

Alkylation of α -methylnaphthalene with long-chain alkenes catalyzed by butylpyridinium bromochloroaluminate ionic liquids

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Abstract

Alkylations of α -methylnaphthalene with long-chain alkenes have been investigated in the presence of various cations bromochloroaluminate room temperature ionic liquids like 1-ethyl-3-methylimidazolium bromochloroaluminate (EMIMBr–AlCl₃), butylpyridinium bromochloroaluminate (BuPyBr–AlCl₃) and organic polycation ionic liquid, methylenedipyridinium bromochloroaluminate (MeDiPyCl–AlCl₃). Effects of anions in ionic liquids on their catalytic performance are also studied. It is found that the BuPyBr–AlCl₃ (0.67–0.75 molar fraction of AlCl₃) ionic liquid exhibits outstanding catalytic properties. The influences of various reaction parameters such as dosage of catalyst, reaction temperature and reaction time on the alkylation catalyzed by BuPyBr–AlCl₃ were investigated. Under the optimum reaction conditions, higher than 90% conversion of alkenes and 100% selectivity for the desired products were obtained. After reaction, the upper organic layer is separated, and the left ionic liquid is reused three times only with a slight decrease in its catalytic activation.

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1. Introduction

Long-chain alkylmethylnaphthalene sulfonate (AMNS) surfactants possess outstanding capability and efficiency of lowering the aqueous solution surface tension and the dynamic interfacial tension between oil and water [1]. AMNS have a great potential for enhanced oil recovery with low costs and high efficiency. Long-chain alkylmethylnaphthalenes are the core intermediates for AMNS. Therefore, studies on the long-chain alkylation of methylnaphthalene are very important from both theoretical and practical viewpoints. To date, alkylation of benzene has already been widely and thoroughly investigated [2–4]. However, naphthalene and its derivatives have not been taken into account. The alkylation of α -methylnaphthalene with long-chain mixed alkenes is a typical Friedel–Crafts reaction. In general, the

reaction is catalyzed by AlCl₃, H₂SO₄, HF and other Lewis acidic catalysts. However, all of the processes have met with common problems, such as heavy environmental pollution, troublesome product recovery and purification, and no recyclability of catalysts. Therefore, to exploit the environmentally friendly catalytic technology have been of keen interest in the development of chemical industry. In recent years, the room temperature ionic liquids are being more and more regarded as relatively clean catalysts and solvents [5–8]. Many organic reactions, such as alkylation [9–11], acylation [12,13], Heck reaction [14], hydroformylation [15], oxidation [16], and Knoevenagel condensation [17], have been reported to proceed in the room temperature ionic liquids with excellent yields and selectivity.

In our laboratory, studies on long-chain alkylations of methylnaphthalene catalyzed by both traditional catalysts [18–21] and novel alkyl ammonium bromochloroaluminate ionic liquid catalysts [22,23] have been done. Compared with traditional catalysts, the ionic liquid catalysts exhibit many

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outstanding advantages, such as simplicity and efficiency of the method, easy product isolation, excellent selectivity for desired products, and no organic solvent needed. Wicelinski and Gale [24] characterized bromochloroaluminate ionic liquid by fast atom bombardment mass spectrometry (FAB–MS), detecting some anions such as AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, AlCl_3OH^- , $\text{Al}_2\text{OCl}_5^-$ and $\text{Al}_2\text{Cl}_6\text{OH}^-$. In the present paper, the alkylations of α -methylnaphthalene in the presence of various ionic liquids were carried out. The synthesized ionic liquids were characterized by electrospray ionization mass spectrometry (ESI–MS). On the basis of analysis results, the possible reaction mechanism is proposed. Gas chromatography and gas chromatography mass spectrometry were used as the appraisal method for alkylation technology [20,21]. The influences of various reaction parameters such as dosage of catalyst, reaction temperature and reaction time on the alkylation catalyzed by butylpyridinium bromochloroaluminate ($\text{BuPyBr}-\text{AlCl}_3$) were investigated. Moreover, reusability of ionic liquid was also studied, and possible reasons for the deactivation of the catalyst are discussed. On the basis of previous studies [18,19,22,23], 5:1 of molar ratio for α -methylnaphthalene to long-chain alkenes was adopted in all cases.

