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Short Communication Isobutane alkylation using acidic ionic liquid catalysts

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ABSTRACT

Alkylation of isobutane with butene (C_4 cut from an industrial alkylation feed) was catalysed by a class of strongly acidic ionic liquids. A dramatic enhancement of the catalytic effect was observed for the ionic liquids containing the SbF_6⁻ anion. The optimal alkylate was obtained using the acidic ionic liquid [HMIm][SbF_6] (47.9 wt.%)/CF_3SO_3H (52.1 wt.%) as the catalyst. The C_8 selectivity was as high as 80% and the research octane number (RON) was 95. These results were better than those obtained by using either neat H₂SO₄ or CF₃SO₃H as the catalyst.

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1. Introduction

The alkylation of isobutane with butene is an important process in the petroleum industry. The products are often used as a premium blending stock for reformulated gasoline since they have high octane number, low vapour pressure, and low contents of aromatics, alkenes and sulfur. However, commercial alkylation processes catalysed by concentrated sulfuric acid or by hydrogen fluoride are gradually being restricted because of environmental pollution and safety problems [1]. Thus, a genuine quest has been spurred to explore safer, cleaner, and more cost-effective alternatives.

Acidic ionic liquids have been extensively applied as catalysts in organic and refinery chemistry due to their unique properties, such as negligible vapour pressure, good solvating ability, and tuneable acid types (Lewis or Brønsted) and strength [2-11]. Owing to their standout acidity, chloroaluminate-based ionic liquids have been investigated as catalysts in isobutane alkylation [3-9]. In 1994, Chauvin et al. [3] reported that the alkylation of isobutane with 2-butene could be efficiently catalysed by the ionic liquid 1-butyl-3-methylinidazolium chloroaluminate. Since then, various chloroaluminate-based ionic liquids have been investigated as catalysts for isobutane-butene alkylation by Yoo et al. [4], Xu et al. [5–7], Zhang et al. [8], Bui et al. [9] and so on. However, Lewis acid chloroaluminate ionic liquids are extremely sensitive to moisture and hydrolyse to release HCl in contact with traces of water [10]. Brønsted acid ionic liquids have also been utilised for isobutane-butene alkylation [10,11]. But, the acidity of common Brønsted acid ionic liquids is usually too low to efficiently catalyse isobutane alkylation by themselves [10]. Therefore, Olah et al. [11] synthesised acidic ionic liquid catalysts with the general formula HF/ [amineH_n]⁺[F_n]⁻ for isobutane alkylation by immobilising HF with amines, which had formed the basis for UOP's commercial alkylation process. Tang et al. [10] have explored binary mixtures of ionic liquids (ILs) and mineral acids as catalysts for isobutane alkylation.

Kim et al. [12] reported that the presence of ILs containing a weakly coordinating anion $(SbF_6^- \text{ or } PF_6^-)$ dramatically enhanced the catalytic activity of Sc(OTf)₃, which was due to the in-situ formation of a strong Lewis acid through anion exchange. Soltner et al. [13] reported that trifluoromethanesulfonic anhydride could react with superacidic solutions AF/SbF_5 (A = H or D) to form the corresponding salts $[CF_3SO_3A_2]^+[SbF_6]^-$, the highest acidity of which in H₀ scale could reach to -18.5. Herein, a series of acidic ionic liquids with a weakly coordinating SbF_6^- anion, including 1-alkyl-3-methylimidazolium hexafluoroantimonate ($[C_nMIm]$ -SbF₆, where n = 4, 6 or 8) and 1alkylpyridinium hexafluoroantimonate ($[C_n Py]$ -SbF₆, where n = 2, 4, 6or 8), was coupled with trifluoromethanesulfonic acid (TFSA) to synthesise a class of acidic ionic liquid catalysts. The catalytic performance of these catalysts for isobutane-butene alkylation was then investigated. In addition, the reaction parameters, such as the composition of the acidic ionic liquid catalyst, the chain length of the cations and the reaction temperature were optimised.

2. Experimental

2.1. Instrumentation and reagents

All chemicals (AR grade) were purchased commercially and were used as received unless otherwise noted. TFSA (>99.9%) was purchased from the 718th Research Institute of China Shipbuilding

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Scheme 1. The structure of the cations and anions of the ionic liquids.

