binding agents, etc. and is one of the most important products of rosin derivatives [1–3]. The dimerization of rosin is actually

the dimerization of abietic acid. Other abietic resin acids and pimaric resin acids are not dimerized due to their large steric hindrance, but the former can be isomerized to abietic acid. Traditionally, Brønsted acid (H_2SO_4 or HCOOH), Lewis acid (BCl_3 or $ZnCl_2$), or their mixture were used in the dimerization of rosin [4,5]. The Brønsted acid is good for the isomerization of the resin acids, and the Lewis acid for the dimerization of abietic acid [5]. The drawbacks of these catalysts include the serious corrosion of equipment, the complicated separation procedure, environmental pollution, and non-recyclability of the catalysts.

In recent years, Brønsted and Lewis acidic ionic liquids (ILs) as environmentally friendly catalysts have received much attention from researchers. Several organic reactions, such as esterification [6–9], carbonylation [10,11], polymerization [12,13], Friedel-Crafts [14–19], Beckmann [20,21], and Diels-Alder [22], have been reported to proceed in acidic ILs with excellent selectivity and yield. However, these ILs only possess either Brønsted acidity or Lewis acidity. Methods for the preparation of Brønsted and Lewis acidic (represented as Brønsted-Lewis acidic) catalyst systems have even been reported by bubbling dried HCl gas into the Lewis acidic ILs [23,24], but these are mixtures and not real Brønsted-Lewis acidic ILs. Moerover, the use of HCl gas is very hazardous, and it is easily lost in the process of reuse because of its high volatility.

In our laboratory, studies on the polymerization of rosin catalyzed by both traditional catalysts and acidic IL catalysts have been performed [25,26]. Compared with traditional catalysts, the IL catalysts exhibited many outstanding advantages, such as simplicity and efficiency of the method and easy product isolation. Therefore, new kinds of stable Brønsted-Lewis acidic ILs ($[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$) were synthesized, characterized, and used in the polymerization of rosin in the present paper.

1 Experimental

1.1 Catalyst preparation

Extra-rosin (pimaric acid 11.9%, isopimaric acid 5.3%, sandarecopimaric acid 1.7%, levopimaric acid 4.7%, neoabietic acid 14.6%, palustric acid 21.5%, dehydroabietic acid 5.0%, and abietic acid 35.2%), 1-methylimidazole (99.8%, Zhejiang Kaile Chemicals Co. Ltd. China), 1,3-propane sultone (1,2-oxathiolane-2,2-dioxide, 99.7%,

Wuhan Fengfan Chemicals Co. Ltd. China), and other chemicals (analytic purity) were commercially available and used without further purification.

Under vigorous stirring, 12.2 g (0.1 mol) 1,3-propane sulfone was dissolved in 50 ml acetate ether, and then 8.2 g (0.1 mol) 1-methylimidazole was dropped slowly in the solution at 50 °C. The mixture was then stirred for 2 h, and the resultant mixture was filtered to get a white precipitate. The precipitate was washed with 30 ml acetate ether three times and dried at 100 °C for 2 h to get 18.6 g MIM-PS as a white powder. Then, 10.2 g (0.05 mol) MIM-PS was dissolved in 15 ml water, and 4.9 g (0.05 mol) hydrochloric acid was dropped slowly at room temperature. After dropping, the mixture was stirred at room temperature for 30 min and further heated in an oil bath at about 90 °C for 2 h. After that, the water of the mixture was removed under vacuum at 90 °C to get 11.6 g 1-(3-sulfonic acid)-propyl-3-methylimidazolechloride ($[HO_3S-(CH_2)_3-mim]Cl$) as a white viscous liquid at room temperature. MIM-PS：IR (KBr): ν = 3464, 3199, 2989, 1629, 1485, 1454, 1222, 1149, 1041, 735, 603, 518 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ = 8.70 (s, 1H), 7.49 (s, 1H), 7.40 (s, 1H), 4.30 (t, J = 7.5 Hz, 2H), 3.81 (s, 3 H), 2.85 (t, J = 7.5 Hz, 2H), 2.25 (m, 2H); ^{13}C NMR (500 MHz, D_2O): δ = 135.82, 123.50, 121.85, 47.41, 46.97, 35.46, 24.73. $HO_3S-(CH_2)_3-mim]Cl$：IR (KBr): ν = 3382, 3142, 3117, 1720, 1653, 1572, 1227, 1171, 1029, 807, 592 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ = 8.53 (s, 1H), 7.32 (s, 1H), 7.25 (s, 1H), 4.16 (t, J = 7.3 Hz, 2H), 3.71 (s, 3H), 2.71 (t, J = 7.3 Hz, 2H), 2.11 (m, 2H)；^{13}C NMR (500 MHz, D_2O)：δ = 134.72, 123.31, 122.16, 47.75, 46.92, 35.26, 24.73.

