Chlorination of Toluene to *o*-Chlorotoluene Catalyzed by Ionic Liquids

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Abstract: Ionic liquids with [BMIM], [Et$_3$NH], and [BPy] cations and Al$_n$Cl$^-_{3n+1}$, Zn$_n$Cl$^-_{2n+1}$, and Cu$_n$Cl$^-_{n+1}$ anions were used as the catalysts for the chlorination of toluene with Cl$_2$. The Zn$_n$Cl$^-_{2n+1}$ containing ionic liquids with high Lewis acid strength had high catalytic activity for the selective chlorination of toluene to *o*-chlorotoluene via the electrophilic substitution reaction. Dichlorotoluenes were favorably formed when the Al$_n$Cl$^-_{3n+1}$ containing ionic liquids with both Lewis and Brönsted acid sites were used as the catalysts. When the Cu$_n$Cl$^-_{n+1}$ containing ionic liquids with weak Lewis acid strength were used as the catalysts, more benzyl chloride was formed via the radical chlorination of methyl group. When the [BMIM]Cl-2ZnCl$_2$ ionic liquid was used as the catalyst, after reacting at 80 °C for 8 h, the conversion of toluene was 99.7% and the selectivities of *o*-chlorotoluene, *p*-chlorotoluene, *m*-chlorotoluene, benzyl chloride, and dichlorotoluenes were 65.4%, 26.0%, 4.0%, 0.4%, and 4.2%, respectively. The [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst had good recycling performance.

Keywords: ionic liquids; toluene; chlorination; *o*-chlorotoluene

1. Introduction

o-Chlorotoluene as an important raw material has been widely used in the production of pharmaceuticals, pesticides, spices, and dyes [1–5]. *o*-Chlorotoluene has been commercially produced by the chlorination of toluene with gaseous chlorine over conventional Lewis acid catalysts, such as FeCl$_3$ and AlCl$_3$, accompanied by the formation of *m*-chlorotoluene, *p*-chlorotoluene, benzyl chloride, and dichlorotoluenes with high yields [6–8]. While using FeCl$_3$ catalyst, only one half of the product is *o*-chlorotoluene. However, the conventional Lewis acid catalysts, FeCl$_3$ and AlCl$_3$, cannot be recycled, causing serious equipment corrosion and environmental pollution [7].

Ionic liquids have attracted considerable attention in recent years because of their negligible vapor pressure, high thermal stability, high ionic conductivity, and composition tunability [9–11]. Ionic liquids have been widely used in the catalysis, electrochemistry, and separation fields [12–19]. When the ionic liquids were used as the catalysts for the polymerization of α-pinene and the redistribution reaction of methyltrichlorosilane with low-boiling residue to dimethyldichlorosilane, the Lewis acid ionic liquids had excellent catalytic activity and good reusability [16,20,21]. The ionic liquid acidities could be adjusted by using different types of cations and anions and changing their mole ratios. Their acidities are crucial for the acid-catalyzed reactions. However, to the best of our knowledge, catalytic chlorination of toluene with gaseous Cl$_2$ to chlorotoluene over ionic liquid catalyst has not been reported until now.

This paper reports the catalytic activities of the ionic liquid catalysts with the cation counterparts, triethylammonium ([Et$_3$NH]), 1-butyl-3-methylimidazolium ([BMIM]), and 1-butylpyridinium ([BPy]) and the anion counterparts, Zn$_n$Cl$^-_{2n+1}$, Al$_n$Cl$^-_{3n+1}$, and Cu$_n$Cl$^-_{n+1}$ for the chlorination reaction

between toluene and gaseous Cl_2. The Fourier transform infrared spectroscopy (FT-IR) technique with the use of pyridine as the molecular probe was used to determine the Lewis and Brönsted acid strengths of these ionic liquid catalysts. The catalytic chlorination reaction was investigated at different reaction temperatures, reaction time periods, and catalyst loadings. The reaction routes were also briefly discussed.

2. Results and Discussion

2.1. Acidity of Ionic Liquid

Pyridine is commonly used as a molecular probe to determine the Lewis and Brönsted acidities of ionic liquids by the IR technique [22]. The IR peak appearing at ca. 1450 cm^{-1} indicates the pyridine molecule coordinated to the Lewis acid site. The IR peak appearing at ca. 1540 cm^{-1} means the formation of pyridinium ions resulting from the Brönsted acid site. The blue shift extent of the peak at ca. 1450 cm^{-1} indicates the increase in Lewis acid strength.

