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Alkylation of isobutane and butene using chloroaluminate imidazolium ionic liquid as catalyst: Effect of organosulfur compound additive

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Abstract−Alkylation of isobutane and butene was carried out in a batch unit using 1-butyl-3-methylimidazolium chloride (BMIC)-aluminium (III) chloride ($AlCl_3$) ionic liquid as catalyst. The effects of additives of butyl thioalcohol and ethyl thioether on the properties of ionic liquids for alkylation were investigated. Improvement of production distribution with high yields of isooctane and selectivity of TMP under a mild reaction condition was observed after addition of butyl thioalcohol. Moreover, the effects of operating variables were investigated and the mechanism was discussed.

Key words: Alkylation, Isobutane, Butene-2, Ionic Liquids, Organosulfur

INTRODUCTION

Isobutane/butene alkylation is an important process being developed by the petroleum refining industry for the production of environmentally friendly gasoline. The resulting mixture of alkylates is an ideal blending constituent of gasoline since it can meet environmental standards concerning high octane number (research octane number (RON) of 92-96), low vapor pressure, and low contents of aromatics, alkenes and sulfur [1,2]. Current commercial alkylation processes are catalyzed by either concentrated sulfuric acid (H_2SO_4) or hydrofluoric acid (HF). Both these processes are highly corrosive and environmentally detrimental associated with spent catalyst disposal. Other problems with cooling and separation, high operating costs and safety aspects also trouble the industry and restrict the effective capacity [3]. It is therefore very necessary to develop a new class of catalyst for alkylation reactions.

Room temperature ionic liquids have been recognized as novel solvents [4] and are receiving increasing attention with potential applications in magnetic materials [5], extraction [6], catalysis [7-9], electrochemistry [10-12], biocatalysis [13], biomaterials [14], inorganic materials [15] and polymerization [16]. The important attributes of these ionic liquids include negligible vapor pressure, potential for recycling, compatibility with various organic compounds and organometallic catalysts, and ease of separation of products from reactions [17].

Alkylation catalyzed by ionic liquids is one focus in catalysis study [18-22]. 1-Alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids have been investigated as catalysts for isobutane/2-butene alkylation. [23,24], The main advantages arising from the use of ionic liquids are high octane number and low unsaturation level of alkylate and simple product separation [23]. The low reaction temperature (about 5 °C), however, weakens its advantages over the conventional liquid acids and consequently increases the cooling cost. It is well known that, due to high acidity of the aluminum chloride-based catalysts, side reactions such as cracking, disproportionation and isomerization become more important when the reaction temperature is increased to room temperature (15-30 °C), resulting in high content of C5-C7 (light ends) and C9+ (heavy ends), low selectivity of C8 (including trimethylpentanes (TMPs) and dimethylhexanes (DMHs)), and low ratio of TMP/DMH in alkylates [23,25]. Thus, for reduction of cooling cost, there should be great interest for improving the catalytic performance of the chloroaluminate ionic liquid at room temperature. As mentioned above, the acidity of aluminum chloride is the key point. It is essential to properly modify the acidity of the active site so as to inhibit the side reactions. We anticipate that adding a certain basic organic compound as additive into the ionic liquids would be an effective method to modify the acidity, leading to improvement of the qualities of alkylates. The organosulfur compounds with a pair of unshared electrons should be good choices owing to the strong interaction with Lewis acid (i.e., aluminum chloride).

Thus, in this research, thioalcohol and thioether were used as the inhibitors for side reactions accompanying alkylation in 1-butyl-3-methylimidazolium chloride-aluminium chloride ionic liquids. The effects of operating variables were investigated. The mechanism was also discussed.

EXPERIMENTAL SECTION

1. Preparation of Ionic Liquids Catalysts

BMIC was prepared as follows: dried and redistilled N-methylimidazolium and 1-chloro-butyl were placed into a dry round-bottomed flask equipped with a reflux cooler, a magnetic agitator and a glass thermometer. The mixture was heated under agitation and the temperature was maintained at 85 °C. After 48 hours of reaction, the mixture was cooled to room temperature. After freezing in a refrigerator, unreacted reactants were decanted. Then, the product was washed by using acetonitrile as solvent. The washed product was dried in a vacuum drying box to remove the residual solvent and water.