Industry Corporation. Isobutane (>99.7%) was purchased from Linggas, LTD. Butene (C_4 cut from an industrial alkylation feed) was supplied by Sinopec Beijing Yanshan Company. NMR spectra were recorded on a JEOL ECA-600 spectrometer. ESI–MS analyses were performed on a Bruker micro TOF-QII spectrometer.

2.2. Preparation of the ionic liquids

The ILs (Scheme 1) were synthesised according to the methods in the literature [14–16]. Pyridine or 1-methylimidazole (1.0 eq) in ethyl acetate was mixed with an alkyl halide (1.2 eq) at room temperature under a nitrogen atmosphere and then refluxed for 20–72 h to produce the crude product [R-MIm][X] or [R-Py][X]. After a series of post-treatment steps, the purified [R-MIm][X] or [R-Py][X] (1.0 eq) was anion-exchanged with NaSbF₆ (1.2 eq) in CH₂Cl₂ (about 150 mL) for 72 h. The filtrate was washed with water until no halogen ions were detected by titration with a concentrated solution of AgNO₃. Then the filtrate was washed two more times with water and the solvent was then removed by evaporation. Finally the product was dried at 100 °C in vacuum for 48 h before use. Yields were generally 70–80% (characterisation data is given in the supporting information).

2.3. Typical alkylation experiment

In a typical alkylation reaction, the autoclave was charged with 25 mL of catalyst, pressurised to 0.5 MPa with argon and cooled to the desired temperature. Approximately 50 mL of the premixed hydrocarbon feed with a 10:1 isobutane/olefin (I/O) molar ratio was pumped into the reactor with stirring at a speed of 1000 r/min. The reaction was stirred continuously for 10 min. After the reaction was

complete, the autoclave was slowly depressurised and the gas hydrocarbon phase was collected for analysis. The liquid phase was allowed to stand for 30 min to separate the catalyst and alkylate layers. The alkylate was then neutralised with a saturated NaHCO₃ solution, washed with water, and finally dried with anhydrous MgSO₄. The products were immediately analysed by GC (detailed information is in the supporting information).

3. Results and discussion

3.1. Isobutane-butene alkylation catalysed by acidic ionic liquids

The effect of the composition of the acidic ionic liquid [C_nMIm]-SbF₆/ TFSA on the quality of alkylate was studied (Table 1) at the optimised catalyst/substrate ratio 0.5 (Fig. 2S in the supporting information). The alkylate quality catalysed by the [BMIm][SbF₆]/TFSA passed through a maximum corresponding to a roughly 49.7 wt.% [BMIm][SbF₆] content, which meant it was of the optimal acidity for isobutane alkylation (Fig. 3S in the supporting information). For this maximum, the [BMIm][SbF₆] (49.7 wt.%)/TFSA (50.3 wt.%) catalyst (Entry 4) gave a higher C₈ selectivity (76.2%), research octane number (RON, 92.6) and yield of alkylate (184.6%) than neat H₂SO₄, TFSA or [BMIm][SbF₆] (Entries 1, 2 and 6). In contrast, a small amount of viscous oligomers (detailed information is in the supporting information) was produced when the [BMIm][CF₃SO₃] (50.0 wt.%)/TFSA (50.0 wt.%) was used as the catalyst (Entry 13). This is probably because the acidity of [BMIm] [CF₃SO₃] (50.0 wt.%)/TFSA (50.0 wt.%) is below the lower limit of the optimal acidity range for isobutane alkylation, which is usually around -8.0 to -13.0 in the H₀ scale. The results indicate there may be a synergetic catalytic effect between [BMIm][SbF₆] and TFSA. According to the references [12,13], we speculate that a strongly acidic salt [CF₃SO₃H₂][SbF₆] may be formed through anion exchange between TFSA and [BMIm][SbF₆], which dramatically enhances the acidity and the catalytic performance of [BMIm][SbF₆]/TFSA.

