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Isobutane/2-butene alkylation catalyzed by chloroaluminate ionic liquids in the presence of aromatic additives

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Abstract

The effect of adding aromatic compounds and varying the $AlCl_3$ molar fraction on the catalytic performance of chloroaluminate ionic liquids in isobutane/2-butene alkylation was investigated. ^{27}Al NMR results and comparison with alkylation catalyzed by solid $AlCl_3$ reveal that the activity of the ionic liquids presumably comes from traces of $AlCl_3$ or Al_2Cl_6. The addition of benzene increases the selectivity of C_8 as well as the TMP:DMH ratio in the alkylate. The performance of the modified catalyst is optimized at high isobutane to 2-butene ratios and low temperatures. The used catalyst can be regenerated by replenishment of the aromatic additives.

Keywords: Alkylation; Isobutane; 2-Butene; Ionic liquids; Aromatics

1. Introduction

Isobutane/2-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, because it can meet environmental standards regarding high octane number (research octane number [RON] of 92–96), low vapor pressure, and low aromatic, alkene, and sulfur content [1,2]. Current commercial alkylation processes are catalyzed by either concentrated sulfuric acid or hydrofluoric acid. Both of 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]. In China, several isoparaffin/olefin alkylation units have been mothballed due to the disadvantages of current catalyst; consequently, a new class of catalysts for alkylation reactions is needed.

Some types of solid acid catalysts, such as modified molecular sieves and immobilized heteropolyacids or superacids, have been investigated as replacements for the conventional liquid acids. Some of these solid catalysts show high catalytic activity and selectivity at the beginning of the reaction, but with rapidly decaying reactivity due to carbon deposition [4]. The alkylation under supercritical condition exhibits a longer catalyst lifetime compared with the reaction in the liquid or gas phase [5].

Chloroaluminate ionic liquids at room temperature also have been suggested as a potential replacement for conventional liquid acid catalysts. Ionic liquids are salts that exist in the liquid state at ambient temperatures. In recent years, significant progress has been made in applications of chloroaluminate room temperature ionic liquids in processes including catalysis [6–8], extractions [9,10], biocatalysis [11,12], and polymerization [13,14]. 1-Alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids have been investigated as catalysts for isobutane/2-butene alkylation [15,16]. The main advantages of the ionic liquid are the high catalytic activity and the negligible solubility of the dominant component of the product, isoparaffin [17]. Moreover, development of alkylation technology using acidic ionic liquids should be very cost-effective, because, unlike solid acid catalysts, they can be used in current units without any modification. Imidazolium-based ionic liquids have the disadvantages of high cost and severe reaction conditions, however. Huang et al. [18] investigated isobutane/2-butene alky-

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lation using triethylamine hydrochloride (Et_3NHCl)-aluminum chloride ionic liquid as a catalyst. CuCl was added to the ionic liquids to inhibit side reactions such as isomerization, cracking, and disproportionation, which produce hydrocarbons of low octane number. However, copper complexes may contaminate the product, and the synthesis of CuCl/Et_3NHCl-$AlCl_3$ is difficult.

Side reactions accompanying alkylation by ionic liquids have been attributed to the high acidity of chloroaluminate. Adding some basic organic substances increases the content of trimethylpentane (TMP) in the product of isobutane/2-butene alkylation [15] and also increases the RON of the alkylate. The superacidic nature of chloroaluminate ionic liquid has been demonstrated by Qiao and Deng [19]. The chloroaluminate ionic liquid is Lewis acid in itself, and the Brønsted acid forms from the interaction of Lewis acid species with HCl or the proton of the Et_3NH^+ cation. The properties of the Lewis acid species determine the acidity of Brønsted acid in the ionic liquid. The poor catalytic performance of 1-alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids reported by Yoo et al. [16] also can be attributed to their high acidity. Some researchers believe that the acidity of ionic liquids can be readily adjusted by varying the molar fraction of aluminum chloride in the mixture [20]. The ionic liquids can be considered acidic when the molar fraction of aluminum chloride is >0.5. The Lewis acid species present are usually considered to include $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, or traces of $AlCl_3$ [21]. The Lewis acid strength of the ionic liquid can be controlled by varying the molar fraction of aluminum chloride in the range 0.5–0.667 [15]. Alternatively, the Lewis acidity of chloroaluminate ionic liquids with a given molar fraction of aluminum chloride can be reduced by the addition of electron-donating organic species; therefore, the property of the Brønsted acid will be changed.

