

# The metal ion modified ionic liquids promoted free-solvent alkylations of $\alpha$ -methylnaphthalene with long-chain olefins

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## Abstract

Alkylations of  $\alpha$ -methylnaphthalene with long-chain olefins in the presence of various synthesized novel ionic liquids have been investigated. The effects of various parameters such as types of cation and anion of ionic liquids, molar fraction of anhydrous aluminum trichloride on the alkylations were studied. It is found that the alkyipyridinium bromochloroaluminate ionic liquids, especially butylpyridinium bromochloroaluminate (0.71–0.75 molar fraction of aluminum trichloride) indicated excellent catalytic performance for long-chain alkylations of  $\alpha$ -methylnaphthalene. It is also found that the anions determine, to a large extent, both physical and chemical properties of ionic liquids, but organic cations mainly influence physical properties, and only have a slight impact on the catalytic performance. Moreover, the effects of type and dosage of transition metal in the modified ionic liquids on the catalytic performances were also investigated. For the less expensive reagents and the easier synthesis process, the  $\text{Cu}^{2+}$  modified butylpyridinium bromochloroaluminate ionic liquid could be a practical catalyst for alkylations of  $\alpha$ -methylnaphthalene with long-chain olefins.

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**Keywords:** Ionic liquids; Butylpyridinium bromochloroaluminate; Alkylation;  $\alpha$ -Methylnaphthalene; Long-chain olefins

## 1. Introduction

The previous research indicated that long-chain alkyl methylnaphthalene sulfonate surfactants possess outstanding capability and efficiency of lowering the surface tensions of aqueous solutions and the dynamic interfacial tensions between crude oil and water, therefore have a great potential to be used in EOR [1,2]. Studies on long-chain alkylations of methylnaphthalene producing alkylmethylnaphthalene intermediates, and therefore are very valuable. To date, alkylations of benzene have already been widely and thoroughly investigated [3–5], but not for naphthalene and its derivatives. In our laboratory, some preliminary studies on long-chain alkylations of methylnaphthalene catalyzed by both traditional catalysts [6–9], novel alkyl-containing amine bromochloroaluminate ionic liquid catalysts [10–12] and zeolite catalysts [13] have been done. The alkylation of

$\alpha$ -methylnaphthalene with long-chain olefins is believed to be a typical Friedel–Crafts reaction, and has conventionally been catalyzed by homogeneous acid catalysts, such as anhydrous  $\text{AlCl}_3$ , concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ ,  $\text{BF}_3$ , etc., which give rise to many problems concerning the handling, health, safety, corrosion, and waste disposal of catalysts. In order to overcome these problems, many efforts have been devoted to the searches environmentally friendly catalytic systems to replace the traditional catalysts. In recent years, the room temperature ionic liquids are being more and more regarded as relatively clean catalysts and solvents [14–17]. Many organic reactions, such as alkylation [18–21], acylation [22,23], Heck reaction [24], hydroformation [25], oxidation [26], and Knoevenagel Condensation [27], have been reported to proceed in the room temperature ionic liquids with excellent yields and selectivity.

Recently, considerable attention has been focused on the use of chloroaluminate room temperature ionic liquids. The acidity of the system can be varied through a wide range depending on the proportions of organic base to Lewis acids

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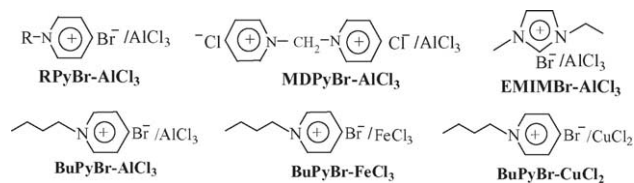


Fig. 1. The used ionic liquids in the present report.

from which it is prepared. If the molar fraction of anhydrous trichloroaluminum is less than 0.5, the system would afford a basic molten salt, and more than 0.5, it would afford an acidic melt. Use of ionic liquids as solvents and catalysts for Friedel–Crafts reactions was first reported in 1976 [28]. Here, we report the alkylations of  $\alpha$ -methyl-naphthalene with long-chain olefins in the presence of various ionic liquids (Fig. 1).