2. Experimental

2.1. Synthesis and characterization of ionic liquids

2.1.1. Synthesis of precursor to ionic liquids

The preparation of the precursor, butylpyridinium bromide (BuPyBr), by reaction of pyridine and 1-bromobutane was performed in a 500 mL oven-dried round bottom flask equipped with stirrer, and a reflux condenser, a drying pipe, a thermometer and a dosing funnel. The mixture containing equimolar amounts (0.6 mol) of commercially available pyridine and 1-bromobutane was heated to 393–453 K in an oil-bath for 10–20 min. During the latter stages of the heating, an exothermic reaction took place forming an emulsion that disappeared in a few minutes to produce a slightly brown viscous liquid. At this point, the oil-bath was removed and the solution was allowed to stir and cool for 10–20 min. The stirred solution was then heated at 393–453 K in an oil-bath for an additional 10–20 min and then the liquid was cooled in an ice bath for a few minutes. Pale brown crystals of BuPyBr were obtained. Preparation of the various precursors like 1-ethyl-3-methylimidazolium bromides (EMIMBr), and organic polycation ionic liquid, methylenedipyridinium dichloride (MeDiPyCl) was carried out by a similar method.

2.1.2. Synthesis and characterization of ionic liquids

$\text{BuPyBr}-\text{AlCl}_3$, $\text{BuPyBr}-\text{FeCl}_3$ and $\text{BuPyBr}-\text{CuCl}_2$ ionic liquids were synthesized by adding 0.5 mol of the synthesized BuPyBr into a 250 mL oven-dried round bottom flask, and then introducing a definite molar metal halide, anhydrous aluminum trichloride, anhydrous iron trichloride and

anhydrous copper chloride, into the batches from a dosing funnel. The reactions were exothermic, and temperature was kept at 303 K with the use of an ice bath. After all of the metal halide was 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. Then the temperature was cooled to room temperature using an ice bath, and the ionic liquid catalysts were produced. 1-Ethyl-3-methylimidazolium bromochloroaluminate ($\text{EMIMBr}-\text{AlCl}_3$) and organic polycation ionic liquid, methylenedipyridinium bromochloroaluminate ($\text{MeDiPyCl}-\text{AlCl}_3$) ionic liquids were prepared by a similar method. Analytical grade anhydrous aluminum trichloride, iron trichloride and copper chloride were used without further purification. The synthesized ionic liquids were characterized with HP 1100 LC/MS.

2.2. Alkylation of α -methylnaphthalene and analysis

First, 30 g of α -methylnaphthalene (>98%) and mixed alkenes C_{11-12} (C_{11} to C_{12} weight ratio 45/55, purchased from Fushun Petrochemical Company) were put into a 100 mL three-necked flask, the molar ratio of aromatic hydrocarbon and alkenes being 5. Then a certain amount of ionic liquid as catalyst was added. After stirring for about 30 min at room temperature to make the agents homodispersed. The reaction time was counted when the mixture was heated to the required reaction temperature. The reaction mixtures were stirred at 273–373 K for about 0–360 min. After the total alkylation, the upper layer containing the alkylated products and unreacted reactants was separated from the ionic liquid catalyst layer at the bottom of the flask simply by decantation. All samples were characterized qualitatively with HP6890/5973 GC/MS equipped with a HP-5MS column, 30 m \times 0.25 mm \times 0.25 μm . Helium was used as the carrier gas at a flow rate of 0.8 mL/min. The injector temperature was 310 °C. The oven temperature was programmed from 120 to 300 °C at a rate of 20 °C/min. The final temperature was held for 2–8 min. Ions were formed for mass spectrometric detection using positive ion electron impact ionization (EI) at the electron energy of 70 eV. Quantitative analyses were carried out with HP6890GC equipped with a HP-5column, 30 m \times 0.32 mm \times 0.25 μm . The initial oven temperature was 100 °C. Then ramped to 300 °C at a rate of 12 °C/min. The final temperature was held for 2–8 min. Nitrogen was used as the carrier gas. Vaporizer and FID detector temperatures were 310 °C. The conversion for olefins (α -methylnaphthalene) was defined as $C_L\%$ ($C_{MN}\%$), which is the wt.% of olefins (α -methylnaphthalene) consumed in the reaction. The selectivity for the desired products, alkylmethylnaphthalene was calculated by: $S_{AMN}\% = W_{AMN}/W_{\text{pro}} \times 100$, where W_{AMN} is the amount of desired monoalkylated products, and W_{pro} is the total amount of the alkylated products, including alkyl-naphthalene, alkylmethyltetrahydronaphthalene, alkyl-dimethylnaphthalene, alkyl-polymethylnaphthalene, etc., other than the desired products.

