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Improved 1-butene/isobutane alkylation with acidic ionic liquids and tunable acid/ionic liquid mixtures

Shengwei Tang [1], Aaron M. Scurto, Bala Subramaniam *

Center for Environmentally Beneficial Catalysis, Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, USA

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ABSTRACT

A new process for 1-butene/isobutane alkylation to yield C_8-alkylates is described using binary mixtures of certain acidic imidazolium ionic liquids (ILs) and strong acids such as sulfuric or trifluoromethanesulfonic (triflic) acid. Equivalent or better conversion (>95%), C_8-alkylates selectivity (>70%) and trimethylpentane/dimethylhexane selectivity (TMP/DMH > 7) were achieved with the IL/acid mixtures over the pure acids themselves. Six types of substituted 3-methyl-imidazolium ionic liquids were investigated, wherein acidity is imparted via either the cation with sulfonic acid groups or the anion (hydrogen sulfate) or both. Long-term studies up to 30+ recycles indicate that the catalyst stability was increased by sometimes greater than 30+% with the IL/acid mixtures over the pure acid. The ionic liquid is believed to tune the acidity, solubility, and interfacial properties, resulting in these enhanced results. In addition, this concept could also be applicable to Friedel–Crafts alkylation, acylation chemistries, or other acid-catalyzed reactions.

1. Introduction

Alkylation of isobutane with various olefins is a major process in the petroleum industry for the production of gasoline. The alkylation of C_3–C_5 olefins with isobutane produces a mixture of highly branched alkanes. This alkylate offers a high octane number, a low Reid vapor pressure (RVP), and low octane sensitivity [difference between research octane number (RON) and motor octane number (MON)]. It contains no aromatics and nearly no sulfur. This alkylate is usually blended with various cuts of refined crude oil. The world-wide installed alkylation production capacity is approx. 102 million tons/year [1], accounting for approximately 10% of the world-wide gasoline usage.

Current commercial alkylation processes are catalyzed primarily by concentrated sulfuric acid or hydrofluoric acid (HF). The sulfuric acid process produces large amounts of spent acid and acid soluble oils. The spent acid is costly to regenerate. Anhydrous HF is highly toxic and its leakage results in dangerously stable aerosols at the ground level. In addition, equipment corrosion, transport, handling of hazards, and environmental liability associated with the disposal of spent acid are disadvantages for both processes. Hence, efforts continue to develop alternative processes that are relatively safe.

Solid acids have shown promise as environmentally-benign alternatives to the strong or mineral acids. However, solid acid catalysts often deactivate rapidly due to fouling of the pores, resulting in low product yield and loss of reaction selectivity [2]. The use of supercritical reaction media was shown to provide an optimum combination of solvent power and transport to mitigate foulant accumulation in the catalyst pores resulting in extended catalyst activity [3]. However, as shown by detailed economic analysis, such efforts are not yet economically competitive with conventional processes. The main challenge is to develop tailored solid acid catalysts that are porous enough to accommodate a high acid site density but with pore sizes that do not impose diffusion limitations on the C_8-alkylate products [4].

Recently, room temperature ionic liquids (RTILs) have been recognized as potentially green solvents for a wide variety of processes. Ionic liquids are organic salts composed of relatively large organic cations and inorganic or organic anions that are liquid near room temperature ($T_m < 100\,^\circ C$). They have virtually no vapor pressure and are molecularly tunable for desired properties. The combination of the cation and anion determines solubility, density, and viscosity of the liquids. There are several major classes of ionic liquid cations, and each offers the possibility to add any number of functional groups. A change in the structure, functional group, or size of the ions leads to different chemical and/or physical properties. We have utilized ionic liquids as efficient medium for homogeneously catalyzed reactions using organometallic complexes [5–7].

Ionic liquids with functional groups providing Lewis or Brønsted acidity have been synthesized for a variety of applications. The use

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* Corresponding author. Fax: +1 785 864 6051.
E-mail address: bsubramaniam@ku.edu (B. Subramaniam).

[1] Present address: College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China.

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of chloroaluminate-based ionic liquids has been reported in patents [8–17] and the open literature [18–25]. Chauvin et al. [18] reported the alkylation of isobutane with 2-butene using 1-butyl-3-methylimidazolium chloride-aluminum chloride molten salts. The chloroaluminate anion serves as a Lewis acid catalyst. Chloroaluminate ionic liquids have also been investigated as catalysts for isobutane/butene alkylation by Yoo et al. [19,20], Xu and coworkers [21–23], Zhang et al. [24] and Bui et al. [1,25]. Chloroaluminate ionic liquids were immobilized on silica (FK 700) or siliceous MCM-41 to form "novel Lewis acid catalysts" (NLACs) and their activities were studied by Kumar et al. [26]. While chloroaluminate ionic liquids have been shown plausible, the selectivity and alkylate quality were seldom greater than those obtained in commercial alkylation processes. Additionally, chloroaluminate ionic liquids are extremely oxophilic, forming adducts with C–O functionalities and reacting irreversibly with traces of water to form HCl.

Few studies exist for the use of non-chloroaluminate ionic liquids for alkylation reactions. Olah and coworkers [27] immobilized HF on an amine-functionalized polymer that forms a poly ammonium catalyst for isobutane/olefin alkylation. Harmer and coworkers [28] have used ionic liquids to sequester or separate novel superacids catalysts from reaction mixtures. The use of pure acidic ionic liquids for alkylation reactions has been shown in the Chinese patent literature [29,30].

For the alkylation of isobutane with butene, the desired attributes of a good homogeneous catalyst and reaction media include acid strength and tunable solubilities of isobutane and 1-butene in the reaction mixture. The ability to protonate the olefinic molecules in the feed depends on the acidity of the catalyst while the concentration of the carbenium ions formed is strongly dependent on the solubility of isobutane [31]. The isobutane and the alkylates are largely insoluble in the strong acids. Hence, the organic phase containing the olefin and excess isobutane is usually dispersed as droplets in the continuous acid phase to obtain substantial rates of mass transfer and high yields of the desired alkylate product.

