

Available online at www.sciencedirect.com



Journal of Catalysis 222 (2004) 511-519

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Ionic liquid-catalyzed alkylation of isobutane with 2-butene

Kyesang Yoo,^a Vasudevan V. Namboodiri,^b Rajender S. Varma,^{b,*} and Panagiotis G. Smirniotis^{a,*}

^a Department of Chemical and Material Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

^b Clean Processes Branch, National Risk Management Research Laboratory, US Environmental Protection Agency, MS 443, Cincinnati, OH 45268, USA

Received 19 May 2003; revised 15 August 2003; accepted 6 November 2003

Abstract

A detailed study of the alkylation of isobutane with 2-butene in ionic liquid media has been conducted using 1-alkyl-3-methylimidazolium halides-aluminum chloride encompassing various alkyl groups (butyl-, hexyl-, and octyl-) and halides (Cl, Br, and I) on its cations and anions, respectively. The emphasis has been to delineate the role of both cations and anions in this reaction. The ionic liquids bearing a larger alkyl group on their cation ($[C_8mim]$) displayed relatively higher activity than a smaller one ($[C_6 \text{ or } C_4mim]$) with the same anionic composition, due to the high solubility of reactants in the former. Among the ionic liquids with different halide groups, bromides ([C₈mim]Br-AlCl₃) showed outstanding activity, because of the higher inherent acidity relative to others. From the 27 Al NMR study, a major peak at ~ 99.5 ppm corresponding to $[AlCl_3Br]^-$ (~ 99.5 ppm) was observed. Moreover, the anion showed a strong acidity based on FT-IR characterization; the largest peak related to acidity (1570 cm^{-1}) was detected. Under various composition conditions, catalytic activity and amount of TMPs increased with concentration of anion. This is mainly attributed to a higher amount of strong acid ions $[Al_2Cl_6Br]^-$ which can react with hydrogen atoms at the 2-position of an imidazolium ion to form Brønsted acid. However, the ionic liquid with strong acidity (X = 0.58) deactivated rapidly due to a higher sensitivity to moisture, causing decomposition. Under various reaction temperature conditions, optimum catalytic activity was observed at 80 °C. The result is also attributed to the effect of anion composition. The strong acidic anion increased with temperature. However, at higher reaction temperatures (120 °C), the ionic liquid showed a lower activity and TMP selectivity, since the solubility and Brønsted acid sites were reduced by decomposition of imidazolium ions. The selected ionic liquid sample ([C₈mim]Br-AlCl₃) was compared with one of the standard commercial catalysts, sulfuric acid. Under optimum experimental conditions, it was observed that both catalysts showed comparable catalytic behavior. However, ionic liquid showed higher activity, and lower TMP selectivity due to a more acidic nature and a lower amount of Brønsted acid sites, respectively.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Alkylation; Ionic liquid; Sulfuric acid; 1-Alkyl-3-methylimidazolium halides-aluminum chloride

1. Introduction

Alkylation of isobutane with 2-butene is an industrially important process, since the ensuing products, alkylates, have high octane numbers and exhibit clean burning characteristics [1]. However, the capacity of the alkylation process is restricted due to constraints imposed by the use of highly corrosive and environmentally detrimental sulfuric and hydrofluoric acid as commercial catalysts. Even though solid acid catalysts have been investigated, they have yet to achieve commercial use as alkylation catalysts because of

* Corresponding authors.

a rapid catalyst decay [2]. The mechanism of deactivation has been attributed to carbonaceous materials depositing inside solid catalysts [3]. The removal of these materials from porous catalysts would be difficult due to their high molecular weights and low diffusion coefficients. Consequently, there is ongoing interest in replacing conventional liquid acids with newer catalysts which have little diffusion limitation.

Ionic liquids have received widespread attention as an alternative to conventional hazardous solvents with potential applications in electrochemistry [4,5], liquid/liquid separations [6,7], extractions [8], catalysis [9–11], biocatalysis [12,13], and polymerization [14,15]. Most of these ionic salts are good and stable solvents for a wide range of organic and inorganic materials [16,17]. The important attributes of

E-mail addresses: Varma.Rajender@epa.gov (R.S. Varma), Panagiotis.Smirniotis@uc.edu (P.G. Smirniotis).



Fig. 1. Structures of ionic liquids employed in this study. $R = C_4H_9$: [C4MIM]⁺; C_6H_{13} : [C6MIM]⁺; C_8H_{17} : [C8MIM]⁺; $X = Cl^-$, Br^- , I^- .