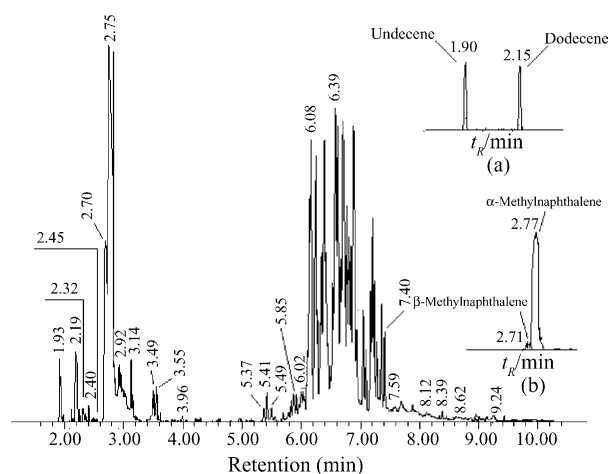


Fig. 1. Total ion current chromatogram of the typical sample for alkylation of methyl naphthalene catalyzed by ionic liquids (reaction conditions: molar ratio of α -methyl naphthalene to olefins = 2:1; $T = 80^\circ\text{C}$; $t = 360$ min; dosage of catalyst = 15%, weight percent of ionic liquid to reagents); (a) and (b) are ion current chromatograms of the starting material, mixed olefins and the α -methyl naphthalene).

3. Results and discussion

The alkylation of α -methyl naphthalene with long-chain mixed alkenes goes through a typical Friedel–Crafts reaction. It is a complex process consisting of reactions. The reaction products were characterized by GC/MS (Fig. 1). The analytical results are listed in Table 1, and the retention times of products in Table 1 corresponding with those in Fig. 1.

The analytical results indicate that the reaction products are quite complex, except for the desired products, a series of isomers of monoalkylated methyl naphthalene, side products, mainly include isomers of monoalkyl naphthalene, monoalkyldimethyl naphthalene, monoalkylmethyl tetrahydronaphthalene and polycyclic aromatic hydrocarbon are included. Under the reaction conditions, the alkylation, isomerization, disproportionation, hydrogenation, etc. take place synchronously. In order to achieve high conversions of reactants and the selectivities for the desired products, the reaction parameters need be optimized.

Alkylations of α -methyl naphthalene, in the presence of different catalytic system, need a similar value for molar

Table 1
GC–MS analysis of the typical sample from alkylation of α -methyl naphthalene catalyzed by ionic liquids

Retention time ^a (min)	Compounds
1.93	Undecene
2.19	Dodecene
2.32	Naphthalene
2.40–2.45	Methyl tetrahydronaphthalenes
2.70	β -Methyl naphthalene
2.75	α -Methyl naphthalene
2.92–3.14	Dimethyl naphthalenes
3.49–3.96	Trimethyl naphthalenes
5.37	Alkylmethyl tetralin (alkylated side products)
5.41	Alkyl naphthalene (alkylated side products)
5.49–6.02	Alkylmethyl tetralins (alkylated side products)
6.08–7.40	Alkylmethyl naphthalenes (desired products)
7.59–8.12	Alkyldimethyl naphthalenes (alkylated side products)
8.39	Alkyltrimethyl naphthalene (alkylated side products)
8.62–9.24	Polycyclic aromatic hydrocarbons

^a The same as those in Fig. 1.

ratio of reagents [18,19,22] to compare their catalytic performance. Therefore, the effects of molar ratio of reagents on the reaction were not investigated in this report. In all cases, molar ratio of 5 for α -methyl naphthalene to olefins is adopted. The BPyBr–AlCl₃ ionic liquid was mainly used as catalyst for alkylation of α -methyl naphthalene with long-chain olefins. The effects of various reaction parameters on the reaction were studied.