The present work investigated the catalytic activity and selectivity of triethylamine hydrochloride-aluminum chloride ionic liquids as catalysts for isobutane/2-butene alkylation. The acidity of the ionic liquids was adjusted by both alterating the molar fraction of aluminum chloride and adding organic species. The mechanism of catalysis by ionic liquids was also studied by means of infrared and nuclear magnetic resonance spectroscopy.

2. Experimental

2.1. Preparation of catalysts

The room temperature ionic liquids were synthesized as described previously [22]. Anhydrous aluminum chloride was purified by sublimation in a sealed tube. Triethylamine hydrochloride was purified by recrystallization from dry, redistilled ethyl acetate–acetonitrile mixtures. A decolorizing charcoal treatment was used in the first two recrystallizations, and the product was finally dried in vacuum at 80 °C. The desired amount of anhydrous aluminum chloride was slowly added to purified triethylamine hydrochloride at 333 K. The entire process was carried out in a dry nitrogen atmosphere in a glove box to avoid hydrolysis of $AlCl_3$. Samples of ionic liquids with molar ratios of $AlCl_3$ to triethylamine hydrochloride of 2.0, 1.8, 1.5, 1.25, and 1.0 were prepared. Benzene (C_6H_6), hexamethylbenzene ($C_{12}H_{18}$), chlorobenzene (C_6H_5Cl), and nitrobenzene ($C_6H_5NO_2$) were introduced into separate samples of the ionic liquids at room temperature, and the mixtures were stored in a dry inert atmosphere.

2.2. Characterization of ionic liquids

Acidity characterizations were carried out by infrared spectroscopy using acetonitrile as the Lewis acid probe at room temperature, along with a Bruker Tensor 27 FT-IR spectrometer [23,24]. All spectra were acquired at a 1-cm^{-1} resolution with a total of 64 scans per spectrum. The samples were prepared by mixing acetonitrile and ionic liquids in a volume ratio of 3:1, and then smeared into liquid films on KBr windows. The reproducibility of the results was confirmed using a Nicolet Nexus-470 spectrometer.

The ^{27}Al NMR measurements were carried out on a Bruker Avance 600 MHz high-resolution liquid nuclear magnetic resonance spectrometer. The spectra were obtained at 156.38 MHz with a preacquisition delay time of 0.5 s.

2.3. Isobutane/2-butene alkylation

Isobutane and 2-butene (a mixture of *cis*- and *trans*-isomers) were purified by passing them through Linde 5A molecular sieves. Reactions were carried out in batch mode in a 500-ml pressure reactor with stirring at 800 rpm. Before the experiment, 30 ml of ionic liquid was put into the reactor. After stirring, the liquid feed (200 ml of isobutane and 2-butene) was charged into the reactor by a means of a plunger pump at a rate of 500 ml/h. The reaction temperature was controlled by a thermostatic water bath with temperature controller. After completion of the reaction with a total reaction time of 30 min, the product and catalyst were decanted from the reactor and allowed to settle for about 30 min, after which the product and catalyst were separated in a separation funnel. The product was fractionated to remove isobutane and distilled in a Claisen flask. The ionic liquid phase was extracted by CCl_4, and then the samples were collected for analysis. The mass of ionic liquids was measured after the reaction to quantify the mass balance.

2.4. Analysis of products

Gaseous products were analyzed using an SP3420 gas chromatograph with a Plot Al_2O_3 S capillary column (Φ, 0.53 mm × 50 m) and a flame ionization detector (FID). The alkylate mixtures were analyzed using 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 a 0.25 mm × 50 m PONA capillary column and a FID. The alkene content of the product was measured by the fluorescent indicator adsorption method (GB/T 11132-2002) at DL1-DSY-404 hydrocarbon types of liquid petroleum analyzer. Within the limits of experimental error, the

Table 1
Effects of different $AlCl_3$ mole fraction on catalytic performance of ionic liquids

