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Alkylation of isobutane/butene promoted by fluoride-containing ionic liquids

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ABSTRACT

In this work, the alkylation of isobutane and butene, catalyzed by sulfuric acid in the presence of the fluoride–containing ionic liquids [Bmim][PF$_6$] and [Bmim][SbF$_6$], was investigated. The use of the binary mixture catalysts brought to a higher C$_8$ selectivity and longer catalyst lifetime, compared with the results obtained when working with sulfuric acid only. This was attributed to the formation of new species when [Bmim][PF$_6$] or [Bmim][SbF$_6$] are added to sulfuric acid. The acidolysis of [Bmim][PF$_6$] and [Bmim][SbF$_6$] was accompanied by the release of hydrogen fluoride (HF) and the decomposition of anions to [PF$_{6-x-2y}$(HSO$_4$)$_x$(SO$_4$)$_y$]$^-$ and [SbF$_{6-x-2y}$(HSO$_4$)$_x$(SO$_4$)$_y$]$^-$, respectively. The presence of these new species after acidolysis was measured and confirmed by ion chromatography, ^{1}H–Nuclear Magnetic Resonance (NMR), ^{19}F–NMR and ^{31}P–NMR. The production of HF and the complexation of anions and carbenium ions both play an important role in stabilizing the carbenium ion and improving the catalytic performance.

1. Introduction

Isobutane/butene alkylation is an important process in the petroleum refining industry from both the economic and environmental viewpoints [1–3]. The gasoline obtained from alkylation is a clean burning fuel and is considered as an ideal blending component for reformed gasoline due to its excellent blending properties such as high octane number, free of aromatic and sulfur–containing compounds [4]. Unfortunately, the current commercial alkylation process relies on the use of the liquid acid catalysts HF and H$_2$SO$_4$, which cause serious environmental and corrosion problems [5–7]. Particularly for HF, several safety measures have to be taken to avoid its leakage, because owing to its high volatility, HF is rapidly dispersed over several kilometers [4]. In the case of H$_2$SO$_4$, the major disadvantages are mostly associated with the high catalyst consumption (70–100 kg of H$_2$SO$_4$ per metric ton of alkylate produced), which requires the presence of a regeneration plant in proximity of the alkylation unit and consequent increases in the operation cost as the regenerated H$_2$SO$_4$ is two to three times more expensive than the fresh acid [8–10]. Therefore, much effort has been devoted to find an alternative catalyst or promoters for the commercial processes [3,6].

Ionic liquids (ILs) are a new class of polar solvents and catalysts with the unique physical and chemical properties of non-volatility, tunable solubility, excellent thermal stability and recyclability [11–17], which are attracting significant attention due to the low environmental impact associated with their use. ILs have been widely applied in various reactions such as hydrogenation, oxidation, Fischer–Crafts and isomerization [18–22]. In recent years they are being regarded as promising alkylation catalysts, improving the reactivity and selectivity of the classical catalysts used until today. In particular, when using acidic choloroaluminate IL catalysts, a high quality alkylate was obtained, presumably because of the adjustable and suitable Lewis and Brønsted acidity [23–26]. On the other hand, this catalyst suffers from extreme oxophilicity and ease of losing hydrogen chloride, which results in its deactivation and reduction of halide content.

Thus, more attention has been devoted to the addition of ILs to strong acids, such as H$_2$SO$_4$ and CF$_3$SO$_3$H, to enhance their catalytic performance [27]. Olah et al. used amine–poly(HF) ILs as additives in the HF alkylation process, obtaining a good yield of alkylate and a research octane number (RON) up to 94 [28]. Tang et al. reported that imidazolium ILs catalyst with HSO$_4$$^-$, OTF$^-$ and Tf$_2$N$^-$ showed a significant promoting effect on the reactivity of the mixture and on the selectivity towards trimethylpentanes (TMPs) in the isobutane/butene alkylation catalyzed by H$_2$SO$_4$ and/or CF$_3$SO$_3$H [29]. Recently, Li et al.

