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Ionic liquid enhanced alkylation of iso-butane and 1-butene

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1. Introduction

The alkylation of *iso*-butane with butene is an important technology to produce branched alkanes for the gasoline pool [1–3]. However, the current alkylation technologies cause both environmental and human health concerns because sulfuric acid and HF are used as catalysts. Thereafter, it is highly desirable to develop safe, green and efficient catalysts for the *iso*-butane alkylation process.

In order to improve the safety and environmental friendliness, solid catalysts were developed for the alkylation process [4–13]. Polymeric acids [5–7], zeolites [8,9], and heteropolyacids [10–13] had been investigated intensively in the last 50 years, and some of them were applied successfully for the *iso*-butane alkylation on a small scale [1]. However, the deactivation of the solid catalysts is still a "bottleneck" for the alkylation process, which limits the industrial application of solid acids. In order to improve the efficiency and depress the waste emission, liquid acidic catalysts, especially acidic ILs have been developed for the alkylation process [2,14,15].

ILs have been applied as solvents and/or catalysts in many research fields [16–19]. Acidic ILs were used widely as efficient catalysts for many reactions such as etherification [20], Friedel–Crafts [21,22], alkylation [2,15,23] and isomerization [24]. In the last decades, chloroaluminated ILs had been investigated extensively for *iso*-butane alkylation in petrochemistry and

ABSTRACT

The alkylation of *iso*-butane with 1-butene was catalyzed by triflic acid (TFOH) coupled with a series of protic ammonium-based ionic liquids (AMILs), and the addition of the AMILs dramatically enhanced the efficiency of TFOH for the alkylation reaction. Up to 85.1% trimethylpentanes (TMP) selectivity and 98 research octane number (RON) were achieved with the optimized TFOH/AMIL catalyst (75 vol.% triflic acid and 25 vol.% triethylammonium hydrogen sulfate), which were much better than that with the commercial H₂SO₄ catalyst (65% TMP selectivity, 97 RON) and pure triflic acid. The addition of AMILs increased the I/O ratio dissolved in the catalyst system and adjusted the acidity of the TFOH/AMILs catalyst system, which were highly beneficial to the alkylation reaction and resulted in high TMP selectivity and high RON.

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petroengineering [25–27]. However, it is difficult to control the acidity of the chloroaluminated ILs. Moreover, chloroaluminated ILs are extremely sensitive to moisture, and deactivated rapidly though the irreversible hydrolysis [26,27]. Therefore, much effort was put into developing highly acidic, non-chloroaluminate systems for the alkylation.

Coupled of six imidazolium-based ILs, TFOH was applied successfully as catalysts for the *iso*-butane alkylation by Tang recently [15]. The coupled catalyst systems were much better (higher selectivity and better reusability) than TFOH, and good conversion (>95%), high C₈-alkylates selectivity (>70%) and high ratio of trimethylpentane/dimethylhexane (TMP/DMH > 7) were achieved with the IL/TFOH mixtures. The fundamental physical-chemical properties of the IL/TFOH system, such as acidity, solubility and interfacial properties were modified to be favorable for the alkylation reaction, as it is well known that the *iso*-butane-olefin (2-butene) ratio (I/O) has significant effect on the TMP selectivity. With higher I/O iso-butane-olefin ratios feed, the alkylation of olefin with iso-butane is faster than the olefin polymerization, resulting in high selectivity of TMP. Moreover Scovazzo [28,29] group reported the solubility property and Henry's law constant for hydrocarbons in imidazolium-, phosphonium-, and ammoniumbased ionic liquids. The ratio of alkane to alkene is higher dissolved in ammonium based ILs than in imidazolium based ILs. Thereafter, ammonium based ILs may be beneficial as co-catalysts of TFOH for the alkylation.

To further improve the quality of alkylate (TMP selectivity and RON), a series of protic ammonium-based ionic liquids with HSO₄⁻ and TFO⁻ anion were synthesized and applied with TFOH as catalysts for the *iso*-butane alkylation. The effects of reaction variables,



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such as the ionic structures and catalyst hydrocarbon ratio for the alkylate compositions, have been investigated and optimized for the alkylation. The addition of the AMILs dramatically enhanced the efficiency of the TFOH for the alkylation reaction, and high selectivity (up to 85.1% of TMP) and high RON (up to 98) were achieved with the optimized TFOH/IL catalyst system.

