Reaction Performance of Isobutane Alkylation Catalyzed by a Composite Ionic Liquid at a Short Contact Time

Zhichang Liu, Xianghai Meng, Rui Zhang, Chunming Xu, Heng Dong, and Yufeng Hu
State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, P.R. China

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Alkylate is an important clean blending component of gasoline due to the increased statutory reduction of the content of aromatics and olefins in commercial gasoline. The alkylation of isobutane with 2-butene catalyzed by a composite ionic liquid was investigated. The composite ionic liquid showed efficient catalytic performance at a short contact time (10–60 s). The optimal conditions were: reaction temperature 15°C, contact time 20 s, ionic liquid to hydrocarbon volume ratio 1:1, and isobutane to olefin mole ratio 54:1. Under these optimal reaction conditions, the butene conversion was 100%, the yields of C8 and trimethylpentanes were 88.9 and 82.0%, respectively, the ratio of trimethylpentane to dimethylhexane was 11.9, and the alkylate research octane number (RON) was 97.3. A correlation model is developed to predict the product yields and the alkylate RON. The correlation model shows a low calculation error. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2244–2253, 2014

Keywords: ionic liquid, alkylation, isobutene, butane, correlation model

Introduction

Isobutane alkylation is an important process in refineries that disposes the C4 fraction from a fluid catalytic cracking unit to produce alkylate. The alkylate predominantly contains isoparaffins and has a high octane number and low-vapor pressure as well as low contents of sulfur, olefins, and aromatics. Therefore, the alkylate burns easily and cleanly, and accordingly it is a good blending component for clean motor gasoline. The current commercial catalysts for isobutane alkylation are concentrated sulfuric acid and hydrofluoric acid. However, the utilization of these liquid Brønsted acid catalysts results in severe corrosion, safety, and environmental issues associated with disposal of spent catalyst and high operating cost.[1,2]

The aforementioned problems have motivated researchers to develop safer catalysts for isobutane alkylation. The search for an effective solid isobutane alkylation catalyst has been ongoing for many years. Hommeltoft[1] reviewed several promising isobutane alkylation technologies with a solid catalyst, including the Alkylene™ process presented by UOP; the fixed-bed alkylation (FBA™) technology developed by Haldor Topsøe A/S; the process developed by Catalytica, Neste Oy and Conoco; and the process proposed by Chemical Research & Licensing.

Most solid catalysts show good initial activity and selectivity. However, these catalysts are quickly deactivated because of carbonaceous deposits and pore mouth plugging.[3–5] The deactivation of solid acid catalysts significantly decelerates when isobutane alkylation is conducted in a supercritical medium. However, the process had several disadvantages such as high capital investment and operating cost because of the supercritical state as well as the formation of undesirable products because of the high temperature required to bring the reaction mixture to supercritical conditions.[6,7]

Ionic liquids, which are also called room-temperature ionic liquids or molten salts, have been widely investigated as new reaction media or catalysts.[8–10] Ionic liquids have the advantages of low-vapor pressure, nonflammability, high thermal stability, Brønsted and Lewis acidity, superacidity in some cases, and a wide liquid-phase temperature range. A number of ionic liquids are used as solvents or catalysts for organic synthesis and catalytic reactions, such as the alkylation of aromatics with olefins,[11,12] the isomerization of light alkanes,[13–16] and the oligomerization of butenes.[17–19]

Acidic ionic liquids can be used to catalyze isobutane alkylation. An overview of reported ionic liquids for isobutane alkylation is given in Table 1. Ionic liquids based on 1-alkyl-3-methylimidazolium halide-aluminum chloride ($C_n$mimX-$AlCl_3$, where X = Cl, Br, I) are reported to catalyze the alkylation of isobutane with 2-butene; the conversion of 2-butene reaches 91.0%, the selectivity of C8 reaches 50.5%, and the selectivity of trimethylpentanes [TMPs, the desired components with research octane number (RON) in the 100–109.6 range] is below 10%.[20] For the alkylation of isobutane with butene mixture, the C8 selectivity is 61.9% for the ionic liquid bmimCl-2$AlCl_3$, and it is 69.9% for the ionic liquid $C_{32}H_{68}P$-2$AlCl_3$.[21] For the alkylation of isobutane with 2-butene catalyzed by the ionic liquid Et_3NHCl-1.5$AlCl_3$, the C8 selectivity is 68.0% and the TMPs selectivity is 58.9%.[22] The highest C8 selectivity is around 70% when the ionic liquid is not modified with any additive.

The work done to improve the catalytic performance of acidic ionic liquids can be classified in three ways.

Correspondence concerning this article should be addressed to C.M. Xu at xcm@cup.edu.cn.

Table 1. Catalytic Performance of Various Lewis Acidic Ionic Liquids for Isobutane Alkylation