Recently, ionic liquids with functional groups containing Brønsted acidity have been reported. However, the application of such ILs in alkylation reactions has not been systematically evaluated. Another possibility that has as yet not been systematically explored is to use mixtures of strong acids with ionic liquids. Here, the ionic liquid may be used to beneficially tune not only the acidity of the mixture but also various thermodynamic and interfacial properties of the acid phase such as better miscibility of reactants in the acid phase, separation of products from the acid phase and reduced volatility of the acid. The solubility of strong acids in ionic liquids and the resulting properties of the mixture are largely unknown at present. In addition, ionic liquid with acidic functional groups may also benefit by mixing with other strong acids. The present work reports on investigations of isobutane/1-butene alkylation with ILs under the following scenarios: (1) acidic ILs; (2) mixtures of acidic ILs with strong acids such as H_2SO_4 or CF_3SO_3H; and (3) neutral ILs mixed with strong acids. The 1-butene conversion and C_8 selectivity obtained in each of these cases is compared with those obtained with pure strong acids at similar pressure, temperature, and feed composition.

2. Experimental

2.1. Ionic liquid synthesis

Six different types of ionic liquids were investigated representing 5 different cations and three different anions as shown in Fig. 1. [BMIm][HSO_4] (1-butyl-3-methyl-imidazolium hydrogen sulfate) was purchased commercially from Sigma–Aldrich Co. The others were synthesized in house.

2.1.1. General method

2.1.1.1. 1-n-Alkyl-3-methyl-imidazolium halide [R-MIm][X]. The ionic liquids used in this study were prepared by anion exchange from the corresponding bromide or chloride salts of the imidazolium cations ([R-MIm][X]) with different *n*-alkyl substituents as described in the literature [32]. The bromide or chloride salt of the imidazolium cation was prepared from a quaternization

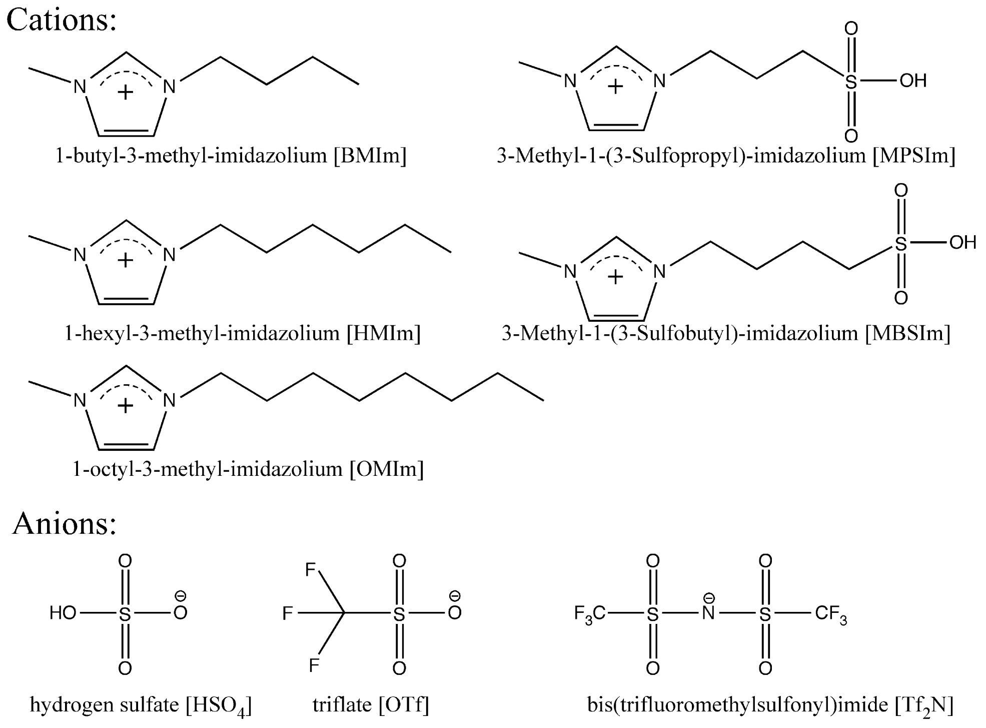

Fig. 1. Structures of the cations and anions of the ionic liquids used in this investigation.

reaction of 1-methylimidazole with a slight excess of the corresponding alkyl halide in acetonitrile at 313.15 K under argon atmosphere with stirring for 3 days. *Caution: These reactions can be highly exothermic and adequate solvent volumes and/or cooling must be provided during the reaction.* The solvent was removed in a rotary evaporator under reduced pressure at 40 °C which was further evacuated by connection to a high vacuum (<10^{-4} Torr) at 50 °C for at least 48 h.

2.1.1.2. 1-Hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf_2N]). [HMIm][Tf_2N] was prepared from the anion exchange of [HMIm][Cl] with Li[Tf_2N] in deionized water as described in the literature [32]. The denser hydrophobic IL phase is decanted and washed six to eight times with approximately twice the volume of water compared to the IL. The IL is then dried under vacuum. ^1H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz (400 MHz, $CDCl_3$, TMS): $\delta = 8.64$ (s, 1H), 7.32–7.36 (m, 2H), 4.13 (t, 2H, $J = 7.5$), 3.89 (s, 3H), 1.83 (t, 2H, $J = 7.18$), 1.28–1.33 (m, 6H), 0.84 (t, 3H, $J = 6.96$).