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 [18]. From this point of view, ionic liquids with strong acidity can be potential alternatives to conventional alkylation catalysts without the usual diffusion limitation drawback. Moreover, they are known to possess interesting tunable physical and chemical properties depending on the organic cations and inorganic anions employed. The organic cation determines the solubility, the density, and the viscosity of the ionic liquids. Even while working with a single cation, the properties of the liquid ion are highly variable through the different possibilities of alkyl groups. The acidity of the ionic liquid is dependent on the metal halide employed and the ratio of metal halide to organic base [18,19]. The possibility of modifying the acidity of the ionic liquids is very interesting from a catalytic point of view in the alkylation of isobutane with 2-butene, since the salient features of a good homogeneous catalyst and reaction media are the acid strength and the solubility of reactants in the catalyst [1]. However, the alkylation of isobutane with butene has been barely studied with the exception of the use of 1-butyl-3-methylimidazolium chloride-aluminum chloride ([C₄mim]Cl–AlCl₃) as a catalyst [20].

In the present study, we have investigated the performance of various ionic liquids by varying the component of anions and cations for alkylation of isobutane with 2butene. A number of 1-alkyl-3-methylimidazolium halides– aluminum chloride $[C_n mim]X$ -AlCl₃ (where n = 4, 6, and 8) have been prepared. The catalytic activity and selectivity were carefully determined with prepared samples under identical conditions. The acidity of ionic liquids was characterized thoroughly to identify the catalytic performance by FT-IR and ²⁷Al NMR spectroscopy. Furthermore, the selected ionic liquid is compared with one of commercial catalyst, sulfuric acid, under various experimental conditions to determine its potential as an alternative catalyst to liquid acids.

2. Experimental

2.1. Preparation of ionic liquids

The 1-methylimidazole (mim) and alkyl halides were obtained from Aldrich Chemical Company and were used as such. The 1-alkyl-3-methylimidazolium halides–aluminum chloride ($[C_n mim]X$ -AlCl₃ where X = Cl, Br, I) (see Fig. 1) were prepared and characterized using protocols described earlier [18,21–23]. GC-MS analyses of the products were carried out by using a Hewlett-Packard 6890 gas chromatograph using a HP-5, 5% phenyl methyl siloxane capillary column (30 m \times 320 µm \times 0.25 µm) and a quadruple mass filter equipped HP 5973 mass selective detector under a temperature-programmed heating from 313 to 473 K at 10°/min.

In a typical representative method, anhydrous aluminum chloride (107.0 mmol) was slowly added to a round-bottomed flask containing dry 1-butyl-3-methylimidazolium chloride (100.0 mmol) under a nitrogen atmosphere in a glove box. The reaction being exothermic and the flask was cooled during addition and mixing.

2.2. Characterization of ionic liquids

Infrared spectra were obtained using a Bio-Rad highresolution FT-IR spectrometer (FTS-40) to investigate the nature of acidity quantitatively. All spectra were acquired at 2-cm⁻¹ resolution with a total 4 scans acquired per spectrum. The preheated samples were placed in a portable, stainless-steel path-length cell (ThermoNicolet) with NaCl windows ($50 \times 25 \times 6$ mm) suitable for FT-IR spectroscopy. All spectra were manipulated by Bio-Rad Win-ir software (ver. 4.14). All the ²⁷Al NMR measurements were carried out using a Bruker WB-400 AMX spectrometer to investigate the species of aluminum complex qualitatively. The ²⁷Al NMR chemical shifts were referenced to an external Al(H₂O)₆³⁺ standard.

2.3. Characterization of dissolved hydrocarbons

The spent ionic liquid (1 g) or the sulfuric acid (1 g) were added to water (10 mL) and the product was extracted with ether. The ether layer was washed with water to remove traces of catalyst and dried over sodium sulfate. The filtrate was then analyzed with TLC and GC-MS. For spent sulfuric acid, the remaining acid-soluble materials in water were extracted with ether after neutralization. The amount weighed after evaporation of ether was 0.4 g.

2.4. Catalytic experiment

In a typical reaction, liquid catalyst samples (15 mL) were placed in a 100-mL double-walled glass reactor (Pyrex). Dead volume in this reactor was decreased using glass beads (Kimble Glass Inc., 3 mm diameter). The isobutane/2-butene mixture (molar ratio of 20) was then introduced into the reactor with various flow rates to adjust the liquid hourly space velocity (LHSV) of system. The flow rate of feed was controlled by a gas-flow controller; thus, all experiments have been performed precisely. The residence time of feed was determined by LHSV of feed stream with no stirring in the reactor. The reaction temperature was controlled by a thermostatic water bath with temperature controller. The reactor effluent was sent to a 16-port sampling valve (Vici-Valco)



Fig. 2. Catalytic conversion of 2-butene versus reaction time over various ionic liquids: $[C_8mim]Br-AlCl_3$ (\blacklozenge), $[C_8mim]Cl-AlCl_3$ (\blacklozenge), $[C_8mim]I-AlCl_3$ (\blacksquare), $[C_6mim]Br-AlCl_3$ (\circlearrowright), $[C_6mim]Cl-AlCl_3$ (\bigcirc), $[C_4mim]Br-AlCl_3$ (\bigcirc), and $[C_4mim]Cl-AlCl_3$ (\blacktriangle). Reactions were performed at LHSV = 24 h⁻¹ and 80 °C.

and the product samples were taken periodically and stored in heated loops. After completion of the reaction, the samples were sent to a gas chromatograph (Hewlett-Packard, 6890). The GC column used for separation is a Supelco Petrocol DH capillary column (50 m \times 0.1 mm \times 0.1 µm). Initial qualitative identifications of the products were accomplished with the help of a gas chromatograph (Hewlett-Packard, 5890 Series II) equipped with a mass spectrometer (Hewlett-Packard, 5972 Series II).