3.1. Effects of ionic liquid catalyst type on the alkylation of α -methyl naphthalene

For their excellent chemical and physical properties, ionic liquids are attracting a great deal of attention as possible replacement for conventional catalysts and solvents. By a judicious combination of cations and anions, it is possible to adjust the catalytic performance to the requirement of the reaction, thus creating an almost indefinite set of “designer medium”. In the present paper, effects of cations and anions composing ionic liquids on the alkylation were studied.

Table 2
Effect of type of cation on the catalytic performance of ionic liquids

Entries	Catalyst	Molar fraction of AlCl ₃	C _L %	C _{MN} %	S _{AMN} %
1	EMIMBr–AlCl ₃	0.67	88.4	18.3	100
2	EMIMBr–AlCl ₃	0.71	90.9	22.6	96.2
3	EMIMBr–AlCl ₃	0.75	91.8	26.6	84.6
4	BuPyBr–AlCl ₃	0.67	85.9	10.1	100
5	BuPyBr–AlCl ₃	0.71	90.3	23.7	100
6	BuPyBr–AlCl ₃	0.75	90.5	24.5	100
7	MeDiPyCl–AlCl ₃	0.67	88.8	19.5	100
8	MeDiPyCl–AlCl ₃	0.71	89.7	21.0	100
9	MeDiPyCl–AlCl ₃	0.75	91.0	25.0	92.4

Reaction conditions: molar ratio α -methyl naphthalene to long-chain olefins = 5:1; $W_{\text{cat}} = 15\%$; $T = 353$ K; $t = 30$ min.

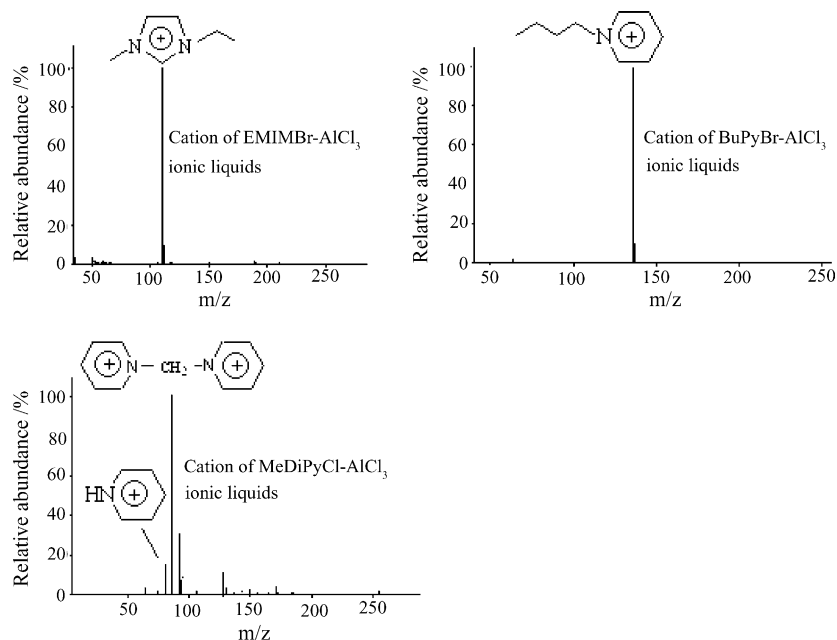


Fig. 2. The ESI-MS of ionic liquids with different cations.

3.1.1. Effects of cations on the alkylation

On the basis of previous studies [18–20,22,23], the alkylation in the presence of various ionic liquids comprising EMIMBr–AlCl₃, BuPyBr–AlCl₃ and MeDiPyCl–AlCl₃ was investigated (Table 2). The cations of ionic liquids were analyzed by ESI/MS (Fig. 2).