Ionic liquid	Conversion of 2-butene	Yield (wt% on olefin)[a]	Composition of alkylate mixtures (wt%)			TMP/DMH	Alkene content (wt%)
			C_5–C_7 alkanes	C_8 alkanes	C_{9+}		
$1.0AlCl_3/Et_3NHCl$	0	0	–	–	–	–	–
$1.25AlCl_3/Et_3NHCl$	95%	157	23.6	45.6	30.8	2.2	<1.5
$1.5AlCl_3/Et_3NHCl$	98%	162	24.1	48.8	27.1	2.7	<1.5
$1.8AlCl_3/Et_3NHCl$	99%	164	21.9	52.5	25.6	2.6	<1.5
$2.0AlCl_3/Et_3NHCl$	99%	163	24.2	49.6	26.2	2.8	<1.5

Note. Reaction temperature = 303 K, ratio of isobutane to 2-butene = 10.

[a] Theoretical yield 204%.

results were quantitative. The RON of the alkylate mixtures was calculated as described previously [15].

3. Computational method

The optimization of geometries and the calculations of Mulliken atomic charge of the aromatic species were performed by density functional theory (B3LYP method) at the 6-31G(d, p) level, to determine the electron donor ability of the different aromatic compounds. The Gaussian 03 [25] software package was used in all calculations.

4. Results and discussion

4.1. *Effect of varying the molar fraction of $AlCl_3$ on the products of isobutane/2-butene alkylation*

The effects of different $AlCl_3$ molar fractions on the catalytic performance of the ionic liquids in alkylation are listed in Table 1. It can be seen that ionic liquids with ratios of $AlCl_3$ to $Et_3NHCl > 1.0$ exhibit high catalytic activity. The conversion of 2-butene is >95%, the selectivities to isooctane (C_8) in the alkylate mixtures are around 50%, and the ratios of trimethylpentane (TMP) to dimethylhexane (DMH) are in the range of 2.2–2.8, indicating that the RON of the products is <90. The hydrocarbon extracted from the ionic liquid phase after reaction is <0.1 wt% of the product. The mass of ionic liquid after the reaction is almost unchanged from that before the reaction. Moreover, the alkene content of the alkylate is very low, indicating a low level of unsaturation in the alkylate catalyzed by chloroaluminate ionic liquid. GC–MS analysis reveals that overall alkene is found in heavy ends (C_{9+}).

4.2. *Comparison of the acidity of ionic liquids with different $AlCl_3$ molar fractions*

The apparent acidity of chloroaluminate ionic liquids can be characterized by FI-IR using acetonitrile as a probe molecule [23,24]. Pure acetonitrile gives two characteristic CN stretching bands at 2293 cm^{-1} (band 2) and 2252 cm^{-1} (band 1). The addition of acetonitrile to Lewis acidic ionic liquids results in the appearance of a new band (band 3) at 2300–2400 cm^{-1}. Bands 1, 2, and 3 all shift to higher wavenumbers with increasing acidity of ionic liquids, with band 2 being more sensitive than band 1 or band 3 [23,24]. The FT-IR spectra in Fig. 1 show that the $1.0AlCl_3/Et_3NHCl$ ionic liquid has no Lewis acidity, as demonstrated by the absence of band 3. For $1.25AlCl_3/Et_3NHCl$, $1.5AlCl_3/Et_3NHCl$, $1.8AlCl_3/Et_3NHCl$, and $2.0AlCl_3/Et_3NHCl$ mixtures, the acidity of the ionic liquids increases monotonically with increasing $AlCl_3$ molar fraction, as indicated by band 1 at 2254, 2254, 2254, and 2255 cm^{-1}; band 2 at 2294, 2203, 2304, and 2306 cm^{-1}; and band 3 at 2332, 2333, 2333, and 2334 cm^{-1}. These results are consistent with the literature [23,24].