2.1.1.3. 1-Octyl-3-methyl-imidazolium hydrogen sulfate ([OMIm][HSO_4]). [OMIm][HSO_4] was prepared from the anion exchange of [OMIm][Cl] with H_2SO_4 in cooled anhydrous methylene chloride as proposed by Fraga-Dubreuil and coworkers [33]. The IL is then dried under vacuum. ^1H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz (400 MHz, $CNCD_3$): $\delta = 10.75$ (s, 1H), 8.76 (s, 1H), 7.40–7.44 (m, 2H), 4.18 (t, $J = 7.3$, 2H), 3.9 (s, 3H), 1.84 (t, $J = 1.98$, 2H), 1.28–1.32 (m, 10H), 0.90 (t, $J = 6.6$, 3H).

2.1.1.4. 3/4-(3-Methyl-imidazoliumyl)propyl (or butyl)-1-sulfonate. Brønsted acidic imidazolium ionic liquids were prepared by attaching alkyl-sulfonic acid to the imidazolium ring through a zwitterionic intermediate. 1,3-Propane sultone or 1,4-butane sultone was combined with 1-methyl imidazole in equimolar quantities in toluene forming the zwitterionic imidazolium sulfonate which precipitates upon formation. After the reaction, the solid was washed three times with diethyl ether and toluene to remove any unreacted starting materials, and the solid was dried *in vacuo*.

2.1.1.5. 3-Methyl-1-(3-sulfobutyl)-imidazolium hydrogen sulfate ([MBSIm][HSO_4]). [MBSIm][HSO_4] was prepared by a method described in the literature [34]. A stoichiometric amount of H_2SO_4 was added drop wise to the zwitterionic intermediate as described above and stirred for several hours at 70 °C until the solid liquefies to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ethyl ether to remove non-ionic residues, and dried in vacuum (393 K, 0.01 Torr). ^1H NMR chemical shifts and coupling constants (relative to TMS internal standard) from a Bruker 400 NMR Spectrometer: J/Hz (400 MHz, $CNCD_3$): $\delta = 10.89$ (bs, 2H), 8.55 (s, 1H), 7.43 (s, 1H), 7.36 (s, 1H), 4.21 (t, $J = 7.0$, 2H), 3.88 (s, 3H), 3.09 (t, $J = 7.6$, 2H), 1.97 (m, 2H), 1.83 (m, 2H).

2.1.1.6. 3-Methyl-1-(3-sulfobutyl)-imidazolium trifluoro methylsulfonate ([MBSIm][OTf]). [MBSIm][OTf] was prepared following a method described in the literature [35]. The zwitterionic intermediate as described above was added in a stoichiometric ratio to trifluoromethylsulfonic acid (triflic acid) and stirred at 40 °C until the solid liquefies to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried *in vacuo*. ^1H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz (400 MHz, $CNCD_3$): $\delta = 9.10$ (s, 1H), 8.51 (s, 1H), 7.42 (t, $J = 1.80$, 1H), 7.37 (t, $J = 1.74$, 1H), 4.20 (t, $J = 7.10$, 2H), 3.88 (s, 3H), 3.18 (t, $J = 7.60$, 2H), 2.01 (m, $J = 7.46$, 2H), 1.84 (m, $J = 7.56$, 2H).

2.1.1.7. 3-Methyl-1-(3-sulfopropyl)-imidazolium trifluoromethylsulfonate ([MPSIm][OTf]). [MPSIm][OTf] was prepared using a method described in the literature [35]. The zwitterionic intermediate as described above was added in a stoichiometric ratio to trifluoromethylsulfonic acid (triflic acid) and stirred at 40 °C until the solid liquefies to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried *in vacuo*. ^1H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz (400 MHz, $CNCD_3$): $\delta = 9.33$ (s, 1H), 8.53 (s, 1H), 7.45 (t, $J = 1.84$, 1H), 7.38 (t, $J = 1.76$, 1H), 4.32 (t, $J = 7.12$, 2H), 3.88 (s, 3H), 3.16 (q, $J = 7.48$, 2H), 2.37 (m, $J = 7.32$, 2H).

2.2. Materials and reagents

Solvents and chemicals used in the synthesis of the ILs and in the reaction experiments were commercially available and used without further purification unless otherwise stated. *N*-methylimidazole, 1,4-butane sultone, trifluoromethanesulfonic acid, sulfuric acid, anhydrous dichloromethane, diethyl ether, 1-chlorooctane and bis(trifluoromethylsulfonyl)amide lithium salt were purchased from Sigma–Aldrich Co.

2.3. Alkylation apparatus and procedure

Isobutane/1-butene alkylations were performed in a 50 mL stirred autoclave reactor as shown in Fig. 2 and explained in detail elsewhere [36]. Temperature and pressure were controlled and monitored with a Camile 2500 data acquisition system. Cooling was provided by a recirculating chiller using ethylene glycol. Due to the exothermicity of the reaction, there was a 2–4 °C increase in temperature upon reaction for the various catalyst mixtures. The isobutane and 1-butene feeds (Matheson, 99+%) were premixed in a storage vessel to a specified I/O ratio, analyzed offline, and then transferred to a syringe pump and cooled to −5 °C. The reactor effluent was collected in a trap chilled by a dry ice and acetone bath. The products were analyzed offline by gas chromatography (GC) with a Varian CP-3380 GC, equipped with a flame ionization detector, and a DB-Petro 100 m column (J&W Scientific). Helium is used as the GC carrier gas and as the flame ionization detector (FID) makeup gas. The analysis conditions were: split ratio = 50:1, injector temperature = 250 °C, detector temperature = 300 °C, carrier gas flow rate = 0.8 sccm. The temperature program for GC analysis is as follows: initial column temperature 30 °C/hold for 15 min, 0.5 °C/min to 100 °C, then 5 °C/min to 300 °C/hold for 15 min. An alkylate reference standard (Supelco) allowed identification of the trimethylpentanes (TMP) and dimethylhexanes (DMH). The GC area percent was equated to weight percent since all hydrocarbons in the reactor effluent have response