No.	Ionic Liquid	Additive	Butene	Reactor	Reaction Mode	Temperature (°C)	I/O Ratio	IL/HC Ratio	Reaction Time/ Space Velocity	Activity (Butene Conversion, %)	Selectivity				References
											C5–7 (wt %)	C8 (wt %)	C9+ (wt %)	TMP/DMH	
1	C_8mimBr-$AlCl_3$	–	2-Butene	Tank	Batch	80	20:1		24 h^{-1}	91.0	53.7	45.4	0.9	0.5	20
2	$C_{32}H_{68}P$-2$AlCl_3$	–	Mixture	Tank	Batch	80	110:1		90 min	>99	12.4	68.9	18.7		21
3	omimBr-1.5$AlCl_3$	0.67 mol % CuCl	2-Butene	Tank	Batch	−5	13:1		60 min		14.2	34.5	51.3	13.4	22
4	omimBr-1.5$AlCl_3$	30 ppm H_2O in HCs	2-Butene	Tank	Batch	−5	13:1		60 min		18.3	45.6	36.1	9.9	22
5	Et_3NHCl-1.5$AlCl_3$	0.67 mol % CuCl	2-Butene	Tank	Batch	−5	13:1		15 min		12.5	77.6	9.9	13.6	22
6	bmimCl-1.8$AlCl_3$	0.2 mol % H_2O in feed	2-Butene	Tank	Batch	−20	13:1		80 min	~92	~22	~21	~57	~2.0	23
7	bmimCl-1.8$AlCl_3$	0.5 mol % tert-butyl bromide	2-Butene	Tank	Batch	−20	13:1		4 min	100	~27	~22	~51	~8.1	23
8	bmimCl-1.8$AlCl_3$	0.4 mol % HCl	2-Butene	Tank	Batch	5	50:1			92–95	14–17	73–74	9–13	5.2–7.2	24
9	Et_3NHCl-2$AlCl_3$	1 wt % benzene	2-Butene	Tank	Batch	30	10:1	0.15:1	~40 min	98	13.4	80.9	5.7	8.1	25
10	Et_3NHCl-1.85$GaCl_3$	5 mol % CuCl	Mixture	Tank	Batch	15	10:1	0.4:1	15 min		13.0	70.1	26.9	3.5	26
11	Et_3NHCl-2$AlCl_3$	–	2-Butene	Tank	Semicontinuous	30	10:1		10 h^{-1}	97	22.8	56.2	21.0	2.8	27
12	Et_3NHCl-2$AlCl_3$	5 mol % CuCl	2-Butene	Tank	Semicontinuous	30	10:1		10 h^{-1}	96	13.0	74.8	12.2	6.4	27
13	Composite IL	–	2-Butene	Tank	Batch	20	23:1	0.15:1	~45 min	98	3.2	95.8	1.0	16.7	28
14	Composite IL	–	2-Butene	Tank	Batch	15	9:1	0.3:1	~30 min	100	1.7	97.3	1.0	17	29
15	Composite IL	–	2-Butene	Static mixer	Continuous	15	1:1	1.2:1	10 min		3.6	95.6	0.8	14.9	30
16	Composite IL	–	2-Butene	Tank	Batch	15	54:1	1:1	20 s	100	5.28	88.86	5.86	11.87	This work

Note: ~: data are read from figures and are not accurate.
No. 1: the alkylate contains C8 olefins with a mass amount of 18.2%.
No. 8: TMP/DMH ratio is TMP/(C8-TMP) ratio.
No. 10: butene mixture contains 66% of 2-butene, 26% of 1-butene, and 8% of isobutene.
No. 15: the outer I/O ratio is 1:1, and the inner I/O ratio is about 500:1.

- The first way is to adjust the acidity of ionic liquids by the addition of suitable amounts of Brønsted acid, for example by addition of a Brønsted acid, such as HCl, or by addition of a reagent that can produce Brønsted acid in reaction with the IL, such as H_2O, or by addition of a functional group containing Brønsted acid, such as $-SO_3H$. The addition of Brønsted acids to ionic liquids accelerates the carbocation formation by the addition of a proton to butene. The addition of anhydrous HCl into the ionic liquid bmimCl-$AlCl_3$ can enhance reaction rate and improve both the TMPs selectivity and the alkylate RON, and the addition of anhydrous HCl is possible to reactivate a deactivated ionic liquid with respect to activity and selectivity.[24] While the addition of large amount of HCl (5 mol %) to the ionic liquid Et_3NHCl-$AlCl_3$ is reported to increase the selectivity of C5–7 and to reduce the selectivities of C8 and C9+.[31] The addition of 0.2 mol % water in the feed improves the butene conversion from 25% to about 92% for the alkylation of isobutane with 2-butene catalyzed by the ionic liquid bmimCl-1.8$AlCl_3$.[23] The TMPs selectivity increases from 21.3 to 41.4% and the alkylate RON increases from 90.5 to 93.7 for the isobutane/2-butene alkylation catalyzed by the ionic liquid omimBr-1.5$AlCl_3$ with a water content of 30 ppm in hydrocarbons.[22] The TMPs selectivity increases from 21.3 to 52.7% and the alkylate RON increases from 90.5 to 94.8 for the isobutane/2-butene alkylation catalyzed by the ionic liquid omimBr-1.5$AlCl_3$ with the addition of 50 wt % of [HO_3Sb-mim][HSO_4] in the ionic liquid.[32] In addition, some aromatics, such as benzene and hexamethylbenzene, are reported to modify the acidity of ionic liquids and improve product distribution. For isobutane alkylation with 2-butene catalyzed by ionic liquid Et_3NHCl-2$AlCl_3$ with the addition of 1.0 wt % of benzene, the selectivities of C8 and TMPs increase from 49.6 and 36.5 to 80.9 and 72.0%, respectively.[25]
- The second way is to promote the formation of tert-butyl carbocations by the addition of alkyl halides such as tert-butyl chloride and tert-butyl bromide. Such promoters are able to speed up the reaction rate of the isobutane/2-butene alkylation catalyzed by the ionic liquid bmimCl-$AlCl_3$ significantly and shift the C8-selectivity towards TMPs.[23] A patent by Chevron also discloses that alkyl halides can promote Lewis acidic chloroaluminate ionic liquid catalyzed alkylation.[33]
- The structural adjustment of ionic liquids by the introduction of transition metal salts (CuCl, $CuCl_2$, and $NiCl_2$) is the third way. For the alkylation of isobutane with 2-butene, the selectivities of C8 and TMPs increase from 68.0 and 58.9 to 77.6 and 72.3%, respectively, when the ionic liquid Et_3NHCl-1.5$AlCl_3$ is modified with CuCl.[22] Also in case of the ionic liquid Et_3NHCl-1.85$GaCl_3$, the addition of CuCl increased the selectivity.[26]

The above three ways are effective to improve the activity and selectivity of Lewis acidic ionic liquids.