The effects of acidity (different molar fraction of anhydrous AlCl<sub>3</sub>,  $N_{\text{AlCl}_3}$ ) and the types of cations and anions in ionic liquids were studied. On the basis of optimal reaction conditions, high conversion of alkylating agent and excellent selectivity (without solvent) for the desired product might be obtained. The products and unreacted reactants were easily isolated by extraction with cyclohexane. Moreover, the roles of types of cations and anions composing ionic liquids were discussed. For the less expensive reagents and easier synthesis process, the Cu<sup>2+</sup> modified BuPyBr-AlCl<sub>3</sub> ionic liquids could be practical novel catalysts for long-chain alkylation of methyl-naphthalene with alkenes.

## 2. Experimental

### 2.1. Synthesis of precursors to ionic liquids

On the basis of the previous report [29], the preparation of the precursor, butylpyridinium bromide (BuPyBr), by reaction of pyridine and 1-bromobutane in a 500 mL oven-dried round bottom flask with stirrer, and reflux condenser equipped with drying pipe, thermometer and a dosing funnel. The mixture containing equal molar amounts (0.6 mol) of commercially available pyridine and 1-bromobutane was heated to 393–453 K in an oil-bath for about 10 min. During the later stages of the heating, an exothermic reaction took place forming an emulsion that disappeared in a few minutes to produce a brown slightly viscous liquid. At this point, the oil-bath was removed and the solution was allowed to stir and cooled for 10–20 min. The stirred solution was then heated in the 393–453 K oil-bath for an additional 10–20 min and then the liquid was cooled with the use of an ice bath for a few minutes. Slightly brown BuPyBr crystals were obtained. The various precursors like 1-ethyl-3-methylimidazolium bromides (EMIMBr), organic polycation precursor, methylenedipyridinium chloride (MDPyCl) and a series of alkylpyridinium bromide (RPyBr) containing various length alkyl groups were prepared with a similar method.

### 2.2. Synthesis and characterization of various ionic liquids

Butylpyridinium bromochloroaluminate (BuPyBr-AlCl<sub>3</sub>), bromochloroferrate (BuPyBr-FeCl<sub>3</sub>) and bromochlorocuprate (BuPyBr-CuCl<sub>2</sub>) ionic liquids were synthesized by adding 0.5 mol of the synthesized BuPyBr into a 250 mL oven-dried round bottom flask with stirrer, and reflux condenser equipped with drying pipe and thermometer, and then introducing a definite molar metal halide, anhydrous aluminum trichloride, anhydrous iron trichloride and anhydrous copper chloride, into batches from a dosing funnel respectively. The reactions were exothermic, and temperature was kept at 303 K with the use of an ice bath. After all of the metal halide had been added, the mixture was stirred at room temperature for 5 min, and then it was heated in an oil-bath at about 353 K for 5 h. After that, the temperature was cooled to ambient temperature by using an ice bath, and the ionic liquids were produced. 1-Ethyl-3-methylimidazolium bromochloroaluminate (EMIMBr-AlCl<sub>3</sub>) ionic liquid and organic polycation ionic liquid, methylenedipyridinium chloroaluminate (MDPyCl-AlCl<sub>3</sub>) ionic liquid and the other alkylpyridinium bromochloroaluminate (RPyBr-AlCl<sub>3</sub>) ionic liquids may be prepared with a similar method. The ionic liquids were modified by adding a certain amount of metal ions, Cu<sup>2+</sup> and Fe<sup>3+</sup>, into the liquids. Analytical grade anhydrous aluminum trichloride, anhydrous iron trichloride and anhydrous copper chloride were used without further purification. The synthesized ionic liquids were characterized with HP 1100 LC/MS [11,30]. The ESI-MS for both the cations of EMIMBr-AlCl<sub>3</sub>, BuPyBr-AlCl<sub>3</sub> and MDPyCl-AlCl<sub>3</sub> and the anions of BuPyBr-AlCl<sub>3</sub>, BuPyBr-FeCl<sub>3</sub> and BuPyBr-CuCl<sub>2</sub> of ionic liquids had been given in previous report [11]. It is found that there exist polynuclear anions in the anion species, which may play an important role in its catalytic performances. Butylpyridinium Lewis acid ionic liquids, including BuPyBr-AlCl<sub>3</sub>, BuPyBr-FeCl<sub>3</sub> and BuPyBr-CuCl<sub>2</sub> (0.71 molar fraction of metal chloride) were characterized by IR by using acetonitrile as a probe.