BMIC-$2AlCl_3$ was prepared by slow addition of the desired amount

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Table 1. Effects of thioalcohol and thioether addition on alkylate composition

Composition of alkylate mixtures (wt%)	Ionic liquid		
	BMIC-2.0AlCl$_3$	BMIC-2.0AlCl$_3$+butyl thioalcohol	BMIC-2.0AlCl$_3$+butyl thioether
2-Methylbutane	5.9	2.7	5.7
2,3-Dimethylbutane	4.9	3.3	5.1
C_6-C_7 (others)	11.7	4.8	12.3
2,2,4-Trimethylpentane	24.6	35.1	23.5
2,2,3-Trimethylpentane	0.1	0.3	0.1
2,3,4-Trimethylpentane	7.0	15.6	7.3
2,3,3-Trimethylpentane	5.6	14.9	6.0
Total TMP	37.3	65.9	36.9
Total DMH	14.2	10.0	15.0
2,2,5-Trimethylhexane	7.9	5.3	7.8
C_{9+} (others)	18.1	8.0	17.2
TMP/DMH	2.6	6.6	2.5
Conversion of 2-butene	99	99	99
Yield (wt% on olefin)	163	179	162

Reaction temperature was 30 °C, molar ratio of isobutane to 2-butene was 10, total reaction time was 40 min, S content in ionic liquid was 1,000 ppmw, and theoretical yield is 204%.

of waterless aluminum chloride to the imidazolium salt. The molar ratio of AlCl$_3$ to 1-butyl-3-methylimidazolium chloride is 2 : 1. The reaction was left stirring overnight at room temperature, in order to allow a perfect homogenization of the resulting ionic liquid. The whole process was kept under a dry nitrogen atmosphere to avoid the hydrolysis of AlCl$_3$. The ionic liquids, once prepared, could be stored for a long time in a dry inert atmosphere.

Butyl thioalcohol ($C_4H_{10}S$), ethyl thioether ($C_4H_{10}S$) were introduced into separate samples of the ionic liquids at −10 °C and the mixtures were also stored in a dry inert atmosphere.

2. Alkylation of Isobutane and Butene

The catalytic performance of the catalysts was evaluated by means of batch alkylation. In all experiments, the alkylation reactions were carried out in a 500 ml stirred pressure reactor and about 30 ml ionic liquid was charged into reactor and brought to the proper temperature before experiment. The feedstocks, i.e., the mixtures of isobutane and butene, were stored over 3 Å molecular sieves to ensure the water content in the feedstocks at a very low degree. After start of stirrer, 400 ml mixture was charged into the reactor by means of a plunger pump in 24 minutes. After finishing feeding, stirring was maintained for a certain time and then turned off. The liquid and gas hydrocarbon phase were collected for analysis. In all experiments, the rate of agitation was 800 rpm and the reaction temperature was controlled by a thermostatic water bath with temperature controller.

3. Analytical Procedures

The gaseous products were analyzed with an SP3420 gas chromatograph with a Plot Al$_2$O$_3$ S capillary column (Φ0.53 mm×50 m) and flame ionization detector. The alkylate mixtures were analyzed by a Shimadzu QP5000 mass spectrometer (with an ion source temperature of 180 °C, in the range 40-400 amu, with scan rate of 1.4 s^{-1}) and a Varian CP3800 chromatograph with 0.25 mm×50 m PONA capillary column and flame ionization detector. S detection was carried out on Varian CP3800 chromatograph with Plus Flame Photometric Detector.

RESULTS AND DISCUSSIONS

1. Effects of Thioalcohol and Thioether

The effect of addition of butyl thioalcohol and ethyl thioether on product distribution was investigated at 30 °C. 2-Butene was used as alkylating agent in this section. The molar ratio of isobutane to 2-butene was 10. The reaction time was 40 min including the feeding time and stirring-holding time. Sulfur content in the ionic liquid was 1,000 ppmw. The typical results are listed in Table 1. In the case of pure BMIC-2.0AlCl$_3$ as catalyst, high butene conversion was obtained. The selectivity of TMP in the alkylate was only 37.3% and ratio of TMP/DMH was 2.6. The contents of heavy ends and light ends were 26.0% and 22.5%, respectively. It is well known that the octane number of alkylate is primarily a direct function of the TMP content. High TMP content in alkylate leads to high octane number, i.e., high quality of the alkylate. Whereas, the DMH, light ends and heavy ends are undesirable. Thus, from the data in Table 1, the quality of the alkylate obtained from alkylation catalyzed by pure BMIC-2.0AlCl$_3$ was poor. In commercial alkylation catalyzed by concentrated sulfuric acid, the content of isooctane is about 72% and ratio of TMP/DMH is about 7 in alkylate typically.