3. Result and discussion

3.1. Comparison of ionic liquids

Catalytic activities determined for the alkylation of isobutane with 2-butene using various ionic liquids are depicted in Fig. 2. The ionic liquids with the same chemical composition, defined as X = [anion]/([anion] + [cation]), were used in this study. The ionic liquids bearing a larger alkyl group on their cation ($[C_8mim]$) exhibit higher activity than a smaller one ([C₆ or C₄mim]) with the same anionic composition, either Cl-AlCl3 or Br-AlCl3 for the entire reaction time. This is mainly attributable to the high solubility of reactants in ionic liquid which can be adjusted by variation of the alkyl group on the cation. This study corroborates the earlier report that with increasing length of the alkyl group, the solubility of hydrocarbons increases significantly [24]. It has been observed that the solubility of 1-octene increases with increasing length of the alkyl group on the cation at 80 °C. This entails that the ionic liquid bearing longer alkyl groups on its cation could catalyze larger amount of reactants under identical conditions, thus, enhancing its catalytic activity.

In the FT-IR characterization results (Fig. 3), it was observed that most of peaks $(1500-700 \text{ cm}^{-1})$ correspond to cationic components (see Table 1) [25] in ionic liquid samples with various lengths of alkyl groups. The height of

Table 1

The list of IR spectra of 1-alkyl-3-methylimidazolium halides-aluminum chloride

Band assignment	Peak frequency (cm ⁻¹)
Complex of AlCl ₃	1568
Ring-stretching symmetrical	1455, 1366, 1326, 1159
Me C-H-bending asymmetrical	1390
Me C–H-bending symmetrical	1336
N–H in-plane bending	1246
Ring C–H in-plane bending	1108
N–H/C–H in-plane bending	956
C–H in-plane bending	832
Ring out of plane asymmetrical	740



Fig. 3. FT-IR spectra of ionic liquids with different cations obtained at $80\,^{\circ}\text{C}.$

peaks representing "ring-stretching symmetrical" increased with length of the alkyl group on the cation. However, the peak at 1571 cm⁻¹ representing a complex of AlCl₃ [26] was barely changed. Consequently, the difference of these samples in terms of catalytic properties is dependent mainly on the anion part. This trend was confirmed from ²⁷Al NMR characterization illustrated in Fig. 4. The major signal of these samples was located around 99.2 ppm representing the presence of [AlCl₃Br]⁻ species [27].

The influence of the anion on the ionic liquid was investigated by adjusting halide with the same alkyl group on its cation. Among the ionic liquids with different halides (Cl, Br, and I), the sample with bromide as a halide ($[C_8mim]Br$ – AlCl₃) has outperformed other ionic liquids under identical experimental conditions. The higher activity is believed to be a result of the enhanced acidic nature of the catalyst determined by an anion group. According to the accepted mechanism [1], the primary alkylation reaction is facilitated by a strong acid strength that is crucial for maintaining a stable activity for this reaction. From the FT-IR results (see Fig. 5), it was observed that the area of peak indicat-



Fig. 4. ²⁷Al NMR spectra of ionic liquids with different cations.

ing acidity (~ 1568 cm⁻¹) varied with halide ion on the anion part. The peak for ionic liquid with Br as a halide was the largest among the samples. This means that the Al anion formed in [C₈mim]Br-AlCl₃ is a stronger acidic anion. Various Al complex anions were identified in ionic liquid samples with different halides in the NMR characterization (Fig. 6). As described earlier, [AlCl₃Br]⁻ anion was dominant in the [C₈mim]Br-AlCl₃. For the [C₈mim]Cl-AlCl₃ sample, AlCl₄ $^-$ (103.5 ppm) ion was detected as the main anion species. The linewidth of the AlCl₄⁻ peak indicates very little Al₂Cl₇ present [28]. For [C₈mim]I-AlCl₃, three peaks were detected as the anions equilibrated. Each peak represents AlCl₄⁻ (103.1 ppm), AlCl₃I⁻ (86.8 ppm), and AlCl₂I₂⁻ (59.4 ppm) ions. As we discussed above, the [AlCl₃Br]⁻ ion is stronger than other major anions among the various ionic liquids used in this study. It is also reported that the bromide-containing aluminates are more acidic than the corresponding chloride ones [18]. The present study also shows that the activity of the bromide-based aluminates is higher than the corresponding tetrachloroaluminates. In addition, it should be noted that the cationic part of the ionic liquid could play a role in the acidity of the system. The imidazolium ion itself shows a weak Lewis acid [29] and the hydrogen atom in the 2-position of an imidazolium ion displays Brønsted acidity [30]. However, the effect of cations on acidity could be ignored since the same imidazolium ion was used in this case.