Our research group has studied the ionic liquid catalyzed isobutane alkylation since 2000.[31] The ionic liquids Et_3NHCl-$AlCl_3$ synthesized from the triethylamine hydrochloride and the anhydrous $AlCl_3$ are also used to catalyze the alkylation of isobutane with 2-butene. The selectivities of C8 and TMPs are 56.2 and 41.4%, respectively, at 30°C with a isobutane to olefin mole ratio (I/O molar ratio) of 10:1.[27] To improve the catalytic performance, the ionic liquid Et_3NHCl-$AlCl_3$ was modified with various additives, such as HCl, CuCl, $CuCl_2$, $ZnCl_2$, $FeCl_3$, and $NiCl_2$.[27,34,35] It is found that CuCl is the best additive and the selectivities of C8 and TMPs reach 74.9 and 64.8%, respectively, when the ionic liquid Et_3NHCl-$AlCl_3$ is modified with CuCl.[27] Based on this, a composite ionic liquid is developed, which has anions in the form of ligands with two or more metallic centers, such as the anion of $[AlCuCl_5]^-$.[30,36] The composite ionic liquid shows good catalytic performance for isobutane alkylation with 2-butene, and the selectivities of C8 and TMPs reach up to 95.8 and 90.4%, respectively.[28] Under better reaction conditions, the selectivities of C8 and TMPs reach up to 97.3 and 92.0%, respectively.[29]

The composite ionic liquid developed by our research group shows the best catalytic performance among the reported Lewis acidic ionic liquids in spite of different reactors, reaction modes, and reaction conditions. The novel composite ionic liquid alkylation (CILA) process was demonstrated by us in a continuous flow pilot plant with 4 L/h equivalent alkylate production for 60 days and subsequently in a retrofitted 65 kt/a sulfuric acid alkylation unit in China.[30] Our next plan was to develop a dedicated CILA plant for which the improved understanding of the reaction conditions was required to optimally design the reactor.

Isobutane alkylation follows the carbonium ion mechanism regardless of the catalyst (concentrated sulfuric acid, hydrofluoric acid, or ionic liquid).[37,38] The rate of carbonium ion induced reactions is relatively fast. The need for a long contact time is still in question for isobutane alkylation. Besides, contact time (residence time) is an important factor in the reactor design. A short contact time is essential to reduce reactor volume and to enhance processing capacity. Thus, the capital investment and the operating cost can be minimized. For the isobutane alkylation catalyzed by Lewis acidic ionic liquid, can the contact time be shortened? And what about the reaction performance at a short contact time? To answer these questions, this article investigates the isobutane alkylation performance catalyzed by the composite ionic liquid at short contact time ($\leq$60 s).

Experimental

Feed and catalyst

The feedstocks of isobutane and 2-butene were obtained from the alkylation unit of Lanzhou Refinery, PetroChina. Tables 2 and 3 show the composition of the two feeds. The feedstocks in the experiments were obtained by blending the two feeds in various ratios.

The composite ionic liquid developed by China University of Petroleum was used as catalyst. The composite ionic liquid was synthesized from triethylamine hydrochloride (Et_3NHCl), anhydrous $AlCl_3$, and CuCl.[39] The composite ionic liquid was brown and was maintained free from moisture.

Table 2. Composition of Isobutane Feedstock (wt %)

Component	Content
i-Butane	98.20
n-Butane	1.42
Others	0.38

Table 3. Composition of 2-Butene Feedstock (wt %)

Component	Content
i-Butane	2.78
n-Butane	3.24
t−2-Butene	46.28
c−2-Butene	43.16
1-Butene	1.04
i-Butene	1.30
Others	2.20

Alkylation apparatus and process

Figure 1 shows the alkylation apparatus. The feed with a certain I/O molar ratio was stored in the feed storage tank. The feed was pumped into a dryer to remove the moisture and then the water content in the feed was below 10 mg/L. The feed was then entered into the feed tank. The amount of feed was controlled by a plunger pump. A certain volume of the composite ionic liquid was added into a 500-mL autoclave, after which the stirrer was started. The autoclave and the feed tank were controlled at the set temperatures. The valve for high-pressure nitrogen and the one between the feed tank and the autoclave were opened, thus forcing the feed into the autoclave while the time meter was started. The pressure in the autoclave was maintained at 0.6 MPa to keep the reactant and the product in a liquid phase.

After the reaction, stirring was stopped, and the autoclave was cooled. The reaction system was immediately separated into two phases because of the large density difference. Thus, the contact time started from the instantaneous feeding, and ended at the switch-off of the stirrer button. The gas sample was collected through the drainage method. The liquid sample hardly dissolved in the composite ionic liquid and was separated by decantation.

The experiments were conducted in batch mode, with a reaction temperature ranging from 0 to 40°C, a contact time from 10 to 600 s, an ionic liquid to hydrocarbon volume ratio (IL/HC volumetric ratio) from 0.5:1 to 1.5:1, an I/O molar ratio from 15:1 to 54:1, and a stirrer speed from 600 to 1800 r/min.

Analysis methods of reaction samples

The volume percentage of components in the gas sample were measured by a refinery gas analyzer, which is an Agilent 6890 Gas Chromatograph that was equipped with a hydrogen flame ionization detector, a thermal conductivity detector, and a ChemStation software.

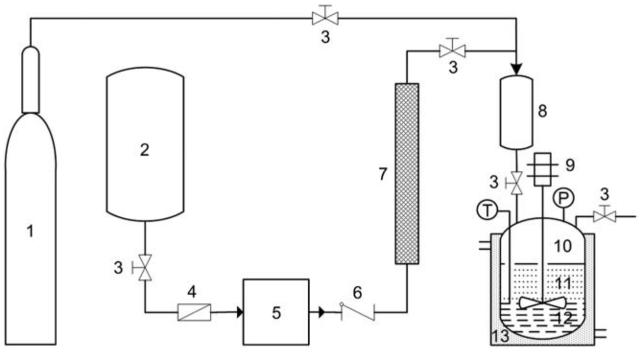

Figure 1. Apparatus for isobutane alkylation (1-constant pressure nitrogen, 2-feed storage tank, 3-cut-off valve, 4-filter, 5-plunger pump, 6-one-way valve, 7-dryer, 8-feed tank, 9-stirrer, 10-autoclave, 11-reactant and product, 12-composite ionic liquid, and 13-constant temperature circulating water).