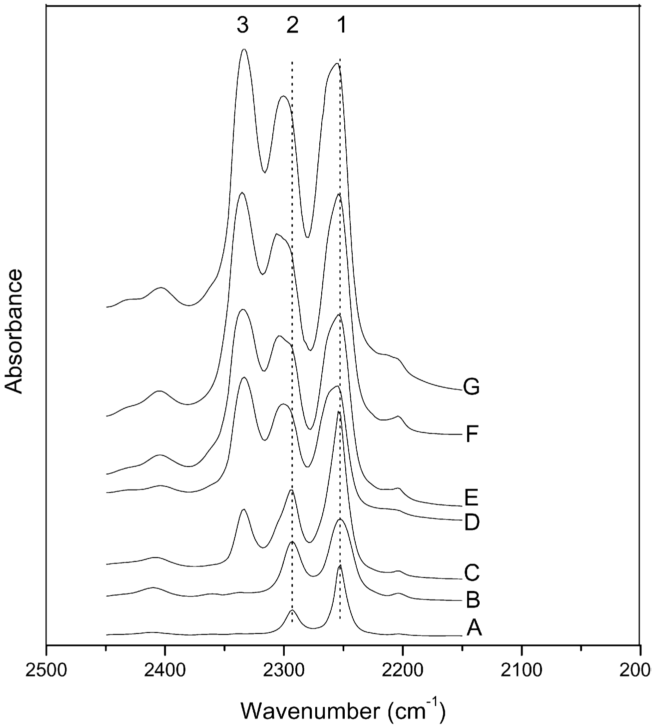

Fig. 1. FT-IR spectra of ionic liquids using acetonitrile as an acidity probe: (A) pure acetonitrile, (B) $1.0AlCl_3/Et_3NHCl$, (C) $1.25AlCl_3/Et_3NHCl$, (D) $1.5AlCl_3/Et_3NHCl$, (E) $1.8AlCl_3/Et_3NHCl$, (F) $2.0AlCl_3/Et_3NHCl$, (G) $2.0AlCl_3/Et_3NHCl$ + benzene.

4.3. *Effect of benzene addition on the catalytic performance of ionic liquids*

Table 2 shows that the high catalytic activity of $2.0AlCl_3/Et_3NHCl$ was maintained after addition of 1% benzene by weight. The conversion of 2-butene remained at 99%. It also can be seen that after introduction of benzene, formation of side

Table 2
Effect of benzene addition on alkylate composition

Composition of alkylate mixtures (wt%)	Ionic liquid	
	$2.0AlCl_3/Et_3NHCl$	$2.0AlCl_3/Et_3NHCl$ + benzene
2-Methylbutane	6.3	4.1
2,3-Dimethylbutane	4.5	2.6
C_6–C_7 (others)	13.4	6.7
2,2,4-Trimethylpentane	23.5	39.6
2,2,3-Trimethylpentane	0.1	0.3
2,3,4-Trimethylpentane	6.7	15.9
2,3,3-Trimethylpentane	6.2	16.2
Total DMH	13.1	8.9
2,2,5-Trimethylhexane	9.2	2.1
C_{9+} (others)	17.0	3.6
Yield (wt% on olefin)	163	188
Calculated RON	88.4	95.6

Note. Reaction temperature = 303 K, ratio of isobutane to 2-butene = 10.

Table 3
Effects of different aromatic additives on catalytic performance of ionic liquids

Aromatic additive	Conversion of 2-butene	Yield (wt% on olefin)	Composition of alkylate mixtures (wt%)			TMP/DMH
			C_5–C_7 alkanes	C_8 alkanes	C_{9+}	
Benzene	98%	183	16.1	76.2	7.7	8.8
Hexamethylbenzene	99%	185	12.6	78.6	8.8	9.7
Nitrobenzene	98%	151	38.2	43.4	18.4	1.1
Chlorobenzene	99%	154	28.7	47.5	23.8	1.3

Note. Reaction temperature = 303 K, ratio of isobutane to 2-butene = 10, 0.8 wt% aromatic.

products was significantly reduced, and, as a result, the RON of the alkylate mixture was increased from 88.4 to 95.6. GC–MS analysis of the product revealed that a part of benzene added into ionic liquid was converted to an alkyl benzene, such as di- or tri-*tert*-butyl benzene, which presented in the heavy ends (C_{9+}), which should be a good promoter as well.

4.4. Effect of benzene addition on the acidity of ionic liquids

Fig. 1 also shows the FT-IR spectrum of $2.0AlCl_3/Et_3NHCl$ ionic liquid mixed with 1% benzene by weight. The presence of band 3 at 2333 cm^{-1} indicates that the ionic liquid mixed with benzene retains a Lewis acid character. The position of band 2 at 2303 cm^{-1} is 3 cm^{-1} lower than that for pure $2.0AlCl_3/Et_3NHCl$, indicating that the apparent Lewis acidity of $2.0AlCl_3/Et_3NHCl$ seems to be comparable to that of $1.5AlCl_3/Et_3NHCl$.