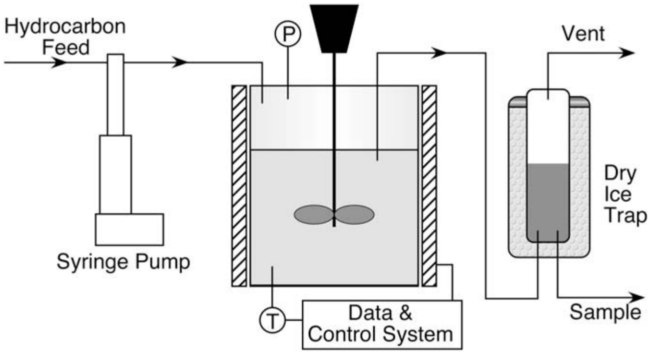

Fig. 2. Schematic of batch alkylation reactor unit.

factors close to unity. The combined mass of TMP and DMH is referred to as the "alkylate product". As discussed elsewhere [37], propane, an impurity in the isobutane feed, was used as an internal standard for butene conversion calculations. The butene isomers were lumped together when calculating butene conversion.

All experiments were performed in batch mode. A typical experiment begins with the addition of the acid, ionic liquid, or acid/IL mixture. The reactor was sealed and cooled to a desired temperature. Approximately 20 mL of the premixed hydrocarbon feed at a desired isobutane/1-butene ratio was pumped into the reactor at a flowrate of 5 mL/min with stirring of the liquid phase. After a certain reaction time (10–30 min), stirring was stopped and the mixture allowed to settle for 5 min to let the catalyst separate from the hydrocarbons. The hydrocarbon layer was then led to an external trap cooled with a dry ice/acetone solution. Care was taken to avoid outflow of the catalyst layer. For recycling studies, the vessel was filled with fresh hydrocarbon feed and the procedure repeated.

3. Results and discussion

The isobutane/1-butene alkylation was investigated using three different acidic catalytic systems including acidic ionic liquids, mixtures of acidic ionic liquids with strong acids such as H_2SO_4 and triflic acid (CF_3SO_3H), and neutral ionic liquids mixed with strong acids.

3.1. Isobutane/1-butene alkylation benchmark: sulfuric acid and triflic acid

To provide benchmarks for the ionic liquid-based acid systems, the alkylation of isobutane with 1-butene was performed with traditional catalysts: sulfuric acid and triflic acid. The results are shown in Entries 1 and 2 of Table 1. At 8 °C and a molar isobutane (I) to 1-butene (O) ratio of 10, nearly quantitative conversion is achieved in just over 10 min for both catalysts. However, the selectivity for each is markedly different. Sulfuric acid provided a selectivity of nearly 60% to octanes with a trimethylpentanes (TMP)/dimethylhexanes (DMH) ratio of approximately 6. These results are consistent with the alkylate quality of a typical commercial plant [31] (60–65% octanes and TMP:DMH $\sim$ 4–6). However, the C_8 selectivity and the TMP/DMH ratio obtained with triflic acid were approximately 41% and 1.4, respectively. These values are similar to those reported by Olah and coworkers [38] (20 °C, isobutane/1-butene = 14, 20 min, 22.7% C_8 selectivity (TMP + DMH + methyl heptanes) and TMP:DMH = 0.17). Selectivity and alkylate quality are strong functions of acid strength. Olah and coworkers [38] reported that the highest C_8-alkylates selectivity occurred at an acid strength, given by the Hammett acidity scale, of $H_0 = -10.7$. At higher acidity however, cracking reactions are favored and hence lighter components are also observed in the product stream. Triflic acid is a strong acid with $H_0 = -14.1$. Consequently, the C_8-alkylates selectivity obtained with pure triflic acid is lower.

3.2. Isobutane/1-butene alkylation using acidic ionic liquids

Davis and coworkers [39] covalently tethered sulfonic acid groups to ionic liquid cations to produce Brønsted acidic ionic liquids. Such ionic liquids have shown high activities in esterification [35], alkylation of phenol with tert-butyl alcohol [34] and Friedel–Crafts alkylation of aromatic compounds with alkene [40]. We have synthesized three different types of acidic ionic liquids, where the acidic group is found in either the cation or anion or both: [MPSI-

Table 1
Isobutane /1-butene alkylation results.