The liquid sample was analyzed by a SP3420 Gas Chromatograph that was equipped with a flame ionization detector. The chromatographic column is a PONA capillary column (50 m × 0.25 mm × 0.25 μm). The temperatures of the injector and the detector were 250 and 300°C, respectively. The temperature program was as follows: holding at 40°C for 2 min, increasing to 60°C at a speed of 2°C/min, increasing to 120°C at a speed of 1°C/min, increasing to 180°C at a speed of 2°C/min, and finally holding at 180°C for 13 min. The qualitative analysis was conducted based on the holding time of the peak, whereas the quantitative analysis was conducted through the area normalization method.

The alkylate RON was calculated according to Eq. 1

$$\mathrm{RON}=\sum_{i=1}^{n} \mathrm{C}_i \cdot \mathrm{RON}_i \tag{1}$$

In Eq. 1, i is a component in alkylate; RON_i is the RON of component i; and C_i is the relative volume percentage of component i in alkylate, vol %, which is calculated on the basis of the mass percentage and the relative density of component i. Table 4 lists the RON[40] and the relative density[41] of the components in alkylate. Hence, RON is the calculated from Eq. 1 unless otherwise defined.

Reliability of experiments

Table 5 lists the data of a group of experiments at the same reaction conditions (reaction temperature of 15°C, contact time of 60 s, stirrer speed of 1500 r/min, IL/HC volumetric ratio of 1:1, and I/O molar ratio of 54:1). The standard deviation was below 1% and the relative standard deviation was below 8% except for 3,4-DMH, indicating that the repeatability of experiments was good.

Table 4. RON and Relative Density of the Components in Alkylate

Carbon Number	Components	RON	Relative Density
C5	*i*-C5	93.0	0.617
	n-C5	61.8	0.626
C6	2,2-DMB	91.8	0.649
	2,3-DMB	104.3	0.662
	2-MP	73.4	0.654
	3-MP	74.5	0.664
	n-C6	24.8	0.660
C7	2,2-DMP	92.8	0.674
	2,4-DMP	83.1	0.675
	2,2,3-TMB	112.1	0.690
	3,3-DMP	80.8	0.693
	2,3-DMP	91.1	0.695
	2-MH	42.4	0.679
	3-MH	52.0	0.687
C8	2,2,4-TMP	100.0	0.692
	2,2,3-TMP	109.6	0.716
	2,3,4-TMP	102.7	0.719
	2,3,3-TMP	106.1	0.726
	2,5-DMH	55.5	0.694
	2,4-DMH	65.2	0.703
	2,3-DMH	71.3	0.712
	3,4-DMH	76.3	0.719
	2-MH	21.7	0.698
	3-MH	26.8	0.706
C9+	2,2,5-TMH	91.0	0.707
	Others	70.0	0.740

Table 5. Repeatability of Four Experiments at the Same Conditions

Item	1#	2#	3#	4#	Average Value	Standard Deviation (wt %)	Relative Standard Deviation (%)
Component yield (wt %)							
C5	1.36	1.20	1.32	1.24	1.28	0.07	5.71
C6	1.88	1.90	1.79	1.98	1.89	0.08	4.05
C7	1.91	1.80	2.01	2.04	1.94	0.11	5.57
C8	86.41	87.18	86.23	87.16	86.74	0.50	0.57
C9+	8.44	7.92	8.65	7.59	8.15	0.48	5.93
C8 distribution							
TMPs	79.31	80.19	79.06	79.80	79.59	0.50	0.63
2,2,4-TMP	43.84	45.09	43.88	44.63	44.36	0.61	1.37
2,3,3-TMP	18.38	18.02	17.71	18.21	18.08	0.29	1.59
2,3,4-TMP	17.09	17.08	17.47	16.96	17.15	0.22	1.29
DMHs	7.10	6.99	7.17	7.34	7.15	0.15	2.05
2,3-DMH	1.54	1.58	1.64	1.72	1.62	0.08	4.83
2,4-DMH	1.82	1.72	1.65	1.53	1.68	0.12	7.26
2,5-DMH	3.50	3.42	3.67	3.77	3.59	0.16	4.43
3,4-DMH	0.24	0.27	0.21	0.32	0.26	0.05	18.04
TMPs/DMHs	11.17	11.47	11.03	10.86	11.13	0.26	2.34
Alkylate RON	96.56	96.77	96.44	96.67	96.61	0.14	0.15

Results and Discussion

The reaction performance of isobutane alkylation catalyzed by the composite ionic liquid was investigated, for example the effects of stirrer speed, reaction temperature, IL/HC volumetric ratio, I/O molar ratio, and contact time on product distribution, butene conversion and alkylate RON, were studied. A correlation model was proposed for the prediction of alkylation performance.

Effect of stirrer speed

It is important to first ensure that sufficient mixing is applied when studying the reaction parameters. The effect of stirrer speed on product distribution and alkylate RON is shown in Figures 2 and 3. At 1500 r/min, the selectivity reached a maximum and remained more or less constant at further increase to 1800 r/min. This indicated that a stirrer speed above 1500 r/min was unnecessary.

The distribution of TMP isomers was similar to the reported data on isobutane alkylation catalyzed by the ionic liquid $Et_3NHCl-AlCl_3$,[25,27] or the ionic liquid $Et_3NHCl-AlCl_3$ modified with CuCl[27] or benzene.[25] However, the distribution of TMP isomers differed from the data on isobutane alkylation catalyzed by the ionic liquid $C_8mimCl-AlCl_3$.[20] Among the DMH isomers, the contents of 2,3-DMH, 2,4-DMH, and 2,5-DMH were high, and that of 3,4-DMH was the lowest. This agrees with the data on isobutane alkylation catalyzed by the ionic liquid $C_8mimCl-AlCl_3$.[20] The TMP/DMH ratio ranged from 10.61 to 11.20, and increased slightly with increasing stirrer speed.