The acidity of ionic liquids is a key aspect in alkylation reactions. The generally accepted mechanism of catalytic alkylation involves carbonium-ion formation initiated by Brønsted acids [15]. It is believed that the Brønsted acid comes from interaction of Lewis acid species with HCl (produced by hydrolysis of chloroaluminate with traces of water in the reactant) or the proton of the Et_3NH^+ cation [26]. The nature of the Lewis acid centers will influence the properties of the Brønsted acid sites. On the basis of the foregoing infrared spectra and alkylation results, it can be proposed that the acidity of the ionic liquids depends on two factors: the concentration of acid sites and the electronic properties of acid sites. Changing the molar fraction of $AlCl_3$ in the ionic liquid affects only the quantity of acid site itself and leads to changes in acidity of ionic liquids as a whole. Because the properties of the acid sites remain unchanged, however, no significant effect on the catalytic behavior of ionic liquids in isobutane/2-butene alkylation (Table 1) by changing the molar fraction of $AlCl_3$ is observed.

It can be postulated that the addition of benzene to chloroaluminate ionic liquids leads to π-complexation of Lewis acid sites with the π-cloud of the aromatic ring, likely resulting in modification of the electronic properties of Lewis acid sites. Such a complexation process is presumably beneficial for alkylation because it inhibits side reactions. Meanwhile, aromatic additives may be stabilize alkyl carbenium through the addition of an alkyl carbenium ion to the aromatic ring, resulting in obvious improvement in the product composition shown in Table 2.

4.5. Effects of different aromatic additives on the catalytic performance of ionic liquids

To investigate the influence of the electron donor ability of the π-cloud of the aromatic ring on the catalytic properties of the ionic liquids, aromatic species with different ring substituents were added to the ionic liquid. Comparing the results, given in Table 3, with the data in Table 1 shows that whereas the presence of benzene and hexamethylbenzene additives leads to an improved selectivity to C_8 and greatly increased ratio of TMP to DMH, the addition of chlorobenzene or nitrobenzene leads to poorer catalytic performance. Moreover, hexamethylbenzene is the preferred inhibitor because it does not consume butene and can be recovered from the product without any change in chemical structure.

Table 4
Atomic charges of the different aromatics

Aromatics	Charges of carbon atom of benzene ring (e)					
	C_1[a]	C_2	C_3	C_4	C_5	C_6
Benzene	0	0	0	0	0	0
Hexamethylbenzene	0	0	0	0	0	0
Nitrobenzene	−0.167	0.061	0.007	0.031	0.007	0.060
Chlorobenzene	−0.120	0.041	0.014	0.010	0.014	0.041

[a] The carbon atom connecting nitro group or chlorine.

Although the presence of the aromatic additives had a marked effect on the catalytic properties of the ionic liquids, only negligible changes were induced in the IR spectra. Consequently, the origin of the effect of different aromatic compounds on the acidity of the ionic liquid was studied by comparing their electron-donating ability, which can be related to the distribution of electronic charges of atoms. The Mulliken atomic charges calculated for the different aromatic species are given in Table 4. Atomic charges of hydrogens and substituents are summed into the corresponding carbon atom of the benzene ring.

The electronic effect (inductive effect, conjugative effect, or hyperconjugation) of the substituent can influence the π-cloud of the benzene ring. For nitrobenzene and chlorobenzene, a negative electric charge is concentrated into C–NO_2^- or C–Cl^-, with delocalization of the π-cloud electron to the substituent, confirming the expected electron-withdrawing effect of NO_2^- or Cl_2^-. Because methyl exhibits a very weak electron-releasing effect through hyperconjugation, the π-cloud of hexamethylbenzene is almost the same as that of benzene, with no difference in charge distribution. This suggests that the effect of different aromatic additives on the catalytic performance of the ionic liquids shown in Table 3 may be rationalized by the ineffectiveness of the electron-poor π-cloud in chlorobenzene and nitrobenzene in coordinating Lewis acid sites, whereas coordination of the electron-rich π-cloud of benzene or hexamethylbenzene with these sites leads to enhanced catalytic properties in isobutane/2-butene alkylation.