$[HO_3S-(CH_2)_3-mim]Cl$ was reacted with various amounts of $ZnCl_2$ at 60 °C for 2 h to get $[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ as a viscous liquid at room temperature. With an increase of the $ZnCl_2$ mass, the viscosity of the obtained ILs also increased. The Lewis acidity of IL was varied by the $ZnCl_2$ mass. When the molar fraction of $ZnCl_2$ (x) was less than 0.5, the ILs only processed Brønsted acidity and no Lewis acidity. When the molar fraction of $ZnCl_2$ was over 0.5, the Lewis acidic behavior of ILs was controlled largely by the reaction in Scheme 1. $[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (x = 0.64): IR (KBr): ν = 3452, 3158, 3117, 2973, 1627, 1580, 1467, 1249, 1171, 1046, 838, 751, 628, 533 cm^{-1}. ^1H NMR (500 MHz, DMSO)：δ = 8.50 (s, 1H), 7.29 (s, 1H), 7.24 (s, 1H), 4.14 (t, J = 7.5 Hz, 2H), 3.65 (s, 3H), 2.67 (t, J = 7.5 Hz, 2H), 2.08 (m, 2H). ^{13}C NMR (500 MHz, DMSO):
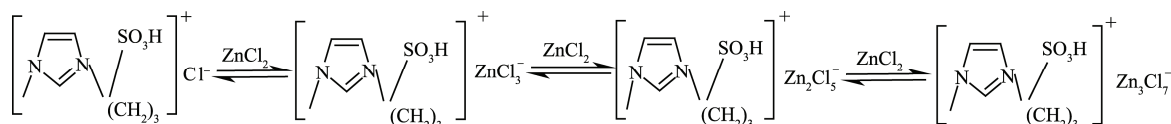

Scheme 1. ILs based on trichlorozincinate anions.

$\delta = 133.81, 121.28, 120.04, 46.57, 45.86, 34.32, 23.35$; Zn^{2+} = 23.50% (GB1625-79). ESI-MS: m/z (+) 204.9 and 286.8, m/z (−) 170.7 and 306.6.

1.2 Catalyst characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 510P FT-IR spectrometer in the range of 4 500–400 cm^{-1}. NMR spectra were taken on a Bruker AV500 Fourier-transform spectrometer with reference to SiMe$_4$ using solvent dimethyl sulphoxide (DMSO) containing 5% sample. Electrospray ionization-mass spectrometry (ESI-MS) was performed by a Shimadzu LC-MS 2010A equipped with a Shimpeck VP-ODS 15 cm × 2.0 mm and a Shimpack GVP-ODS guard column 5 cm × 2.0 mm, using a mixed solvent of DMSO and methanol containing 1% sample. Ions were formed for mass spectrometric detection using positive ion electron impact ionization (EI) at the electron energy of 70 eV.

1.3 Catalytic performance

In a typical experiment, 5 g rosin, 15 g solvent toluene, and 1 g catalyst were reacted at 110 $^{\circ}$C for 4 h. After reaction, the upper layer (solvent and unreacted reactant) containing the polymerized rosin was separated from the ILs catalyst layer at the bottom of the flask simply by decantation. The ILs catalyst layer was reused without any disposal. Without adding water, the product of the polymerized rosin was obtained after removing the solvent by distillation. The softening point of product was measured by a SDY-2806 asphalt softening point machine according to the circular ball method [4]. The color and acid value were measured by the Gardena color method and a chemical titrant method, respectively. The yield of product in all experiments was about 95% and not given in this paper. The dimerization reaction is shown in Scheme 2.
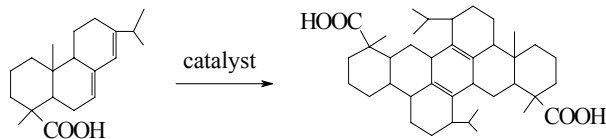
Scheme 2. The dimerization of abietic acid.