A high stirrer speed enhances the dispersion of isobutane and butenes in the ionic liquid, and modifies the contact effect between the feed and the ionic liquid catalyst. Therefore, a high stirrer speed favors the product distribution. The optimal stirrer speed for the tested geometry was 1500 r/min. This stirring speed was applied in the further study of the reaction parameters.

Effect of reaction temperature

The increase of reaction temperature leads to lower selectivity of C8, lower alkylate RON and higher selectivities of C5, C6, C7, and C9+ as shown in Figure 4. The results are in accordance with the literature.[29,42] High temperature accelerates such side reactions as cracking and disproportionation, resulting in increasing yields of light ends (C5–C7) and heavy ends (C9+).

The increase of reaction temperature leads to lower selectivity of TMPs and lower TMP/DMH ratio as shown in Figure 5. Chauvin et al. report the similar results in the

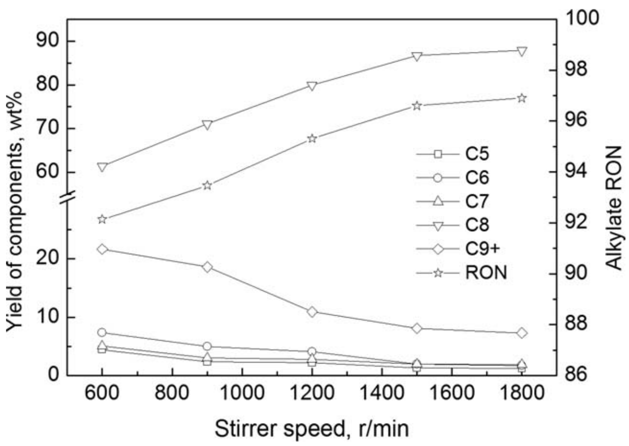

Figure 2. Yields of components and alkylate RON as a function of stirrer speed (T = 15°C, *t* = 60 s, IL/HC = 1:1 v:v, and I/O = 54:1 mol:mol).

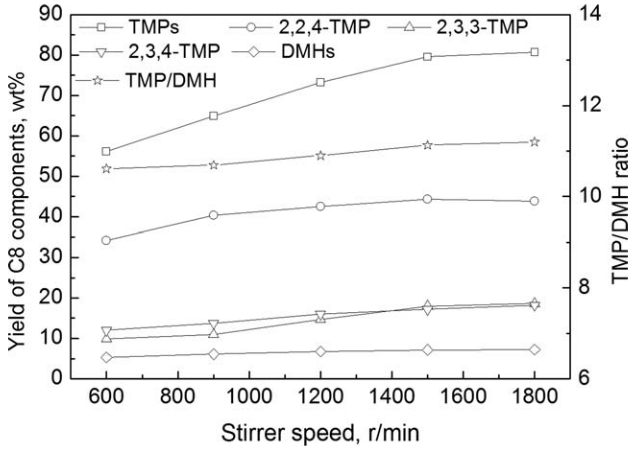

Figure 3. Yields of C8 components and TMP/DMH ratio as a function of stirrer speed (T = 15°C, *t* = 60 s, IL/HC = 1:1 v:v, and I/O = 54:1 mol:mol).

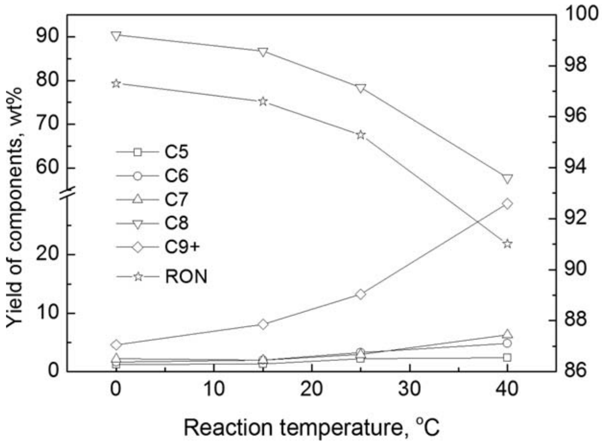

Figure 4. Yields of components and alkylate RON as a function of reaction temperature (R = 1500 r/min, *t* = 60 s, IL/HC=1:1 v:v, and I/O=54:1 mol:mol).

temperature range of −5°C to 15°C, but the product distribution at −15°C is a bit worse than that at −5°C, which may be due to high viscosity of ionic liquid at −15°C.[43] Zhang and coworkers report that the TMP/DMH ratio in alkylate increases with decreasing reaction temperature when chloroaluminate ionic liquid is used as catalyst with 1 wt % of benzene as additive.[25] Isobutane alkylation is exothermic, so low temperatures favor the balance distribution of TMPs. Low temperatures also inhibit side reactions, and accordingly, favor the formation of C8 and TMPs. Both the product distribution and the alkylate RON were favorable at 0°C. However, the viscosity of the composite ionic liquid was high at 0°C. Therefore, the optimal reaction temperature was 15°C.

Effect of IL/HC volumetric ratio

The product distribution and the alkylate RON at IL/HC volumetric ratios of 1:1, 1.2:1, and 1.5:1 were similar, and they were better than those at the IL/HC volumetric ratios of 0.5:1 and 0.75:1 as shown in Figures 6 and 7.

Hydrocarbons can dissolve in chloroaluminate ionic liquid and the solubility increases with decreasing chain length of hydrocarbons.[23,44] The volume of ionic liquid phase will increase with dissolving hydrocarbons. Therefore, for the IL/HC volumetric ratio above 1:1, the ionic liquid is most likely in the continuous phase and the hydrocarbon is in the dispersed phase. These conditions favor alkylation reactions. However, for the IL/HC volumetric ratios of 0.5:1 and 0.75:1 in this research, the hydrocarbon is likely in the continuous phase and the ionic liquid is in the dispersed phase. These conditions are unfavorable for alkylation reactions that occur at the phase interface. As long as the IL/HC volumetric ratio was equal to or greater than 1:1, the system was maintained ionic liquid continuous, good alkylation performance was achieved, and IL/HC volumetric ratio showed little effect on product distribution and the alkylate RON. This agrees well with the alkylation performance of isobutane with 1-butene using sulfuric acid as catalyst.[45] The optimal IL/HC volumetric ratio was 1:1 from the perspective of the reactor volume.