2. Experimental

2.1. Material

TFOH (>99.9% in purity) was purchased from 718th Research Institute of China Shipbuilding Industry Corporation. The mixture of *iso*-butane and 1-butene with a mole ratio of 10:1 was obtained from Airgas, Ltd., USA. Other chemicals including sulfuric acid (98 wt.%), N,N-dimethyl isopropanolamine, N,Ndimethyl ethanolamine, N-methyl diethanolamine, N,N-diethyl ethanolamine and triethylamine were purchased from Alfa Aesar. All reagents were used as received without further purification. The research octane number (RON) of alkylate was calculated according to the method applied in Ref. [30].

2.2. Ionic liquid synthesis

2.2.1. General procedure for the synthesis of protic ionic liquids

N,*N*-diethyl ethanolammonium triflate [DEEA] [*C*F₃SO₃]: The ammonium-based ionic liquids were synthesized by neutralization of the amines and the TFOH. In a typical procedure, 100 mL N,N-diethyl ethanolamine was added into a three-neck flask. Then 63.7 mL TFOH was dropped into the flask with vigorous stirring under nitrogen atmosphere in a cold water bath. After the reaction was complete, the ionic liquid was dried by vacuum overnight before use. The products were analyzed by ¹H NMR (JOEL JNM – ECA600), ESI/MS (Bruker microTOF Q.), Element analysis (vario EL. cube). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.17–7.13 (s, 1H), 4.02 (t, *J* = 5.34 Hz, 2H), 3.44–3.35 (t, *J* = 6.5 Hz, 2H), 3.04–3.01 (m, 4H), 2.73 (s, 1H), 1.43–1.34 (m, 6H). ESI/MS: *m/z* (+) 118.1226, *m/z* (–) 148.9579. Calculate for C₇H₁₆NO₄SF₃: C, 31.46%; H, 5.99%; N, 5.24%; O, 23.97%; S, 11.99%. Found: C, 30.52%; H, 5.95%; N, 5.38%; O, 25.01%; S, 11.92%.

N,*N*-dimethyl isopropanolammonium hydrogen sulfate[*DMIPA*] [*HSO*₄]: [DMIPA] [HSO₄] was synthesized from N,N-dimethyl isopropanolamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.12–7.06 (s, 1H), 4.13–4.07 (m, 1H), 3.10–2.98 (m, 2H), 2.87 (s, 1H), 2.84–2.81 (s, 6H), 2.10–2.07 (s, 1H), 1.14 (d, *J* = 6.42 Hz, 3H). ESI/MS: *m*/*z* (+) 104.1072, *m*/*z* (-) 96.9618. Calculate for C₅H₁₅NO₅S: C, 29.85%; H, 7.46%; N, 6.96%; O, 39.80%; S, 15.92%. Found: C, 28.22%; H, 7.81%; N, 6.92%; O, 40.06%; S, 15.41%.

N,*N*-dimethyl ethanolammonium hydrogen sulfate [*DMEA*] [*HSO*₄]: [DMEA] [HSO₄] was synthesized from N,N-dimethyl ethanolamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.12–7.06 (s, 1H), 3.58 (t, *J*=5.22 Hz, 2H), 1.98 (t, *J*=5.22 Hz, 2H), 2.64 (s, 1H), 2.61 (s, 6H), 2.12–2.06 (s, 1H). ESI/MS: *m/z* (+) 90.0915, *m/z* (-) 96.9623. Calculate for C₄H₁₃NO₅S: C, 25.67%; H, 6.95%; N, 7.49%; O, 42.78%; S, 17.11%. Found: C, 25.22%; H, 7.20%; N, 7.80%; O, 43.62%; S, 16.82%.

Ethanolammonium hydrogen sulfate [MEA] [HSO₄]: [MEA] [HSO₄] was synthesized from ethanolamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.17–7.11 (s, 3H), 4.11 (t, *J*=5.28 Hz, 2H), 3.74 (t, *J*=4.92 Hz, 2H), 2.33–2.29 (s, 1H), 2.13–2.08 (s, 1H). ESI/MS: *m/z* (+) 62.0613, *m/z* (-) 96.9624. Calculate for C₂H₉NO₅S: C, 15.09%; H, 5.66%; N, 8.81%;

O, 50.32%; S, 20.12. Found: C, 14.97%; H, 6.00%; N, 8.87%; O, 50.68%; S, 19.95%.