2 Results and discussion

2.1 Characterization

The ESI-MS results showed that the cations of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) were mainly [HO$_3$S-(CH$_2$)$_3$-mim]$^+$ (m/z: 204.9) and [mim-HO$_3$S-(CH$_2$)$_3$-mim]$^+$

(m/z: 286.8). The latter was the complex of the [HO$_3$S-(CH$_2$)$_3$-mim]$^+$ and 1-methylimidazole. [HO$_3$S-(CH$_2$)$_3$-mim]$^+$ possessed sulfonic acid as a Brønsted acid. The anions of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) were mainly [ZnCl$_3$]$^-$ (m/z: 170.7) and [Zn$_2$Cl$_5$]$^-$ (m/z: 306.60), and Cl$^-$ was not found, which indicated that Cl$^-$ was completely reacted with ZnCl$_2$. The anion [Zn$_2$Cl$_5$]$^-$ resulting from the reaction of [ZnCl$_3$]$^-$ and ZnCl$_2$ has Lewis acidity. Therefore, it can be concluded that ZnCl$_2$ did not react with the sulfonic acid of [HO$_3$S-(CH$_2$)$_3$-mim]Cl, and [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) was Brønsted and Lewis acidic.

Acetonitrile is a weak base and usually used as the FT-IR spectroscopy probe to characterize the acidic strength of Lewis acids. In general, the nitrile group is reacted with the Lewis acid to produce a CN-Lewis complex, which shows a new absorption peak at 2200–2400 cm^{-1} in the FT-IR spectra. With the increase of the Lewis acidic strength, this absorption peak moves to higher wavenumbers. Thus, acetonitrile has been used as a probe to characterize the Lewis acidic strength of ILs [16,27]. Here, this method was also employed to indicate the Lewis acidic strength of the synthesized ILs. As shown in Fig. 1, the peaks of acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.5) were nearly the same as that of acetonitrile. They both had two absorption peaks at 2260 and 2285 cm^{-1}, which indicated that [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.5) was not Lewis acidic. In the spectra of acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.6) and acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64), new absorption peaks at 2314 and 2316 cm^{-1} appeared besides the two peaks mentioned above, respectively. The new absorption peak was the characteristic absorption peak of the CN-Lewis complex. This means that
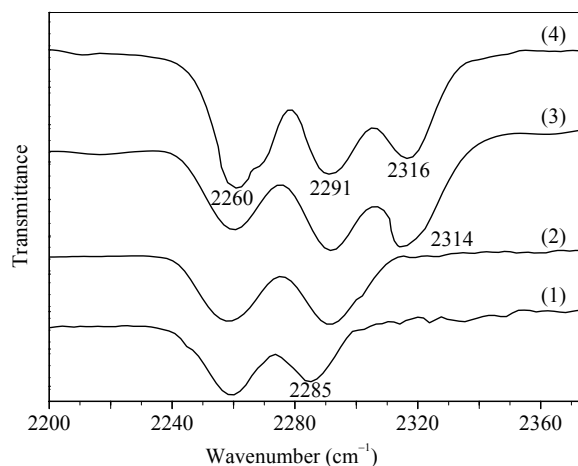

Fig. 1. FT-IR spectra of ILs using acetonitrile as probe. (1) Pure acetonitrile; (2) Acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.5); (3) Acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.6); (4) Acetonitrile/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64). Acetonitrile is 1/2 in volume in the samples of (2)–(4).

both [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.6) and [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) had Lewis acidity. More-over, the wavenumber of the peak of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) was higher than that of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.6), which meant that the Lewis acidity of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) was stronger than that of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.6).