The optimal C₈ selectivity and trimethylpentanes (TMP)/ dimethylhexanes (DMH) ratio were achieved with the [HMIm][SbF₆] (47.9 wt.%)/TFSA (52.1 wt.%) (Entry 8). The literature has reported that better quality alkylate in terms of C₈ selectivity and RON were obtained by using [BMIm]Cl-AlCl₃ (86.8 wt.% and 96.9 wt.% respectively) [3] or [(C₂H₅)₃NH]Cl-AlCl₃/CuCl (98.1 wt.% and 99.7 wt.% respectively) [6]. However, pure 2-butene and a high I/O ratio (15 [3] or 30 [6]) were used in their studies, which has a positive effect on improving the quality of alkylate. In addition, our results are different from those reported for imidazolium-based acidic ionic liquids where the ILs with an octyl group ([OMIm]) had the best catalytic performance [4]. Therefore, the effect of the chain length on the alkylate quality was investigated.

Table 1 The distribution of alkylate catalysed by H_2SO_4 , CF_3SO_3H and $[C_nMIm][SbF_6]/TFSA^a$.

Entry	ILs	IL (wt.%)	Acid (wt.%)	C ₅ -C ₇ (wt.%)	C ₈ selectivity (wt.%)	C ₉₊ (wt.%)	TMP/DMH	RON	Yield of alkylate (%)
1 ^b	None		100.0	10.5	49.6	39.9	5.0	89.8	154.3
2 ^c	None		100.0	22.6	32.2	45.2	1.3	85.0	95.0
3	[BMIm][SbF ₆]	29.7	70.3	6.7	64.9	28.4	4.5	90.5	176.6
4	[BMIm][SbF ₆]	49.7	50.3	7.2	76.2	16.6	5.4	92.6	184.6
5	[BMIm][SbF ₆]	66.7	33.3	3.8	59.6	36.6	5.2	89.8	177.1
6	[BMIm][SbF ₆]	100.0	0.0	-	-	-	-	-	0.0
7	[HMIm][SbF ₆]	31.8	68.2	18.7	48.6	32.6	2.5	87.8	168.2
8	[HMIm][SbF ₆]	47.9	52.1	4.9	80.1	14.5	7.2	95.6	180.6
9	[HMIm][SbF ₆]	68.9	31.1	5.1	76.5	19.4	5.4	92.6	172.9
10	[OMIm][SbF ₆]	27.4	72.6	11.8	63.8	24.4	4.2	90.7	159.5
11	[OMIm][SbF ₆]	46.8	53.2	8.3	70.1	21.7	6.1	92.1	176.6
12	[OMIm][SbF ₆]	64.1	35.9	4.5	70.7	24.9	5.3	91.7	161.4
13	[BMIm][CF ₂ SO ₂]	50.0	50.0	-	_	_	_	_	0.0

^a Reaction conditions: volume of hydrocarbon feed (molar I/O = 10) = 50 mL, volume of catalyst = 25 mL, P = 0.5 MPa, T = 10 °C, agitation = 1000 r/min, reaction time = 10 min.

^b Entry 1 acid = H_2SO_4 (96.8 wt.%).

^c Entries 2–13 acid = CF_3SO_3H .



Fig. 1. The alkylation catalysed by [EPy][SbF₆] (50 wt.%)/TFSA (50 wt.%), [BPy][SbF₆] (50 wt.%)/TFSA (50 wt.%), [HPy][SbF₆] (50 wt.%)/TFSA (50 wt.%) and [OPy][SbF₆] (50 wt.%)/TFSA (50 wt.%). Conditions: 50 mL C₄ feed; 25 mL catalyst; 0.5 MPa; 1000 r/min; 10 min; 10 °C.