4.6. ^{27}Al NMR characterization

It is noteworthy that significant improvements in catalytic performance can result from the addition of small quantities of benzene or alkylbenzene derivatives. Adding 0.8 wt% of benzene increases the selectivity to C_8 from 49.6% (Table 1) to 76.2% (Table 3) and increases the TMP:DMH ratio from 2.8 (Table 1) to 8.8 (Table 3). The structures of the chloroaluminate species present in the ionic liquids (1.5$AlCl_3$–Et_3NHCl, 2.0$AlCl_3$–Et_3NHCl, and 2.0$AlCl_3$–Et_3NHCl–benzene) were investigated by ^{27}Al NMR spectroscopy. The amount of benzene added was 20 wt%, to produce significant changes in the spectra. The results are shown in Fig. 2.

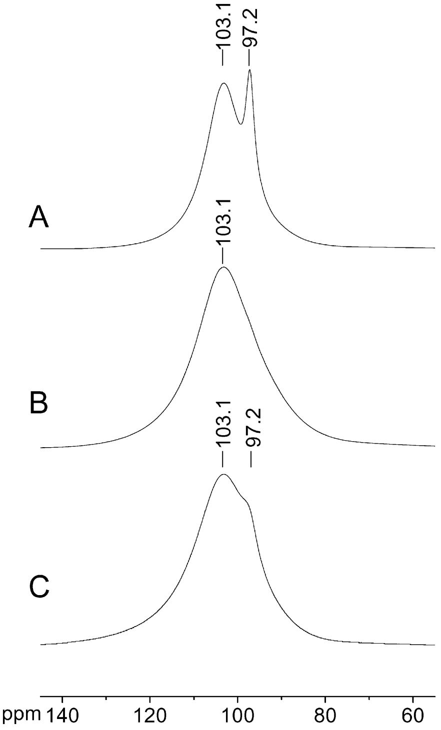

Fig. 2. ^{27}Al NMR spectra of various ionic liquids: (A) 1.5$AlCl_3$/Et_3NHCl, (B) 2.0$AlCl_3$/Et_3NHCl, (C) 2.0$AlCl_3$/Et_3NHCl + benzene.

On the basis of their chemical shifts, the two peaks in the spectrum of 1.5$AlCl_3$–Et_3NHCl can be assigned to $AlCl_4^-$ (97.2 ppm) and $Al_2Cl_7^-$ (103.1 ppm) [27,28]. In contrast, $Al_2Cl_7^-$ is the dominant Al species in 2.0$AlCl_3$–Et_3NHCl. Moreover, traces of $AlCl_3$ (or dimeric Al_2Cl_6), originating from dissociation of $Al_2Cl_7^-$, cannot be detected by NMR. The equilibrium mixture in 2.0$AlCl_3$–Et_3NHCl ionic liquids can be expressed as [20]

$$2Al_2Cl_7^- \leftrightarrow Al_2Cl_6 + 2AlCl_4^-, \quad K = 10^{-16}\text{–}10^{-17}.$$

After the addition of benzene to 2.0$AlCl_3$–Et_3NHCl, the appearance of a shoulder at about 97 ppm in Fig. 2C indicates some interaction between benzene and aluminum-containing species. It is generally believed that $AlCl_4^-$ is neutral and cannot coordinate with the aromatics. In the experiments mentioned above, adding a small amount of benzene dramatically improved the catalytic performance of 2.0$AlCl_3$–Et_3NHCl by reducing the side reactions, indicating that $Al_2Cl_7^-$ could not function as the active site to interact with the additive, because the dominant $Al_2Cl_7^-$ was present in a much greater quantity than the additive.

A conceivable mechanism involves the Al_2Cl_6 as the actual active origin coordinating with benzene, resulting in a shift of the equilibrium to the right with formation of $AlCl_4^-$, which is responsible for the shoulder peak shown in Fig. 2C. Peaks arising from the Al_2Cl_6 coordinated with benzene could not be detected in the spectra and may be obscured by bands of $Al_2Cl_7^-$ and $AlCl_4^-$. In the experiments, the stoichiometry between the Lewis acid sites, i.e. traces of Al_2Cl_6, and the small amount of additive is reasonable.

