

Friedel–crafts alkylation of α -methylnaphthalene in the presence of ionic liquids

Zhong-Kui Zhao*, Wei-Hong Qiao, Zong-Shi Li, Gui-Ru Wang, Lü-Bo Cheng

State Key Laboratory of Fine Chemicals, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, PR China

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Abstract

Alkylations of α -methylnaphthalene with long-chain alkenes (mixed C_{11-12} olefins) in the presence of room temperature ionic liquids and zeolite catalysts have been investigated. The influences of various parameters, such as type and dosage of catalyst, molar ratio of α -methylnaphthalene to alkenes, reaction temperature, and reaction time were studied. The $Et_xNH_{4-x}Cl-AlCl_3$ ($x = 1-3$, 0.67–0.75 molar fraction of aluminum trichloride) ionic liquids, compared with HY, USY zeolite and the other ethylamine-containing ionic liquids, were found to catalyze the reaction with high conversion of long-chain olefins and good selectivity for monoalkylated methylnaphthalene.

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Keywords: Ionic liquids; Alkylation; α -Methylnaphthalene; Long-chain alkenes; HY and USY

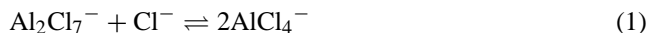
1. Introduction

Alkyl naphthalene sulfonates are one of the most important anionic surfactants for various industrial purposes. By using them as a chemical oil-displacing agent for enhanced oil recovery, satisfactory results could be obtained, and the ultralow interfacial tension between oil and water could be achieved. Moreover, because of their eminent surface activity, they may be used in many fields, such as cleaning, dyeing and printing, emulsifying, ore milling, and nanotechnology. Long-chain alkylmethylnaphthalenes are the key intermediates for alkyl naphthalene sulfonate anionic surfactants. The alkylation of methylnaphthalene with long-chain olefins is of both industrial importance and academic relevance. To date, alkylation of benzene has already been widely and thoroughly investigated [1–3]. But naphthalene and its derivatives have not been taken into account. In particular, alkylation of methylnaphthalene was rarely conducted [4]. In our laboratory, the alkylation of methylnaphthalene catalyzed by $AlCl_3$ had already been studied [5]. The alkylation of α -methylnaphthalene with long-chain mixed alkenes is a typ-

ical Friedel–Crafts reaction. In general, this reaction is catalyzed by $AlCl_3$, H_2SO_4 , HF and other Lewis acid catalysts. However, all of the processes have met with some common problems, such as heavy environmental pollution, and troublesome product recovery and purification, and catalysts cannot be reused. Therefore, investigation and development of environmentally friendly catalytic technology have attracted great interest from chemical industry. In recent years, the room temperature ionic liquids are being more and more regarded as relatively clean catalysts and solvents [6–9]. Many organic reactions, such as alkylation [10–13], acylation [14–15], Heck reaction [16], hydroformylation [17], oxidation [18], and Knoevenagel Condensation [19], have been reported to proceed in the room temperature ionic liquids with excellent yields and selectivity. One remarkable character of ionic liquids is their changeable properties. Based on “tailoring technology”, the cation and anion composing the ionic liquids could be designed at molecular level; the desirable physical and chemical performance could be obtained. Recently, considerable attention has been thus focused on the use of chloroaluminate room temperature ionic liquids. The acidity of the system can be varied in a wide range depending on the proportions of organic base to Lewis acids. If the mole fraction of trichloroaluminium is less than 0.5, the sys-

* Corresponding author. Tel.: +86 411 88993878; fax: +86 411 83683229.
E-mail address: zkzhao2000@yahoo.com (Z.-K. Zhao).

tem would afford a basic molten salt, and if more than 0.5, it would afford an acidic melt. The acid/base behavior of the melts is controlled largely by the reaction in Eq. (1).