As a FT-IR spectroscopy probe, pyridine can react with Brønsted and Lewis acids and to produce the cation [PyH]$^+$ and the Py-Lewis complex, respectively. [PyH]$^+$ has an absorption peak near 1540 cm^{-1} in the FT-IR spectra, and the absorption peak of Py-Lewis is close to 1450 cm^{-1}. By observing these two peaks, the acidic type of the sample can be deduced. This method has been used to characterize the acidic type of solid acids and Lewis acidic ILs [28]. Therefore, this method was also used to characterize [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64). As shown in Fig. 2, compared with the spectra of [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64), two new absorption peaks of 1535 and 1452 cm^{-1} appeared in the FT-IR spectra of pyridine/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64), which indicated that [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) was Brønsted and Lewis acidic.
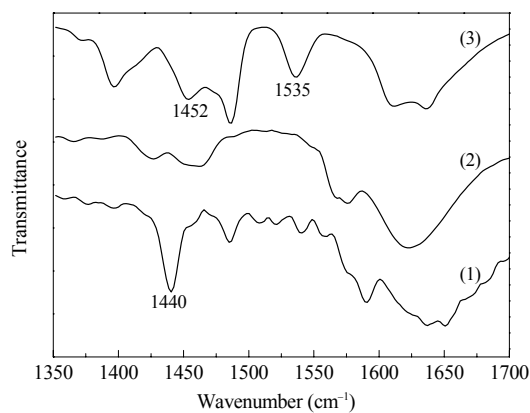
Fig. 2. FT-IR spectra of samples using pyridine as probe. (1) Pure pyridine; (2) [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64); (3) Pyridine/[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64). Pyridine is 1/2 in volume.

2.2 Effect of different catalysts on the polymerization of rosin

The catalytic performance of different catalysts is shown in Table 1. When the catalyst was H$_2$SO$_4$-ZnCl$_2$, the softening point of polymerized rosin reached 134 ^{o}C, but the acid value was less than 140 mg/g, and the color was black. In particular, the separation of the acidic sludge or emulsion during work-up in this process was very troublesome. When Lewis acidic ZnCl$_2$ and Brønsted acidic IL [HO$_3$S-(CH$_2$)$_3$-mim]Cl were used as catalysts, the dimerization reaction was slight, and the softening points of the products were

Table 1 Effect of different catalysts on the dimerization of rosin

Catalyst	Softening point (^{o}C)	Acid value (mg/g)
None	97	163.7
H$_2$SO$_4$-ZnCl$_2$ (x = 0.42)	134	138.2
ZnCl$_2$	102	159.2
[HO$_3$S-(CH$_2$)$_3$-mim]Cl	100	160.1
[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.50)	100	154.8
[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.60)	114	148.9
[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64)	118	148.7
[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.67)	102	157.8
[HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.69)	98	157.3

Reaction conditions: rosin 5 g, toluene 15 g, reaction time 4 h, reaction temperature 110 ^{o}C, catalyst 1 g.

102 and 100 ^{o}C, respectively. Compared with the blank experiment, these had almost no catalytic activity. The Lewis acidic ILs depended on the amount of ZnCl$_2$ in the [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$. With an increased amount of ZnCl$_2$, the Lewis acidity of ILs became stronger. Among the investigated ILs, the IL had no Lewis acidity when the molar fraction of ZnCl$_2$ was 0.5, and the softening point of the polymerized rosin was only 100 ^{o}C. This was equal to that of [HO$_3$S-(CH$_2$)$_3$-mim]Cl. When the molar fraction of ZnCl$_2$ was increased to 0.64, the softening point of the polymerized rosin reached 118 ^{o}C, which was 21 ^{o}C higher than that without the catalyst. It was concluded that the softening point of the product can be increased by an increase in Lewis acidity. However, the softening point of the polymerized rosin was decreased to about 100 ^{o}C when the Lewis acidity of ILs was too strong (x = 0.67 and 0.69). This may be because the viscosity of the ILs increased with the increase of ZnCl$_2$ mass. When the molar fraction of ZnCl$_2$ was more than 0.64, the IL dispersion was very bad in the reaction mixture. In all the experiments using ILs as the catalysts, the color of polymerized rosin was 8–9 ghana, and the acid value was close to 150 mg/g, which showed that there was almost no oxidation and decarboxylation of the rosin acids. Therefore, it was concluded that the Brønsted-Lewis acidic IL [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) gave good catalytic performance for the dimerization of rosin.

