Catalysis Today 200 (2013) 30–35

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

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ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form 1 June 2012
Accepted 13 June 2012
Available online 4 August 2012

Keywords:
Ionic liquids
Alkylation
iso-Butane
Butene
Triflic acid

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 H_2SO_4 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.

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 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 C_8-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 ammonium-based 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 HSO_4^- 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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http://dx.doi.org/10.1016/j.cattod.2012.06.008

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,N-dimethyl 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] [CF_3SO_3]: 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 ^{1}H NMR (JOEL JNM – ECA600), ESI/MS (Bruker microTOF Q.), Element analysis (vario EL. cube). ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_7H_{16}NO_4SF_3$: 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] [HSO_4] was synthesized from N,N-dimethyl isopropanolamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_5H_{15}NO_5S$: 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] [HSO_4] was synthesized from N,N-dimethyl ethanolamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_4H_{13}NO_5S$: 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] [HSO_4]: [MEA] [HSO_4] was synthesized from ethanolamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_2H_9NO_5S$: 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] [HSO_4]: [DEEA] [HSO_4] was synthesized from N,N-diethyl ethanolamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_6H_{17}NO_5S$: 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] [HSO_4]: [MDEA] [HSO_4] was synthesized from N-methyl diethanolamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_5H_{15}NO_6S$: 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] [HSO_4]: [TEA] [HSO_4] was synthesized from triethylamine and sulfuric acid according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_6H_{17}NO_4S$: 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] [CF_3SO_3]: [DMIPA] [CF_3SO_3] was synthesized from N,N-dimethyl isopropanolamine and TFOH according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_6H_{14}NO_4SF_3$: 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] [CF_3SO_3]: [MDEA] [CF_3SO_3] was synthesized from N-methyl diethanolamine and TFOH according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_6H_{14}NO_5SF_3$: 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_3SO_3]: [TEA] [CF_3SO_3] was synthesized from triethylamine and TFOH according to the typical procedure. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_7H_{16}NO_3SF_3$: 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 C_4 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 Al_2O_3 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