The equilibrium constant for this is in the order of 10^{16} at ambient temperature [20]. As a result, in melts that contain more than a slight excess of AlCl_3 , the Cl^- concentration is very small. Thus, the Al_2Cl_7^- anions are powerful Cl^- acceptors and are the source of a high Lewis acidity. When the AlCl_3 mole fraction approaches or exceeds 0.67, even more strongly acidic chloroaluminate species, such as $\text{Al}_3\text{Cl}_{10}^-$ and Al_2Cl_6 should be taken into account. When HCl is dissolved into acidic chloroaluminate ionic liquids, the Brønsted superacid at ordinary temperature and pressure can be obtained [21–22]. It is similar in strength to liquid HF ($H_0 = -15.1$). Use of low-melting ionic liquids composed of an organic chloride and aluminium chloride as solvents and catalysts for Friedel–Crafts reactions was first reported in 1976 [23]. However, the relative alkylation reactions of naphthalene and its derivatives catalyzed by ionic liquids have not been reported. In the present paper, we first report an efficient method for preparing long-chain monoalkylated methylnaphthalene intermediates through alkylation of α -methylnaphthalene with long-chain olefins (C_{11-12}) catalyzed by alkyl-containing amine room temperature ionic liquids. The effects of various reaction parameters like type and dosage of catalysts, reactant ratio, the reaction temperature and reaction time are investigated. The present work revealed that ionic liquids $\text{R}_x\text{NH}_{4-x}\text{Cl}\cdot\text{AlCl}_3$ ($x = 1, 2, 3$) have potential applications in the synthesis of long-chain monoalkyl methylnaphthalene intermediates. Room temperature ionic liquids, especially those based on the ethylammonium cation, have shown great promise as attractive alternatives to conventional homogeneous catalysis systems. Catalyzed by ionic liquid under the optimal reaction conditions, the alkylation reaction of α -methylnaphthalene with long-chain olefins (C_{11-12}) becomes simple, and many side reactions, such as disproportionation, hydrogenation and so on, were restrained effectively. The high purity of desired products, a series of isomers of long-chain monoalkyl methylnaphthalene intermediates could be achieved under optimal reaction conditions, and no solvent was needed. Furthermore, the products and unreacted reagents do not dissolve in the ionic liquids, and therefore could be isolated easily. Moreover, some useful basal data for investigating and exploiting green alkylation catalysis technology for naphthalene and its derivatives are provided.

2. Experimental

2.1. Synthesis of ionic liquids

A series of ionic liquids, comprising alkylamine hydrochloride $\text{Et}_x\text{NH}_{4-x}\text{Cl}$ ($x = 1, 2, 3$) and the different co-

valently bonded metal halide, anhydrous aluminum trichloride, anhydrous iron trichloride and anhydrous zinc trichloride, were synthesized by adding 0.5 mol alkylamine hydrochloride 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 in batches from a dosing funnel. The reaction was exothermic, and temperature was kept at ca. 313 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. At the end, dried HCl gas, prepared by mixing concentrated H_2SO_4 and sodium chloride was bubbled into the ionic liquids. Analytical grade alkylamine hydrochloride, anhydrous aluminum trichloride, anhydrous iron trichloride and anhydrous zinc trichloride were used without further purification.

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, bought from Fushun Petrochemical Company) were put into a 100 mL 3-neck flask equipped with a stirrer, a reflux condenser with a drying pipe and a thermometer, the molar ratio of aromatic hydrocarbon and alkenes (N_{rea}) varying from 2 to 8. 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. The reaction mixtures were stirred at 273–373 K for about 0–360 min, depending on specific reaction parameters. 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 flask simply by decantation.

All samples were characterized qualitatively with HP6890/5973 GC/MS equipped with a HP-5MS column, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$; quantitative analyses were carried out with HP6890GC equipped with a 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 methylnaphthalene, were used as evaluation standards. The conversion of olefins was defined as $C_L\%$, which is the wt.% of olefins consumed in the reaction. The selectivity of monoalkylmethylnaphthalene was calculated by: $S_{\text{AMN}}\% = W_{\text{AMN}}/W_{\text{pro}} \times 100$, 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 dimethyl naphthalene,

alkylpolymethylnaphthalene, etc., other than the desired products.