Pure pyridine shows a well resolved band at 1437 cm^{-1} (Figure 1a). When pyridine was mixed with the [BMIM]Cl-nAlCl$_3$, [Et$_3$NH]Cl-nAlCl$_3$, and [BPy]Cl-nAlCl$_3$ (n = 1, 2, and 2.5) ionic liquids, the absorption peaks appearing at 1448, 1449, 1449; 1445, 1445, 1447; 1449, 1449, 1449 cm^{-1} were observed, respectively, indicating the presence of Lewis acid sites. In addition, for the [Et$_3$NH]Cl-nAlCl$_3$, [BMIM]Cl-nAlCl$_3$, and [BPy]Cl-nAlCl$_3$ (n = 1, 2, and 2.5) ionic liquids, the IR peaks at 1538 cm^{-1} attributed to the Brönsted acid sites were also observed, due to the interaction between AlCl$_3$ and water from air [22].
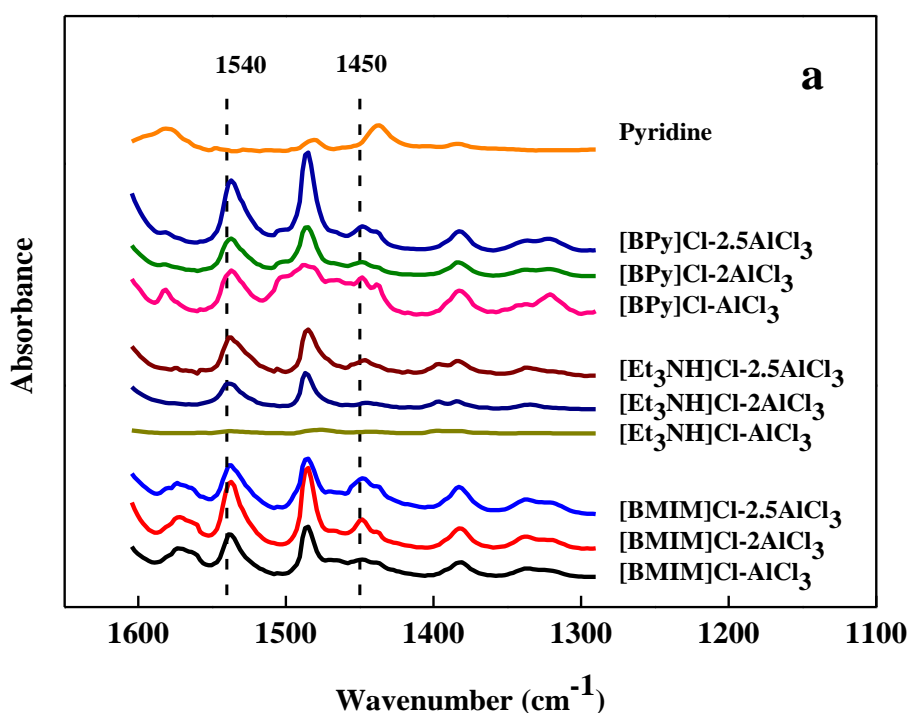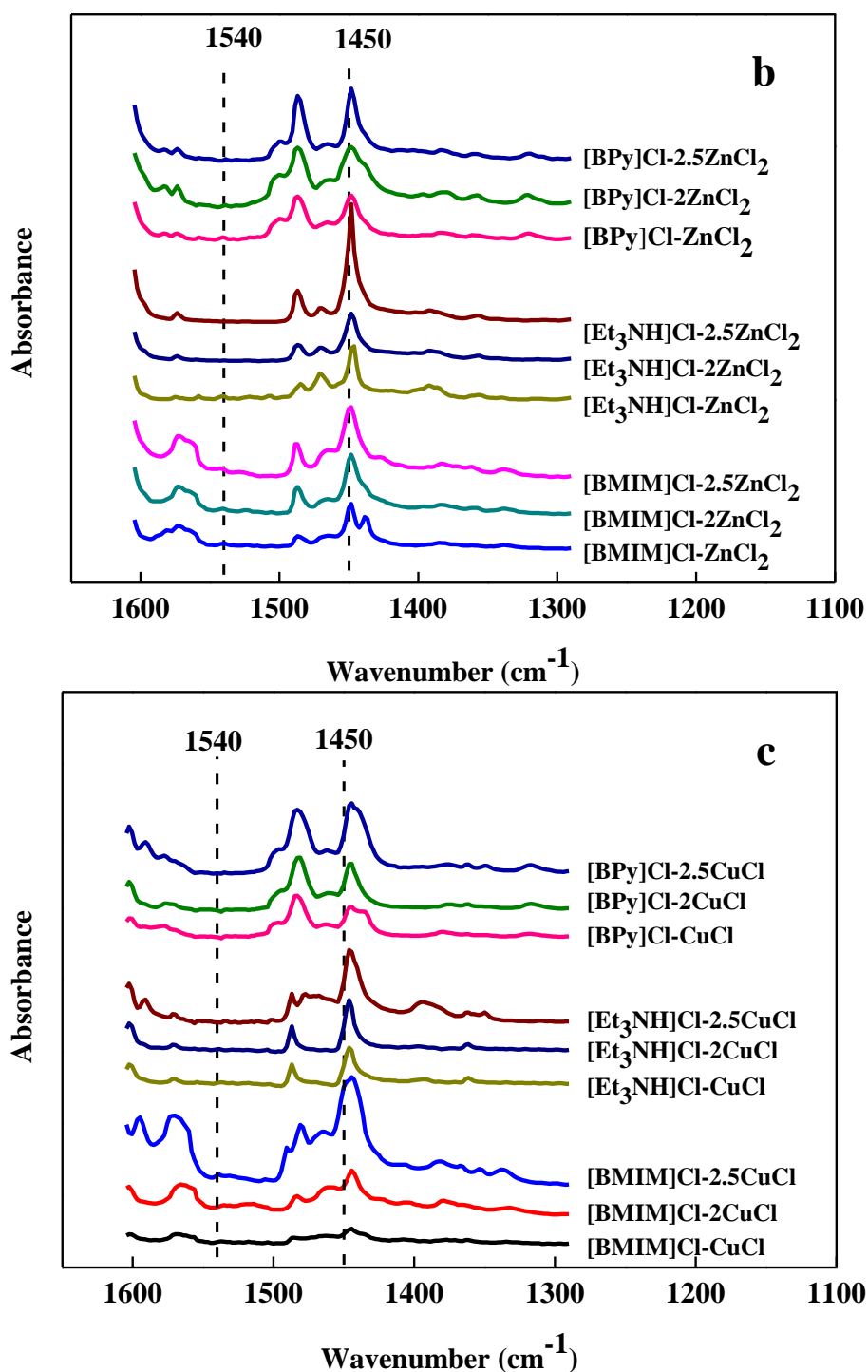

Figure 1. *Cont.*

Figure 1. Fourier transform infrared spectroscopy (FT–IR) spectra of (**a**) pyridine/$Al_nCl^-_{3n+1}$ anion-containing ionic liquids; (**b**) pyridine/$Zn_nCl^-_{2n+1}$ anion-containing anion ionic liquids; and (**c**) pyridine/$Cu_nCl^-_{n+1}$ anion-containing ionic liquids. The volume ratio of pyridine to ionic liquid is 1:1.

When the [BMIM]Cl-nZnCl$_2$, [Et$_3$NH]Cl-nZnCl$_2$, and [BPy]Cl-nZnCl$_2$ (n = 1, 2, and 2.5) ionic liquids were mixed with pyridine, IR peaks at 1448, 1449, 1449; 1447, 1448, 1449; 1449, 1449, 1449 cm^{-1} were observed (Figure 1b). When the [BMIM]Cl-nCuCl, [Et$_3$NH]Cl-nCuCl, and [BPy]Cl-nCuCl (n = 1, 2, and 2.5) ionic liquids were mixed with pyridine, IR peaks at 1444, 1444, 1444; 1446, 1446, 1446; 1445, 1445, 1445 cm^{-1} were observed (Figure 1c). The results indicated that only Lewis acid sites are present in the $Zn_nCl^-_{2n+1}$, and $Cu_nCl^-_{n+1}$ anion-containing ionic liquids.

According to the blue shift extent of the IR absorption bands attributed to the Lewis acid sites, it could be found that the Lewis acid strengths of the as-synthesized ionic liquids were in an order of $Zn_nCl^-_{2n+1}$ anion-containing ionic liquids > $Al_nCl^-_{3n+1}$ anion-containing ionic liquids > $Cu_nCl^-_{n+1}$ anion-containing ionic liquids. The intensities of those absorption peaks attributed to the Lewis acid sites increased with the increase in anion content, meaning that the Lewis acid amount increased upon increasing the anion content. It was interesting to find that the intensities of the IR peaks at 1537 cm^{-1} attributed to the Brönsted acid sites present in [BMIM]Cl-nAlCl$_3$, [Et$_3$NH]Cl-nAlCl$_3$, and [BPy]Cl-nAlCl$_3$ ionic liquids also increased with the increase in $Al_nCl^-_{3n+1}$ content, indicating that the Brönsted acid amount also increased upon increasing the $Al_nCl^-_{3n+1}$ content.