3.2. The effect of cation chain length in $[C_n Py][SbF_6]$ (n = 2, 4, 6 or 8) on the alkylate quality

As shown in Fig. 1, the yield of alkylate catalysed by $[C_nPy]$ -SbF₆/ TFSA (n=2, 4, 6 or 8) increased as the length of the alkyl group increased from 2 to 6 and then decreased for n = 8. Maximum yield (171.8%), highest C₈ selectivity (79%) and best RON (94) were obtained with [HPy]-SbF₆/TFSA, which is in agreement with the results obtained for the [C_nMIm]-SbF₆/TFSA catalyst. This may be mainly attributed to a complex interplay of the acidity of the coupled catalysts and the solubility of isobutane, the reaction intermediates and products in the coupled catalysts. The longer the chain length of the alkyl group of ionic liquid is, the higher the solubility of hydrocarbon is in the ionic liquid and its solution [17]. A high isobutane solubility increases the rate of the hydrogen transfer from the isobutane to the C_8^+ carbonium, which accelerates the generation of the desired C₈ fraction and inhibits side reactions, such as cracking and oligomerisation. However, high alkylate solubility is not beneficial for the production and separation of alkylate. The coupled catalyst [HPy][SbF₆]/TFSA which has a moderate chain length of alkyl group, probably has the most suitable solubility for isobutane and the reaction intermediates, thus produces the best quality and the maximum amount of alkylate.

3.3. Effect of reaction temperature on the alkylate quality

The effect of temperature on the alkylate quality was investigated by using [HMIm][SbF₆] (47.9 wt.%)/CF₃SO₃H (52.1 wt.%) as the catalyst (see Fig. 2). As the temperature increased, the amount of light ends (C₅-C₇ products) and heavy ends (C₉₊ products) increased from 1.7%



Fig. 2. Effect of reaction temperature on the alkylate quality. Conditions: 50 mL C_4 feed; 25 mL [HMIm][SbF₆] (47.9 wt.%)/CF₃SO₃H (52.1 wt.%) catalyst; 0.5 MPa; 1000 r/min; 10 min.

to 7.2% and from 11.5% to 42.3% respectively. This was caused by an accelerated rate of polymerisation and cracking. Conversely, the C₈ selectivity decreased from 85.6% (at -5 °C) to 45.2% (at 30 °C). This trend is similar to alkylation catalysed by sulfuric acid [17,18] or by chloroaluminate-based ionic liquids [4].

3.4. Reusability of catalyst

The reusability of the [HMIm][SbF₆] (47.9 wt.%)/CF₃SO₃H (52.1 wt.%) catalyst was studied at the conditions of 0.5 catalyst/substrate ratio, 0 °C and 10 min. The alkylate distribution and the RON are displayed in Fig. 3. The quality and yield of alkylate varied slowly in the four runs and then dropped dramatically after the fifth run. The amount of heavy ends (C₉₊) started to increase in the fifth run, and reached 47 wt.% by the eighth run. The colour of catalyst changed from light yellow into dark brown because of the accumulation of acid soluble oils (ASOs) (Fig. 4 S in the supporting information). In addition, the volume of the catalyst was reduced from 25 to 22 mL in the eighth run, which may be due to the vaporisation of catalyst or its dissolution/entrainment in the alkylate during the batch operation. These may be the main reasons for the reduction of the acidity. Vice versa, low acidity of the catalyst accelerated the formation of heavy ends and ASOs.

4. Conclusions

Alkylation of isobutane with industrial butene feed using a class of strongly acidic ionic liquid catalysts had been investigated. The ionic liquid catalyst showed superior performance over pure CF_3SO_3H and H_2SO_4 . A dramatic enhancement in catalytic effect was observed for the ILs containing SbF_6^- anion compared with the ILs containing $CF_3SO_3^-$ anion. The optimal alkylate with a C_8 selectivity of up to 80% and RON of 95 was obtained using the acidic ionic liquid [HMIm] $[SbF_6]$ (47.9 wt.%)/CF_3SO_3H (52.1 wt.%) as the catalyst. A complex



Fig. 3. The reuse of catalysts [HMIm][SbF₆] (47.9 wt.%)/CF₃SO₃H (52.1 wt.%). Conditions: 50 mL C₄ feed; 25 mL catalyst; 0.5 MPa; 1000 r/min; 10 min; 0 °C.

interplay of acidity and solubility effects in the ionic liquid-based coupled catalyst may contribute to the quantity and quality of the alkylate produced. These results suggest that the catalytic performance of the coupled ionic liquid/acid system can be easily adjusted by varying the cation/anion combination or by modifying the structures of the cation or anion. It may offer a new way of thinking about the design of acid-base catalysts for a specific reaction.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.04.022.

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