3. Results and discussion

Alkylation reaction of α -methylnaphthalene with long-chain alkenes is a typical acid-catalyzed reaction. The reaction, catalyzed by AlCl_3 , is very complex. In addition to alkylation reaction, some of side reactions, such as isomerization, disproportionation, hydrogenation, polyalkylation, etc., took place simultaneously. The products are very complex. Except for the desired products, monoalkylmethylnaphthalene, a series of by-products, such as alkyl naphthalene, alkylmethyltetrahydronaphthalene, alkyl dimethylnaphthalene, alkylpolymethylnaphthalene, and mutialkylated products were detected by GC/MS [5,24–26]. Especially, the boiling points of alkyl naphthalene and alkylmethyltetrahydronaphthalene are too similar with those of the desired products to be separated with satisfactory results. Therefore, novel alkylation technology should be sought. In the present study, alkylation of methylnaphthalene with olefins in $\text{Et}_x\text{NH}_{4-x}\text{Cl}-\text{AlCl}_3$ ($x = 1, 2, 3$) ionic liquids gave a mixture, including of the isomers of monoalkylated products in terms of carbon chain and the position of alkyl substituent, which are all desired products. A major advantage for the use of an ionic liquid for this reaction is that the selectivity towards monoalkylmethylnaphthalene was higher than those catalyzed by anhydrous aluminum trichloride.

Alkylation reaction of α -methylnaphthalene with long-chain alkenes, catalyzed by chloroaluminate ionic liquid modified with HCl, adheres to proton acid catalysis mechanism. The possible catalysis processes are given in Scheme 1.

The superacid properties of protons in acidic chloroaluminate melts could be explained by the reaction between the dissolved HCl and the acidic species (i.e. Al_2Cl_7^- in the melts), which releases protons with extremely low solvation and therefore high reactivity Eq. (1) [8]. Highly dispersed superacid protons in ionic liquids are the active species for the alkylation reactions, which play a decisive role in enhancing rates and selectivities. The molar fraction of AlCl_3 exerts a decisive influence on the acidity of the catalyst system. The effects of various parameters, such as type and dosage of catalysts, molar ratio of α -methylnaphthalene to alkenes, reaction temperature, and reaction time, were studied.

Table 1

Results of alkylations of α -methylnaphthalene with long-chain alkenes catalyzed by different catalysts

Entry	Catalyst	C_L (%)	S_{AMN} (%)
1	USY a	59	100
2	HY b	91	100
3	HY c	11	100
4	HY d	0	–
5	AlCl_3	89	76
6	AlCl_3	92	100 e
7	FeCl_3	56	100 f
8	$\text{Et}_3\text{NHCl}-\text{FeCl}_3$	7	29
9	$\text{Et}_3\text{NHCl}-\text{AlCl}_3$	91	100
10	$\text{Et}_3\text{NHCl}-\text{ZnCl}_2$	0	–

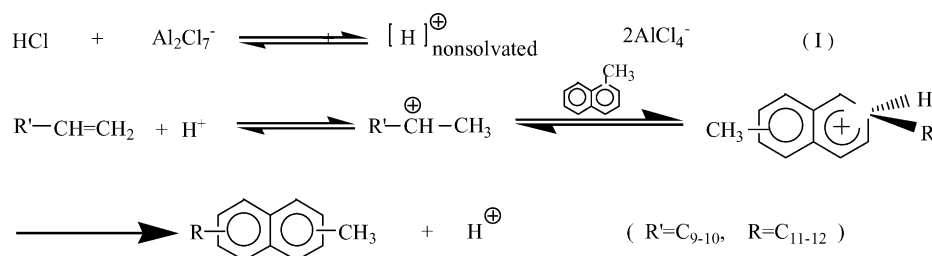
Entries 1–4, molar ratio of α -methylnaphthalene to olefins: 4:1; dosage of catalysts = 20% weight of reactants; reaction time: 240 min; temperature: (a, b) 523 K; (c) 473 K; (d) 453 K. Entries 5–10, reaction conditions: molar ratio of α -methylnaphthalene to olefins: 5:1; dosage of catalysts: 12% weight of reactants; temperature: 353 K; time: 30 min. (e, f) Cyclohexane, used as solvents, were added, molar ratio of cyclohexane to α -methylnaphthalene: 4:1.