2.2. Chlorination Reaction Catalyzed by Ionic Liquids

Figure 2 shows the conversions of toluene and the selectivities of *o*-chlorotoluene, *m*-chlorotoluene, *p*-chlorotoluene, benzyl chloride, and dichlorotoluenes in the chlorination reaction between toluene and gaseous Cl$_2$ catalyzed by the ionic liquids.
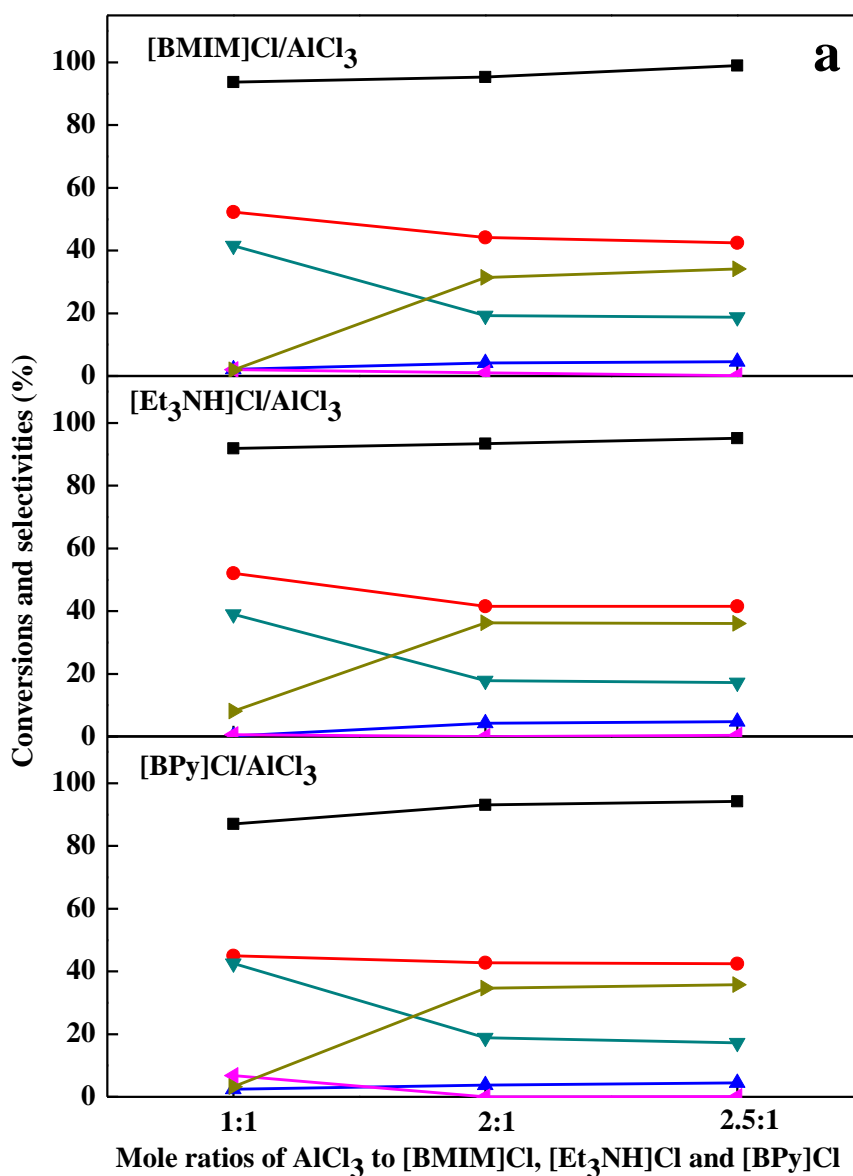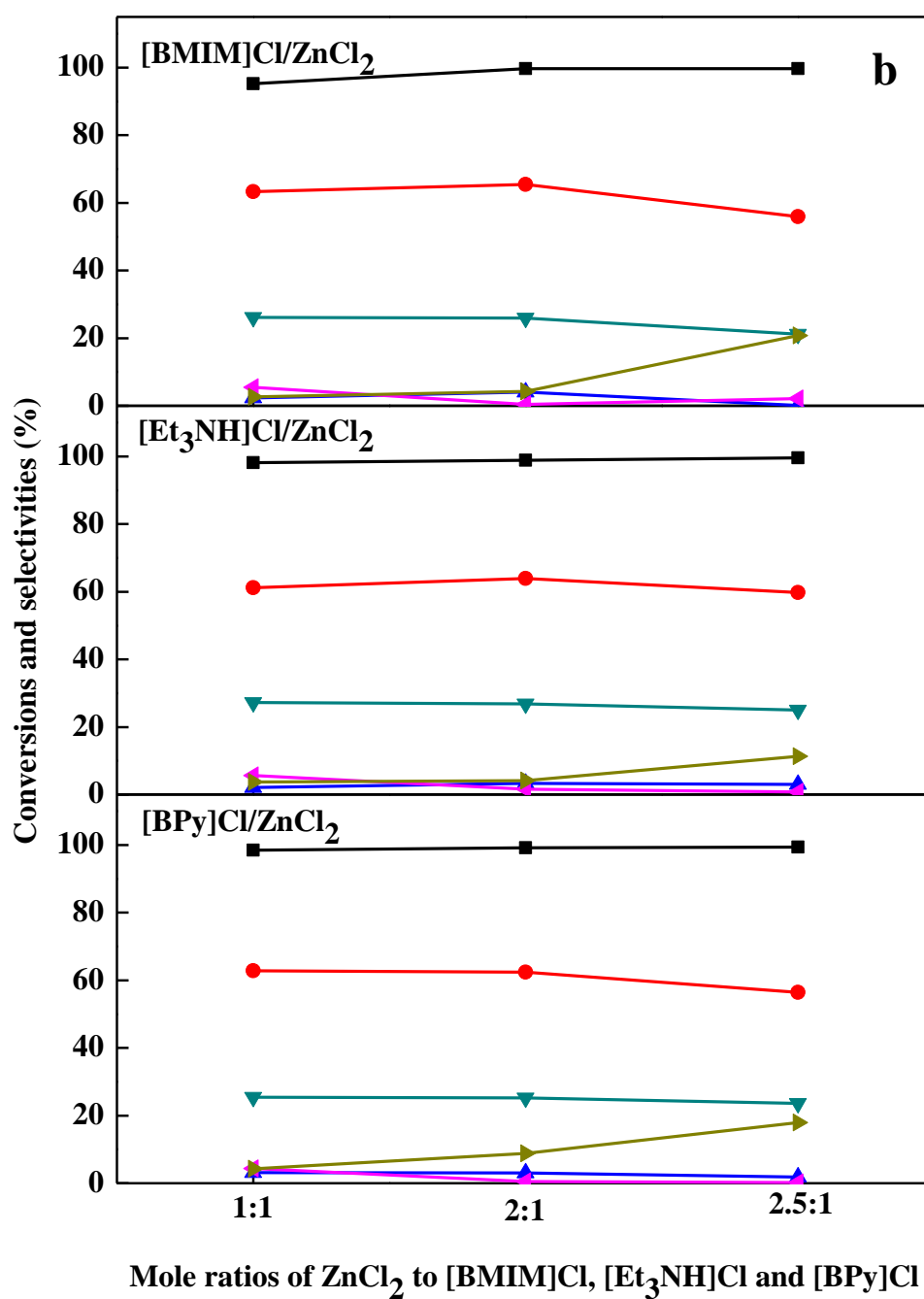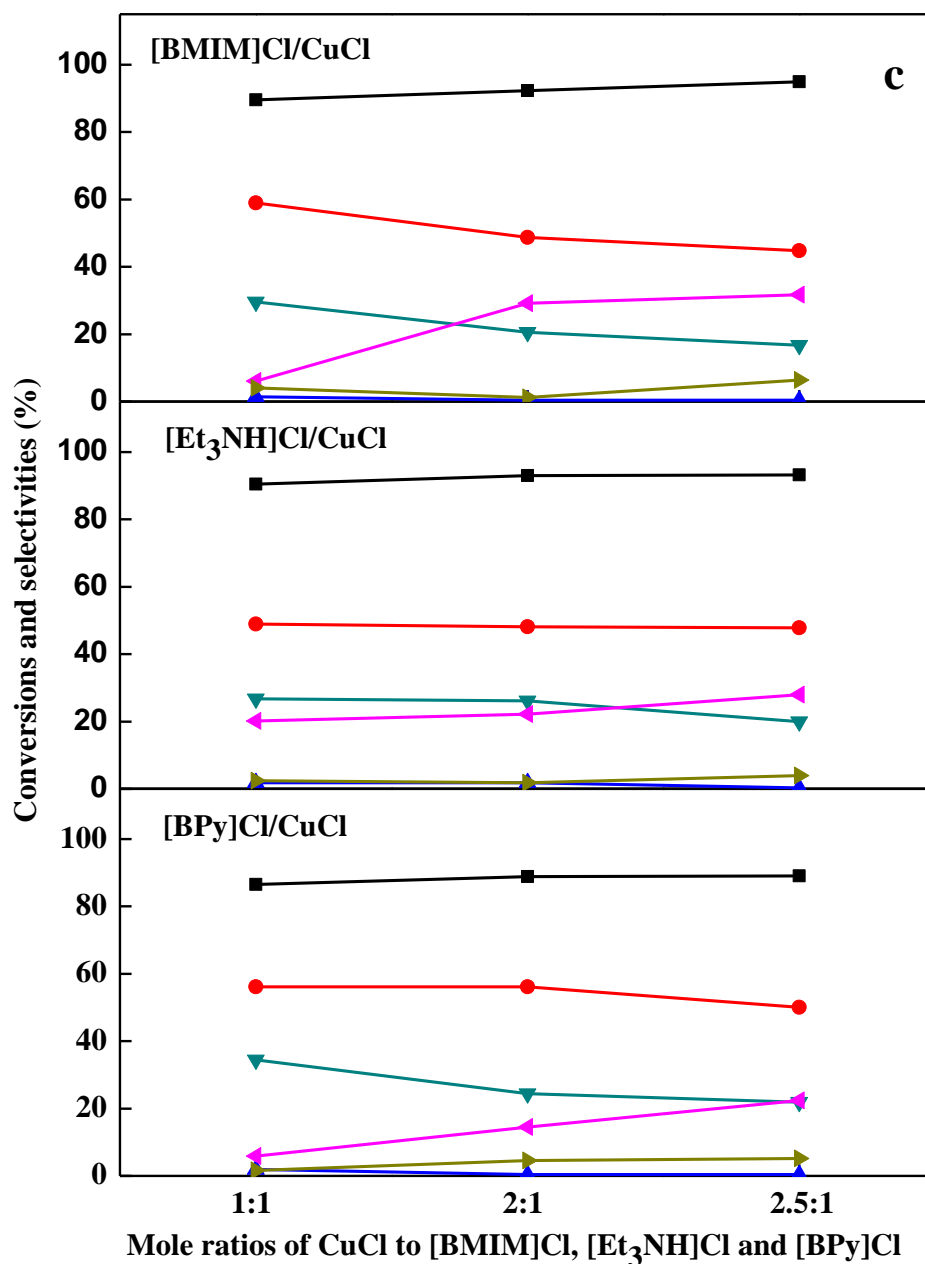