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also found that the selectivity of C_8 increased from 80% to 88% in the presence of caprolactamium hydrogen sulfate ILs in the alkylation of isobutane/butene catalyzed by H_2SO_4 [30]. In our previous work, various kinds of ILs coupled with strong acids mixtures were investigated in the isobutane/butene alkylation [28,31]. For example, compared to pure CF_3SO_3H, the use of the binary mixture catalyst consisting of CF_3SO_3H and $[N(C_2H_5)_3][HSO_4]$ was found to lead to a 20% increase in TMPs selectivity and an increase by 1 of the RON [28]. Even more strikingly, when $[Hmim][SbF_6]$ was added to CF_3SO_3H, the C_8 selectivity and RON increased by 47% and 10, respectively [32]. It is worth mentioning that, in addition to the good performance related to RON and alkylates yield, the catalyst lifetime of H_2SO_4 was dramatically prolonged when it was coupled with traces of $[Bmim][SbF_6]$. The acid buffer effect of $[Bmim][SbF_6]$ was assumed to be responsible for the excellent performance [33]; however, the roles of these ILs in the binary catalytic mixtures were still unclear, and more efforts were necessary to understand their influence.

As mentioned previously, the presence of ILs dramatically enhanced the catalytic performance of liquid acid catalysts, especially in the case of the fluoride–containing ILs. These results inspired us to further investigate the role of ILs in the catalytic isobutane/butene alkylation, focusing on the mechanisms on molecular lever rather than on the influence of acidity only. In this work, $[Bmim][PF_6]$ and $[Bmim][SbF_6]$ were selected as additives and the properties and catalytic features of the binary mixtures formed with H_2SO_4 were investigated in detail, taking into account their acidity, stability, composition, and catalytic performance during recycling. A possible promoting mechanism was proposed based on the classic carbonium alkylation mechanism.

2. Experimental section

2.1. Materials and instruments

Sulfuric acid (H_2SO_4, $\geq$ 98 wt%) was obtained from Beijing Chemical Works (China). Deionized water (H_2O) was purified by a Millipore system (Milli–Q, 18.2 MΩ•cm). $[Bmim][PF_6]$ and $[Bmim][SbF_6]$ (ILs) were provided by Linzhou Keneng Material Technology Co. Ltd. (Linzhou, China). D_6–dimethyl sulfoxide (DMSO) and trichlorofluoromethane ($CFCl_3$) were purchased from Aladdin Chemistry Co. Ltd. (Beijing, China). All other chemicals were from commercial sources and of analytical reagent grade unless indicated otherwise. Isobutane was purchased from LingGas, Ltd (Beijing, China). Butene was obtained from Sinopec Beijing Yanshan Company (Beijing, China). The isobutane/butene mixtures (mole ratio = 9:1) were premixed to obtain the composition detailed in Table 1.

$[Bmim][PF_6]$ and $[Bmim][SbF_6]$ were measured by ^{1}H–NMR. ^{1}H–NMR (500 MHz, d_6–DMSO), δ = 7.46 (d, J = 22.4 Hz, 1H), 6.47 (t, 2H), 3.49–3.15 (m, 2H), 2.98 (d, 3H), 0.92 (dt, 2H), 0.51–0.26 (m, 2H), −0.03 (dt, 3H). The H_2O concentration of $[Bmim][PF_6]$ and $[Bmim][SbF_6]$ was less than 440 ppm, as detected by the Karl Fischer Moisture Titrator.