The ratio of trimethylpentanes (TMPs) to dimethylhexanes (DMHs) is considered as an important criterion for examining the performance of alkylation catalysts. A high TMPs/DMHs ratio is desirable as it typically re-



Fig. 5. FT-IR spectra of ionic liquids with different anions obtained at 80 °C.



Fig. 6. ²⁷Al NMR spectra of ionic liquids with different anions.

sults in the highest octane yield. Moreover, this ratio describes the relative extent of real alkylation in comparison to the oligomerization reaction [31]. The TMP/DMH ratio for all ionic liquids was almost constant during entire reaction time (not shown) and the trend of selectivity (TMPs/DMHs) was comparable with that of catalytic activity (see Fig. 7). Furthermore, it should be noted that the ionic liquids with the same anion group yielded comparable values of TMPs/DMHs regardless of the chain length of the cation on the ionic liquid. From the product distribution described in Table 2, it is obvious that the length of cation barely affected the entire selectivity of C8 product. A small change of cracking product distribution is observed



Fig. 7. Catalytic results of ionic liquid samples at time on stream 200 min.

Table 2 Product distribution obtained using various ionic liquid samples (TOS = 30 min)

	[C ₄ mim] Br–AlCl ₃	[C ₆ mim] Br–AlCl ₃	[C ₈ mim] Br–AlCl ₃	[C ₈ mim] Cl–AlCl ₃	[C ₈ mim] I–AlCl ₃
Olefin conversion (%)	32.1	73.2	91.0	69.5	52.4
C5 (wt%)	13.8	15.2	18.9	11.2	8.7
C6 (wt%)	23.4	22.7	20.1	22.5	24.3
C7 (wt%)	17.4	15.7	14.7	16.2	15.5
C8 (wt%)	45.1	45.9	45.4	50.3	50.5
C9 ⁺ (wt%)	0.3	0.5	0.9	0.4	1.0
C8 distribution					
TMPs (wt%)	8.8	9.4	9.3	6.9	2.3
2,2,3-TMP	0.0	0.0	0.0	0.0	0.0
2,2,4-TMP	5.4	5.8	5.6	0.3	1.0
2,3,3-TMP	0.9	1.0	1.1	2.2	0.5
2,3,4-TMP	2.5	2.6	2.6	4.4	0.8
DMHs (wt%)	18.8	18.0	18.1	22.7	13.6
2,2-DMH	0.0	0.0	0.0	0.0	0.0
2,3-DMH	2.2	2.1	2.0	3.4	1.6
2,4-DMH	6.1	6.2	5.8	8.1	4.6
2,5-DMH	9.9	9.4	9.5	10.0	6.9
3,3-DMH	0.0	0.0	0.1	0.0	0.0
3,4-DMH	0.6	0.3	0.5	1.2	0.5
C8 olefins (wt%)	17.5	18.5	18.2	20.7	34.6

Reactions were performed at 80 $^{\circ}C$ (LHSV_{total} = 24 h^{-1} and i/o_{molar} ratio = 20).

using these samples with the same anionic part. For ionic liquids with different anion compositions, significant changes in product selectivity occurred. The higher amount of cracking products (C5–C7) and alkylation products (TMPs) was obtained over $[C_8mim]Br-AlCl_3$ possessing strong acidic anions. The acidity influences the selectivity of products and essentially the anionic part on the ionic liquid is of significance.

3.2. Effect of composition

Experiments were conducted with various compositions of ideal ionic liquid ($[C_8mim]Br-AlCl_3$), which showed the most desirable performance profile to critically examine the effect of anion species. For a more acidic sample (X = 0.58), it was found that the catalytic activity was high initially



Fig. 8. Catalytic conversion of 2-butene versus reaction time over $[C_8mim]Br-AlCl_3$ with various concentrations of anion species. Reactions were performed at LHSV = 240 h⁻¹ and 80 °C.