Figure 2. *Cont.*

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Figure 2. Chlorination of toluene with gaseous Cl_2 over the ionic liquid catalysts, with different mole ratios of (**a**) $AlCl_3$, (**b**) $ZnCl_2$, and (**c**) CuCl to [BMIM]Cl, [Et_3NH]Cl, and [BPy]Cl, respectively. ■, conversion of toluene; ●, selectivity of *o*-chlorotoluene; ▲, selectivity of *m*-chlorotoluene; ▼, selectivity of *p*-chlorotoluene; ◀, selectivity of benzyl chloride; ▶, selectivity of dichlorotoluenes. Reaction conditions: toluene, 0.5 mol; chlorine, 25 mL min^{-1}; catalyst loading, 3 mol/100 mol toluene; reaction temperature, 80 °C; reaction time, 8 h.

When the [BMIM]Cl-nAlCl$_3$, [Et_3NH]Cl-nAlCl$_3$, and [BPy]Cl-nAlCl$_3$ ionic liquids were used as the catalysts, after reacting at 80 °C for 8 h, the conversions of toluene increased from 93.7% to 98.9%, 91.9% to 95.2%, and 87.0% to 94.3%, respectively, with increasing the *n* values from 1 to 2.5 (Figure 2a). The selectivities of *o*-chlorotoluene decreased from 52.3% to 42.5%, 52.1% to 41.6%, and 45.0% to 42.4%. The selectivities of *p*-chlorotoluene decreased from 41.6% to 18.8%, 39.0% to 17.3%, and 42.5% to 17.3%. However, the selectivities of dichlorotoluenes rapidly increased from 1.9% to 34.1%, 8.1% to 36.1%, and 3.2% to 35.7%. The selectivities of *m*-chlorotoluene and benzyl chloride were less than 4.7% and 6.8%, respectively.

When the [BMIM]Cl-nZnCl$_2$, [Et$_3$NH]Cl-nZnCl$_2$, and [BPy]Cl-nZnCl$_2$ ionic liquids were used as the catalysts, after reacting at 80 °C for 8 h, the conversions of toluene increased from 95.2% to 99.7%, 98.2% to 99.6%, and 98.5% to 99.4%, respectively, with increasing the n values from 1 to 2.5 (Figure 2b). Over the [BMIM]Cl-nZnCl$_2$ catalysts, the selectivities of *o*-chlorotoluene increased from 63.4% to 65.4% and then decreased to 55.9% with increasing the n values from 1 to 2 and 2.5 while over [Et$_3$NH]Cl-nZnCl$_2$ catalysts, the selectivities of *o*-chlorotoluene increased from 61.2% to 63.9% and then decreased to 59.8%. When the [BPy]Cl-nZnCl$_2$ ionic liquids were used as the catalysts, the selectivities of *o*-chlorotoluene decreased from 62.9% to 56.4%. The selectivities of *p*-chlorotoluene decreased from 26.1% to 21.1%, 27.2% to 25.0%, and 25.4% to 23.6% with increasing the n values. However, the selectivities of dichlorotoluenes increased from 2.6% to 20.8%, 3.8% to 11.3%, and 4.3% to 17.9%. The selectivities of *m*-chlorotoluene and benzyl chloride were less than 4.0% and 5.7%, respectively.

When the [BMIM]Cl-nCuCl, [Et$_3$NH]Cl-nCuCl, and [BPy]Cl-nCuCl ionic liquids were used as the catalysts, after reacting at 80 °C for 8 h, with increasing the n values of the ionic liquids from 1 to 2.5, the conversions of toluene increased from 89.6% to 94.9%, 90.4% to 93.2%, and 86.6% to 89.0%, respectively (Figure 2c). The selectivities of *o*-chlorotoluene decreased from 58.9% to 44.7%, 48.9% to 47.8%, and 56.2% to 50.1%. The selectivities of *p*-chlorotoluene decreased from 29.6% to 16.8%, 26.8% to 20.0%, and 34.4% to 21.9%. However, the selectivities of benzyl chloride increased from 6.1% to 31.7%, 20.1% to 27.9%, and 5.8% to 22.4%. The selectivities of *m*-chlorotoluene and dichlorotoluenes were less than 1.9% and 6.4%, respectively.