N,*N*-diethyl ethanolammonium hydrogen sulfate [DEEA] [HSO₄]: [DEEA] [HSO₄] was synthesized from N,N-diethyl ethanolamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.19–7.16 (s, 1H), 3.68–3.62 (m, 4H), 3.15–3.12 (t, 2H), 2.99–2.96 (t, 2H), 2.74 (s, 1H), 2.65 (m, 6H), 2.12–2.07 (s, 1H). ESI/MS: *m*/*z* (+) 118.1230, *m*/*z* (–) 96.9620. Calculate for C₆H₁₇NO₅S: C, 33.49%; H, 7.91%; N, 6.51%; O, 37.21%; S, 14.88%. Found: C, 33.30%; H, 8.06%; N, 7.55%; O, 37.80%; S, 14.50%.

N-methyl diethanolammonium hydrogen sulfate [MDEA] [HSO₄]: [MDEA] [HSO₄] was synthesized from N-methyl diethanolamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.15–7.10 (s, 1H), 3.73 (t, *J* = 5.34 Hz, 4H), 3.16–3.06 (t, *J* = 7.11 Hz, 4H), 2.63 (s, 2H), 1.17–1.10 (s, 3H), 2.10–2.06 (s, 1H). ESI/MS: *m*/*z*(+) 120.1018, *m*/*z*(-) 96.9618. Calculate for C₅H₁₅NO₆S: C, 27.65%; H, 6.91%; N, 6.45%; O, 44.24%; S, 14.75%. Found: C, 27.46%; H, 7.16%; N, 7.02%; O, 44.99%; S, 14.81%.

Triethylammonium hydrogen sulfate [TEA] [HSO₄]: [TEA] [HSO₄] was synthesized from triethylamine and sulfuric acid according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.11–7.07 (s, 1H), 3.07–3.03 (m, 6H), 1.13 (m, 9H), 2.13–2.08 (s, 1H). ESI/MS: *m/z* (+) 96.9618, *m/z* (–) 102.1271. Calculate for C₆H₁₇NO₄S: C, 36.18%; H, 8.54%; N, 7.04%; O, 32.16%; S, 16.08%. Found: C, 36.28%; H, 8.54%; N, 7.16%; O, 32.81%; S, 15.60%.

N,*N*-dimethyl isopropanolammonium triflate [*DMIPA*] [*C*F₃SO₃]: [DMIPA] [*C*F₃SO₃] was synthesized from N,N-dimethyl isopropanolamine and TFOH according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.21–7.16 (s, 1H), 4.27–4.24 (m, 1H), 3.24–3.15 (d, *J* = 6.54 Hz, 2H), 2.98 (s, 6H), 2.83 (s, 1H), 1.31 (d, *J* = 6.36 Hz, 3H). ESI/MS: *m*/*z* (+) 104.1064, *m*/*z* (–) 148.9580. Calculate for C₆H₁₄NO₄SF₃: C, 28.46%; H, 5.53%; N, 5.53%; O, 25.27%; S, 12.65%. Found: C, 27.96%; H, 5.75%; N, 5.62%; O, 25.84%; S, 12.52%.

N-methyl diethanolammonium triflate [*MDEA*] [*C*F₃SO₃]: [MDEA] [*C*F₃SO₃] was synthesized from N-methyl diethanolamine and TFOH according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.18–7.13 (s, 1H), 4.09–4.07 (t, *J*=8.71 Hz, 4H), 3.61–3.57 (t, *J*=8.54 Hz, 4H), 3.11 (s, 3H), 2.61 (s, 2H). ESI/MS: *m/z* (+) 120.1020, *m/z* (-) 148.9581. Calculate for C₆H₁₄NO₅SF₃: C, 26.77%; H, 5.20%; N, 5.20%; O, 29.74%; S, 11.90%. Found: C, 25.99%; H, 5.14%; N, 5.52%; O, 30.27%; S, 11.88%.

Triethylammonium triflate [TEA] [*CF*₃SO₃]: [TEA] [*CF*₃SO₃] was synthesized from triethylamine and TFOH according to the typical procedure. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ (ppm) 7.10–7.06 (s, 1H), 3.15–3.12 (m, 6H), 1.12 (m, 9H). ESI/MS: *m*/*z* (+) 102.1269, *m*/*z* (-) 148.9583. Calculate for C₇H₁₆NO₃SF₃: C, 33.47%; H, 6.38%; N, 5.58%; O, 19.12%; S, 12.75%. Found: C, 33.32%; H, 6.62%; N, 5.75%; O, 20.01%; S, 13.01%.