As can be seen from Table 2, the ionic liquids consisting of different cations and the same molar fraction *N* (*N*, 0.67–0.75 molar fraction of AlCl₃; for EMIMBr–AlCl₃ and BuPyBr–AlCl₃, which is calculated by: $N = n_{\text{AlCl}_3} / (n_{\text{AlCl}_3} + n_{\text{ILs}})$, where n_{AlCl_3} is the amount of AlCl₃; n_{ILs} is the amount of EMIMBr or BuPyBr; for MeDiPyCl–AlCl₃, $N = n_{\text{AlCl}_3} / (n_{\text{AlCl}_3} + 2n_{\text{MeDiPy}})$, where n_{MeDiPy} is the amount of MeDiPyCl) of AlCl₃ exhibit similar catalytic activities and selectivities. Therefore, it is concluded that organic cation type mainly influence selectivity, and have little effect on the catalytic activity. The possible reason should be further studied. It is found that BuPyBr–AlCl₃ (*N* is 0.67–0.75) exhibits the best catalytic performance among the ionic liquids comprising various cations. Moreover, because of inexpensiveness and simple preparation method, BuPyBr–AlCl₃ could be a practical catalyst for alkylation of α -methyl-naphthalene with long-chain mixed alkenes.

3.1.2. Effects of anions on the alkylation

Table 3 shows the effects of anions of ionic liquids on their catalytic performance. It is found that the anions affected the catalytic performance of ionic liquids to a large extent. Bromochloroalumininate ionic liquid showed the best catalytic performance. No reaction occurred when catalyzed by BuPyBr–2.5CuCl₂ ionic liquid was used.

The anionic species of ionic liquids were characterized by ESI-MS, and are shown in Figs. 3–5. There

Table 3

Effect of anions on the catalytic performance of ionic liquids

Entries	Catalyst ^a	C _L %	C _{MN} %	S _{AMN} %
1	BuPyBr–AlCl ₃	90.3	23.7	100
2	BuPyBr–FeCl ₃	28.2	5.2	83.7
3	BuPyBr–CuCl ₂	0	0	–

Reaction conditions: molar ratio α -methyl-naphthalene to olefins = 5:1; $W_{\text{cat}} = 15\%$; $T = 353\text{ K}$; $t = 30\text{ min}$.

^a 0.71 molar fraction of metal halide.

exist both mononuclear and polynuclear anion species. Because of sensitivity to air, bromochloroalumininate ionic liquid mainly contains oxybromochloroalumininate anion species such as AlCl₂BrOH[–], Al₂OCl₅[–], Al₃Cl₆O₂[–], etc. Both BuPyBr–2.5FeCl₃ and BuPyBr–2.5CuCl₂ are stable towards air, no oxychloride ions being detected. The order of Lewis acidity for the studied ionic liquids is: Al₂Cl₇[–] > Fe₂Cl₃[–] > Cu₂Cl₅[–]. Moreover, molar fraction of

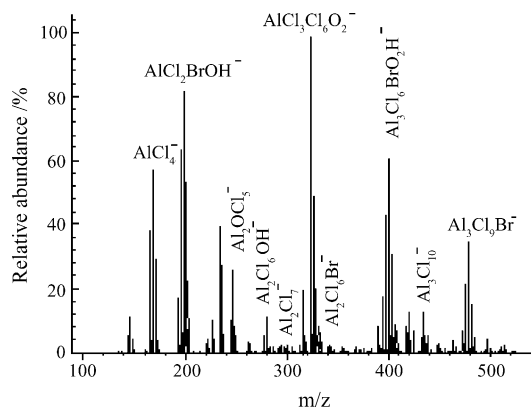


Fig. 3. The ESI-MS of anion of BuPyBr–AlCl₃ ionic liquids (molar fraction of AlCl₃ is 0.71).