### 2.3. Alkylations of $\alpha$ -methyl-naphthalene and analysis

First, 30 g of  $\alpha$ -methyl-naphthalene (>98%) and mixed alkenes C<sub>11–12</sub> (C<sub>11</sub> to C<sub>12</sub> weight ratio is 45/55 by GC, bought from Fushun Petrochemical Company) were put into a 100 mL 3-necked flask equipped with a stirrer, a reflux condenser with a drying pipe and a thermometer. In all cases, the molar ratio of aromatic hydrocarbon and olefins was 5. Then a certain amount of ionic liquid as catalyst was added. After stirring for about 30 min at room temperature to make the reaction agents homodispersed. The reaction time was noted when the mixture was heated to the required reaction temperature. In all cases, the having been reaction conditions, 5:1 molar ratio of  $\alpha$ -methyl-naphthalene to olefins, 15% dosage of catalyst, at 353 K for 30 min, were

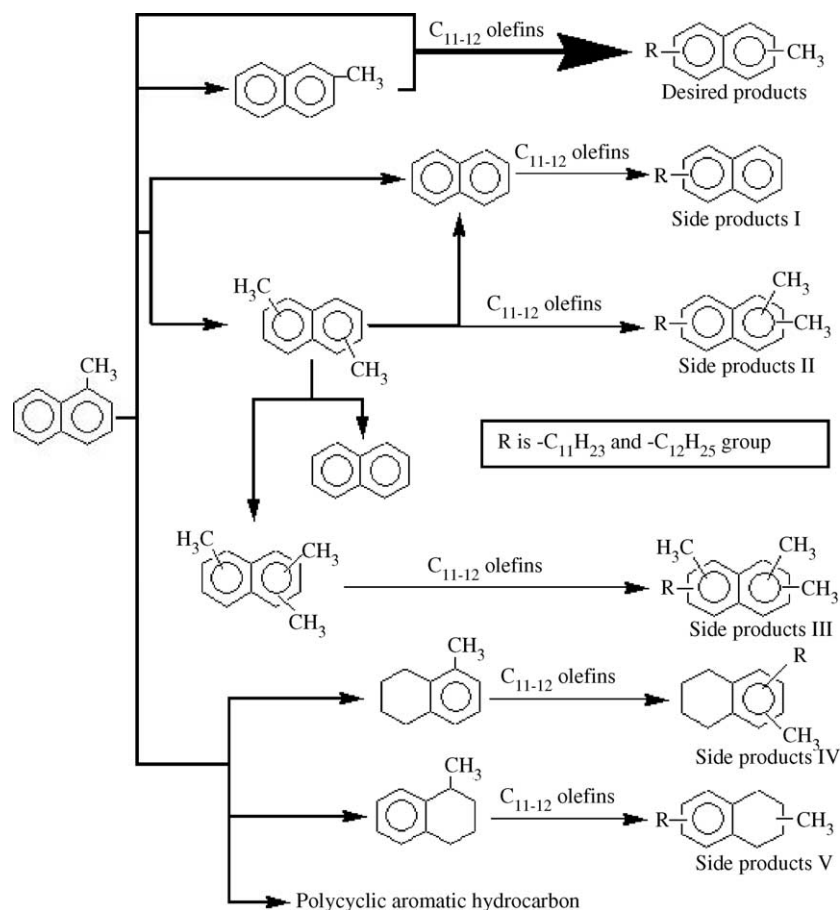
adopted based on previous report [11]. After the alkylation reaction, the upper layer containing the alkylated products and unreacted reactants was separated from the ionic liquid catalyst layer at the bottom of flask simply by decantation. All samples were characterized qualitatively with HP6890/5973 GC/MS equipped with an HP-5MS column,  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ; quantitative analyses were carried out with HP6890 GC equipped with an HP-5 column,  $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ . The concentrations of reactants and products were directly given by the system of GC chemstation (in this departmental laboratory) according to the area of each chromatograph peak. The conversion of alkenes and selectivity of the desired products, monoalkylated methyl-naphthalene, were used as evaluation standards. The conversion for olefins was defined as  $C_L\%$ , which is the wt.% of olefins consumed in the reaction. The selectivity for the desired products, alkylmethyl-naphthalene (AMN) was calculated by:  $S_{AMN}\% = W_{AMN}/W_{pro} \times 100$ , where  $W_{AMN}$  is the amount of desired AMN products, and  $W_{pro}$  the total amount of the alkylated products, including alkyl-naphthalene, alkyl-methyl-tetrahydronaphthalene, alkyl-dimethyl-naphthalene, alkyl-polymethyl-naphthalene, etc., other than the desired products. The analysis results of the typical reaction mixture,