3.1. Effects of kinds and dosage of catalysts on alkylation reaction

3.1.1. Effects of different catalysts on the alkylation reaction

Results of alkylation of α -methylnaphthalene with long-chain alkenes catalyzed by different ionic liquids, produced by comprising triethylamine hydrochloride and different metal halides, molar fraction of metal halides 0.67, are listed in Table 1.

Under optimal reaction conditions, higher than 90% conversions of olefins were obtained by $\text{Et}_3\text{NHCl}-\text{AlCl}_3$, HY, and AlCl_3 . Compared with anhydrous AlCl_3 , remarkably higher selectivities towards monoalkylated methylnaphthalene were obtained when catalyzed by $\text{Et}_3\text{NHCl}-\text{AlCl}_3$ ionic liquids and HY. The reaction, catalyzed by AlCl_3 , is very complex. In addition to alkylation reaction, some of the side-reactions, such as isomerization, disproportionation, hydrogenation, polyalkylation, etc., took place simultaneously. Expect for hydrogenation, the other side-reactions can be explained. At present, the mechanism of hydrogenation in alkylation of aromatic hydrocarbon was not reported. The alkylation of MN was catalytically carried out by zeolite, but no hydrogenated products were found, even at high temperature and pressure. In order to postulate the hydrogenation



Scheme 1. Possible catalysis processes of Friedel–Crafts alkylation reaction of α -methylnaphthalene with long-chain alkenes.

mechanism, a blank experiment under the same alkylation condition, without adding any alkyl agent, was performed. The reaction mixture was detected by GC/MS. Polynuclear aromatic hydrocarbon, benzene, toluene, methyltetrahydronaphthalene, etc. were found. This result indicates that, polymerizations of methylnaphthalene release hydrogen, which offers hydrogen sources for hydrogenations of methylnaphthalene. When the reaction was carried out in the presence of AlCl_3 , a great amount of solvents also cause high selectivity towards monoalkylated products to be obtained. It's obvious that ionic liquids played dual roles in the reaction. Ionic liquids could be used as novel and efficient catalysts and solvents for the alkylation of methylnaphthalene.

Moreover, the different ionic liquids, comprising different metal halides and the same alkylamine hydrochloride, will produce completely different reaction results. The ionic liquids, from entry 8 to entry 10, comprise the same cations, Et_3NH^+ and Et_2NH_2^+ , characterized by fast atom bombardment mass spectrometry (FAB-MS) [27], possess completely different catalytic performance, which owe to the important role of anions. The complexing ability of Al_2Cl_7^- , mainly anionic species in $\text{Et}_3\text{NHCl-AlCl}_3$ acidic ionic liquids, with Cl^- is stronger than that of Fe_2Cl_7^- and ZnCl_3^- , which is the source of a high Lewis acidity. The alkylations of methylnaphthalene with long-chain olefins require more powerful acidity; alkylations of benzene with ethylene can be effectively carried out in $\text{Et}_3\text{NHCl-FeCl}_3$ [28], but the alkylations of methylnaphthalene with long-chain olefins cannot be effectively catalyzed. On the other hand, the anions Al_2Cl_7^- are powerful Cl^- acceptors, which strengthen the acidity of proton in the ionic liquids.

Though high conversion of olefins and excellent selectivity for desired products are obtained when catalyzed both by HY and by $\text{Et}_3\text{NHCl-AlCl}_3$ ionic liquids, alkylamine chloroaluminate ionic liquids show more excellent catalytic performance for its high activity at low temperature.