The results showed that the conversions of toluene over the ionic liquid catalysts were in an order of Zn$_n$Cl$^-_{2n+1}$ anion-containing ionic liquids > Al$_n$Cl$^-_{3n+1}$ anion-containing ionic liquids > Cu$_n$Cl$^-_{n+1}$ anion-containing ionic liquids, being consistent with that of their Lewis acid strengths. The Zn$_n$Cl$^-_{2n+1}$ anion-containing ionic liquids with high Lewis acid strength showed high catalytic activity for the chlorination of toluene with gaseous chlorine. The Al$_n$Cl$^-_{3n+1}$ anion-containing ionic liquids favored the chlorination of the resultant monochlorotoluene to dichlorotoluenes as compared to the other ionic liquid catalysts. The explanation for this could be that the co-presence of Brönsted and Lewis acid sites was beneficial to the formation of dichlorotoluenes. For the Cu$_n$Cl$^-_{n+1}$ anion-containing ionic liquids, their catalytic activities for the chlorination of toluene were less than the Zn$_n$Cl$^-_{2n+1}$ and Al$_n$Cl$^-_{3n+1}$ anion-containing ionic liquids. The explanation for this could be that the Cu$_n$Cl$^-_{n+1}$ anion-containing ionic liquids with low Lewis acid strength gave low catalytic activity for the chlorination reaction. However, benzyl chloride was formed in a large scale while the Cu$_n$Cl$^-_{n+1}$ anion-containing ionic liquids were used as the catalysts. The results revealed that the chlorination of toluene to chlorinated toluene and the chlorination of toluene to benzyl chloride are competitive reactions. The Zn$_n$Cl$^-_{2n+1}$ and Al$_n$Cl$^-_{3n+1}$ anion-containing ionic liquids with high Lewis acid strength favored the chlorination of toluene to chlorinated toluene via the electrophilic substitution reaction, suppressing the formation of benzyl chloride via the free radical reaction. It was also found that the toluene conversions and the product selectivities over these ionic liquid catalysts with different cation counterparts but with the same anion counterpart were similar to each other, indicating that the cation counterparts of these ionic liquids had little effect on their catalytic activities in the chlorination reaction.

2.3. Effect of Catalyst Loading

Among the ionic liquids, the [BMIM]Cl-2ZnCl$_2$ ionic liquid exhibited the highest catalytic activity for the formation of *o*-chlorotoluene. Therefore, it was selected as the model catalyst to investigate the effect of other experimental parameters on the toluene chlorination reaction.

The conversions of toluene and the selectivities of products in the catalytic chlorination reaction over the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst with different loadings are shown in Figure 3. When the mole ratios of [BMIM]Cl-2ZnCl$_2$ ionic liquid to toluene were 1:100, 3:100, and 5:100, the conversions of toluene were 84.4%, 99.7%, and 99.7% and the selectivities of *o*-chlorotoluene were 65.0%, 65.4%, and 62.1%, respectively. The selectivities of *p*-chlorotoluene decreased from 26.8% to 24.1% upon increasing the catalyst loading while the selectivities of dichlorotoluenes increased from 2.2% to

10.9%. Only a small amount of *m*-chlorotoluene and benzyl chloride were formed with the selectivities of less than 4.4% and 1.7%, respectively. The results showed that high catalyst loading not only favored the chlorination reaction between toluene and gaseous Cl_2, but also caused the chlorination of monochlorotoluenes to dichlorotoluenes.
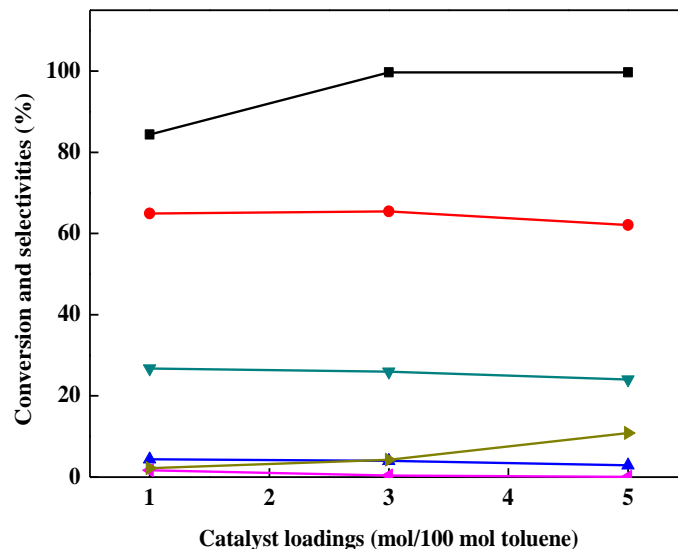

Figure 3. Chlorination of toluene with gaseous Cl_2 over the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst with different loadings. ■, conversion of toluene; ●, selectivity of *o*-chlorotoluene; ▲, selectivity of *m*-chlorotoluene; ▼, selectivity of *p*-chlorotoluene; ◄, selectivity of benzyl chloride; ►, selectivity of dichlorotoluenes. Reaction conditions: toluene, 0.5 mol; chlorine, 25 mL min^{-1}; reaction temperature, 80 °C; reaction time, 8 h.

2.4. Effect of Reaction Temperature

The conversions of toluene and the selectivities of products in the catalytic chlorination reaction over the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst at different reaction temperatures are shown in Figure 4.

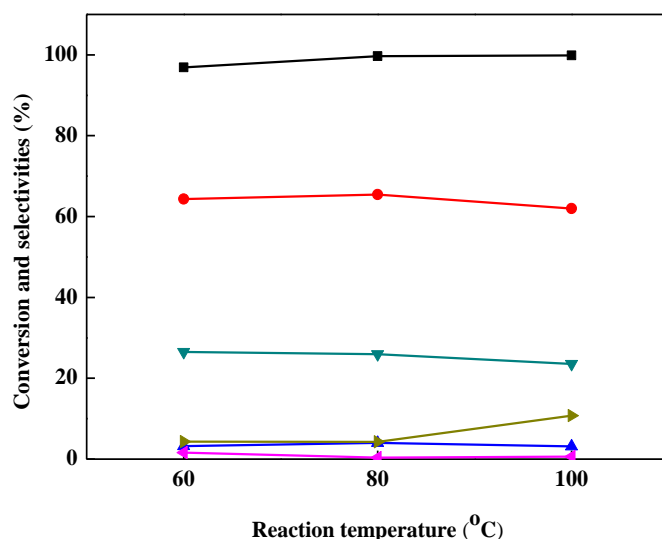**Figure 4.** Chlorination of toluene with gaseous Cl_2 over the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst at different reaction temperatures. ■, conversion of toluene; ●, selectivity of *o*-chlorotoluene; ▲, selectivity of *m*-chlorotoluene; ▼, selectivity of *p*-chlorotoluene; ◄, selectivity of benzyl chloride; ►, selectivity of dichlorotoluenes. Reaction conditions: toluene, 0.5 mol; chlorine, 25 mL min^{-1}; [BMIM]Cl-2ZnCl$_2$, 3 mol/100 mol toluene; reaction time, 8 h.