Fig. 9. FT-IR spectra of $[C_8mim]Br-AlCl_3$ with various concentrations of anion species obtained at 80 °C.

and then deactivated gradually with time on stream (see Fig. 8). This is mainly attributed to the moisture sensitivity of ionic liquids and the decomposition of the organic components [18]. From the FT-IR spectra illustrated in Fig. 9, the peak representing an anionic component ($\sim 1570 \text{ cm}^{-1}$) is displayed as two different anion species in this composition, such as $[AlCl_3Br]^-$ and $[Al_2Cl_6Br]^-$ presumably. The existence of stronger acidic species, [Al₂Cl₆Br]⁻, is attributed to an excess of anion compound also confirmed from ²⁷Al NMR. The appearance of a broad peak (98.7 ppm) in ²⁷Al NMR (Fig. 10) is supportive of the fact that the concentration of [Al₂Cl₆Br]⁻ increased under strong acidic conditions. For ionic liquids with a lower amount of anionic component (X = 0.48), the catalytic performance was lower than other samples. This is mainly attributed to a lower amount of available acidic sites, as is obvious from the FT-IR spectra; a weak peak ($\sim 1570 \text{ cm}^{-1}$) was detected.



Fig. 10. ²⁷Al NMR spectra of $[C_8mim]Br-AlCl_3$ with various concentrations of anion species: (A) X = 0.58, (B) X = 0.52, (C) X = 0.48.

Table 3 Product distribution obtained over $[C_8mim]Br-AlCl_3$ with various compositions

			Comp	osition		
	0.48		0.52		0.58	
TOS (min)	10	300	10	300	10	300
Olefin conversion (%)	18.0	17.4	40.5	39.6	70.4	35.1
C5 (wt%)	4.5	4.3	18.9	17.9	32.5	24.5
C6 (wt%)	10.3	10.2	20.1	20.1	26.6	22.2
C7 (wt%)	14.1	15.0	14.7	13.7	16.6	18.1
C8 (wt%)	30.3	31.4	45.2	45.4	23.7	22.7
C9 ⁺ (wt%)	40.8	39.1	1.1	2.9	0.6	12.5
C8 distribution						
TMPs (wt%)	0.7	0.7	9.4	9.2	8.7	5.7
2,2,3-TMP	0.0	0.0	0.0	0.0	0.2	0.3
2,2,4-TMP	0.2	0.2	5.8	5.6	4.7	3.0
2,3,3-TMP	0.2	0.2	1.2	1.1	1.2	1.0
2,3,4-TMP	0.3	0.3	2.5	2.5	2.6	1.4
DMHs (wt%)	7.3	7.2	18.2	18.2	8.3	8.9
2,2-DMH	0.0	0.0	0.0	0.0	0.0	0.0
2,3-DMH	1.1	1.0	2.0	2.0	1.1	1.3
2,4-DMH	2.6	2.6	5.7	5.9	3.0	3.6
2,5-DMH	3.4	3.5	9.6	9.7	3.9	3.6
3,3-DMH	0.0	0.0	0.3	0.1	0.0	0.0
3,4-DMH	0.2	0.1	0.6	0.5	0.3	0.4
C8 olefins (wt%)	22.3	23.5	17.8	18.0	6.7	8.1

Reactions were performed at 80 °C (LHSV_{total} = 240 h^{-1} and i/o_{molar} ratio = 20).

From the product distribution summarized in Table 3, a trend was observed. With increasing acidity, the amount of cracking products (C5–C7) increased with a concomitant decrease in oligomerization products (olefins and heavy products). It should be noted that the ratio of TMPs/DMHs



Fig. 11. Catalytic conversion of 2-butene versus reaction time over $[C_8mim]Br-AlCl_3$ at various reaction temperatures. Reactions were performed at LHSV = 240 h⁻¹.

increased with the amount of anionic component of the ionic liquid. This means that higher numbers of Brønsted acid sites responsible for producing TMPs exist in more acidic ionic liquid (X = 0.58) as corroborated by results obtained earlier [20]. It is well known that strong Lewis acid, [Al₂Cl₆Br]⁻, can react with hydrogen atoms at the 2-position of an imidazolium ion to form Brønsted acid [30,32] as described in the reaction:

$$[Al_2Cl_6Br]^- + H^+ \leftrightarrow [AlCl_3Br]^- + [AlHCl_3]^+.$$
(1)

Moreover, it was observed that a small amount of TMP (about 0.7 wt%) was formed using ionic liquid with a lower anionic composition (X = 0.48). This is attributed to the fact that there is a paucity of strong acidic anion, $[Al_2Cl_6Br]^-$, which can be transformed to Brønsted acid sites in this sample. This result supports the aforementioned discussion.

3.3. Effect of temperature

In terms of olefin consumption, the maximum activity was observed at 80°C (Fig. 11), thereby suggesting that the acidity of ionic liquid, as determined by the formation of anions, is influenced by the reaction temperature. In the FT-IR results illustrated in Fig. 12, the peak heights representing acidity ($\sim 1570 \text{ cm}^{-1}$) under varying temperatures were similar for the anion composition (see Fig. 9). Apparently, the concentration of strong acidic anion increases with the temperature as has been observed by others [28, 33]. However, under favorable reaction conditions in terms of acidity, the catalytic activity was low at 120 °C. This is mainly attributed to decomposition of the cation part of the ionic liquid [18]. In the FT-IR data shown in Fig. 12, it was seen that the diminution of peaks corresponded with cations $(1000-1100 \text{ and } 1300-1400 \text{ cm}^{-1})$. As a result of this reduction, the solubility of reactant deceased. Thus, the lower catalytic performance was observed at this temperature.