while the reaction parameters not being optimized, had been given in my previous report [11].

### 3. Results and discussion

The alkylation of  $\alpha$ -methyl-naphthalene with long-chain mixed alkenes goes through a typical Friedel–Crafts reaction. It is a complex competitive process between the main and side reactions (Scheme 1).

Ionic liquids (ILs) are known to have interesting, more important, tuneable properties. Depending on the organic cation and inorganic anion the ionic liquids consist of. They would have different physical and chemical properties by varying the components of ionic liquids. On the basis of varying the organic cation, the properties of the ILs might be highly variable through the different possibilities of alkyl groups. The Lewis acidity of ILs is dependent on the metal halide chosen and its molar fraction. In the present report, effects of various parameters, designing ILs to meet the reaction, like cations of ILs, metal halide chosen and the molar fraction of metal halide, type and amount of modification metal ion on the reaction were studied. In all cases, on the



Scheme 1. The whole competing process for alkylation of  $\alpha$ -methyl-naphthalene with long-chain olefins catalyzed by ionic liquids.

Table 1  
Effects of types of anion and cation of ionic liquids on the alkylation of  $\alpha$ -methylnaphthalene

Entries	Ionic liquids	$C_L$ %	$S_{AMN}$ %
1	BuPyBr-CuCl <sub>2</sub>	0	–
2	BuPyBr-FeCl <sub>3</sub>	28.2	83.7
3	BuPyBr-AlCl <sub>3</sub>	90.3	
4	EMIMBr-AlCl <sub>3</sub>	90.9	96.2
5	MDPyBr-AlCl <sub>3</sub>	89.7	100

0.71 mol fraction of metal halide was adopted.

basis of previous researches [6,10,11], the optimum reaction conditions for this long-chain alkylation reaction were: molar ratio of 4–5:1 for aromatic hydrocarbon to alkenes, in the presence of 15% of ILs catalysts at 313 K for 30 min.

### 3.1. Effects of type of cation and anion on the alkylation

The ILs containing various cations and anions, MDPyCl-AlCl<sub>3</sub>, EMIMBr-AlCl<sub>3</sub>, BuPyBr-AlCl<sub>3</sub>, BuPyBr-FeCl<sub>3</sub>, BuPyBr-CuCl<sub>2</sub> were synthesized (Fig. 1), the composition of these materials are the same as the previous report [11]. Table 1 exhibits their catalytic performance for the alkylation of  $\alpha$ -methylnaphthalene with olefins in the presence of various ILs.

It is found that the anions determine, to a large extent, catalysis properties of ionic liquids, but organic cations mainly influence physical properties, and have a little impact on the catalytic performance. The catalysis performance of pyridinium bromochloroaluminate is better than that of imidazolium bromochloroaluminate ILs. Compared with bromochloroferrate (BuPyBr-FeCl<sub>3</sub>), bromochloroaluminate ILs (BuPyBr-AlCl<sub>3</sub>) indicates the better catalytic performance. No reaction takes place when catalyzed by bromochlorocuprate (BuPyBr-CuCl<sub>2</sub>) ILs.

The analysis results of ILs by ESI-MS indicate that there exist both mononuclear and polynuclear anion species. Because of sensitivity to air, bromochloroaluminate ionic liquid mainly contains oxybromochloroaluminate anion species such as AlCl<sub>2</sub>BrOH<sup>-</sup>, Al<sub>2</sub>OCl<sub>5</sub><sup>-</sup> and Al<sub>3</sub>Cl<sub>6</sub>O<sub>2</sub><sup>-</sup>, etc. Because both bromochloroferrate and bromochlorocuprate ILs are stable to air, no oxychloride ions were detected [11]. In order to explore the reasons, the Lewis acidities of the ILs containing different metal halide was determined by using acetonitrile as IR spectroscopy probe (Fig. 2) [31–34].