Toluene was almost completely converted when the reaction temperature was raised to 80 °C. The selectivities of *o*-chlorotoluene gradually increased from 64.3% to 65.4% upon increasing the reaction temperatures from 60 to 80 °C. Further increasing the reaction temperature to 100 °C, the selectivity decreased to 62.0%. The selectivities of *p*-chlorotoluene decreased from 26.5% to 23.5% while the selectivities of dichlorotoluenes increased from 4.4% to 10.7% upon increasing the reaction temperatures from 60 to 100 °C. The selectivities of *m*-chlorotoluene and benzyl chloride were less than 4.0% and 1.6%, respectively. The results showed that the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst had stable activity for the catalytic chlorination of toluene to *o*-chlorotoluene at the reaction temperatures ranging from 60 to 100 °C.

2.5. Effect of Reaction Time

The toluene conversions and the product selectivities at 80 °C and different reaction time periods are shown in Figure 5. Upon prolonging the reaction time to 8 h, toluene was almost completely converted. When the reaction time periods ranged from 2 to 8 h, the selectivities of *o*-chlorotoluene, *m*-chlorotoluene, *p*-chlorotoluene, and dichlorotoluenes were around 65%, 5%, 26%, and 4%, respectively. The selectivity of benzyl chloride was less than 2.3%. The results showed that reaction time had little effect on the product selectivity.
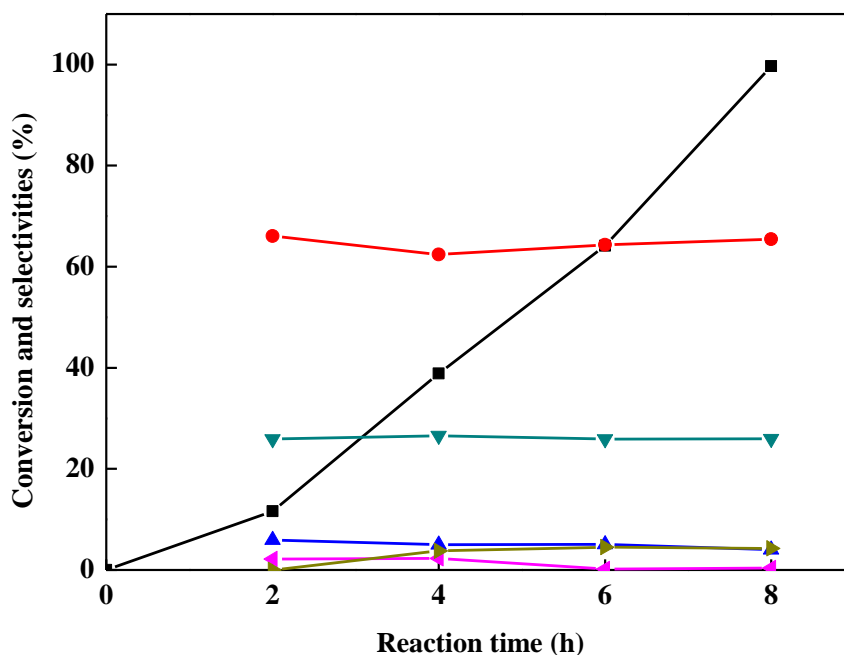

Figure 5. Chlorination of toluene with gaseous Cl$_2$ over the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst at different reaction times. ■, conversion of toluene; ●, selectivity of *o*-chlorotoluene; ▲, selectivity of *m*-chlorotoluene; ▼, selectivity of *p*-chlorotoluene; ◄, selectivity of benzyl chloride; ►, selectivity of dichlorotoluenes. Reaction conditions: toluene, 0.5 mol; chlorine, 25 mL min^{-1}; [BMIM]Cl-2ZnCl$_2$, 3 mol/100 mol toluene; reaction temperature, 80 °C.

2.6. Recycling Performance

To investigate the recycling performance of the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst, the recycling experiments were also conducted. After reaction, the reaction mixture and the ionic liquid catalyst were separated with a funnel. The recovered ionic liquid was reused as the catalyst for next run. Figure 6 shows the recycling performance of the ionic liquid catalyst.
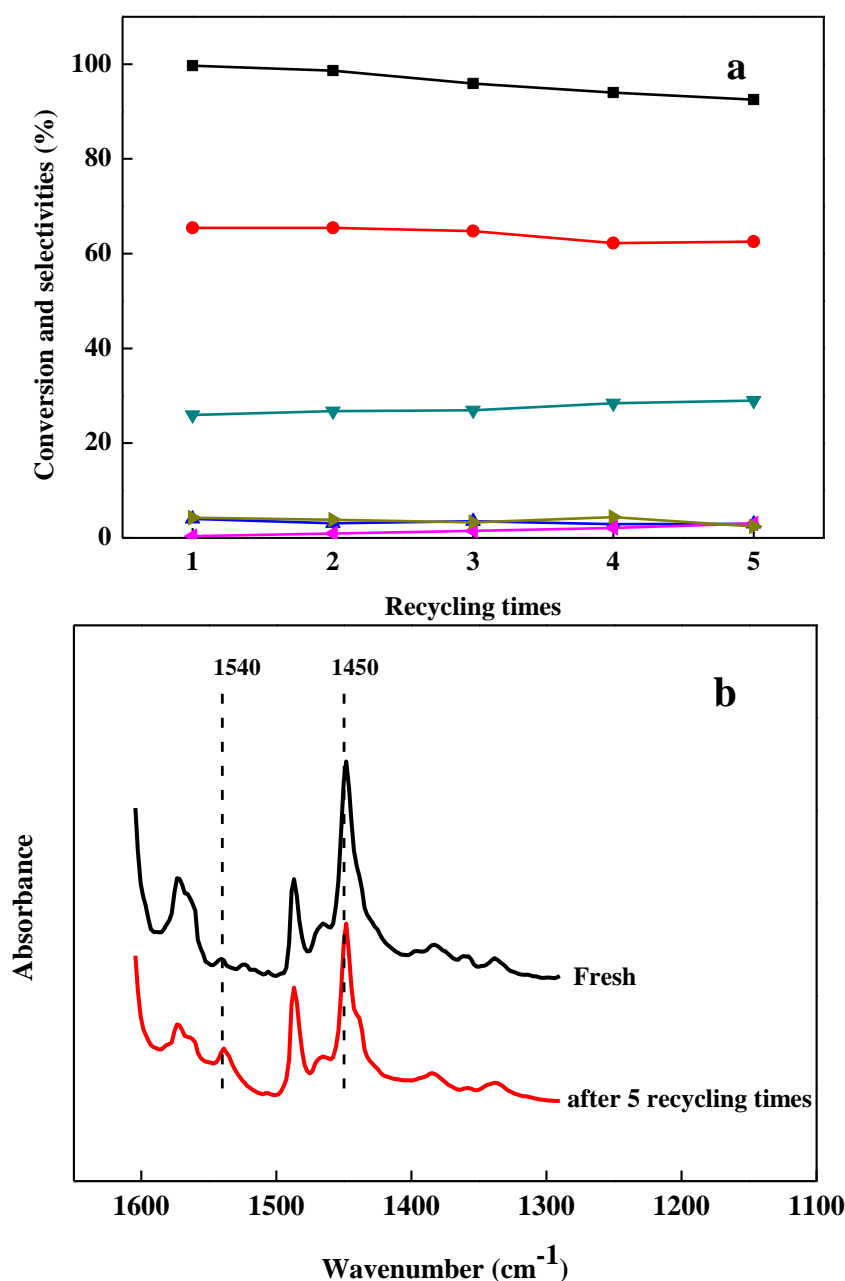
Figure 6. (**a**) Recycling performance of the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst in the chlorination of toluene with gaseous Cl$_2$. ■, conversion of toluene; ●, selectivity of *o*-chlorotoluene; ▲, selectivity of *m*-chlorotoluene; ▼, selectivity of *p*-chlorotoluene; ◄, selectivity of benzyl chloride; ►, selectivity of dichlorotoluenes. Reaction conditions: toluene, 0.5 mol; chlorine, 25 mL min^{-1}; [BMIM]Cl-2ZnCl$_2$, 3 mol/100 mol toluene; reaction temperature, 80 °C; reaction time, 8 h; (**b**) FT–IR spectra of pyridine/fresh [BMIM]Cl-2ZnCl$_2$ ionic liquid and pyridine/spent [BMIM]Cl-2ZnCl$_2$ ionic liquid recycled for 5 times. The volume ratio of pyridine to ionic liquid is 1:1.