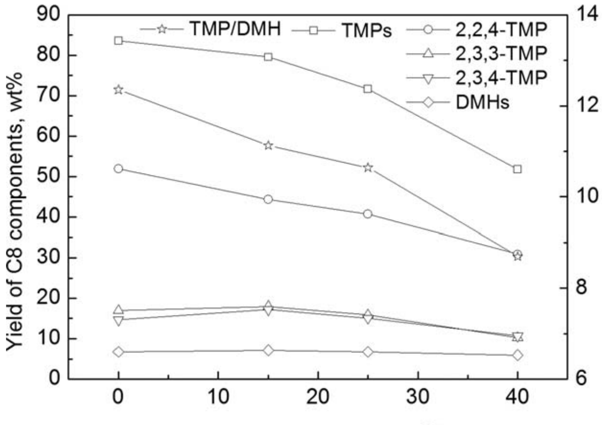

Figure 5. Yields of C8 components and TMP/DMH ratio as a function of reaction temperature (R = 1500 r/min, *t* = 60 s, IL/HC=1:1 v:v, and I/O=54:1 mol:mol).

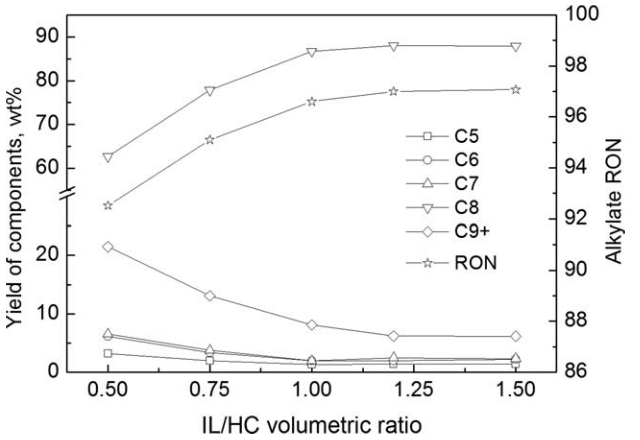

Figure 6. Yields of components and alkylate RON as a function of IL/HC volumetric ratio (R = 1500 r/min, T = 15°C, *t* = 60 s, and I/O=54:1 mol:mol).

Effect of I/O molar ratio

The increase of I/O molar ratio leads to higher alkylate RON, higher selectivities of C8 and TMPs and lower selectivities of C5, C6, C7, and C9+ as shown in Figures 8 and 9.

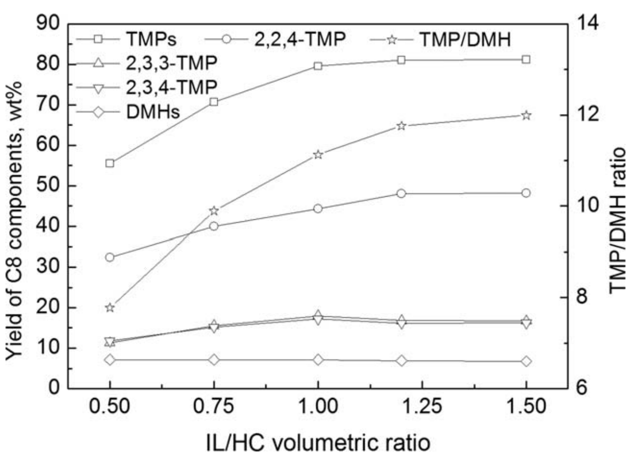

Figure 7. Yields of C8 components and TMP/DMH ratio as a function of IL/HC volumetric ratio (R = 1500 r/min, T=15°C, *t* = 60 s, and I/O=54:1 mol:mol).

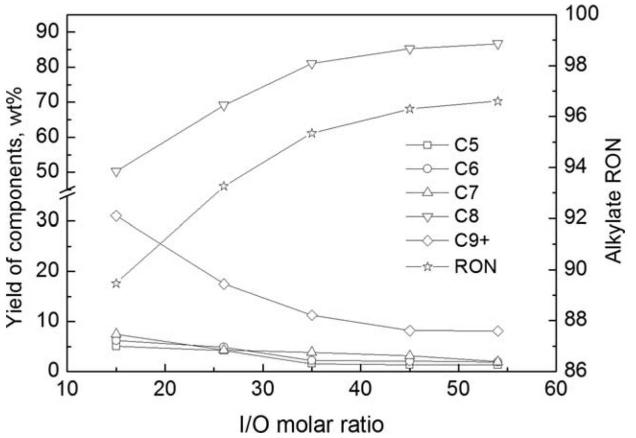

Figure 8. Yields of components and alkylate RON as a function of I/O molar ratio (R = 1500 r/min, T = 15°C, *t* = 60 s, and IL/HC=1:1 v:v).

The optimal I/O molar ratio was as high as possible and was above 50:1.