After addition of butyl thioalcohol, enhanced catalytic performance was observed. The conversion of butene was still high. The TMP selectivity increased from 37.3% to 65.9%, the selectivity of DMH decreased from 14.2% to 10.0%, and the ratio of TMP/DMH in isooctane increased from 2.6 to 6.6. The quality of the alkylate was drastically improved. Besides, the yield of liquid product was increased from 163% to 179%, indicating that the butene dimerizations and hydrogen transfer were inhibited. These results led to the conclusion that butyl thioalcohol had a beneficial effect on the catalytic property of the ionic liquid. However, the product distribution of the alkylate obtained from the alkylation catalyzed by BMIC-2AlCl$_3$ with thioether additive was very similar to that of the alkylate obtained from pure BMIC-2AlCl$_3$ system. This result revealed that thioether additive could not inhibit the side reactions and had no positive effect on the catalytic performance of the ionic liquid. In addition, in all experiments, no S species was detected in the liquid products, indicating S stayed in ionic liquid through a certain interaction with ionic liquid. This conjecture was confirmed by observed exotherm of chloroaluminate ionic liquids after addition of butyl thioalcohol and ethyl thioether. In all alkylates, a trace of olefin was detected by means of mass spectrometer, which indicated that the level of saturation in the alkylates was high.

The mechanism about thioalcohol drastically altering the composition of the alkylate obtained from the BMIC-2AlCl$_3$ system is a question. It is well known that BMIC-2AlCl$_3$ is acid, while BMIC-AlCl$_3$ is neutral [26]. In BMIC-2AlCl$_3$ ionic liquid, 1-butyl-3-methylimidazolium is the only kind of cation, $Al_2Cl_7^-$ is the dominant anion, and there are traces of $Al_3Cl_{10}^-$, $AlCl_4^-$ and $AlCl_3$. The equilibrium among the Al species can be expressed as [17]:

$$Al_2Cl_7^- \leftrightarrow AlCl_3+AlCl_4^- \tag{1}$$

$$Al_3Cl_{10}^- \leftrightarrow AlCl_3+Al_2Cl_7^- \tag{2}$$

Lewis acidity in the chloroaluminate ionic liquid originates from dissociation of AlCl$_3$ from di- and trimeric anions [23]. Furthermore, Lewis acid BMIC-2AlCl$_3$ ionic liquid could be regarded as a homogeneous system containing Lewis acid species (i.e., AlCl$_3$) and solvent - so-called “neutral” BMIC-AlCl$_3$ ionic liquid [27]. Thus, dissociative AlCl$_3$ can be regarded as the origin of the catalytic activity in chloroaluminate ionic liquid. However, isobutane alkylation is a typical Brønsted acid catalyzed reaction. So, Lewis acid should be transformed to Brønsted acid firstly and then to catalyze the reaction. In this system, AlCl$_3$ could be transformed to Brønsted acid via interaction between AlCl$_3$ and HCl, which came from the reaction of AlCl$_3$ and trace of water in feedstock. However, no interaction occurs between pure AlCl$_3$ and pure HCl, excepting in the presence of a basic compound (i.e., a proton acceptor) [28]. With a proton acceptor, a complex forms in which AlCl$_3$ and HCl are associated with molar ratio of 1 : 1 as follows:

$$AlCl_3+\text{proton acceptor}+HCl \leftrightarrow [\text{Hproton acceptor}]^+AlCl_4^- \tag{3}$$

It is believed that the resulting ionized complex acts as the Brønsted acid site to catalyze alkylation [29]. Obviously, the property of this Brønsted acid site is only influenced by the nature of the proton acceptor. In the catalysis systems of this study, butene or thioalcohol with their unshared electrons is a proton acceptor. Association occurs as follows:

$$AlCl_3+C_4H_8+HCl \leftrightarrow [HC_4H_8]^+AlCl_4^- \tag{4}$$

$$AlCl_3+C_4H_{10}S+HCl \leftrightarrow [HC_4H_{10}S]^+AlCl_4^- \tag{5}$$

In these complexes, the availability of the electron of the proton acceptors, i.e., the electron-donating ability, influences the strength of interaction among HCl, proton acceptor and AlCl$_3$, and consequently determines the acidity of the Brønsted acid site.