From the product distribution point of view, it was observed that the nature of acidity could be altered with reaction temperature as shown in Table 4. Predominant yields



Fig. 12. FT-IR spectra of $[\mathrm{C}_8\mathrm{mim}]\mathrm{Br-AlCl}_3$ obtained at various temperatures.

Table 4

Product distribution obtained under various temperature conditions for both samples (TOS = 300 min)

Sample:		[C8mim]Br-AlCl3			
Temperature (°C):	50	80	120		
Olefin conversion (%)	30.2	39.6	27.8		
C5 (wt%)	10.1	17.9	15.8		
C6 (wt%)	21.1	20.1	18.7		
C7 (wt%)	18.8	13.7	17.6		
C8 (wt%)	46.2	45.4	44.2		
C9 ⁺ (wt%)	3.8	2.9	3.7		
C8 distribution					
TMPs (wt%)	1.8	9.2	4.1		
2,2,3-TMP	0.0	0.0	0.0		
2,2,4-TMP	1.4	5.6	3.7		
2,3,3-TMP	0.0	1.1	0.0		
2,3,4-TMP	0.4	2.5	0.4		
DMHs (wt%)	4.7	18.2	3.5		
2,2-DMH	0.0	0.0	0.0		
2,3-DMH	0.7	2.0	0.3		
2,4-DMH	1.7	5.9	2.7		
2,5-DMH	2.3	9.7	0.5		
3,3-DMH	0.0	0.1	0.0		
3,4-DMH	0.0	0.5	0.0		
C8 olefins (wt%)	39.7	18.0	36.6		

Reactions were performed at $LHSV_{total} = 240 \ h^{-1}$ and i/o_{molar} ratio = 20.

of olefins (85%) were observed when the reaction was performed at 50 and 120 °C possibly due to oligomerization activity that dominates over Lewis acids under these conditions. The fragmentation of the cationic component decreases the number of Brønsted acid sites, thus affecting the selectivity as discussed above. In contrast, a relatively large amount of primary product (TMPs) was obtained in alkylation activity at 80 °C. Based on a well-known alkylation mechanism [1], both alkylation and oligomerization are strongly dependent on the nature of acidity. Alkylation



Fig. 13. Catalytic conversion of 2-butene versus reaction time over $[C_8mim]Br-AlCl_3$ (\Box) and H_2SO_4 (\diamondsuit). Reactions were performed at LHSV = 240 h⁻¹ and 80 °C over ionic liquid and 18 °C over H_2SO_4 .

and oligomerization usually occur over Brønsted and Lewis acids, respectively. Hence, the existence of [AlHCl₃]⁺ as a Brønsted acid could maintain the optimum acidity of ionic liquid determining catalytic performance at this temperature.

3.4. Ionic liquid versus sulfuric acid

The change in olefin conversion with time on stream for H₂SO₄ and the ideal ionic liquid ([C₈mim]Br-AlCl₃) is illustrated in Fig. 13. For a fair comparison, the reaction with sulfuric acid was performed under optimum conditions, delineated in the literature [1,34–36] such as sulfuric acid of 95% purity and at 18 °C. At temperatures above (25 °C), oligomerization of olefin becomes significant and the activity decreases with temperature. It can be seen that both catalysts showed comparable catalytic behavior under optimum reaction conditions. For the sulfuric acid system, the olefin conversion gradually decreased and the color of the catalyst changed with time on stream. It is mainly attributed to the formation of acid-soluble oil (ASO) also referred to as conjunct polymers or red oil. These materials have been described to have empirical compositions of about $(C_{1.0}H_{1.75})_n$, where *n* averages from about 10 to 30 [34]. These highly unsaturated cyclic hydrocarbons relatively rapidly deactivate the acid catalyst [35].

In the case of bromide-bearing ionic liquid, the olefin conversion barely changed and remained higher than sulfuric acid during the entire reaction time. The higher activity of ionic liquid is attributable its higher acid strength which is higher than 100% sulfuric acid [24]. Moreover, the catalytic stability can be explained by the tunable coordinating ability of the anions at this temperature (80 °C). A highly electrophilic metal center involved as the active sites can be stabilized in the solvent without loss of their activity [37]. Moreover, the ionic liquid employed in this study can be considered as a biphasic system. In the case of a biphasic catalysis it is assumed that the active catalytic species is soluble in the solvent but reaction products, especially heavier hydrocarbons, are not [38]. The hydrocarbon materials dissolved in ionic liquid were identified to support the above discussion. Most of the ex-



Fig. 14. Catalytic conversion of 2-butene versus reaction time with various LHSV over (A) H_2SO_4 at 18 °C and (B) $[C_8mim]Br-AlCl_3$ at 80 °C.

tracted carbon from spent ionic liquid are smaller than C8 hydrocarbon, e.g., 2,3-dimethylbutane, 3-methylpetane, 2-methyl-2-pentene, *n*-hexane, 3-methylhexane, and isoheptane. This means that larger hydrocarbons causing deactivation of acidic sites, such as ASO, were barely formed in ionic liquid and hence, ionic liquid can be used as a stable catalyst for this reaction.