2.3. The alkylation procedure

The alkylation was carried out in a 200 mL autoclave with a PTEF lining. A low temperature thermostat bath was used to control the reaction temperature with ethanol as a working fluid. The ILs and TFOH were premixed at the desired temperature with stirring under argon (0.5 Mpa). And then the liquefied C₄ gas was injected into the liquid phase using a pump at a flow rate of 500 mL/h with stirring. The reaction mixture was stirred for 10 min at the desired temperature under argon. After the reaction completed, the tail gas was collected and analyzed by a SP-6890 gas chromatography (GC), equipped with a flame ionization detector and a HP-PLOT Al₂O₃ S column (50 m × 0.53 mm × 15 µm). The analysis conditions were: split ratio = 100:1, constant column temperature 100 °C hold for 20 min, injector temperature = 250 °C, detector temperature = 250 °C. The changes of the 1-butene contents in the feed



Fig. 1. The optimization of catalyst volume in the reaction system. (A), the product distribution on the IL content in the catalyst system; (B), the ratio of TMP to DMH and the RON on the IL content in the catalyst system.

Reaction conditions: the reaction temperature, $10 \degree C$; argon pressure, 0.5 MPa; reaction time, $10 \min$; stirring speed, 1000 rpm; the TFOH/[DMIPA] [HSO₄] (75/25 by vol.) catalyst, 50 mL; the premixed hydrocarbon feed (*iso*-butane: 1-butene = 10:1), 50 mL; I/O, $10. (\triangledown) C_5-C_7; (\bigcirc) C_8; (\triangle) C_{9^+}; (\square) TMP/DMH; (\diamondsuit) RON.$ Data were obtained at full conversion of 1-butene for optimized IL contents.

gas and tails gas was used to calculate the 1-butene conversion as the *iso*-butane in feed gas is far excessive.

The alkylate oil was immediately separated from the catalyst phase (TFOH/IL). The oil was washed with water and then analyzed by GC (gas chromatography, SHIMADZU GC 2014), equipped with a flame ionization detector and a DB-petro capillary column ($100 \text{ m} \times 0.25 \text{ mm}$). The analysis conditions were: split ratio = 100:1, injector temperature = $250 \degree$ C, detector temperature = $280 \degree$ C, carrier gas flow rate = 1 mL/min. The temperature program for GC analysis was as follows: initial column temperature $40 \degree$ C, $2 \degree$ C/min to $100 \degree$ C, then $25 \degree$ C/min to $250 \degree$ C hold for 20 min. Products were identified on an HP 6890/5975 gas chromatography/mass spectrometry (GC/MS) system. For all the GC analysis, nitrogen is used as carrier gas and with flame ionization detector. S content (light triflic ester) in the products of every cycle was determined by elemental analysis.

3. Results and discussions

3.1. The effect of catalyst system to hydrocarbon ratio

For the alkylation of *iso*-butane and 1-butene, the acid/hydrocarbon ratio is an important process variable. Herein, the ratio of the catalyst system/hydrocarbon was firstly investigated

using the TFOH/[DMIPA] [HSO4] catalyst system ([DMIPA] [HSO4], 25 vol.%). With 50 mL of the hydrocarbon feed, the catalyst system varied from 20 mL to 60 mL, and the results are shown in Fig. 1. Good selectivity of C_8 (79%) and high RON (95) were obtained with 50 mL of the catalyst system at 100% conversion of 1-butene, and the optimized ratio of the TFOH/IL catalyst to hydrocarbon was 1:1. Side products were increased with more or less the TFOH/IL catalyst system. It is generally believed that the alkylate is produced at the interfaces of the acid/hydrocarbon. Hence, a high interfacial surface area between the acid catalyst and the hydrocarbon is beneficial to the production of alkylate. However, the interfacial area is decided by acid/hydrocarbon ratio, acid composition, agitation rate and temperature generally. Additionally, a continuous dispersion of the acid in the hydrocarbon is highly desirable to reduce the consumption of acid and improve the TMP selectivity. For the H₂SO₄ catalyst system, the optimized acid/hydrocarbon ratio is in the range of 45-60%. Below this acid/hydrocarbon ratio, an emulsion of H₂SO₄ in the hydrocarbon was formed continuously, which resulted in poor product selectivity and potential runaway of the acid. In the TFOH/[DMIPA] [HSO₄] catalyst system, similar optimized acid/hydrocarbon ratio was obtained for the alkylation. At this acid/hydrocarbon ratio, full conversion, good selectivity and high RON were obtained due to a combination effect of the acidity, the interfacial area and the solubility. Thus, the 1:1 ratio of the TFOH/IL to hydrocarbon was used for further investigation.