Mosby and Albright report that I/O molar ratio has a significant effect on alkylation catalyzed by sulfuric acid, and increased ratios favor the formation of TMPs, but disfavor the formation of light ends and heavy ends.[45] The effect of I/O molar ratio on alkylation is similar for both sulfuric acid catalyst and the composite ionic liquid catalyst. Liu et al. report that the TMPs yield increases slightly from 84% at an I/O molar ratio of 3:1 to 92% at an I/O molar ratio of 40:1 (the composite ionic liquid, reaction temperature of 12°C).[29] The TMPs yield is much higher than that in this research (43.35–79.55%). It is the experimental method difference that leads to the alkylation result difference. For the experiment of Liu et al.,[29] isobutane (250 g) and composite ionic liquid (140 mL) were first charged into the reactor, and then 2-butene was pumped into the reactor gradually in 30 min. The composite ionic liquid catalyzed alkylation is a fast reaction, which occurs during the feeding time. This results in a very low content of butene and much higher infinite inner I/O molar ratio in reactor. Therefore, the TMPs yield increases slightly with the outer I/O molar ratio of the feed. However, for the experiment of this research, the mixed isobutane and butene feed was instantly pressured into the reactor. The initial inner I/O molar ratio in reactor equals the outer I/O molar ratio of the feed and it may increase with the gradual consumption of butene. The inner I/O ratio reflects the real alkylation conditions and it determines the product distribution in a large extent. For the pilot-scale experiment of Liu et al., the inner I/O molar ratio is so higher about 500:1, and then the TMPs yield reaches 90%.[30]

Increasing the I/O molar ratio is useful for the modification of product distribution and for the enhancement of alkylate RON. This method is the same one applied for commercial isobutane alkylation catalyzed by sulfuric acid or hydrofluoric acid. High I/O molar ratio in the hydrocarbon phase decreases the butene concentration. Thus, the rate of undesired reactions such as the polymerization of olefin is reduced, which yields an improved alkylate. High I/O molar ratio favors the product distribution and the alkylate RON, but it requires more isobutane recycles in a commercial unit. So there are penalties of operating expense and capital expenditure, and thus a compromise needs to be taken.

Effect of contact time

A number of reactions continue at the interface between hydrocarbon and ionic liquid even after the stirrer button is turned off. However, the extent of such reactions is low because the interface area is significantly smaller than that while stirring. The experiments showed that the effect of contact time on product distribution was negligible when the stirrer button was turned off.

Butene conversion reached 100% when the contact time was longer than 15 s as shown in Figure 10. This shows that the isobutane alkylation catalyzed by the composite ionic liquid is a fast reaction. In Figures 10 and 11, the yields of C5, C6, and C7 showed a slightly decreasing trend with increasing contact time before 50 s, after which the values increased slightly. The yields of C8 and TMPs, the TMP/DMH ratio, and the alkylate RON showed a maximum value at 20 s of 88.86 wt %, 81.96 wt %, 11.87, and 97.26, respectively. The product distribution and the alkylate RON worsened with prolonged contact time (above 60 s).

An alkylate component can convert to other alkylate components at the presence of chloroaluminate ionic liquid.[43] The content of TMPs in alkylate decreases with increasing contact time when concentrated sulfuric acid or acidic ionic

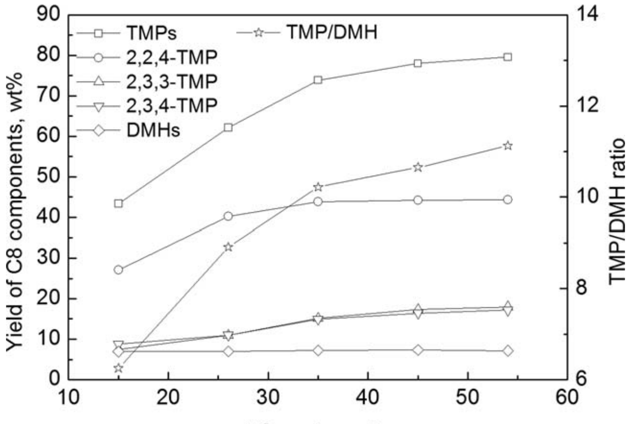

Figure 9. Yields of C8 components and TMP/DMH ratio as a function of I/O molar ratio (R = 1500 r/min, T = 15°C, *t* = 60 s, and IL/HC=1:1 v:v).

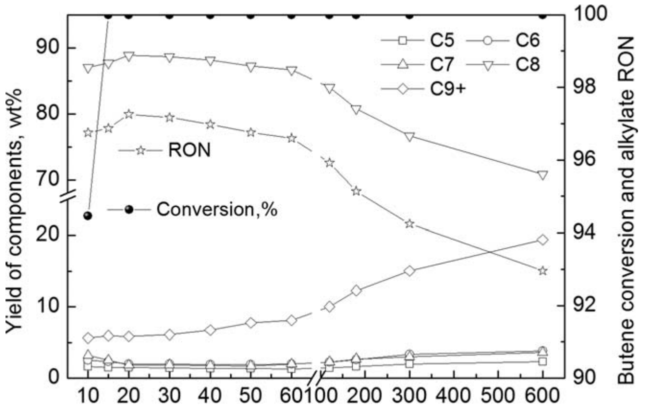

Figure 10. Yields of components, butene conversion, and alkylate RON as a function of contact time (R = 1500 r/min, T = 15°C, IL/HC=1:1 v:v, and I/O=54:1 mol:mol).

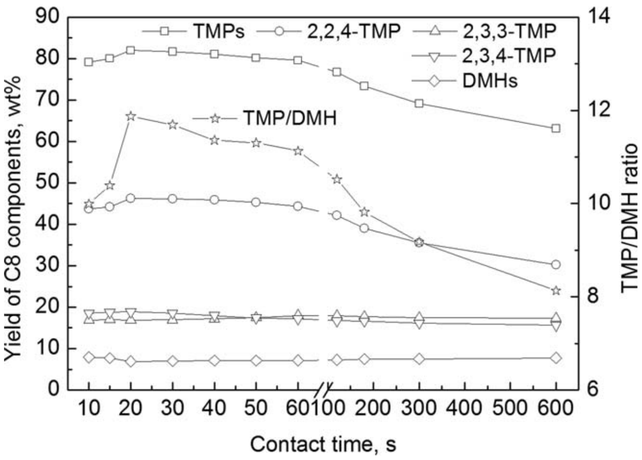

Figure 11. Yields of C8 components and TMP/DMH ratio as a function of contact time (R = 1500 r/min, T = 15°C, IL/HC=1:1 v:v, and I/O=54:1 mol:mol).

liquids is used as catalyst.[46] The alkylation reaction of isobutane with 2-butene is completed at a short contact time (15 s), and then the hydrocarbons are rearranged at longer contact time (>15 s). The rearrangement tends to form more TMPs before 20 s, which results in a higher TMP/DMH ratio and a higher alkylate RON. However, the rearrangement converts the TMPs to other products because of disproportionating reactions, which results in a lower TMP/DMH ratio and a lower alkylate RON. The optimal contact time was 20 s.