Entry	Total catalyst weight (g)	Ionic liquid (IL)	IL (wt%)	Acid	Acid (wt%)	Batch time (min)	1-Butene conversion (%)	C_s selectivity (%)	TMP/DMH selectivity
1	27.01	None		H_2SO_4	100.0	10	97.3	61.7	6.1
2	24.87	None		CF_3SO_3H	100.0	10	98.7	41.1	1.4
3	25.84	[HMIm][Tf_2N]	100.0	None	0.0	30	0.3	15.4	0.5
4	27.61	[HMIm][Tf_2N]	93.6	H_2SO_4	6.4	10	2.2	15.9	0.6
5	45.43	[HMIm][Tf_2N]	60.8	H_2SO_4	39.2	30	59.0	19.2	5.8
6	30.75	[HMIm][Tf_2N]	42.0	H_2SO_4	58.0	20	89.4	31.1	4.8
7	39.01	[HMIm][Tf_2N]	8.7	H_2SO_4	91.3	20	89.7	60.2	5.1
8	31.05	[MPSIm][OTf]	100.0	None	0.0	20	6.3	11.0	0.8
9	31.84	[MPSIm][OTf]	43.6	H_2SO_4	56.4	20	93.7	43.6	3.6
10	36.43	[MPSIm][OTf]	26.8	H_2SO_4	73.2	20	92.2	63.9	5.1
11	28.86	[MBSIm][OTf]	100.0	None	0.0	20	2.2	6.6	0.0
12	30.22	[MBSIm][OTf]	70,4	H_2SO_4	29.6	20	8.2	31.2	2.7
13	32.86	[MBSIm]|OTf]	46.7	H_2SO_4	53.3	20	91.3	41.0	3.8
14	37.39	[MBSIm][OTf]	28.1	H_2SO_4	71.8	20	91.1	57.0	4.8
15	24.47	[BMIm][HSO_4]	100.0	None	0.0	20	11.4	8.7	0.1
16	27.61	[BMIm][HSO_4]	67.6	H_2SO_4	32.4	20	51.8	22.4	5.2
17	30.93	[BMIm][HSO_4]	41.7	H_2SO_4	58.3	20	91.0	60.3	4.9
18	33.29	[BMIm][HSO_4]	20.9	H_2SO_4	79.1	20	90.4	41.0	7.9
19	33.20	[OMIm][HSO_4]	16.0	H_2SO_4	84.0	10	98.0	51.3	6.6
20	27.10	[MBSIm][HSO_4]	100.0	None	0.0	20	5.4	62.0	7.2
21	25.49	[MBSIm][HSO_4]	63.9	H_2SO_4	36.1	20	12.1	27.2	8.1
22	30.26	[MBSIm][HSO_4]	40.9	H_2SO_4	59.2	20	89.5	25.9	2.6
23	36.14	[MBSIm][HSO_4]	26.0	H_2SO_4	74.0	20	95.6	62.3	6.4
24	26.85	[MBSIm][OTf]	96.6	CF_3SO_3H	3.4	20	1.1	59.5	8.8
25	26.45	[MBSIm][OTf]	81.3	CF_3SO_3H	18.7	10	68.3	57.9	6.2
26	29.11	[MBSIm][OTf]	48.3	CF_3SO_3H	51.7	10	95.2	64.7	5.1
27	31.79	[MBSIm][OTf]	33.3	CF_3SO_3H	66.7	10	93.3	72.1	5.7
28	29.32	[BMIm][HSO_4]	23.2	CF_3SO_3H	76.8	10	98.1	72.4	8.1
29	20.58	[OMIm][HSO_4]	67.6	CF_3SO_3H	32.4	10	85.1	61.9	6.2
30	24.51	[OMIm][HSO_4]	59.6	CF_3SO_3H	40.4	10	91.2	65.6	6.8
31	25.07	[OMIm][HSO_4]	23.7	CF_3SO_3H	76.3	10	96.3	75.8	6.8

Experimental conditions: initial volume of hydrocarbon feed = 20 mL; molar I/O in feed = 10; P = 2 bar; initial T = 8 °C. For entry 19, I/O in feed = 7.5, second recycle.

m][OTf], [MBSIm][OTf], [MBSIm][HSO_4], [BMIm][HSO_4] and [OMIm][HSO_4] (see Fig. 1). [MPSIm][OTf] and [MBSIm][OTf] have an acidic sulfonic acid group tethered by either a propyl or butyl group to the imidazolium cation. [BMIm][HSO_4] and [OMIm][HSO_4] have acidity from the hydrogen sulfate group, which have shown good activities in acetalization [41] and other acid-catalyzed reactions [42–44]. The alkylation using [BMIm][HSO_4] as the catalyst (Entry 15) resulted in a low conversion, ~11%, even after 20 min (compared with 10 min for the pure H_2SO_4) with a C_8 selectivity of only 8.7% and almost no trimethylpentanes produced. H_2SO_4 is obviously a much stronger acid than [HSO_4] as the aqueous pK_a of H_2SO_4 is −3 and for [HSO_4] is 1.92. [MBSIm][OTf], with a butylsulfonic acid group attached to the cation and the triflate anion (Entry 11), also yielded low conversions and C_8 selectivity while [MPSIm][OTf] with a propylsulfonic acid group (Entry 8), yielded only slightly better conversion and selectivities. Thus, the conversions and selectivities with these acidic ILs alone are much lower than that those obtained using just the strong acids. It should be noted that this is based upon an equal mass basis. When converted to a unit of concentration based upon acidic protons, the disparity in the results becomes much smaller. For example, the acidic protons for entries 15, 11, and 1 are 0.1, 0.08, and 0.55 moles, respectively. Thus for the pure sulfuric acid case, the molar quantity of catalyst is more than five times that of the acidic ionic liquids.

When acidity is manifested in both the cation and anion, as in the case of [MBSIm][HSO_4] (Entry 20), the C_8 selectivity and TMP/DMH ratio were actually slightly better than that for pure sulfuric acid (Entry 1). However, the olefin conversion was still significantly lower. It thus appears that the acidity of these ILs is not enough to catalyze the alkylation of isobutane/1-butene to match the olefin conversion rate and selectivities of the strong acids.

3.3. Isobutane/1-butene alkylation using mixtures of ionic liquids and strong acids

3.3.1. Sulfuric acid

The addition of strong acids to ionic liquid solvents to catalyze various reactions is reported in the literature [45,46]. However, in all of these cases the acid represents a small fraction of the total mass/moles. Here, we have found that large amounts of either H_2SO_4 or triflic acid can be dissolved with ionic liquids. For instance, mixing with even the hydrophobic IL, [HMIm][Tf_2N], with equal moles or mass of H_2SO_4 results in a single homogeneous phase. This behavior allows fine tuning of the acidity and properties of the ionic liquid phase. Solutions of both neutral and acidic ILs with the strong acids were used for the isobutane/1-butene alkylation. When the alkylation is performed in the neutral ionic liquid, [HMIm][Tf_2N], without the addition of any catalyst (Entry 3), there was virtually no reaction (<0.5% olefin conversion). As a greater fraction of H_2SO_4 was used, higher conversions were obtained (Entries 4–7) until approximately 50 wt% of the acid, after which little improvement is seen in the activity. Thus, less acid catalyst seems to suffice to achieve the same level of activity/conversion. The selectivity and TMP/DMH ratio significantly increase with increased fraction of the acid. This trend is possibly due to the preferential solubility of 1-butene over isobutane in the IL relative to the pure acid. This neutral IL is known to have moderate solubility of alkenes and lower solubility of alkanes. This equilibrium partitioning would lead to isobutane starvation in the catalytic phase and encourage 1-butene dimerization, adversely affecting the C_8 and TMP selectivity.