3.1.2. Effects of the type of cations and the molar fraction of AlCl_3 in ionic liquids

Alkylation reactions of α -methylnaphthalene with long-chain olefins were carried out in ethyl-containing chloroaluminate ionic liquid $\text{Et}_x\text{NH}_{4-x}\text{-AlCl}_3$ ($x = 1, 2, 3$). Molar fraction of aluminum trichloride, n , varies from 0.55 to 0.80. The results are listed in Table 2.

The ionic liquids which can be obtained by mixing the preferred compounds having the generic formula R_3NHCl , where at least one of the "R" groups is ethyl, and the covalently bonded metal halide is aluminum trichloride. Both type of organic cation and molar fraction of AlCl_3 exert a marked influence on the physical and chemical properties of ionic liquids. The former is a critical factor deciding the melting points of the molten salts, and the latter has a crucial effect on the acidity of ionic liquid, which decides the catalysis activity. The melting points of $\text{EtNH}_3\text{Cl-AlCl}_3$ ($n = 0.67$) and $\text{Et}_2\text{NH}_2\text{Cl-AlCl}_3$ ($n = 0.67$) are 38°C and 33°C , respectively. However, $\text{Et}_3\text{NHCl-AlCl}_3$ ($n = 0.67$) has a low

Table 2

Effects of the kinds of catalysts on the alkylation reaction

Entry	Catalyst	n	C_L (%)	S_{AMN} (%)
1	$\text{Et}_3\text{NHCl-AlCl}_3$	0.55	0	–
2	$\text{Et}_3\text{NHCl-AlCl}_3$	0.60	44	100
3	$\text{Et}_3\text{NHCl-AlCl}_3$	0.67	91	100
4	$\text{Et}_3\text{NHCl-AlCl}_3$	0.71	91	100
5	$\text{Et}_3\text{NHCl-AlCl}_3$	0.75	91	100
6	$\text{Et}_3\text{NHCl-AlCl}_3$	0.80	76	90
7	$\text{Et}_2\text{NH}_2\text{Cl-AlCl}_3$	0.67	91	100
8	$\text{EtNH}_3\text{Cl-AlCl}_3$	0.67	90	100

Molar ratio of α -methylnaphthalene to long-chain olefins: 5:1; $W_{\text{cat}} = 12\%$; $T = 353\text{ K}$; $t = 30\text{ min}$.

melting point, and it remains fluid liquid form until -8°C . Furthermore, molar fraction n has also an influence on melting points. As far as $\text{Et}_3\text{NHCl-AlCl}_3$ is concerned, when n is less than 0.60, the molten salts remained viscous glassy material at room temperature and atmospheric pressure. It is reported that the ionic liquids show acidity as long as n is more than 0.5 [14]. However, the results showed that no reaction took place when n is equal to 0.55. By increasing the n value, the acidity was raised. When n value reached 0.67, alkylation reaction of α -methylnaphthalene was effectively catalyzed. α -Methylnaphthalene is difficult to be alkylated, and the reaction needs a certain acid strength. Therefore, the reaction does not take place whereas those ionic liquids are acid ($0.55 \geq n > 0.5$). The x value (alkyl number in organic cation) had also a slight influence on the reaction results of alkylation. The most preferred low temperature molten salt was a compound consisting essentially of triethylamine hydrochloride and aluminum trichloride. Mole fraction of AlCl_3 n was about 0.60–0.75, preferably about 0.67; 91% of conversion of olefins and 100% of selectivity of monoalkylated products were achieved.

3.1.3. Effects of dosage of catalysts on alkylation reaction

The dosage of $\text{Et}_3\text{NHCl-AlCl}_3$ ($n = 0.67$) catalyst, W_{cat} , has also been studied. The results are given in Fig. 1.