Function mechanism of composite ionic liquid

The composite ionic liquid showed good catalytic performance, the selectivity of TMPs in alkylate reached up to 82%, and the alkylate RON exceeded 97 in this research, and the results are even better at higher inner I/O molar ratio.[29,30] The catalytic performance of the composite ionic liquid is much better than that of the Et_3NHCl-$AlCl_3$ ionic liquids.[25,27] The composite ionic liquid was synthesized on the basis of the Et_3NHCl-$AlCl_3$ ionic liquid with the addition of CuCl at suitable conditions. A new Al-Cu complex anion is proved to exist in the composite ionic liquid.[29] It is assumed that the new anion can inhibit side reactions, and hence it can modify the selectivity of TMPs. Bui et al. conjecture that there is a combination of CuCl with Et_3NHCl in the composite ionic liquid, resulting in an increase of the Brønsted acidic site density and a decrease of the Lewis acidic site density.[22] The Brønsted acidic sites suppress such side reactions of cracking, polymerization, and isomerization. Therefore, the composite ionic liquid shows good catalytic performance. The structure of the Al-Cu complex anion and/or the combination way of CuCl with Et_3NHCl are worthy of deep study to explain the function mechanism of the composite ionic liquid.

Correlation model

The composite ionic liquid shows good catalytic performance for isobutane alkylation at a short contact time. The product distribution and the alkylate RON vary with the reaction conditions. Equation 2 shows a correlation model that was proposed to predict product distribution and alkylate RON in terms of reaction temperature (0–40°C), IL/HC volumetric ratio (0.5:1–1.5:1), I/O molar ratio (15:1–54:1), and contact time (10–60 s). The stirrer speed was kept constant at 1500 r/min to provide a favorable mixing status

$$y=a+b\cdot T^2+c\cdot T+d\cdot\left(\frac{\mathrm{IL}}{\mathrm{HC}}\right)^2+e\cdot\left(\frac{\mathrm{IL}}{\mathrm{HC}}\right)+f\cdot\left(\frac{\mathrm{I}}{\mathrm{O}}\right)^2 +g\cdot\left(\frac{\mathrm{I}}{\mathrm{O}}\right)+h\cdot t^2+i\cdot t \tag{2}$$

In Eq. 2, y refers to the yield of components in alkylate (wt %) or the alkylate RON; T is the reaction temperature in °C; t is the contact time in s; a, b, c, d, e, f, g, h, and i are the correlation coefficients.

Table 6 shows the correlation coefficients that were estimated according to the least-square regression of 21 groups of data, obtained at reaction temperature of 0 to 40°C, IL/HC volumetric ratio of 0.5:1 to 1.5:1, I/O molar ratio of 15:1 to 54:1, and contact time of 10–60 s. The above boundaries are also the applicable scope of the model. Table 6 also lists the calculation errors. The average absolute error for the predicted product yields is below 0.5% and the average relative error is below 6%. Both the average absolute error and the average relative error for the alkylate RON are below 0.1%. This result shows that the correlation model can effectively predict the product yields and the alkylate RON.

Conclusions

The optimal conditions of the CILA have been determined successfully in a 500-mL autoclave. The optimal reaction temperature, contact time, IL/HC volumetric ratio, and I/O molar ratio were 15°C, 20 s, 1:1 and 54:1, respectively. Under these optimal reaction conditions, the butene conversion, the yields of C8 and TMPs, the TMP/DMH ratio, and the alkylate RON were 100%, 88.86%, 81.96%, 11.87, and 97.26, respectively. A correlation model is proposed to

Table 6. Coefficients and Calculation Errors of the Correlation Model

Coefficient	C5–7	TMP	DMH	C9+	Alkylate RON
a	64.73	−60.42	6.97	88.71	71.10
b	7.00×10^{-3}	-2.03×10^{-2}	-1.74×10^{-3}	1.50×10^{-2}	-4.40×10^{-3}
c	-6.27×10^{-2}	2.04×10^{-2}	4.73×10^{-2}	-4.32×10^{-2}	2.15×10^{-2}
d	21.47	−43.80	−0.74	23.05	−7.24
e	−52.26	112.44	1.07	−61.21	18.93
f	9.14×10^{-3}	-2.94×10^{-2}	-5.10×10^{-4}	2.08×10^{-2}	-5.59×10^{-3}
g	−0.97	2.95	4.14×10^{-2}	−2.02	0.57
h	2.26×10^{-3}	-3.48×10^{-3}	7.71×10^{-4}	4.64×10^{-4}	-6.65×10^{-4}
i	−0.19	0.24	-6.70×10^{-2}	1.55×10^{-2}	4.18×10^{-2}
Average absolute error (%)	0.40	0.45	0.10	0.20	0.08
Average relative error (%)	5.83	0.59	1.34	2.10	0.09

predict the alkylate selectivity and RON based on the reaction conditions. The model agrees well with the experimental data. The results have been used in the design of an isobutane alkylation demonstration unit with an alkylate production capacity of 120 kt/a.

The reaction mode carried out in this research, such as methods of the instant feeding and the starting and stopping experiment, is approved effective to control reaction conditions, especially the contact time, IL/HC volumetric ratio, and I/O molar ratio. Therefore, this reaction mode is recommended to compare the alkylation performance across different Lewis acidic ionic liquids.

Compared with the basis ionic liquid Et_3NHCl-$AlCl_3$, the composite ionic liquid significantly enhances the selectivity of the desired products. The mechanism is worthy of further research. The alkylation reaction of isobutane with 2-butene is completed at a short contact time (15 s). The conversion of alkylate components occurs after the alkylation reaction. Therefore, the conversion performance of reaction products, such as the conversion of TMPs into other products, is also worthy of further study.

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