For ILs with the sulfonic acid group, [MPSIm][OTf] and [MBSIm][OTf] (Entries 8–10 and 11–14, respectively), higher proportions of sulfuric acid increase both the conversion and selectivities throughout the concentration range. Note that at approximately 70 wt% of H_2SO_4 in the IL mixture, the conversion and selectivities are similar to those obtained with the pure acid. This suggests the possibility of a significant reduction in acid usage for commercial alkylations. When using the slightly acidic [HSO_4] anion in [BMIm][HSO_4] with H_2SO_4 (Entries 15–18), the olefin conversion increases up to approximately 50 wt% acid. However, a maximum in the C_8 selectivity is seen at approximately 58 wt% H_2SO_4 with moderate TMP/DMH ratios. At ~79 wt% H_2SO_4, the C_8 selectivity significantly drops, but yields higher TMP/DMH ratios. Increasing the alkyl-chain length of the ionic liquids from butyl- to octyl- ([OMIm][HSO_4] Entry 19) seems to increase the conversion and selectivity slightly. The [OMIm][HSO_4]/sulfuric acid system represents some of the best performance and was hence investigated for its reuse and recyclability.

The IL, [MBSIm][HSO_4] (Entries 20–23) that has acidic groups in both the cation and anion, intrinsically yields selectivities higher than pure sulfuric acid, but with markedly lower olefin conversion. Higher proportions of H_2SO_4 in the IL increase the conversion, but initially degrades the selectivities. However, at approximately 60 wt% H_2SO_4 in the IL, the conversion seems to plateau, but the selectivities are at a minimum. The selectivities increase with further amounts of acid, and at ~74 wt% acid, the conversion and selectivities match those of pure H_2SO_4. The foregoing results clearly demonstrate that the catalytic IL/acid mixtures can be highly tunable for conversion, C_8 selectivity, and TMP/DMH ratio by changing the structure and acidity of the cation and anion and by varying the proportion of acid.

3.3.2. Triflic acid

Mixtures of the acidic ionic liquids with triflic acid were investigated for the isobutane/1-butene alkylation using the cation, [MBSIm]. [MBSIm][OTf], when mixed with triflic acid (Entries 24–27), increased the conversion while maintaining consistent C_8 selectivity and only a slight drop in the TMP:DMH ratio. The selectivities obtained with roughly 67 wt% triflic acid are significantly better than those obtained with either the neat triflic acid (Entry 2) or neat IL (Entry 11). The long-chain 1-octyl-3-methyl-imidazolium hydrogen sulfate IL ([OMIm][HSO_4]), which has a slightly acidic anion, when mixed with triflic acid at approximately 36 and 76 wt% acid again yielded conversion and selectivities that surpass those obtained with pure triflic acid (Entries 29–31). The acidic ionic liquids appear to mitigate the poorer selectivity found with triflic acid, by possibly adjusting (i.e., lowering) the high acid value of the pure triflic acid.

The addition of IL to strong acids helps tune not only the acidity, but also other characteristics such as reactant/product solubility, surface activity, density and viscosity. Wasserscheid et al. [45] observed interplay of acidity and solubility effects caused by the ionic liquid additive in the Friedel–Crafts-alkylation of benzene with 1-decene. Low amounts of ionic liquid result in a dramatic improvement of product yield. The acidity of the catalyst can be fine-tuned by the choice of the amount of ionic liquid additive and by the choice of its anion. In a similar manner, it should be possible to tune the solubilities of the alkylation reactants and products by a suitable choice of the ions of the ionic liquid and by the amount of added ionic liquid. Among the ILs used for creating the binary mixtures with conventional acids, the [OMIm][HSO_4] (Entry 29–31) showed the best combination of activity and C_8 alkylate selectivity presumably because of improved isobutane solubility in the binary mixture compared to other IL/acid mixtures. For isobutene + 2-butene alkylation, Yoo et al. [19] observed with imidazolium ionic liquids with the Lewis acid chloroaluminate anion, that the ionic liquids bearing a larger alkyl group on their cation ([OMIm]) displayed relatively higher activity than a smaller one ([HMIm] or [BMIm]) with the same anionic composition. This was presumably due to the higher solubility of reactants, especially isobutane, in the [OMIm]-based IL. In general, the solubility of hydrocarbons increases significantly with increasing length of the alkyl group in the ILs. For a series of 1-alkyl-3-methyl-imidazolium cations, increasing the alkyl-chain length from butyl to hexyl to octyl increases the hydrophobicity [32]. Olivier-Bourbigou and Magna [47] also observed that changing the [BMIm] cation for the longer-chain [HMIm] with a [BF_4] anion converts a hydrophilic ionic liquid to a hydrophobic IL. These reports further indicate that the IL with a cation of [OMIm] may have a better miscibility with isobutane. It therefore appears that in the present work, the IL addition not only tunes the acidity of strong acids, but also has a strong effect on the isobutane solubility in the catalyst mixture. It has been shown previously by our group and others that higher I/O ratios favor isooctane yields [3].