The influence of liquid hourly space velocity (LHSV) based on feed mixture on olefin conversions with respect to the time on stream is illustrated in Fig. 14 for sulfuric acid as well as ionic liquid. Both catalysts displayed a quite comparable catalytic pattern. In lower LHSV conditions (24 h^{-1}), the catalytic activity was very high without further deactivation. With increasing LHSV, the catalytic activity decreased gradually. This reduction of catalytic activity is mainly attributed to the fact that resident time of reactants decreased with LHSV. At higher LHSV condition, some of reactant passed over acidic sites without undergoing any reaction. Interestingly, using ionic liquid, higher than 240 h^{-1} of LHSV, the activity remained at the same level (see Fig. 14B). Thus, the ionic liquid invariably yields higher than 40% of olefin conversion at this reaction temperature (80 °C). For sulfuric acid, however, olefin conversion still decreased with LHSV. Therefore, the activity of both catalysts can be determined by changing reaction conditions.

Table 5
Product distribution obtained with various LHSV conditions over both same
ples (TOS = 300 min)

Sample:	H ₂ SO ₄			[C ₈ n	nim]Br–A]Br–AlCl ₃	
LHSV:	24	60	240	24	60	240	
Olefin conversion (%)	74.6	40.1	24.5	84.1	57.1	39.6	
C5 (wt%)	13.6	9.7	5.8	18.1	17.3	17.9	
C6 (wt%)	16.3	12.8	11.4	19.3	20.0	20.1	
C7 (wt%)	12.5	13.1	16.7	13.5	14.8	13.7	
C8 (wt%)	42.8	51.9	52.4	46.1	44.6	45.4	
C9 ⁺ (wt%)	14.8	12.5	13.7	3.0	3.3	2.9	
C8 distribution							
TMPs (wt%)	28.1	30.8	28.5	9.2	9.4	9.2	
2,2,3-TMP	0.7	1.0	1.0	0.0	0.0	0.0	
2,2,4-TMP	11.5	12.8	13.5	6.0	5.4	5.6	
2,3,3-TMP	7.4	8.7	7.1	0.8	1.3	1.1	
2,3,4-TMP	8.5	8.3	6.9	2.4	2.7	2.5	
DMHs (wt%)	12.4	17.2	18.8	18.1	18.7	18.2	
2,2-DMH	0.0	0.0	0.0	0.0	0.0	0.0	
2,3-DMH	2.6	2.9	2.8	1.8	1.8	2.0	
2,4-DMH	3.7	6.6	7.1	5.7	6.1	5.9	
2,5-DMH	5.5	6.8	7.9	9.8	10.2	9.7	
3,3-DMH	0.0	0.0	0.0	0.0	0.0	0.1	
3,4-DMH	0.6	0.9	1.0	0.8	0.6	0.5	
C8 olefins (wt%)	2.3	3.9	5.1	18.8	16.5	18.0	

Reactions were performed at 80 °C (i/o_{molar} ratio = 20).

The product selectivity over various LHSV is shown in Table 5. Both catalysts showed different patterns with LHSV. For sulfuric acid, cracking (C5-C7) and alkylation (TMPs/DMHs) products formed by strong acid sites decreased with increasing of LHSV. Moreover, an increase of olefin products by oligomerization was observed. Using ionic liquid, even though olefin conversion varied with LHSV, the distribution of products was comparable. This means that the nature of acidity, determined by the anion part on ionic liquid, hardly changed regardless of reaction conditions at this temperature. This result supports the stability of ionic liquid as well. However, the amount of primary products (TMPs) obtained is much smaller using ionic liquid than sulfuric acid. This is because of the lower concentration of Brønsted acid sites in the case of ionic liquid. Therefore, ionic liquid with a higher amount of Brønsted acid sites is more feasible as a commercial alkylation catalyst.

4. Conclusion

Alkylation of isobutane with 2-butene using various 1-alkyl-3-methylimidazolium halides–aluminum chloride catalysts has been successfully demonstrated. Among theses ionic liquids, $[C_8mim]Br-AlCl_3$ displayed the best performance in terms of activity and selectivity for this reaction. From various parametric studies, such as anion compositions and temperature, optimum catalytic activity was observed at 80 °C and X = 0.52. Based on FT-IR and ²⁷Al NMR analyses, it was found that the formation of anions was crucial for determining the catalytic performance. Especially, the existence of strong acidic anion, $[Al_2Cl_6Br]^-$, maintains the

higher activity and TMP selectivity. In the comparison with sulfuric acid, the selected ionic liquid showed higher catalytic activity but lower TMP selectivity. Consequently, an ionic liquid possessing a larger amount of Brønsted acid sites would be ideally suited as a commercial alkylation catalyst.