3.2. The effect of the content and cation types of ILs with hydrogen sulfate anion

Coupled with TFOH, six ILs with hydrogen sulfate anion were examined for the alkylation of iso-butane with butene. The ILs contents in the catalyst system were optimized, and the typical results (ILs [DMIPA] [HSO₄] and [TEA] [HSO₄] as additives for the alkylation) are shown in Fig. 2. The results (using other ILs) were added in supporting information (SI Figs. 1s-4s). As shown from Fig. 2, the optimized content of [DMIPA] [HSO4] and [TEA] [HSO4] in the catalyst systems were around 15 vol.% and 25 vol.% respectively for the alkylation. According to Tang [15], the best results (conversions and selectivity) were obtained with around 25 wt.% IL (around 30 vol.%) [Omim] [HSO₄]/TFOH catalytic system. For the AMILs with hydroxyl group, including [DMIPA] [HSO₄], [DMEA] [HSO₄], [MEA] [HSO₄], [DEEA] [HSO₄] and [MDEA] [HSO₄], the optimized ILs' contents were less and typically around 15 vol.%. And this may be due to the hydroxyl group reacted with triflic acid and more TFOH was required in the alkylation process. The optimized contents of all ILs are listed and compared in Table 1. We were delighted that all the six catalyst systems (TFOH/ILs) exhibited high selectivity of C_8 (88–92%) with high RON (up to 98) at full conversion of 1-butene (see Table 1). The I/O solubility ratio maybe played an important role for the alkylation, since the ammonium-based ionic liquids have a higher I/O solubility ratio than imdazolium based ionic liquids [28,29]. The I/O ratio has significant effect on the TMP selectivity [31] for the alkylation. With higher I/O ratios feed, the alkylation of olefin with iso-butane was much faster than the polymerization of the butene, which results in higher selectivity of the C₈ product. Thus high selectivity of C₈ (88–92%) and high RON (up to 98) were obtained in our catalyst system, as ammonium-based ionic liquids were used as co-catalysts in the TFOH catalyst system for the alkylation.

3.3. The effect of the content and anion types of ILs

Then ILs with triflate anion (TFO⁻) were also synthesized and applied for the *iso*-butane/1-butene alkylation. The contents of ILs in the catalyst systems were optimized, and the results with ILs [DEEA] [CF₃SO₃] and [TEA] [CF₃SO₃] are shown in Fig. 3. Other



IL content (vol.%) IL content (vol.%)

Fig. 2. The optimization of [DMIPA] [HSO₄] and [TEA] [HSO₄] content in the catalyst system. (A) and (C), the product distribution on the IL content in the catalyst system; (B) and (D), the ratio of TMP to DMH and the RON on the IL content in the catalyst system.

Reaction conditions: the reaction temperature, 10°C; argon pressure, 0.5 MPa; reaction time, 10 min; stirring speed, 1000 rpm; the catalyst, 50 mL (A and B, TFOH/[DMIPA] $[HSO_4]$; C and D, TFOH/[TEA] $[HSO_4]$; the premixed hydrocarbon feed (*iso*-butane: 1-butene = 10:1), 50 mL; I/O, $10. (\nabla) C_5 - C_7$; $(\bigcirc) C_8$; $(\bigtriangleup) C_{9+}$; $(\square) TMP/DMH$; $(\diamondsuit) RON$. Data were obtained at full conversion of 1-butene for optimized IL contents.

Table 1

The alkylate compositions produced by the optimized TFOH/IL with HSO4-.

Entry	Ionic liquid	C ₅ -C ₇ (%)	C ₈ (%)	C ₉₊ (%)	TMP/DMH	RON
1	[DMIPA] [HSO ₄] (15 vol.%)	3.8	88.9	7.3	12.1	97.4
2	[MDEA] [HSO ₄] (15 vol.%)	2.5	92.1	5.4	12.0	97.8
3	[DEEA] [HSO ₄] (15 vol.%)	3.5	87.3	9.1	13.5	97.4
4	[DMEA] [HSO ₄] (15 vol.%)	3.8	89.6	6.6	12.9	97.7
5	[MEA] [HSO ₄] (15 vol.%)	2.9	87.9	9.1	10.4	97.0
6	[TEA] [HSO ₄] (25 vol.%)	1.9	91.5	6.6	13.5	98.0