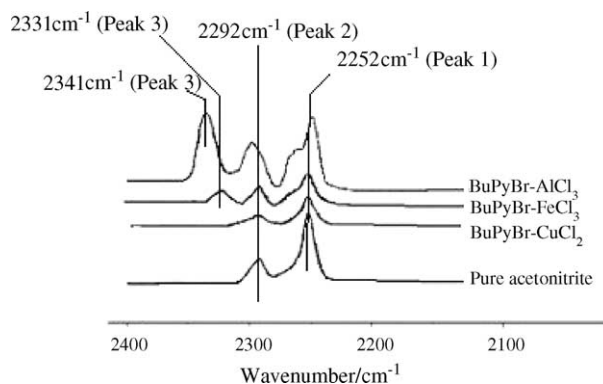
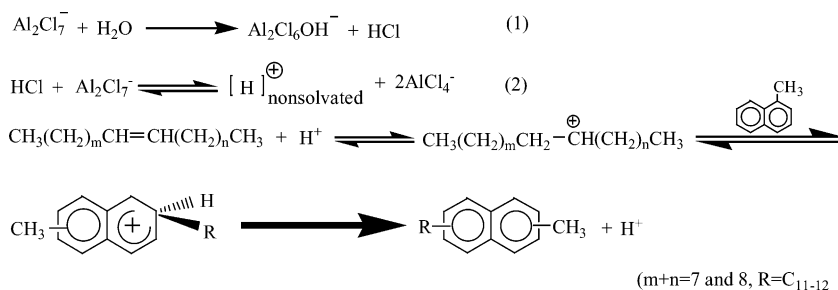


Fig. 2. FT-IR of butylpyridinium Lewis acid ionic liquids containing different metal chlorides.

As can be seen from Fig. 2, there exist two expanding vibration peaks, 2292 cm<sup>-1</sup> (peak 2) and 2252 cm<sup>-1</sup> (peak 1) for acetonitrile. The positions of peaks for BuPyBr-CuCl<sub>2</sub> are entirely same as that of acetonitrile. It is proved that BuPyBr-CuCl<sub>2</sub> does not possess acidity. Moreover, not like Al<sub>2</sub>Cl<sub>6</sub>Br<sup>-</sup> and Fe<sub>2</sub>Cl<sub>3</sub>Br<sup>-</sup>, Cu<sub>2</sub>Cl<sub>4</sub>Br<sup>-</sup> is so stable to air that it cannot react with the microwater in the air. The third peak, 2341 cm<sup>-1</sup> (peak 3) for BuPyBr-AlCl<sub>3</sub> and 2331 cm<sup>-1</sup> (peak 3) for BuPyBr-FeCl<sub>3</sub>, exists in the IR of ILs, besides peak 1 and peak 2. The third peak is the characteristic peak of Lewis acid. The result indicates that both BuPyBr-AlCl<sub>3</sub> and BuPyBr-FeCl<sub>3</sub> possess Lewis acidity, and the Lewis acidity of BuPyBr-AlCl<sub>3</sub> is stronger than that of BuPyBr-FeCl<sub>3</sub>. On the basis of the above results, the reaction mechanism for alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins (mixed alkenes,  $m+n=7$  and 8, mass ratio of C11 to C12 is 45/55) catalyzed by ionic liquids is proposed in Scheme 2. HCl is produced by the reaction of ionic liquid and adventitious water in the air (Eq. (1)). The activated proton is produced by the reaction of HCl and anion species Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> or Al<sub>3</sub>Cl<sub>10</sub><sup>-</sup> etc. For this reason the activity of BuPyBr-AlCl<sub>3</sub> is obviously higher than those of BuPyBr-FeCl<sub>3</sub> and BuPyBr-CuCl<sub>2</sub>. As is known to all, the absolutely dry AlCl<sub>3</sub> cannot effectively catalyze the Friedel–Crafts alkylation reaction of arene with olefins, and the microwater is indispensable for the reaction even though catalyzed by traditional AlCl<sub>3</sub>. However, too much water must be avoided in the process of the alkylation reaction, or else the activated species would be destroyed by water, which also is the main reason for deactivation of



Scheme 2. The possible reaction mechanism for alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins catalyzed by ionic liquids (main reaction).