^{1}H–NMR, ^{13}C–NMR, ^{19}F–NMR and ^{31}P–NMR spectra were obtained with a Bruker Avance III 500WB spectrometer (Germany). The ^{1}H–NMR spectra were tested at 25 °C with DMSO internal standard and 16 scans; the relaxation delay and pulse width were 2.0000 and 10.0000, respectively. The ^{13}C-NMR spectra were tested at 25 °C without internal standard and with 256 scans, the relaxation delay and pulse width were 1.5000 and 10.0000. The ^{19}F–NMR spectra with standard reference trichlorofluoromethane were tested at 25 °C with 512 scans, the

relaxation delay and pulse width were 1.0000 and 12.5000. The parameters of the ^{31}P–NMR spectra were: 25 °C with 513 scans, the relaxation delay and pulse width were 2.0000 and 11.1000. Quantitative analyses of fluorine ion content were conducted using an ion chromatograph (ICS–900, Dionex, America) equipped with IonPac AS22 Analytical Column (4 × 250 mm).

2.2. Acidity evaluation

The ^{13}C–NMR spectra were employed to determine the Hammett acidity (H_0) through the chemical shift of C_β and C_α ($\triangle\delta$) of 4–methyl–3–pentene–2–one (mesityl oxide), as reported in the literature [34]. The intercept, $\triangle\delta^0$, was obtained by the linear correlation between $\triangle\delta$ and mesityl oxide contents. The H_0 was determined through Eqs. (1) or (2), according to $\triangle\delta^0$ values [35].

$$\Delta\delta^0 = -62.190H_0 - 9.968H_0^2 - 0.7419H_0^3 - 0.0211H_0^4$$
$$- 75.538 \ (50.22 < \Delta\delta0 < 80.3) \tag{1}$$

$$\Delta\delta^0 = -57.805H_0 - 5.0885H_0^2 - 0.14934H_0^3 - 138.0706 \ (\Delta\delta^0 > 80.37) \tag{2}$$

2.3. Alkylation experiment

The isobutane/butene alkylation reactions catalyzed by H_2SO_4 coupled with either $[Bmim][PF_6]$ or $[Bmim][SbF_6]$ were carried out in a 250 ml batch autoclave immersed in the cooling groove (DC 2010, ethanol employed as cycling media), as illustrated in Fig. 1. The catalysts, consisting of H_2SO_4 (40 ml) and either $[Bmim][PF_6]$ or $[Bmim][SbF_6]$, were charged into the reactor, the mixture was then brought to 5 °C and stirred at a speed of 1000 rpm at 0.4 MPa in nitrogen atmosphere. 50 ml isobutane/butene were pumped into the reactor at a flow rate of 500 ml/h using a precision double metering pump plunger (2ZB–1L10) and held for 10 min. After the reaction, the reactor was depressurized slowly. The hydrocarbon phase in the lighter solution was separated from the binary mixture catalysts by stewing and washing with deionized water.

The hydrocarbon products were analyzed by gas chromatography (GC, GC–2010 Plus, Shimadzu (China) Co.,Ltd) with a capillary column (Rtx-DHA, 100 m × 0.25 mm × 0.5 μm). The analysis conditions were the following: split ratio = 100:1, injector temperature = 250 °C, detector temperature = 300 °C, chromatographic column flow rate = 0.95 ml/min, pressure = 177.0 kPa. The GC column was initially held at 45 °C for 10 min, it was then heated through three heat ramps: to 60 °C at a rate of 1 °C/min, to 120 °C at 2 °C/min and to 180 °C at 5 °C/min. Nitrogen was employed as carrier gas. The quantitative analysis of alkylates was carried out by studying the ratio of peak areas through the area normalization method. The TMPs selectivity was determined as the mass ratio between TMPs and the total alkylates. The RON was calculated based on the individual RON value and volume fraction, y_i, of each component i as follows RON $= \sum_{i=1}^{n} y_i RON_i$ [23].

3. Results and discussion

3.1. Properties of the binary mixtures in the presence of fluoride–containing ILs

The ILs containing halogens were sensitive to the presence of water and hydrolysis of the halogen usually accompanied the reaction [36].

Table 1
The composition (wt%) of isobutane/butene mixtures.

Item	Isobutane	1–butane	Trans–2–butene	1–butene	Isobutene	Cis–2–butene
wt%	82.27	7.75	3.79	3.65	0.08	2.46