2.3 Effect of reaction conditions on the rosin polymerization

Table 2 shows the effects of amount of catalyst [HO$_3$S-(CH$_2$)$_3$-mim]Cl-ZnCl$_2$ (x = 0.64) on the polymerization of rosin. The dosage of the catalyst is the concentration of the catalyst in the reaction mixture. When the dosage of catalyst was 5.0%, 118 ^{o}C as the softening point was achieved. However, no obvious increase in the softening point was

observed with the further increase of the catalyst dosage. Therefore, the optimal dosage of catalyst was 5.0%.

The effect of reaction temperature on the polymerization was investigated by varying the reaction temperature from 90 to 120 °C. The results are also given in Table 2. The catalyst exhibited outstanding catalytic properties at 110 °C, and the softening point of polymerized rosin reached 118 °C. Therefore, 110 °C was the optimal reaction temperature.

The effect of reaction time on the polymerization was investigated by varying the reaction time from 3 to 6 h. As shown in Table 2, no obvious change was observed after 4 h of reaction. Therefore, the optimal reaction time was 4 h.

Table 2　Effect of reaction conditions on the dimerization of rosin

| Catalyst dosage (%)	Reaction temperature (°C)	Reaction time (h)	Softening point (°C)	Acid value (mg/g)
2.5	110	4	102	164.6
5.0	110	4	118	148.7
7.5	110	4	117	144.3
10.0	110	4	120	136.6
5.0	90	4	106	161.5
5.0	100	4	112	152.4
5.0	110	4	118	148.7
5.0	120	4	120	138.7
5.0	110	3	112	150.6
5.0	110	4	118	148.7
5.0	110	5	119	142.2
5.0	110	6	118	136.5

Reaction conditions: rosin 5 g, toluene 15 g.

2.4　Reuse of the ionic liquid

$[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (x = 0.64) was selected to investigate the reusability of the ILs. The results are given in Table 3. It can be seen that the softening point of the polymerized rosin was almost unchanged after $[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (x = 0.64) was repeatedly used five times, which indicated that the Brønsted-Lewis acidic ILs had excellent recyclability in the dimerization of rosin. This result was explained in terms of two aspects. First, in the $[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (x = 0.64), an alkane sulfonic acid group was catalytically active for the isomerization. This was covalently tethered to the IL cation, and this group

Table 3　Reuse of Brønsted-Lewis acidic ILs

Cycle	Softening point (°C)	Acid value (mg/g)
1	116	151.7
2	118	148.2
3	116	150.1
4	117	154.8
5	115	151.9

cannot be easily lost. Second, the $[Zn_2Cl_5]^-$ anion of the IL was the site of catalytic activity for the dimerization. It was inert and stable in water or Brønsted acid, so its activity was also not easily lost. In order to show the intactness of the repeatedly used ILs, the FT-IR spectra are shown in Fig. 3. As shown in Fig. 3, the FT-IR spectra of the reused (five times) IL were almost similar to that of the unused IL. It was clear that the structure of the reused IL was retained.
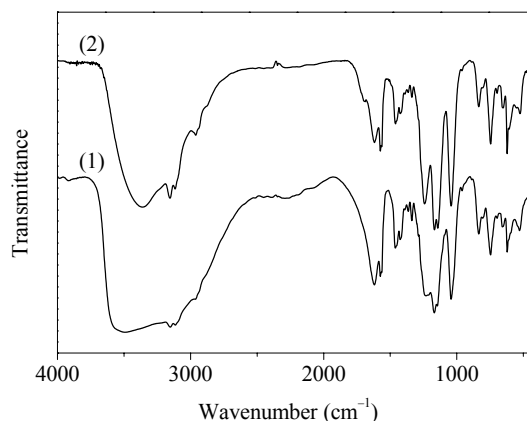
Fig. 3. FT-IR spectra of $[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (x = 0.64). (1) Unused IL; (2) Repeatedly used five times.

3　Conclusions

Brønsted-Lewis acidic ILs were synthesized, characterized, and used in the dimerization of rosin. The cation contributed to Brønsted acidity and mainly catalyzed the isomerization of the non-abietic acids. The anion gave Lewis acidity to the ILs and catalyzed the dimerization reaction of abietic acid. Compared with traditional catalysts, the Brønsted-Lewis acidic ILs exhibit many outstanding advantages, such as simplicity, efficiency, and easy product isolation. However, the softening point of the product was less than that of the traditional catalysts. Thus, more research should be done to improve the catalytic performance of these Brønsted-Lewis acidic ILs.

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