3.4. Recycling studies of the acid/IL mixtures

The ability of the IL/acid mixtures to be recycled was investigated as to the conversion, selectivity, and TMP/DMH ratio of the alkylate. [OMIm][HSO_4] and H_2SO_4 were used in initial studies with a feed I/O ratio of 7.5. The isobutane/1-butene mixtures were reacted and the reactant/product phase was decanted and removed. Fresh reactants were then added to start the next run. Fig. 3 illustrates the results of recycling the IL/acid mixture up to nine times as compared with the results of just the pure sulfuric acid. Similar conversion and selectivity were observed for both the IL/acid mixture and the pure acid for about four recycles; however, the TMP/DMH ratio is better in the IL/acid mixture. After four recycle runs, the pure sulfuric acid conversion and selectivities sig-

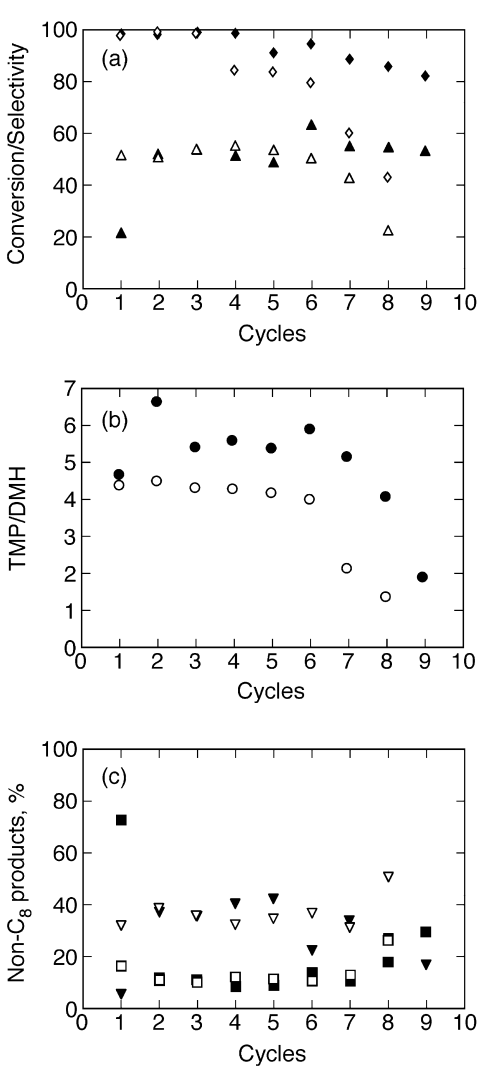

Fig. 3. Effects of reuse of pure H_2SO_4 and mixtures of [OMIm][HSO_4]/H_2SO_4: (a) conversion and selectivity; (b) TMH:DMH; and (c) non-C_8 products. *Catalysts*: 33.2 g of [OMIm][HSO_4] (16 wt%) + H_2SO_4 (84 wt%) or 26.6 g of H_2SO_4. *Reaction parameters*: temperature = 8 °C; pressure ~2 bar; batch reaction time = 10 min; volume of hydrocarbon fed = 20 mL with a molar I/O in feed = 7.5. *Legend*: (♦) 1-butene conversion with IL/acid mixture; (◇) 1-butene conversion with H_2SO_4; (▲) C_8 selectivity with IL/acid mixture; (△) C_8 selectivity with H_2SO_4; (●) TMP/DMH selectivity with IL/acid mixture; (○) TMP/DMH selectivity with H_2SO_4; (■) the concentration of light compounds (C_7 and C_{7-}) with IL/acid mixture; (□) the concentration of light compounds (C_7 and C_{7-}) with H_2SO_4; (▼) the concentration of heavy compounds (C_9 and C_{9+}) with IL/acid mixture; and (▽) the concentration of heavy compounds (C_9 and C_{9+}) with H_2SO_4.

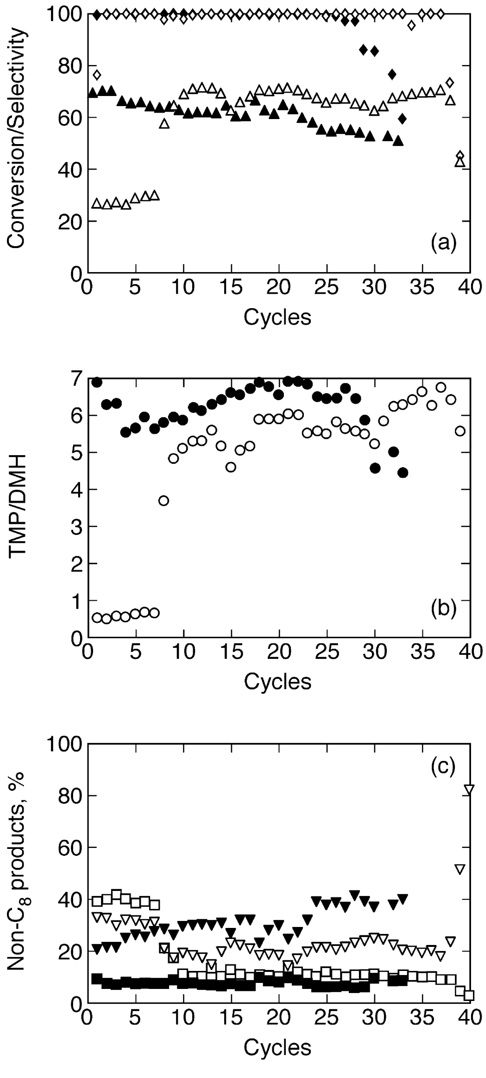

Fig. 4. Comparison of the reuse of catalysts based on trifluoromethanesulfonic acid: (a) conversion and selectivity; (b) TMH:DMH; and (c) non-C_8 products. *Catalysts*: Either 26 g of a mixture of [OMIm][HSO_4] (22.6 wt%) and 77.4 wt% CF_3SO_3H or 33.9 g of neat CF_3SO_3H. *Reaction parameters*: initial temperature: 8 °C; pressure: ~2 bar; batch reaction time = 10 min; volume of hydrocarbon fed = 20 mL with a molar I/O in feed = 7.5. *Legend*: (♦) 1-butene conversion with IL/acid mixture; (◇) 1-butene conversion with neat CF_3SO_3 H; (▲) C_8 selectivity with IL/acid mixture; (△) C_8 selectivity with neat CF_3SO_3 H; (●) TMP/DMH with IL/acid mixture; (○) TMP/DMH with neat CF_3SO_3H; (■) the concentration of light compounds (C_7 and C_{7-}) with IL/acid mixture; (□) the concentration of light compounds (C_7 and C_{7-}) with neat CF_3SO_3H; (▼) the concentration of heavy compounds (C_9 and C_{9+}) with IL/acid mixture; and (▽) the concentration of heavy compounds (C_9 and C_{9+}) with neat CF_3SO_3H.