In the alkylation without thioalcohol additive, butene was the proton acceptor for association with HCl and AlCl$_3$ to catalyze the reaction. In the presence of thioalcohol inhibitors, thioalcohol with stronger electron-donating ability was more basic than butene and tended to bind the HCl and AlCl$_3$ more strongly, forming in turn a carbonium ion of lower acid strength: $[HC_4H_8S]^+AlCl_4^-$. The net effect was to buffer the acidity of ionic liquid to a proper level and thereby decreased the side reactions.

The other question is focused on thioether additive in this ionic liquid catalyzed system. Although thioether is also a basic organic compound with strong electron-donating ability, no improvement of the catalytic performance of BMIC-2AlCl$_3$ was observed after addition of thioether. The reason for this may be that the basicity (i.e., the availability of the unshared electron pair) of thioether is too strong (stronger than thioalcohol at least), leading to complete deactivation of AlCl$_3$ via association of AlCl$_3$ and thioether. The unshared electron pairs of thioether and thioalcohol molecules are both mainly offered by S atom. However, the basicities of thioether and thioalcohol should be pronouncedly different owing to the difference in chemical structure, resulting in different intensity of complexation of AlCl$_3$ and the organosulfur compounds. Actually, in previous study about solid AlCl$_3$ catalyst, the researchers found that the complex of $AlCl_3 \cdot CH_3OH$ was catalytically active for alkylation [25], whereas the equimolar complexes of AlCl$_3$ with dialkyl ethers were catalytically inert [30]. The strong complex of AlCl$_3$ with ether completely deactivated AlCl$_3$, resulting in no available space for HCl adding to form the ionized effective catalyst for alkylation. The electron-donating ability of alcohol seemed weaker than ether, leading to the extent of interaction of HCl with alcohol being lower than ether. Thereby, HCl could interact with the equimolar complexes of $AlCl_3 \cdot$alcohol to form an effective Brønsted acid site to catalyze alkylation. Obviously, thioalcohol is similar to alcohol in chemical structure, and thioether is also similar to ether. Thus, in the case of thioether as additive, AlCl$_3$ would be deactivated by thioether via strong complexation with molar ratio of 1 : 1 due to analogous mechanism mentioned above and no new Brønsted acid site formed. $[HC_4H_8]^+AlCl_4^-$ still acted as the catalytically active site to catalyze isobutane alkylation, resulting in no improvement of the alkylate’s quality. Whereas, a new Brønsted acid site was formed to substitute $[HC_4H_8]^+AlCl_4^-$ in the presence of thioalcohol additive in the chloroaluminate ionic liquid, leading to improvement of the catalytic performance of BMIC-2AlCl$_3$ for isobutane/2-butene alkylation.

2. Effects of Different Butenes on the Alkylation Product Composition with Thioalcohol Additive

In section 3.1, it was found that butyl thioalcohol was a good additive for isobutane/2-butene alkylation catalyzed by BMIC-2AlCl$_3$ ionic liquid. However, for 1-butene and isobutene as reactants, the composition of the alkylates would be different. Analysis of the alkylate produced with various butene is shown in Table 2.

For 1-butene as alkylating agent, the content of trimethylpentane of the alkylate obtained from alkylation catalyzed by BMIC-2AlCl$_3$/thioalochol was very low, but the content of DMH was high, and the ratio of TMP/DMH was lower than 0.2, indicating that the quality of the alkylate was bad. Moreover, the contents of light ends and heavy ends in the alkylate produced by 1-butene were higher than that in the alkylate produced by 2-butene. Thus, 1-butene is not suitable for isobutane alkylation catalyzed by BMIC-2AlCl$_3$/thioalochol and must be removed from the feedstock to obtain the maximum octane number in a future industrial process. For isobutene as alkylating agent, the distributions of hydrocarbons in the alkylate were better than that in alkylate produced by 1-butene, but worse than that in alkylate produced by 2-butene. For isobutene, the lower TMP content may be caused by the tendency of isobutene to polymerize and form heavy ends that crack to products other than TMP.