As shown in Figure 6a, the conversions of toluene slightly decreased from 99.7% to 92.5% when the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst was recycled five times. The selectivities of *o*-chlorotoluene slightly decreased from 65.4% to 62.6% while the selectivities of *p*-chlorotoluene slightly increased from 26.0% to 29.0%. The selectivities of *m*-chlorotoluene, benzyl chloride, and dichlorotoluenes were around 3.5%, 2.0%, and 4.0%, respectively. The results showed that the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst had good recycling performance for the chlorination reaction.
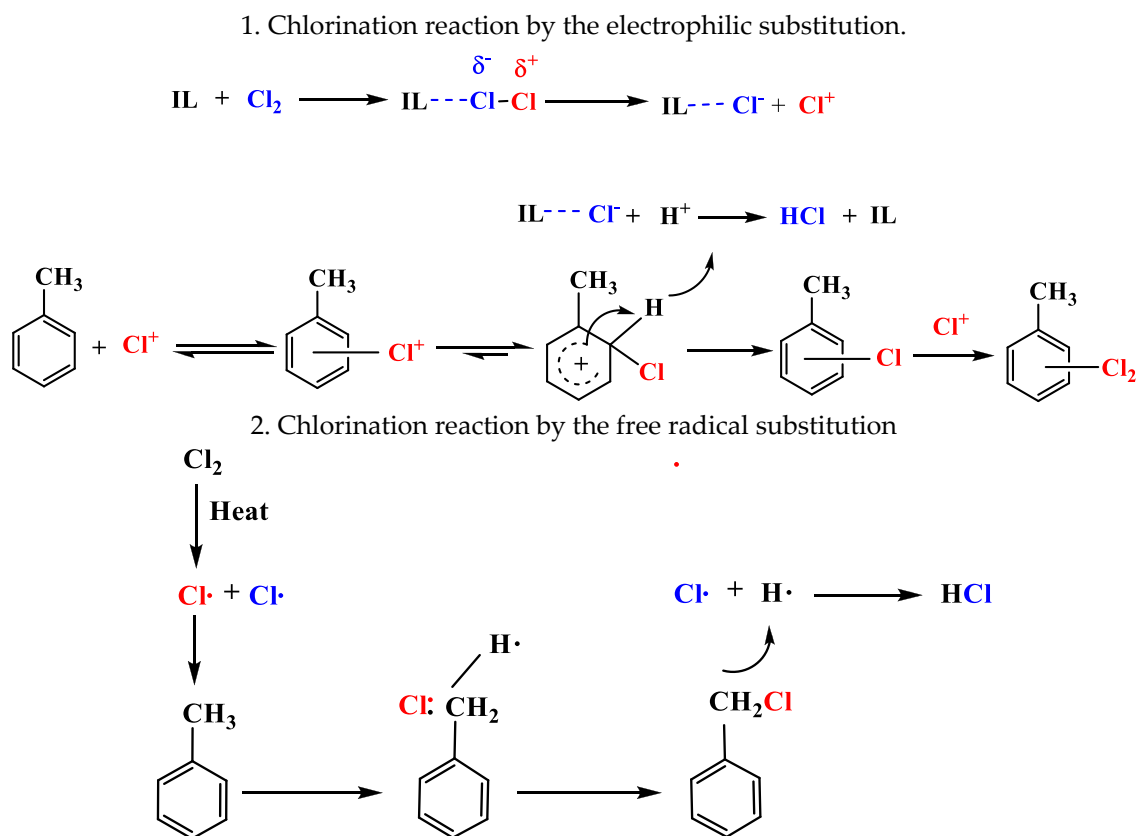
When pyridine was mixed with the fresh [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst or the spent [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst was recycled 5 times, the IR absorption peaks at 1449 cm^{-1} were observed in both samples (Figure 6b), indicating that the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst was stable in the chlorination of toluene.

It was reported that K-L zeolite catalysts could catalyze the toluene chlorination with gaseous Cl$_2$ at 70–80 °C to *o*-chlorotoluene with selectivities in a range of 20–49% [6,8]. When NaK-L zeolite catalyzed the toluene chlorination with the use of the expensive SO$_2$Cl$_2$ as the chlorinating agent at 50 °C, *p*-chlorotoluene was favorably formed with the *p*-chlorotoluene/*o*-chlorotoluene ratio of more than 3:1 [7]. As compared with the previous work, it was clear that the [BMIM]Cl-2ZnCl$_2$ ionic liquid catalyst exhibited excellent catalytic activity for the toluene chlorination with gaseous Cl$_2$ to *o*-chlorotoluene.

2.7. Reaction Routes

Chlorination of toluene is a typical electrophilic substitution reaction. The methyl group of toluene as the electron-donating substitute can activate the phenyl ring, being beneficial to the electrophilic phenyl chlorination reaction [7,8]. *o*-Chlorotoluene and *p*-chlorotoluene are easily formed in the toluene chlorination reaction because methyl is a usual *ortho/para* directing group.

The reaction routes in the toluene chlorination with gaseous Cl$_2$ catalyzed by the ionic liquid catalyst are suggested as Scheme 1.

Scheme 1. The reaction routes in the chlorination of toluene with gaseous chlorine over the ionic liquid catalyst.

Firstly, chlorine molecules were polarized by the ionic liquid catalyst to form Cl$^-$ anions and Cl$^+$ cations. The positive Cl$^+$ cation as an electrophile attacked the phenyl ring of toluene to form a π-complex while the Cl$^-$ anion was harbored by the ionic liquid catalyst to form a chlorinated anion, IL ... Cl$^-$. Then, the π-complex evolved into a σ-complex. Finally, the reactive intermediate was

converted to monochlorotoluene by the deprotonation. The resulting proton reacted with the IL . . . Cl^- anion to form HCl and the Lewis acidic ionic liquid catalyst was recovered. The monochlorotoluenes could be further chlorinated to form dichlorotoluenes. Benzyl chloride was produced as a by-product via the free-radical reaction [6].