Acknowledgments

The authors thank Dr. Elwood Brook for the NMR analyses. V.V.N. is a postgraduate research participant at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and the US Environmental Protection Agency.

References

- [1] A. Corma, A. Martinez, Catal. Rev. 35 (1993) 483.
- [2] J. Weitkamp, Y. Traa, Catal. Today 49 (1999) 193.
- [3] J. Weitkamp, S. Maxiner, Zeolites 7 (1987) 6.
- [4] C.L. Hussey, Molten Salt Chem. 5 (1983) 185.
- [5] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.
- [6] R.P. Swatloski, A.E. Visser, W.M. Reichert, G.A. Broker, L.M. Farina, J.D. Holbrey, R.D. Rogers, Green Chem. 4 (2002) 81.
- [7] L.A. Blanchard, D. Hancu, E.J. Beckmann, J.F. Brennecke, Nature 399 (1999) 28.
- [8] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Chem. Commun. (1998) 1765.
- [9] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 124 (2002) 4974.
- [10] A.C. Cole, J.L. Jensen, I. Ntai, K. Loan, K.L. Tran, T.K.J. Weaver, D.C. Forbes, J.H. Davis Jr., J. Am. Chem. Soc. (2002) 5962.

- [11] D. Zhao, M. Wu, Y. Kon, E. Min, Catal. Today 74 (2002) 157.
- [12] S.G. Cull, J.D. Holbrey, V. Vargas-Mora, K.R. Seddon, G. Lye, J. Biotechnol. Bioeng. 69 (2000) 227.
- [13] R.A. Sheldon, R. Maderia Lau, M.J. Sorgedrager, F. van Rantwijk, K.R. Seddon, Green Chem. 4 (2002) 147.
- [14] C. Hardacre, J.D. Holbrey, S.P. Katdare, K.R. Seddon, Green Chem. 4 (2002) 143.
- [15] A.J. Carmichael, D.M. Haddleton, S.A.F. Bon, K.R. Seddon, Chem. Commun. (2000) 1237.
- [16] S.J. Nara, J.R. Harjani, M.M. Salunkhe, J. Org. Chem. 66 (2001) 8616.
- [17] L. Green, I. Hemeon, R.D. Singer, Tetrahedron Lett. 41 (2000) 1343.
- [18] T. Welton, Chem. Rev. 99 (1999) 2071.
- [19] K.R. Seddon, J. Chem. Technol. Biotechnol. 68 (1997) 351.
- [20] Y. Chauvin, A. Hirschauer, H. Olivier, J. Mol. Catal. 92 (1994) 155.
- [21] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.
- [22] R.S. Varma, V.V. Namboodiri, Chem. Commun. (2001) 643.
- [23] V.V. Namboodiri, R.S. Varma, Org. Lett. 4 (2002) 3161.
- [24] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3773.
- [25] S. Tait, R.A. Osteryoung, Inorg. Chem. 23 (1984) 4352.
- [26] S. Csihony, A. Bodor, J. Rohonczy, I.T. Hovath, J. Chem. Soc. Perkin Trans. 1 (2002) 2861.
- [27] H. Haraguchi, S. Fujiwara, J. Phys. Chem. 73 (1969) 3467.
- [28] J.L. Gray, G.E. Maciel, J. Am. Chem. Soc. 103 (1981) 7147.
- [29] J. Howarth, K. Hanlon, D. Fayne, P. McCormac, Tetrahedron Lett. 38 (1997) 3097.
- [30] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
- [31] A. Corma, A. Martinez, C. Martinez, J. Catal. 146 (1994) 185.
- [32] P.R. Gifford, J.B. Palmisano, J. Electrochem. Soc. 134 (1987) 610.
- [33] K. Ichikawa, M. Izumi, T. Jin, T. Matsumoto, Chem. Lett. (1992) 1651.
- [34] L.F. Albright, Ind. Eng. Chem. Res. 41 (2002) 5627.
- [35] L.F. Albright, M.A. Spalding, C.G. Kopser, R.E. Eckerty, Ind. Eng. Chem. Res. 27 (1988) 386.
- [36] K.W. Li, R.E. Eckert, L.F. Albright, Ind. Eng. Chem. Process Des. Dev. 9 (1970) 434.
- [37] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182–183 (2002) 419.
- [38] P.B. Hitchcock, T.J. Mohammed, K.R. Seddon, J.A. Zora, C.L. Hussey, E.H. Ward, Inorg. Chem. Acta 113 (1986) L25.