Table 2. Effects of different butenes on the alkylation product composition with thioalcohol additive

Composition of alkylate mixtures (wt%)	Butenes		
	1-Butene	Isobutene	2-Butene
2-Methylbutane	4.6	5.2	2.7
2,3-Dimethylbutane	3.7	3.6	3.3
C_6-C_7 (others)	15.5	17.9	4.8
2,2,4-Trimethylpentane	4.3	31.8	35.1
2,2,3-Trimethylpentane	0.0	0.2	0.3
2,3,4-Trimethylpentane	1.2	5.0	15.6
2,3,3-Trimethylpentane	1.8	7.9	14.9
Total TMP	7.3	44.9	65.9
Total DMH	42.8	9.0	10.0
2,2,5-Trimethylhexane	10.1	6.3	5.3
C_{9+} (others)	16.0	13.1	8.0
TMP/DMH	0.17	5.0	6.6
Conversion of butene	99	99	99
Yield (wt% on olefin)	161	167	179

Reaction temperature was 30 °C, molar ratio of isobutane to butene was 10, total reaction time was 40 min, S content in ionic liquid was 1,000 ppmw, and theoretical yield is 204%.

Table 3. Effect of reaction temperature on the alkylation product composition with thioalcohol additive

Composition of alkylate mixtures (wt%)	Reaction temperature (°C)				
	15	30	40	50	60
2-Methylbutane	1.6	2.7	3.0	3.4	9.5
2,3-Dimethylbutane	3.1	3.3	4.5	5.6	6.1
C_6-C_7 (others)	2.8	4.8	6.1	6.9	7.8
2,2,4-Trimethylpentane	38.2	35.1	24.0	19.1	11.3
2,2,3-Trimethylpentane	0.3	0.3	0.2	0.2	0.2
2,3,4-Trimethylpentane	18.2	15.6	12.4	9.7	6.7
2,3,3-Trimethylpentane	17.4	14.9	11.5	8.5	6.5
Total TMP	74.1	65.9	48.1	37.5	24.7
Total DMH	8.8	10.0	12.7	18.8	22.4
2,2,5-Trimethylhexane	4.1	5.3	8.1	9.5	9.8
C_{9+} (others)	5.5	8.0	17.5	18.3	19.7
TMP/DMH	8.4	6.6	3.8	2.0	1.1
Conversion of 2-butene, %	99	99	99	99	99
Yield (wt% on olefin)	189	179	170	162	155

Molar ratio of isobutane to 2-butene was 10, total reaction time was 40 min, S content in ionic liquid was 1,000 ppmw, and theoretical yield is 204%.

Table 4. Effect of ratio of isobutane to butene on the alkylation product composition with thioalcohol additive

Composition of alkylate mixtures (wt%)	Ratio of isobutane to butene		
	10	20	25
2-Methylbutane	2.7	2.2	2.1
2,3-Dimethylbutane	3.3	3.1	2.4
C_6-C_7 (others)	4.8	4.0	3.7
2,2,4-Trimethylpentane	35.1	36.9	37.2
2,2,3-Trimethylpentane	0.3	0.2	0.4
2,3,4-Trimethylpentane	15.6	16.1	16.2
2,3,3-Trimethylpentane	14.9	17.3	18.7
Total TMP	65.9	70.5	72.5
Total DMH	10.0	9.5	9.2
2,2,5-Trimethylhexane	5.3	5.2	4.8
C_{9+} (others)	8.0	5.5	5.3
TMP/DMH	6.6	7.4	7.9
Conversion of butene	99	99	99
Yield (wt% on olefin)	179	186	187

Reaction temperature was 30 °C, total reaction time was 40 min, S content in ionic liquid was 1,000 ppmw, and theoretical yield is 204%

In these experiments, high conversion of butene was obtained. Liquid product yield of alkylation with 2-butene as alkylating agent was higher than that of alkylation with 1-butene and isobutene.