We suggested that the $Zn_nCl^-_{2n+1}$ anion-containing ionic liquids with a higher Lewis acid strength favored the chlorination of toluene to *o*-chlorotoluene. The co-presence of the Lewis and Brönsted acid sites in the $Al_nCl^-_{3n+1}$ anion-containing ionic liquids favored the further chlorination of monochlorotoluene to dichlorotoluene. The reactions of toluene chlorination to chlorotoluene and benzyl chloride are competitive. Therefore, when the $Cu_nCl^-_{n+1}$ anion-containing ionic liquids with weak Lewis acid strength were used as the catalysts, more benzyl chloride was formed via the free-radical substitution reaction.

3. Experimental

3.1. Materials

Liquid Cl_2 of industrial grade was purchased from Jiangsu SOPO Co., Ltd. Zhenjiang, China. *N*-Methylimidazole with the purity of 99% was supplied by Yancheng Medical Factory, Yancheng, China. Anhydrous $AlCl_3$, CuCl, $ZnCl_2$, *n*-chlorobutane, triethylamine, pyridine, ethyl acetate, toluene, hydrochloric acid, and isopropanol were purchased from the Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals were of reagent grade and were used as received without further purification.

3.2. Synthesis of Ionic Liquids

3.2.1. Synthesis of 1-Butyl-3-methylimidazolium Chloride ([BMIM]Cl)

According to the reported method [23,24], [BMIM]Cl was synthesized as follows. 1.7 mol of *n*-chlorobutane and 1.5 mol of *N*-methylimidazole were added into a three-necked flask (500 mL) under stirring. A nitrogen stream at a flow rate of 10 mL min^{-1} was introduced into the flask. The reaction was carried out under reflux for 48 h. When the reaction mixture was cooled to 0 °C, the [BMIM]Cl turned to be solid. The as-synthesized [BMIM]Cl was filtrated and repeatedly washed with ethyl acetate at least two times. The remaining ethyl acetate was evaporated at 80 °C from [BMIM]Cl. The [BMIM]Cl sample was dried at 70 °C for 24 h in a vacuum oven.

3.2.2. Synthesis of Triethylammonium Chloride ([Et3NH]Cl)

The synthesis of [Et3NH]Cl was done according to the method reported in reference [25]. The synthesis procedures are briefly stated as follows. Firstly, triethylamine (1.5 mol) and concentrated hydrochloric acid (1.7 mol) were added into a three-necked flask (500 mL). The reaction was carried out at ambient temperature for 3 h under stirring. After reaction, the reaction mixture was filtrated and repeatedly washed with anhydrous ethanol at least two times. The remaining ethanol was evaporated at 80 °C from [Et3NH]Cl. The prepared [Et3NH]Cl sample was dried at 70 °C for 24 h in a vacuum oven.

3.2.3. Synthesis of 1-Butylpyridinium Chloride ([BPy]Cl)

[BPy]Cl was synthesized according to the method reported in reference [15]. The synthesis procedures are briefly stated as follows. Firstly, pyridine (1.5 mol) and *n*-chlorobutane (1.7 mol) were added into a 500 mL flask under stirring. A N_2 stream continuously flowed through the reaction system at a flow rate of 10 mL min^{-1}. In a dark fume hood, the reaction took place under reflux for 72 h. After reaction, the reaction mixture was cooled to room temperature and [BPy]Cl crystallized. The [BPy]Cl sample was filtrated and washed with ethyl acetate at least twice. The remained ethyl

acetate was evaporated at 80 °C from the [BPy]Cl sample. The as-prepared [BPy]Cl sample was dried at 70 °C for 24 h in a vacuum oven.

3.2.4. Synthesis of Ionic Liquids

The ionic liquids were synthesized by using [BMIM]Cl, [Et3NH]Cl, [BPy]Cl, AlCl3, ZnCl2, and CuCl as the raw materials. The preparation method of [BMIM]Cl-nAlCl3 is briefly described as follows. In a nitrogen atmosphere, a certain amount of anhydrous AlCl3 was added slowly into a round-bottom flask containing [BMIM]Cl under stirring. The reaction was carried out in a nitrogen atmosphere at 120 °C for 2 h. The [BMIM]Cl-nAlCl3 ionic liquids with the n values of 1, 2, and 2.5 were synthesized by changing the AlCl3/[BMIM]Cl ratios. The synthesis procedures of other ionic liquids were the same as those described above. The synthesized ionic liquid samples were stored in a desiccator.

3.3. Determination of Lewis and Brönsted Acid Strengths of Ionic Liquids

The Lewis acid strength of the ionic liquids was measured according to the blue shift of pyridine infrared (IR) absorption band at ca. 1450 cm^{-1} and the Brönsted acid amount was determined according to the intensity of the band at ca. 1540 cm^{-1} [22,26]. For the FT-IR analysis, all the samples were prepared by mixing pyridine and ionic liquid with a volume ratio of 1:1. The FT-IR spectra of the samples were recorded on a FT-IR spectrophotometer (Nicolet Nexus 470, Thermo Fisher Scientific, Waltham, MA, USA) at ambient temperature.

3.4. Chlorination Reaction

0.5 mol of toluene and a given amount of ionic liquid catalyst were added into a 100 mL four-necked round bottom flask, which was equipped with a thermometer, a chlorine inlet tube, a condenser, and a magnetic stirrer. Before the chlorination reaction, a nitrogen stream at a flow rate of 20 mL min^{-1} was introduced into the reactor to replace air inside. When the reaction solution was heated to a prescribed reaction temperature under stirring at 100 rpm, gaseous Cl$_2$ dried by passing through a concentrated sulfuric acid solution was introduced into the reactor at 25 mL min^{-1}. The exhaust gas was absorbed in a NaOH aqueous solution. In order to avoid the photon-initiated free-radical chlorination, the chlorination reaction was carried out in a dark fume hood.

The compositions of the reaction mixtures were analyzed on a gas chromatograph, equipped with a KR-ELJB capillary column and a flame ionization detector [27]. The conversion of toluene and the selectivities of *o*-chlorotoluene, *p*-chlorotoluene, *m*-chlorotoluene, dichlorotoluene, and benzyl chloride were calculated according to the following equations.

$$Conversion_{(Toluene)} = \frac{[Toluene]_{in} - [Toluene]_{out}}{[Toluene]_{in}} \times 100\% \tag{1}$$

$$Selective_{(Product)} = \frac{[Product]_{out}}{[Toluene]_{in} - [Toluene]_{out}} \times 100\% \tag{2}$$

4. Conclusions

When the ionic liquids with the cation counterparts, [BMIM], [Et$_3$NH], and [BPy] and the anion counterparts, Al$_n$Cl$^-_{3n+1}$, Zn$_n$Cl$^-_{2n+1}$, and Cu$_n$Cl$^-_{n+1}$ were used as catalysts for the chlorination of toluene with Cl$_2$ to *o*-chlorotoluene, the Lewis acid sites present in the ionic liquids catalyzed the chlorination reaction. The selectivity of *o*-chlorotoluene was much higher than those of *p*-chlorotoluene, *m*-chlorotoluene, and benzyl chloride. The Zn$_n$Cl$^-_{2n+1}$ anion-containing ionic liquids showed high catalytic activity and selectivity for the chlorination of toluene to *o*-chlorotoluene. Dichlorotoluenes were favorably formed when the Al$_n$Cl$^-_{3n+1}$ anion-containing ionic liquids were used as catalysts.

When the chlorination reaction was catalyzed by the $Cu_nCl^-_{n+1}$ anion-containing ionic liquids, benzyl chloride was easily formed.

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