Reaction conditions: temperature, 10°C; pressure, 0.5 Mpa; reaction time, 10 min; stirring speed, 1000 rpm; the TFOH/IL coupled catalyst, 50 mL; the premixed hydrocarbon feed, 50 mL; I/O, 10. Data were obtained at full conversion of 1-butene for optimized IL contents.

results are shown in SI (Figs. 5s and 6s). The optimized contents of [DEEA] [CF₃SO₃] and [TEA] [CF₃SO₃] were around 25 vol.% and 40 vol.% respectively for the alkylation. The catalysts of TFOH/ILs with TFO- and TFOH/ILs with HSO4- were compared in terms of RON, total C₈, 2,2,4-TMP, DMH and other products (Table 2). The ILs with TFO⁻ showed lower activity and selectivity. This was presumably because the TFOH/ILs systems with TFO anion can dissolve more hydrocarbons, including reaction intermediates, the products, iso-butane and 1-butene, but with lower I/O ratio. Anions usually play an important role for the solubility of the hydrocarbons in the ILs [32]. The general characteristics of the TFOH/ILs catalysts are very similar to those of the conventional liquid acidic

Table 2

Comparison of	of the alkylate	composition	produced b	y the optimized	TFOH/IL cat	alysts with	TFO] ⁻ and [HS	iO₄]⁻
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Components	[DEEA] [HSO ₄] (15 vol.%)	[DEEA] [CF ₃ SO ₃] (25 vol.%)	[DMIPA] [HSO ₄] (15 vol.%)	[DMIPA] [CF ₃ SO ₃] (25 vol.%)	[TEA] [HSO ₄] (25 vol.%)	[TEA] [CF ₃ SO ₃] (40 vol.%)
C ₅ -C ₇	3.5	3.7	3.8	3.1	1.9	2.0
2,2,4-TMP	51.2	48.0	47.2	44.2	49.9	37.4
Other TMPs	30.1	32.4	34.9	35.5	35.2	42.5
DMH	6.0	5.8	6.8	6.6	6.4	7.3
Total C ₈	87.3	86.2	88.9	86.3	91.5	87.2
C ₉₊ (%)	9.1	6.3	7.3	10.6	6.6	10.7
RON	97.4	97.0	97.4	96.4	98.0	96.9

Reaction conditions: temperature, 10 °C; pressure, 0.5 Mpa; reaction time, 10 min; stirring speed, 1000 rpm; the TFOH/IL coupled catalyst, 50 mL; the premixed hydrocarbon feed, 50 mL; I/O, 10. Data were obtained at full conversion of 1-butene for optimized IL contents.



Fig. 3. The optimization of [DEEA] [CF₃SO₃] and [TEA] [CF₃SO₃] content in the catalyst system. (A) and (C), the product distribution on the IL content in the catalyst system; (B) and (D), the ratio of TMP to DMH and the RON on the IL content in the catalyst system. Reaction conditions: the reaction temperature, 10° C; argon pressure, 0.5 MPa; reaction time, 10 min; stirring speed, 1000 rpm; the catalyst, 50 mL (A and B, TFOH/[DEEA] [CF₃SO₃]; C and D, TFOH/[TEA] [CF₃SO₃]); the premixed hydrocarbon feed (*iso*-butane: 1-butene = 10:1), 50 mL; I/O, $10. (\triangledown) C_5-C_7$; ($\bigcirc) C_8$; ($\bigtriangleup) C_{9+}$; (\square) TMP/DMH; (\diamondsuit) RON. Data were obtained at full conversion of 1-butene for optimized IL contents.

catalysts (H₂SO₄ and HF) for the alkylation reaction. Higher I/O solubility ratio in the catalyst system is highly favorable for the hydride transfer (hydride from i-C₄ to C₈⁺) rather than for the side chain propagation (the formation of C₁₂⁺ and C₁₆⁺ from C₈⁺). In addition, TFO⁻ is a weak coordinating anion and this may be harmful to the stability of carbocations, resulting in low selectivity of C₈ and low RON [33]. During Tang's study [15], the imidazoliumbased ionic liquids with TFO⁻ were also found to produce less C₈ products and more byproducts. In addition, the 2,2,4-sec-TMP⁺ (-314.80211) is the most stable intermediate, formed by degradation and isomerization of other TMP isomers [34]. High *iso*-butane/1-butene solubility ratio is highly favorable for the production of *iso*-octane and 2,2,4-TMP.