3. Effect of Temperature

The effect of reaction temperature on product distribution was investigated by using BMIC-2AlCl$_3$/thioalcohol as catalyst. 2-butene was used as alkylating agent. The typical results are listed in Table 3. Under each temperature in these experiments, high conversion of 2-butene was exhibited, indicating good catalytic activity of the ionic liquid. As temperature increased in the range of 15-60 °C, the percentages of light ends and heavy ends increased and the TMP's fraction decreased, and the fraction of DMH increased. The TMP/DMH ratio dropped from 8.4 to 1.1 with the increase of the temperature, indicating that the quality of the alkylates was reduced. Furthermore, the yield decreased with the increase of reaction temperature, indicating that the dimerization of 2-butene and hydrogen transfer became dominating in relative high temperature. Therefore, it is conclusive that low temperatures are favorable for the alkylation of isobutane/2-butene catalyzed by the BMIC-2AlCl$_3$/thioalcohol ionic liquid. This characteristic is similar to the alkylation catalyzed by sulfuric acid [31,32] or aluminium chloride [24].

4. Effect of Ratio of Isobutane to Butene

The effect of ratio of isobutane to butene on the alkylation product composition was investigated by using BMIC-2AlCl$_3$/thioalcohol as catalyst. 2-butene was used as alkylating agent. The typical results are listed in Table 4. It can be seen that increasing the ratio of isobutane to butene increased the selectivity of TMP from 65.9% to 72.5%. The contents of light ends, heavy ends and DMH were all decreased with the increase of ratio of isobutane and 2-butene. The ratio of TMP/DMH also increased. Thereby, the quality of the alkylate was improved at relatively high ratio of isobutane to butene.

5. Effect of Reaction Time

Some side reactions, such as cracking, disproportionation and isomerization coexist with alkylation in this catalytic system. Due to the difference of reaction rates among these reactions, the reaction time would influence catalytic performance of BMIC-2AlCl$_3$/thioalcohol. Typical results concerning the effect of the reaction time on the catalytic performance of the catalyst are reported in Table 5. The reaction temperature in this experiment was 30 °C. The reaction time included the feeding time and stirring-holding time. As mentioned above, the feeding time was 24 minutes. As the reaction time increased from 34 minutes to 40 minutes, the conversion of 2-butene, the yield, the fraction of TMP and the ratio of TMP/

Table 5. Effect of reaction time on the alkylation product composition with thioalcohol additive

Composition of alkylate mixtures (wt%)	Reaction time (min)			
	34	37	40	50
2-Methylbutane	2.5	2.6	2.7	4.5
2,3-Dimethylbutane	4.6	4.0	3.3	5.7
C_6-C_7 (others)	6.0	5.5	4.8	8.7
2,2,4-Trimethylpentane	30.3	31.2	35.1	28.5
2,2,3-Trimethylpentane	0.2	0.2	0.3	0.3
2,3,4-Trimethylpentane	16.4	16.2	15.6	12.3
2,3,3-Trimethylpentane	14.6	15.3	14.9	11.7
Total TMP	61.5	62.9	65.9	52.8
Total DMH	10.2	10.2	10.0	13.9
2,2,5-Trimethylhexane	6.5	6.0	5.3	5.9
C_{9+} (others)	8.7	8.8	8.0	8.5
TMP/DMH	6.0	6.2	6.6	3.8
Conversion of 2-butene, %	94	95	99	99
Yield (wt% on olefin)	168	171	179	170

Reaction temperature was 30 °C, ratio of isobutene to 2-butene was 10, S content in ionic liquid was 1,000 ppmw, and theoretical yield is 204%.

DMH all increased. At a reaction time of 40 minutes, the conversion of 2-butene was up to 99%. The increase of reaction time to 50 minutes brought no improvement in the yield and the conversion of 2-butene. However, the percentages of light ends and DMH increased, while the fraction of heavy ends, TMP and the ratio of TMP/DMH were less than those at 40 minutes. The increase of DMH content might be the result of isomerization of TMP. And the degradation of isooctane and heavy ends led to the increase of percentage light ends. Therefore, a proper contacting time not only was beneficial to high 2-butene conversion and liquid product yield, but high TMP fraction as well. Similar observations were described when sulfuric acid was used as the catalyst.

CONCLUSION

In summary, it has been found that adding butyl thioalcohol into chloroaluminate imidazolium ionic liquids could improve product distributions of isobutane alkylation, and the alkylate with improved quality was obtained. 2-butene was the suitable alkylating agent for isobutane alkylation catalyzed by BMIC-2$AlCl_3$/thioalcohol to produce high quality alkylate. Low reaction temperature, high ratio of isobutane to butene and proper reaction time were beneficial to isobutane alkylation.

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