Table 2

Effect of  $N_{\text{AlCl}_3}$  on the alkylation of  $\alpha$ -methyl-naphthalene catalyzed by the BuPyBr-AlCl<sub>3</sub> ionic liquids

Entry	$N_{\text{AlCl}_3}$	$C_L\%$	$S_{\text{AMN}}\%$	Entry	$N_{\text{AlCl}_3}$	$C_L\%$	$S_{\text{AMN}}\%$
1	0.50	0	–	6	0.75	90.5	100
2	0.55	0	–	7	0.80	88.6	94.7
3	0.60	36.4	100	8	0.67	83.3	100
4	0.67	80.9	100	9	0.71	90.1	100
5	0.71	90.3	100	10	0.75	91.0	100

Entries 8–10 are for the repeat data for entries 4–6.

chloroaluminate ionic liquids while the reaction were performed without safeguard.

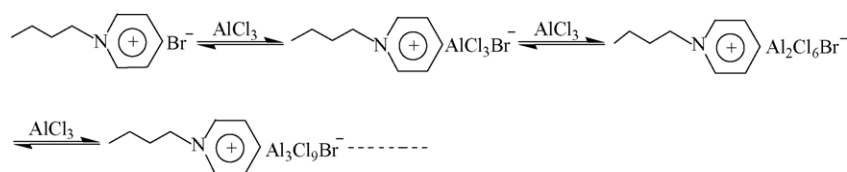
On the basis of the above, it is found that there exists a direct relation between activity and acidity. The stronger the acidity is, the more excellent the activity is. The RPyBr-AlCl<sub>3</sub> exhibits the most excellent catalytic properties and therefore was chosen as catalysts for alkylation of  $\alpha$ -methyl-naphthalene with long-chain olefins.

### 3.2. Effects of molar fraction of anhydrous AlCl<sub>3</sub> on the alkylation

Now that the alkylation of  $\alpha$ -methyl-naphthalene with long-chain olefins goes through the acid-catalyzed mechanism, the reaction is remarkably influenced by catalyst acidity, which is decided by molar fraction of anhydrous AlCl<sub>3</sub> [13–15]. Table 2 shows the effects of molar fraction of anhydrous AlCl<sub>3</sub> ( $N_{\text{AlCl}_3}$ ) on the alkylation.

It is found that there exists an obvious increase in conversion for olefins when the mole fraction of anhydrous AlCl<sub>3</sub> is increased from 0.60 to 0.71. Only a slight change in conversion takes place when the mole fraction of anhydrous AlCl<sub>3</sub> is further increased. But the selectivity for the desired products decreases if the molar fraction of anhydrous AlCl<sub>3</sub> is further increased. No reaction takes place when the mole fraction of anhydrous AlCl<sub>3</sub> is not more than 0.6. The previous report [35] showed that there exists the third peak in FT-IR spectra when the molar fraction of anhydrous AlCl<sub>3</sub> is more than 0.5. It also showed that as the molar fraction of anhydrous AlCl<sub>3</sub> increases, the third peak, Lewis characteristic peak would move to the higher wavenumber, which shows the acidity increases with increasing mole fraction of AlCl<sub>3</sub>. The effects of molar fractions of anhydrous AlCl<sub>3</sub> on the acidity of ILs are illustrated by the equilibrium equation in Scheme 3.

By increasing the molar fraction of anhydrous trichloroaluminum, the bromochloroaluminate ionic liquids would become neutral, acidic and even very strong Lewis acidic melt



Scheme 3. Control of acidity of BuPyBr-AlCl<sub>3</sub> ionic liquids by varying the molar fraction of anhydrous AlCl<sub>3</sub>.