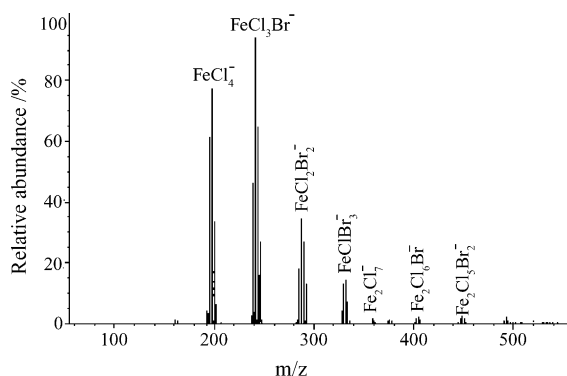


Fig. 4. The ESI-MS of anion of BuPyBr-FeCl₃ ionic liquids (molar fraction of FeCl₃ is 0.71).

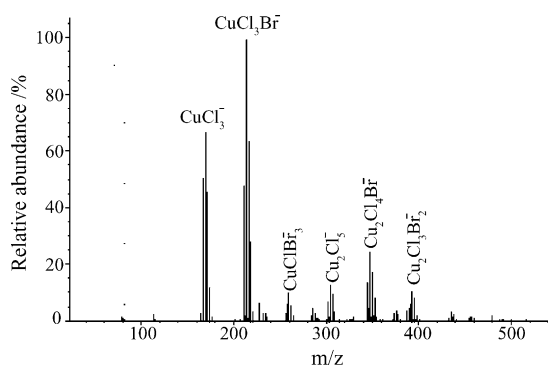
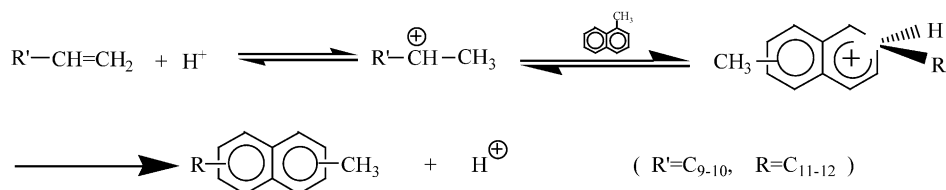
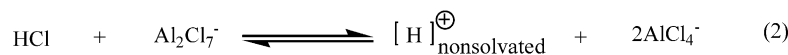


Fig. 5. The ESI-MS of anion of BuPyBr-CuCl₂ ionic liquids (molar fraction of CuCl₂ is 0.71).

AlCl₃ has a decisive influence on the catalytic performance as shown in Table 2. On the basis of previous studies [22,23], the 0.67–0.71 molar fraction of AlCl₃ is optimum for alkylation of α -methyl-naphthalene in the presence of ionic liquids. The effects of molar fraction of AlCl₃ on the reaction are not investigated any longer.

On the basis of the above results, the possible mechanism is proposed (Scheme 1). 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



Scheme 1. Possible catalysis processes of Friedel-Crafts alkylation reaction of α -methyl-naphthalene.

Table 4
Effects of dosage of catalyst alkylation reaction of α -methyl-naphthalene with long-chain olefins

Entries	Dosage of catalyst (%)	C _L %	C _{MN} %	S _{AMN} %
1	5	34.1	6.1	100
2	7	34.7	7.2	100
3	10	53.6	9.7	100
4	12	85.7	16.6	100
5	15	89.3	17.4	100
6	20	89.6	17.5	100

Reaction conditions: molar ratio α -methyl-naphthalene to olefins = 5:1; T = 353 K; t = 30 min.

anion species Al₂Cl₇⁻ or Al₃Cl₁₀⁻, etc. For this reason the activity of BuPyBr-AlCl₃ is obviously higher than those of BuPyBr-FeCl₃ and BuPyBr-CuCl₂.

3.2. Effect of dosage of catalyst on the alkylation of α -methyl-naphthalene

Table 4 shows the effects of dosage of catalyst, BuPyBr-AlCl₃ (0.67 molar fraction of AlCl₃), on the alkylation of α -methyl-naphthalene. The dosage of catalyst is the concentration AlCl₃ in the reaction mixture. The conversions for both α -methyl-naphthalene and olefins obviously increased from 34.1 and 6.1% to 89.3 and 17.4%, respectively, when the dosage of catalyst is increased from 5 to 15%, and then leveled off. Thus optimum dosage of catalyst is 15%.