3.4. The reusability of the catalyst system

The reusability of TFOH/[TEA] [HSO₄] catalyst system was studied in a batch mode and the results are shown in Figs. 4 and 5. After every cycle of the reaction, the catalyst was separated from the hydrocarbon phase through a separation funnel. The TFOH/IL was the lower layer. The recovered catalyst without further treatment was used again for the alkylation of *iso*-butane/1-butene under the same reaction conditions. As shown from Figs. 4 and 5, the catalyst could be reused at least five cycles with full conversion and high selectivity of C₈ (close to 90%), but deactivated rapidly from 6th cycles. The selectivity of C₈, and the RON dropped slowly from 91.5 and 98.0 at the first cycle down to 87.9 and 97.1 at the fifth cycle and then rapidly down to 82.7 and 95.9 at the sixth cycle. The selectivity of 2, 2, 4-trimethylpentane decreased slowly in the 10 cycles. But the selectivity of 2,3,4-trimethylpentane increased gradually from 12.1 wt.% at the first cycle up to 23.2 wt.% at the third cycle and did not change much in the next 7 cycles. After 10 using cycles, the catalyst system became a viscous dark-brown gel. The sulfur content (S) in the products for the 10 reaction cycles was investigated by element analysis (shown in Fig. 6). The S content in the products was relatively low in the first five cycles and increased significantly from 110 ppm at the 6th cycle to 290 ppm at the 7th cycle. The sulfur in the product should be esters of sulfate or triflate formed from the intermediates in the catalyst system. The raising of S content in the products indicated that the acidity of



Fig. 4. The reusability of the TFOH/[TEA] [HSO₄] catalyst. Reaction conditions: the reaction temperature, 10 °C; argon pressure, 0.5 MPa; reaction time, 10 min; stirring speed, 1000 rpm; the TFOH/[TEA] [HSO₄] (75/25 by vol.) catalyst, 50 mL; the premixed hydrocarbon feed (*iso*-butane: 1-butene = 10:1), 50 mL; I/O, 10. (\triangledown) C₅-C₇; (\bigcirc) C₈; (\triangle) C₉₊; (\diamondsuit) RON. Data were obtained at full conversion of 1-butene for first cycles.



Fig. 5. iso-Octane distributions of the products with the reused TFOH/[TEA] [HSO₄] catalyst.

Reaction conditions: the reaction temperature, $10 \degree C$; argon pressure, 0.5 MPa; reaction time, $10 \min$; stirring speed, 1000 rpm; the TFOH/[TEA] [HSO₄] (75/25 by vol.) catalyst, 50 mL; the premixed hydrocarbon feed (*iso*-butane: 1-butene = 10:1), 50 mL; 1/O, 10. $(\triangledown) C_5-C_7$; $(\bigcirc) C_8$; $(\triangle) C_{9+}$; (\diamondsuit) RON. Data were obtained at full conversion of 1-butene for first 7 cycles.



Fig. 6. S content of the products with the reused TFOH/[TEA] [HSO₄] catalyst.

the catalyst system became lower than the optimized acidity range for the *iso*-butane/1-butene alkylation from the 7th cycle, which resulted in decreased selectivity of C_8 and decreased RON since appreciable amount of light acid soluble oil (ASO) was formed. The loss of TFOH in the catalyst system by vaporization, dissolution and entrainment during the transfer operations may be the main reason for the acidity reduction in the first five cycles. And the formation of byproducts, such as light ASO and heavy ASO accelerated the acidity reduction and the deactivation of the catalyst since the 6th cycle.

4. Conclusions

The alkylation of *iso*-butane with 1-butene was catalyzed by TFOH with a series of protic ammonium-based ILs, and the addition of the ILs dramatically enhanced the alkylation reaction. Up to 85.1% trimethylpentane selectivity and a high research octane number of 98 were obtained with the optimized TFOH/AMILs catalyst system (TFOH/[TEA] [HSO₄], 75/25 vol.%), which were far better than those with the commercial H₂SO₄ and pure triflic acid. The ratio of ionic

liquids to TFOH and the anion structure have significant effects on the alkylate composition, and HSO_4^- was much better anion than TFO⁻ in the ILs for the alkylation process. Furthermore, the catalyst system can be reused at least 5 runs without significant loss of activity. It was believed the addition of AMILs increased the I/O ratio in the TFOH/AMILs catalyst system and adjusted the acidity of the TFOH/AMILs catalyst system, which were beneficial for the alkylation reaction. Moreover, the addition of ILs changed the interfacial area and the solubility of the catalyst system with hydrocarbon, which affected the product compositions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod. 2012.06.008.