Concerning the mechanism by which benzene interacts with $AlCl_3$ to improved the composition of the alkylate catalyzed by chloroaluminate ionic liquids, some conjectures have been made. No interaction occurs between pure $AlCl_3$ and pure HCl without a proton acceptor [29]. When a basic substance (i.e., a proton acceptor) is present in the system, a complex is formed

Table 5
Alkylation catalyzed by solid $AlCl_3$ and the effects of benzene addition

Catalyst	Conversion of 2-butene	Yield (wt% on olefin)	Composition of alkylate mixtures (wt%)			TMP/DMH
			C_5–C_7 alkanes	C_8 alkanes	C_{9+}	
$AlCl_3$	96%	168	20.2	56.2	27.3	1.9
$AlCl_3$ + 0.20 g benzene	95%	172	15.2	66.7	18.1	4.8
$AlCl_3$ + 0.39 g benzene	95%	179	11.6	76.2	12.2	7.6
$AlCl_3$ + 0.59 g benzene	95%	174	10.4	73.1	16.5	7.7

Note. Reaction temperature = 303 K, ratio of isobutane to 2-butene = 10; 1 g $AlCl_3$ was used in each experiment.

Table 6
Effect of varying the amount of benzene added to the ionic liquids

Benzene (wt%)	Yield (wt% on olefin)	Composition of alkylate mixtures (wt%)			TMP/DMH
		C_5–C_7 alkanes	C_8 alkanes	C_{9+}	
0.2	171	24.5	64.0	11.5	6.7
0.4	173	19.2	68.4	12.4	8.2
0.6	173	21.6	66.3	12.1	8.4
1.0	188	13.4	80.9	5.7	8.0
2.0	183	15.9	76.2	7.9	8.7
3.0	184	11.4	77.6	11.0	14.5
4.0	184	14.2	76.8	9.0	15.7

Note. Reaction temperature = 303 K, ratio of isobutane to 2-butene = 10.

in which the $AlCl_3$ and HCl are coordinated with ratio of 1:1. The complex can be illustrated as follows:

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

It is believed that the resulting ionized complex acts as the Brønsted acid site to catalyze alkylation [30]. The property of this Brønsted acid site is influenced by the nature of Lewis acid site, that is, the complex of proton acceptor and $AlCl_3$. In this alkylation system, HCl comes from the reaction of acidic anion with trace water in feedstock. Butene or benzene, with their unshared electrons, is the proton acceptor in these cases. The association is as follows:

$$AlCl_3 + \text{butene} + HCl \leftrightarrow [\text{Hbutene}]^+ AlCl_4^-,$$

$$AlCl_3 + \text{benzene} + HCl \leftrightarrow [\text{Hbenzene}]^+ AlCl_4^-.$$

In these complexes, the availability of the electron of the proton acceptors (i.e., the electron-donating ability) determines the strength of the interaction among HCl, the proton acceptor, and $AlCl_3$.

In alkylation without the benzene additive, butene is the proton acceptor in association with HCl and $AlCl_3$ to catalyze the reaction. In the case of aromatic inhibitors, benzene or alkylbenzene, with a stronger electron-donating ability, is more basic than butene and tends to bind the HCl and $AlCl_3$ more strongly, forming a carbonium ion of lower acid strength, that is, $[\text{Hbenzene}]^+AlCl_4^-$. The effect is to decrease the acidity of ionic liquid to a lower level and decrease the side reaction. But when nitrobenzene and chlorobenzene are used as additives, no side reaction inhibitions occur, because the availability of the unshared electron in nitrobenzene or chlorobenzene is less than that in butene. Thus, butene still acts as the proton acceptor, and the acid property of the ionic liquids remains unchanged. An analogous understanding can be derived from these results on the effect of varying the molar fraction of $AlCl_3$ on the products of isobutane/2-butene alkylation. Although the $AlCl_3$ molar fractions in ionic liquids changes, there are no alterations in the properties of the active site for the same proton acceptor and the same Lewis acid species in different ionic liquids with different $AlCl_3$ molar fractions. Therefore, the improved quality of the alkylate cannot be determined by varying $AlCl_3$ molar fraction in ionic liquids. These findings are consistent with the discussions in Sections 4.4 and 4.5.