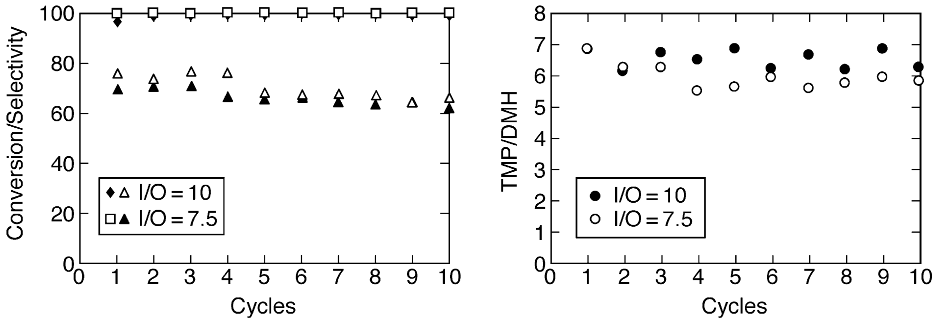

Fig. 5. Comparison of performance of $[OMIm][HSO_4] + CF_3SO_3H$ mixtures at different I/O ratios: catalyst used at I/O = 10:25.1 g of $[OMIm][HSO_4]$ (23.7 wt%) + CF_3SO_3H (76.3 wt%); catalyst used at I/O = 7.5: 26.1 g of $[OMIm][HSO_4]$ (22.6 wt%) + CF_3SO_3H (77.4 wt%). *Reaction parameters*: temperature = 8 °C; pressure = ~2 bar; batch reaction time = 10 min; volume of hydrocarbon feed = 20 mL. *Legend*: (♦, □) 1-butene conversion and (△, ▲) C_8 selectivity; ●, ○: TMP/DMH selectivity.

nificantly decreased. After eight recycles, the conversion and C_8 selectivity were about half of their values observed during the first run (Fig. 3a). With the IL/acid mixture, the conversion only decreased by approximately 20% by recycle 9, with nearly unchanged C_8 selectivity (Fig. 3a), albeit with a much reduced TMP/DMH ratio (Fig. 3b). The formation of lighter (C_7 and C_{7-}) and heavier (C_9 and C_{9+}) compounds showed similar trends with the neat acid and the IL/acid mixture up to seven recycles. However, after seven recycles, the amounts of heavier compounds (C_9 and C_{9+}) decreased for the IL/acid mixture relative to neat sulfuric acid (Fig. 3c) indicating that the addition of $[OMIm][HSO_4]$ to sulfuric acid impedes the formation of acid soluble heavies.

The $[OMIm][HSO_4]$ IL was used in the mixtures of triflic acid with a feed I/O ratio of 7.5. Fig. 4 illustrates that even after 25 recycles, the IL/acid mixture maintains high conversion and C_8 selectivity (Fig. 4a) with better TMP/DMH selectivity (Fig. 4b) than the pure triflic acid. This IL/acid mixture also does not suffer from the initial low conversion and selectivity that hampers the pure triflic acid. The high initial acidity of the pure triflic acid leads to cracking reactions which degrades the selectivity, but the IL seems to moderate this. From Fig. 4c, it may be inferred that after seven recycles, the concentrations of lighter compounds (C_7 and C_{7-}) were about 40% with triflic acid, implying that cracking reactions were prominent. However, the concentrations of these lighter compounds were less than 10% with the IL/acid mixture and the conversion decreased after 29 cycles with a slight increase of heavy (C_9 and C_{9+}) compounds while the C_8 selectivity was stable. In contrast, with neat triflic acid, the presence of these heavier compounds increased sharply when the conversion decreased after 38 cycles. These results clearly show that the addition of IL to the triflic acid inhibits the formation of heavies and the ensuing deactivation. The spent $[OMIm][HSO_4]$/triflic acid catalyst was slightly colored after the recycle runs. In comparison, the spent sulfuric acid was opaque. This suggests that the deactivation of the mixed IL/triflic acid catalyst may only be partly due to the entrainment of heavy compounds in the acidic solution. Further, the C_8 selectivity and the TMP/DMH ratio obtained with the binary $[OMIm][HSO_4]/CF_3SO_3H$ mixture were higher than those obtained with H_2SO_4 and the lifetime of H_2SO_4 was only 3–6 cycles (Fig. 3).

Fig. 5 illustrates that the conversion and selectivities obtained at the higher I/O ratio of 10 were nearly identical to the values obtained at an I/O ratio of 7.5. The ability to use lower I/O ratios without sacrificing alkylate yields and stability is desirable to lower isobutane separation costs.

4. Summary

Six types of ionic liquids and IL/acid mixtures with sulfuric acid and triflic acid were utilized as catalysts in the isobutane/1-butene alkylation reaction. The ionic liquids with inherent acidity in either the cation or the anion resulted in low conversions and poor selectivities. In contrast, the ILs that had acidity in both the cation and the anion provided better selectivities even though the conversions were still low. The mixture of these ILs with sulfuric acid and triflic acid resulted in superior performance over either the ILs themselves, or, importantly, the pure acids. This is especially true for mixtures with the triflic acid, whose acidity is believed to be too high for the high selectivities sought for alkylation reactions. Ionic liquids with longer-chain alkyl groups, such as $[OMIm][HSO_4]$, were found to have better selectivity, which is believed to be due to higher isobutane solubility in the IL. The recyclability of the IL/acid mixtures were also superior to the pure acids even out to 25 different recycling runs. These results suggest that ILs offer the ability to produce liquid acid catalysts with tuned acidity, reactant solubilities, product separation and mass transfer properties that may in turn be exploited to optimize the performance of acid catalyzed transformations.

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