References

- [1] S.I. Hommeltoft, Applied Catalysis A 221 (2001) 421-428.
- [2] T.L.T. Bui, W. Korth, S. Aschauerb, A. Jess, Green Chemistry 11 (2009) 1961–1967.
- [3] J. Weitkamp, Y. Traa, Catalysis Today 49 (1999) 193–199.
- [4] V.R. Sarsani, B. Subramaniam, Green Chemistry 11 (2009) 102-108.
- [5] W. Shen, Y. Gu, H.L. Xu, D. Dube, S. Kaliaguine, Applied Catalysis A 377 (2010) 1-8.
- [6] F. Martinez, G. Morales, A. Martin, R. van Grieken, Applied Catalysis A 347 (2008) 169–178.
- [7] G. Morales, R. van Grieken, A. Martín, F. Martínez, Chemical Engineering Journal 166 (2010) 388–396.
- [8] B.O.D. Costa, C.A. Querini, Applied Catalysis A 385 (2010) 144-152.
- [9] A.S. Chellappa, R.C. Miller, W.J. Thomson, Applied Catalysis A 209 (2001) 359–374.
- [10] T. Blasco, A. Corma, A. Martinez, P. Martinez-Escolano, Journal of Catalysis 177 (1998) 306–313.
- [11] V. Sarsani, Y. Wang, B. Subramaniam, Industrial and Engineering Chemistry Research 44 (2005) 6491–6495.
- [12] M.J. Janik, R.J. Davis, M. Neurock, Journal of Catalysis 244 (2006) 65-77.
- [13] G. Baronetti, H. Thomas, C.A. Querini, Applied Catalysis A 217 (2001) 131-141.
- [14] M.A. Harmer, C.P. Junk, V.V. Rostovtsev, W.J. Marshall, Green Chemistry 11 (2009) 517–525.
- [15] S. Tang, A.M. Scurto, B. Subramaniam, Journal of Catalysis 268 (2009) 243–250.
- [16] J. Esser, P. Wasserscheid, A. Jess, Green Chemistry 6 (2004) 316–322.
- [17] R.D. Rogers, Nature 447 (2007) 917-918.
- [18] A. Ahosseini, W. Ren, A.M. Scurto, Industrial and Engineering Chemistry Research 48 (2009) 4254–4265.
- [19] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, Angewandte Chemie International Edition 43 (2004) 4988–5499.
- [20] J. Bender, D. Jepkens, H.H. Sken, Organic Process Research and Development 14 (2010) 716–721.
- [21] S.V. Malhotra, Y. Xiao, Journal of Organic Chemistry 690 (2005) 3609-3613.
- [22] M.J. Earle, K.R. Seddon, C.J. Adams, G. Roberts, Chemical Communications
- (1988) 2097–2098.
- [23] P. Kumar, W. Vermeiren, J.P. Dath, Applied Catalysis A 304 (2006) 131–141.
- [24] L. Wang, J.J. Zou, X.W. Zhang, L. Wang, Fuel 91 (2012) 164-169.
- [25] J. Zhang, C.P. Huang, B.H. Chen, Journal of Catalysis 249 (2007) 261-266.
- [26] J. Zhang, C.P. Huang, B.H. Chen, J.W. Li, Y.X. Li, Korean Journal of Chemical Engineering 245 (2008) 982–986.
- [27] A.S. Berenblyum, E.A. Katsman, Y.Z. Karasev, Applied Catalysis 315 (2006) 128–134.
- [28] R. Condemarin, P. Scovazzo, Chemical Engineering Journal 147 (2009) 51–57.
- [29] L. Ferguson, P. Scovazzo, Industrial & Engineering Chemistry Research 46 (2007) 1369–1374.
- [30] Y. Chauvin, A. Hirschauer, H. Olivier, Journal of Molecular Catalysis 92 (1994) 155-165.
- [31] W. Chen, Applied Catalysis A 255 (2003) 231–237.
- [32] U. Domańska, Pure and Applied Chemistry 77 (2005) 543-557.
- [33] G.A. Olah, P. Batamack, D. Deffieux, B. Török, et al., Applied Catalysis A 146 (1996) 107–117.
- [34] P. Wang, D.X. Wang, C.M. Xu, J.S. Gao, Applied Catalysis 332 (2007) 22-26.