Table 3

Effects of alkyl chain length ( $N_{\text{carbon}}$ ) for alkylpyridinium bromochloroaluminate ionic liquids on the alkylation of  $\alpha$ -methyl-naphthalene ( $N_{\text{AlCl}_3} = 0.67$ )

Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$	Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$
1	2	79.9	100	5	7	79.7	100
2	4	80.9	100	6	8	80.1	100
3	5	80.1	100	7	10	79.1	100
4	6	81.1	100	8	12	78.9	100

Table 4

Effects of alkyl chain length ( $N_{\text{carbon}}$ ) for alkylpyridinium bromochloroaluminate ionic liquids on the alkylation of  $\alpha$ -methyl-naphthalene ( $N_{\text{AlCl}_3} = 0.71$ )

Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$	Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$
1	2	90.8	100	5	7	89.7	100
2	4	90.3	100	6	8	90.4	100
3	5	89.9	100	7	10	90.4	100
4	6	87.6	100	8	12	89.0	100

from a basic salt. Bromochloroaluminate melts are designated as basic when the molar ratio of anhydrous AlCl<sub>3</sub> is less than 0.5. A neutral melt is referred to at a mole fraction of anhydrous trichloroaluminum of exactly 0.5, where essentially only the anion AlCl<sub>4</sub><sup>−</sup> is present. An acidic ionic liquid is one in which the molar ratio of anhydrous trichloroaluminum is larger than 0.5. In such acidic melts, the anions Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> and Al<sub>3</sub>Cl<sub>10</sub><sup>−</sup> exist, which act as very strong Lewis acids. The acidity of the systems can be varied in a wide range by varying the molar fraction of anhydrous AlCl<sub>3</sub>.

### 3.3. Effects of alkyl chain length of RPyBr-AlCl<sub>3</sub> ionic liquids on the alkylation

On the basis of molecular design, a series of RPyBr-AlCl<sub>3</sub> ILs (varying the molar fraction of anhydrous AlCl<sub>3</sub> from 0.67 to 0.71) containing various cations with different length alkyl groups (carbon number of alkyl groups,  $N_{\text{carbon}}$ ) were prepared. Their catalytic performances for alkylation of  $\alpha$ -methyl-naphthalene were investigated. The reaction results for the effects of various side-chain length of RPyBr-AlCl<sub>3</sub> ILs with various molar fraction of anhydrous AlCl<sub>3</sub> (0.67, 0.71 and 0.75) are given in Tables 3–5 respectively.

It is obviously seen that, effects of length of alkyl group on the catalysis performance of ILs are very slight when the molar ratio of anhydrous AlCl<sub>3</sub> is 0.67. The influence becomes more obvious when the mole ratio of AlCl<sub>3</sub> is increased. But the effects of length of alkyl group on both



Table 5

Effects of alkyl chain length ( $N_{\text{carbon}}$ ) for alkyipyridinium bromochloroaluminate ionic liquids on the alkylation of  $\alpha$ -methylnaphthalene ( $N_{\text{AlCl}_3} = 0.75$ )

Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$	Entry	$N_{\text{carbon}}$	$C_L\%$	$S_{\text{AMN}}\%$
1	2	91.5	94.6	5	7	88.1	100
2	4	90.5	100	6	8	90.0	98.9
3	5	90.0	100	7	10	90.9	98.6
4	6	88.1	96.5	8	12	88.7	100

conversion for olefins and selectivity for the desired products are not disciplinary. The reasons should be further studied. When the mole ratio of  $\text{AlCl}_3$  is 0.71, the  $\text{RPyBr-AlCl}_3$  ILs containing the various lengths of alkyl groups are all excellent catalysts for the alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins. It is also found that  $\text{BuPyBr}$ , the precursor to  $\text{BuPyBr-AlCl}_3$  ILs, would be prepared easily. Therefore,  $\text{BuPyBr-AlCl}_3$  might be a practical catalyst for the alkylations of  $\alpha$ -methylnaphthalene with long-chain olefins.