It can be obviously seen that W_{cat} is crucial for the alkylation reaction. The conversion is nil at the dosage of catalyst

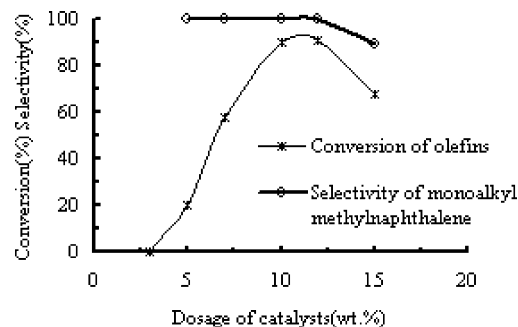


Fig. 1. Effects of the dosages of catalysts on the alkylation reactions. Conditions: molar ratio methylnaphthalene to long-chain olefins = 5:1; $T = 353\text{ K}$; $t = 360\text{ min}$.

less than 3 wt.%. As W_{cat} increased, the conversion of olefins became higher and higher. However, the conversion did not increase monotonously with increasing dosage of catalyst. The possible reason for this is that, at a high dosage of catalyst, the polymerization of aromatic rings produces active hydrogen, which offers hydrogen sources for hydrogenation of olefins. In the mixture, long-chain alkanes were detected. As a result, the conversion of olefins decreased. With the increase of dosage of catalyst, a series of side reactions took place simultaneously, which produces some by-products, such as naphthalene, methyltetrahydronaphthalene, dimethylnaphthalene, polymethylnaphthalene and their further long-chain alkylated products. Furthermore, some polycyclic aromatic hydrocarbons were also detected by GC/MS. Therefore, a large decrease in the selectivity for monoalkyl-methylnaphthalene was obtained. Taking all of these factors into account, the value of 10–12% of W_{cat} was chosen.

3.2. Effects of reaction temperature on alkylation reaction

The effect of reaction temperature on the results of alkylation reaction catalyzed by $\text{Et}_3\text{NHCl-AlCl}_3$ ($n = 0.67$) ionic liquids was investigated in detail. The influence of reaction temperature on the conversion and selectivity is shown in Fig. 2. A dramatic effect on the conversion and a slight effect on the selectivity for monoalkylated products were observed. At 313 K, 91% of high conversion of olefins has been achieved. An obvious decrease in conversion of long-chain olefins took place, when the reaction temperature was further raised. The reason is that, since the alkylation is exothermic, the equilibrium conversion decreases with further increasing reaction temperature. Therefore, 313 K is the optimal reaction temperature.

3.3. Effects of molar ratio of α -methylnaphthalene and long-chain alkenes on alkylation reaction

The influences of mole ratio of methylnaphthalene to alkenes (N_{rea}) on conversion and selectivity in alkylation re-

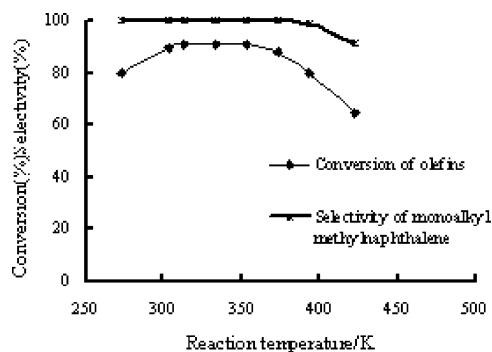


Fig. 2. Effects of the reaction temperatures on alkylation reactions. Conditions: molar ratio methylnaphthalene to long-chain olefins = 5:1; $W_{\text{cat}} = 12\%$; $t = 360$ min.

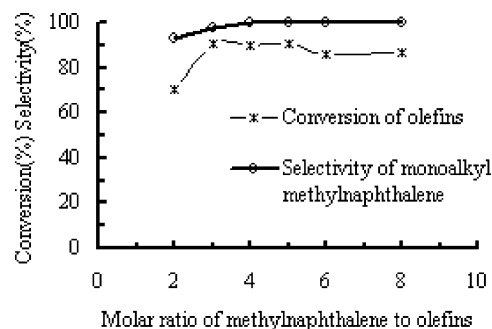


Fig. 3. Effect of N_{rea} values on the results of alkylation reactions. Conditions: $W_{\text{cat}} = 12\%$; $T = 313$ K; $t = 360$ min.

action in $\text{Et}_3\text{NHCl-AlCl}_3$ ($n = 0.67$) ionic liquid are shown in Fig. 3.