3.3. Effect of reaction temperature on the alkylation of α -methyl-naphthalene

Effect of reaction temperature on the alkylation of α -methyl-naphthalene was investigated by varying reaction temperature from 273 to 373 K. The results are given in Table 5. The catalyst exhibits outstanding catalytic properties, and the reaction may be well carried out at low reaction temperatures. Only a slight change was observed when the reaction temperature was increased from 273 to 373 K.

Table 5
Effect of reaction temperature on the alkylation reaction of α -methylnaphthalene

Entries	<i>T</i> (K)	<i>C_L</i> %	<i>C_{MN}</i> %	<i>S_{AMN}</i> %
1	273	88.7	24.0	100
2	298	88.4	30.0	100
3	333	87.6	26.0	100
4	353	89.3	17.4	100
5	373	88.6	31.9	100

Reaction conditions: molar ratio α -methylnaphthalene to olefins = 5:1; *W_{cat}* = 15%; *t* = 30 min; BuPyBr–AlCl₃ (0.67 molar fraction of AlCl₃) ionic liquid were adopted.

Table 6
Effect of reaction time on the alkylation reaction of α -methylnaphthalene with long-chain olefins

Entries	Reaction time (min)	<i>C_L</i> %	<i>C_{MN}</i> %	<i>S_{AMN}</i> %
1	0	79.2	18.3	100
2	30	90.1	22.1	100
3	60	90.1	24.0	100
4	120	90.0	24.7	100

Reaction conditions: molar ratio α -methylnaphthalene to olefins = 5:1; *W_{cat}* = 15%; *T* is room temperature and BuPyBr–AlCl₃ (0.67 molar fraction of AlCl₃) ionic liquid were adopted.

3.4. Effect of reaction time on the alkylation of α -methylnaphthalene

Effect of reaction time on the alkylation of α -methylnaphthalene was investigated by varying reaction time from 0 to 480 min. The results are given in Table 6. No obvious change was observed after 30 min of reaction. Thus the optimum reaction time is 30 min.

3.5. Reusability of BuPyBr–AlCl₃ catalyst for alkylation of α -methylnaphthalene

Hereafter the reusability of BuPyBr–AlCl₃ ionic liquid for alkylation of α -methylnaphthalene was studied. The results are given in Table 7.

The products and unreacted reactants do not dissolve in the ionic liquids, and the ionic liquids could be isolated easily by decantation, and be reused directly. The ionic liquid may be reused three times with a slight decrease in its catalytic activity. However, the conversion obviously decreased for the fourth reaction, possibly due to the deactivation of ionic liquid catalyst as a result of the destruction by water in the air [25].

Table 7
The reaction results of the reusability for ionic liquid catalysts

Recycling times	<i>C_L</i> %	<i>C_{MN}</i> %	<i>S_{AMN}</i> %
1	90.2	19.7	100
2	89.7	19.9	100
3	89.1	17.6	100
4	79.5	15.4	100

Reaction conditions: molar ratio α -methylnaphthalene to olefins = 5:1; *W_{cat}* = 15%; *t* = 30 min; *T* is room temperature, and BuPyBr–AlCl₃ (0.67 molar fraction of AlCl₃) ionic liquid were adopted.

4. Conclusion

The alkylation of α -methylnaphthalene with long-chain alkenes was carried out in the presence of various ionic liquid catalysts. The butylpyridinium bromochloroaluminate (BuPyBr–AlCl₃) ionic liquid exhibits an outstanding catalytic performance. Under the optimum reaction conditions, higher than 90% conversion of olefins and 100% selectivity for the desired products were achieved. Compared with classical reaction media, BPyBr–AlCl₃ ionic liquid exhibited many outstanding advantages, such as simplicity and efficiency of the method, easy product isolation, excellent selectivity for desired products, and no organic solvent needed. After reaction, the upper organic layer is separated, and the left ionic liquid is reused three times only with a slight decrease in its catalytic activity. But the catalytic performance deteriorates when the ionic liquid is further reused. Thus, other ionic liquid systems should be further investigated to improve the reusability of ionic liquids.

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