### 3.4. Effects of modification of $\text{BuPyBr-AlCl}_3$ by transition metal ion

The anion species in  $\text{BPyCl-AlCl}_3$  (0.71 of molar fraction) ionic liquid exist in the form of  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{Al}_3\text{Cl}_{10}^-$ ,  $\text{AlCl}_3\text{OH}^-$ ,  $\text{Al}_2\text{OCl}_5^-$ , etc. The acid and base behavior of the ILs is controlled by the reaction in Eq. (3) [36]:



Because the  $\text{Cl}^-$  is a strong ligand, the acidity might be increased through introducing an amount of transition metal ion into ionic liquid [37]. The added 5% of  $\text{Cu}^{2+}$  ionic liquid exhibited more excellent catalysis performance for alkylation of isobutane with butene [38]. In the present report, effects of modification of  $\text{BuPyBr-AlCl}_3$  by transition metal ion on alkylation were investigated (Fig. 3).

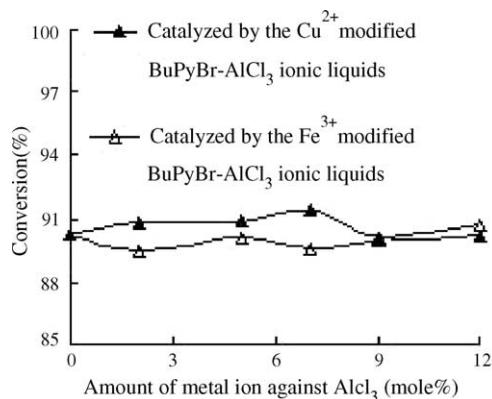


Fig. 3. Effects of transition metal ion amount on the alkylation of  $\alpha$ -methylnaphthalene catalyzed by the modified  $\text{BuPyBr-AlCl}_3$  ionic liquid ( $N_{\text{AlCl}_3} = 0.71$ ).

Table 6

Results of alkylation in the presence of ionic liquid modified by 7%  $\text{Cu}^{2+}$

Entries	$C_L\%$	$S_{\text{AMN}}\%$
1	91.4	100
2	92.1	100
3	91.0	100
4	91.6	100
5 <sup>a</sup>	90.3	100

<sup>a</sup> Is for being catalyzed by unmodified  $\text{BuPyBr-AlCl}_3$  ionic liquid.

It is obviously seen that, 7% of  $\text{Cu}^{2+}$  modified ionic liquid exhibits more excellent catalysis performance for alkylations of  $\alpha$ -methylnaphthalene with long-chain olefins than that of unmodified  $\text{BuPyBr-AlCl}_3$  ionic liquid. But the change is not too remarkable as the reported results [38]. The  $\text{Fe}^{3+}$  modification only has a slight effect on the catalytic properties of ionic liquids.

In order to further corroborate the above results, the experiments for the alkylation in the presence of ionic liquid modified by 7%  $\text{Cu}^{2+}$  were repeatedly performed, the results were given in Table 6. In order to compare, the result catalyzed by unmodified  $\text{BuPyBr-AlCl}_3$  ionic liquid was also listed in the table.

## 4. Conclusion

The alkylation of  $\alpha$ -methylnaphthalene with long-chain mixed alkenes ( $\text{C}_{11-12}$ ) was carried out in a batch mode in the presence of various liquids, performed as both catalyst and solvent. Compared with  $\text{MDPyCl-AlCl}_3$ ,  $\text{EMIMBr-AlCl}_3$ ,  $\text{BuPyBr-FeCl}_3$ ,  $\text{BuPyBr-CuCl}_2$  ionic liquids,  $\text{RPyBr-AlCl}_3$  (0.67–0.75 molar ratio of anhydrous aluminum trichloride) ILs were found to catalyze the reaction with high conversion for long-chain olefins and excellent selectivity for the desired products. The anions of ionic liquids determine, to a large extent, the physical and chemical properties of ionic liquids, but organic cations mainly influence physical properties, and have a slight impact on the catalytic performance. It is also found that the  $\text{Cu}^{2+}$  modified  $\text{BuPyBr-AlCl}_3$  (0.71 of  $\text{AlCl}_3$  mole fraction) ionic liquids by an optimum amount of transition metal indicate more excellent catalytic performances than those of unmodified ionic liquids. The alkylations of  $\alpha$ -methylnaphthalene with long-chain olefins could be well carried out in the presence of the  $\text{Cu}^{2+}$  modified  $\text{BuPyBr-AlCl}_3$  (0.71 of  $\text{AlCl}_3$  mole fraction) ionic liquids, which were used as both high efficient catalyst and novel solvent.

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