The effects of molar ratio of reactants are easily observed from Fig. 3. As N_{rea} increased, the conversion of alkenes reached a maximum and then decline. The maximum of 91% in conversion was observed when N_{rea} was 3. But the selectivity of monoalkylated products, S_{AMN} , is only 98%. When the concentration of α -methylnaphthalene was increased, N_{rea} was not less than 4, 100% of high selectivity for monoalkylated products was obtained. However, the conversion slightly decreased with increasing molar ratios of methylnaphthalene to alkenes. Moreover, with N_{rea} increasing, the cubic capacity effect decreased, therefore the circulation amounts were increased to a great extent, and so production cost would be increased. The reagent molar ratio of 4–5 is preferable.

3.4. Effects of reaction time on alkylation reaction

The influence of reaction time on the conversion and selectivity of alkylation reaction in $\text{Et}_3\text{NHCl-AlCl}_3$ ($n = 0.67$) ambient temperature ionic liquids is given in Fig. 4. It can be readily seen that the reaction time has only a slight influence on the results of alkylation reactions. Within 30 min, the catalysis activity and product selectivity reached an equilibrium (clearly shown in Fig. 4); 90% of conversion of long-chain alkenes and 100% selectivity of desired product were achieved.

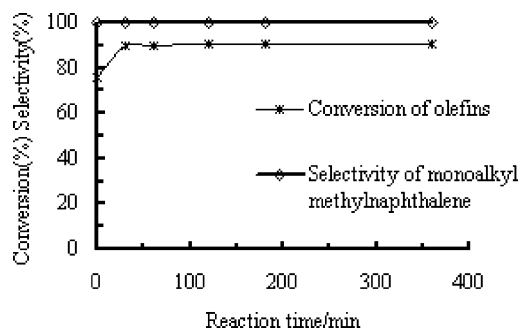


Fig. 4. Effects of reaction time on the alkylation reactions. Conditions: $N_{\text{rea}} = 5:1$; $W_{\text{cat}} = 12\%$; $T = 313$ K.

As can be seen from above, the optimal reaction conditions for this long-chain alkylation reaction were as follows: molar ratio of 4–5:1 for aromatic hydrocarbon to alkenes, in the presence of 12% of ethylamine chloroaluminate ionic liquids at 313 K for 30 min.

4. Conclusions

The alkylation of α -methylnaphthalene with long-chain mixed alkenes (C_{11-12}) was carried out in a batch mode with various catalysts. Compared with HY, USY zeolite and the other ethylamine-containing ionic liquids, ethylamine chloroaluminate ionic liquids, $Et_xNH_{4-x}Cl-AlCl_3$ (0.67–0.75 molar fraction of aluminum trichloride), were found to catalyze the reaction with high conversion of long-chain olefins and excellent selectivity towards monoalkylated methylnaphthalene. The anions of ionic liquids determined, to a large extent, the physical and chemical properties of ionic liquids, but organic cations mainly influenced physical properties, and have little impact on the catalytic performance. Highly dispersed superacid protons in ionic liquids were the active species for the alkylation reactions, which played a decisive role in enhancing rates and selectivities. Under the optimal reaction conditions, more than 90% of conversion for alkenes, and about 100% of selectivity towards monoalkylated methylnaphthalene were obtained. Alkyl-containing amine chloroaluminate ionic liquids could be considered as a novel environmentally friendly alternative to the existing homogeneous catalysts. They could become practical catalysts and efficient solvents for long-chain alkylation of α -methylnaphthalene with olefins.

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