4.7. *Alkylation catalyzed by solid $AlCl_3$ and the effect of benzene addition*

Isobutane/2-butene alkylation catalyzed by solid $AlCl_3$ and the effects of benzene addition were investigated; the product distributions are given in Table 5. The results in Table 5 show that $AlCl_3$ alone has high catalytic activity but low selectivity to trimethylpentane. Obviously, the product distribution of the alkylate catalyzed by solid $AlCl_3$ is analogous to that of ionic liquids. Moreover, the addition of different quantities of benzene (0.0025, 0.005, and 0.0075 mol) to 0.0075 mol $AlCl_3$ significantly enhanced the product distribution in each case, with results comparable to those in reactions catalyzed by ionic liquid with added benzene. In terms of additive effect, it is very important to note that the addition of benzene improved the catalytic performance of both the chloroaluminate ionic liquid and solid $AlCl_3$. Thus, it can be deduced that the mechanism of alkylation catalyzed by the chloroaluminate ionic liquid is analogous to that of alkylation catalyzed by solid $AlCl_3$. This finding supports the aforementioned conclusion that $AlCl_3$ or Al_2Cl_6 is the active origin in chloroaluminate ionic liquids for alkylation.

Table 8
Reuse of ionic liquids with benzene as additive

No. of times used	Yield (wt% on olefin)	Composition of alkylate mixtures (wt%)			TMP/DMH
		C_5–C_7 alkanes	C_8 alkanes	C_{9+}	
1	189	10.8	82.8	6.4	13.5
2	168	27.1	59.6	13.3	2.8
3	164	30.4	52.8	16.8	2.9
4	183	15.1	75.6	9.3	11.2

Note. Reaction temperature = 293 K, ratio of isobutane to 2-butene = 10, content of benzene in original catalyst = 0.8 wt%, an additional 0.8 wt% benzene is introduced into the ionic liquid before the fourth experiment.

Table 7
Effects of varying the isobutane/2-butene ratio and reaction temperature on alkylate composition

Catalyst	Ionic liquid + benzene (1.0 wt%)		
Reaction temperature	303 K	303 K	288 K
Ratio of isobutane to 2-butene	10	25	25
Yield (wt% on olefin)	188	190	193
C_5–C_7 alkanes	13.4	8.2	4.9
C_8 alkanes	80.9	84.6	90.1
C_{9+}	5.7	7.2	5.0
TMP/DMH	8.0	10.3	13.9

4.8. Effect on catalytic performance of varying the amount of benzene added to ionic liquids

The effects of varying the amount of benzene added to ionic liquids on their catalytic performance are characterized in Table 6. The addition of 1% by weight gives the optimum compositions of alkylate.

4.9. Effects of varying the isobutane/2-butene ratio and reaction temperature on alkylation product composition

The affects of varying the isobutane:2-butene ratio and the reaction temperature on alkylation product composition are shown in Table 7. It can be seen that increasing this ratio leads to improved selectivity to isooctane and increased TMP:DMH ratio when using $2.0AlCl_3/Et_3NHCl$ mixed with 1% benzene by weight as a catalyst. With decreasing reaction temperature, more TMP appears in the products. For this catalyst, at a mild reaction temperature of 288 K and an isobutane:2-butene ratio of 25, an alkylate mixture with excellent quality is obtained.

4.10. Reuse of ionic liquids with benzene as an additive

The potential for reuse of $2.0AlCl_3/Et_3NHCl$ with benzene as additive was investigated. The results, given in Table 8, show that the recycled catalyst has worse catalytic performance than the fresh catalyst. After the third reaction, good catalytic performance can be recovered by introducing 0.8 wt% of benzene into the ionic liquid. The catalyst's poor recycling properties may be due to weak complexation between benzene and Al species, causing a partial loss of benzene into the product. Good catalytic performance in a continuous alkylation process can be maintained throughout by regular replenishment of benzene.

5. Conclusion

Adjusting the acidity of ionic liquids by changing the molar fraction of $AlCl_3$ cannot improve catalytic performance in isobutane/2-butene alkylation. Adding a small amount of benzene increases the selectivity of C_8 as well as the TMP:DMH ratio in the alkylate. The catalytic active origin in the ionic liquid is trace amounts of $AlCl_3$ or Al_2Cl_6. Adding benzene also can enhance the catalytic performance of solid $AlCl_3$. At high isobutane:2-butene ratios and low temperatures, maximum benefits can be obtained with a catalyst modified by benzene or alkylbenzene. The performance of the used catalyst can be easily maintained by replenishing the aromatic additives.

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