



## Effects of catalyst composition on the ionic liquid catalyzed isobutane/2-butene alkylation



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### ABSTRACT

Ionic liquid catalyzed isobutane/2-butene alkylation modified with metal compounds was studied. The effect of catalyst composition on the alkylation selectivity was investigated.  $^{27}\text{Al}$  NMR, ESI-MS, and FTIR spectra reveal that the catalytic selectivity of the modified ionic liquid is probably determined by the catalyst composition rather than by the acid strength. The complexation of transition metal with 2-butene can increase the internal isobutane-to-olefin ratio of feed during the alkylation reaction, which results in the better selectivity of the modified ionic liquid. The best ionic liquid catalysts were those containing  $\text{CuAlCl}_4$  complexes, giving the alkylate with 87.5 wt% trimethylpentanes and a calculated research octane number (RON) of 100.5.

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### 1. Introduction

Alkylation of isobutane with  $\text{C}_3$ – $\text{C}_5$  alkenes is an important industrial process for the production of high-octane gasoline with low residual vapor pressure. To date, only sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrofluoric acid (HF) have been extensively commercially applied for the alkylation due to economic considerations [1,2]. However, acid sludge treatments and safety protection may be the most difficult problems that restrict the commercial application of the two acids [3]. Due to the growing awareness of environmental issues, it is necessary to use some safer and easily regenerable materials to catalyze the reaction. Molecular sieves and heteropolyacids are known to possess high catalytic activities and selectivities. These solid acids have been studied as potential catalysts for alkylation of isobutane with alkenes for years. Despite the potential benefits presented by the solid acids, they have still not achieved commercial use as alkylation catalysts due to the fast catalyst decay [4]. In order to enhance the lifetime of solid catalysts, supercritical fluid like supercritical isobutane has been used as media for solid acid catalyzed alkylation [5].

Liquid superacid catalysts such as ionic liquids (IL) are also receiving increased attention [1,6]. The main advantages arising from the use of IL are their clean catalytic properties for alkylation processes. Additionally, the physical and chemical properties

of IL can be readily tuned by using different organic cations or inorganic anions. Compared with solid acids, most IL can maintain high catalytic activity during the whole alkylation reaction without carbon deposition problems. Despite no IL has reached industrial application, the composite IL  $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3-\text{CuCl}$ , which is a chloroaluminate IL modified with cuprous chloride, has been reported for the pilot-scale alkylation test [1].

It is well known that acid strength and catalyst composition will affect the formation of *t*-butyl cation ( $t\text{-C}_4^+$ ) and the rate of hydride transfer [7]. Thus, the acidity and composition of IL are probably the most important parameters affecting alkylation. Recently, influences of the IL acidity on isobutane/2-butene alkylation have been studied. When some metal salts are mixed with the chloroaluminate IL  $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3$ , it is supposed that the change of Lewis acidic site in the IL that results in the alkylate quality increases dramatically [8,9]. Zhang et al. [10] also found that the addition of benzene to  $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3$  could obviously improve the alkylate composition. They consider that benzene leads to modify the Lewis acidity of  $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3$ , and the modification is presumably beneficial for alkylation because it inhibits the side reactions. Additionally, it is believed that increasing the concentration of HCl or the molar fraction of  $\text{AlCl}_3$  in  $[\text{BMIm}]\text{Cl}-\text{AlCl}_3$  will increase its acidity. Such an increase leads to an increase in the butene conversion and a decrease in the rate of side reactions. Adding water in an acidic molten salt can play a similar role to HCl [11]. For non-chloroaluminate based IL, a dramatic enhancement of the catalytic effect was observed when the IL containing the  $\text{SbF}_6^-$  anion [12,13]. Using the binary mixture of acidic imidazolium IL and sulfuric or

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triflic acid has the similar effects [14]. The better catalytic performances of such catalysts may result from the complex acidity and solubility effects of IL. However, the aforementioned studies were essentially focused on discussing the effects of acidity and acid strength, it is necessary to investigate more characteristics of the catalyst composition to better understand the behavior of IL during the alkylation.

In this study, we report our studies on the effect of the IL composition on the alkylation of isobutane with 2-butene. Chloroaluminate IL [BMIm]Cl–AlCl<sub>3</sub>, [BMIm]Br–AlCl<sub>3</sub>, and [Et<sub>3</sub>NH]Cl–AlCl<sub>3</sub> were used as catalysts in the studies. They were also modified with transition metal salts, metal complexes, and metallic oxides. The catalytic selectivities of the IL catalysts were compared with those obtained in pure strong acids under the identical reaction conditions. The acid strength and composition of the IL were also investigated by means of FTIR, <sup>27</sup>Al NMR, and electrospray ionization-mass spectrometry (ESI-MS).

## 2. Experimental

### 2.1. Preparation of catalysts

Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 wt%) and trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H) were purchased from Sinopharm Chemical Reagent (SCRC). Before use, CF<sub>3</sub>SO<sub>3</sub>H were distilled under dry nitrogen.

The triethylamine hydrochloride ([Et<sub>3</sub>NH]Cl), chloride or bromide salts of the 1-butyl-3-methylimidazolium cations ([BMIm]Cl, [BMIm]Br) were all obtained from Sigma-Aldrich Chemical Company and dried under vacuum at 383 K. [Et<sub>3</sub>NH]Cl–AlCl<sub>3</sub>, [BMIm]Cl–AlCl<sub>3</sub>, and [BMIm]Br–AlCl<sub>3</sub> chloroaluminate IL were prepared and characterized using methods described earlier [15]. The molar ratio of AlCl<sub>3</sub> to organic salt is 1.8:1 in this work.

The IL/additive systems were prepared by directly adding additives to the chloroaluminate IL. Additives included transition metal salts, metal complexes, and metallic oxides. They were added to the IL at the beginning of the alkylation reaction. Most of IL/additive catalysts were suspension. According to the literature preparation [16,17], the mixed-metal chloride CuAlCl<sub>4</sub> can be readily synthesized in high yield from the melt of CuCl and AlCl<sub>3</sub> (<523 K).

[BMIm]Cl–AlCl<sub>3</sub>–CuCl, [BMIm]Br–AlCl<sub>3</sub>–CuCl, and [Et<sub>3</sub>NH]Cl–AlCl<sub>3</sub>–CuCl were composite IL used in this study. They were prepared by introducing cuprous chloride to the chloroaluminate IL [18]. In a typical method of preparing composite IL, anhydrous aluminum chloride (1.8 mol) was slowly added to a round-bottomed flask containing dry 1-butyl-3-methylimidazolium chloride (1 mol) under a nitrogen atmosphere at 383 K. After formation of chloroaluminate ionic liquid, 0.5 mol of cuprous chloride was added to the above ionic liquid. The reaction mixture was stirred at 383 K overnight to allow a complete homogenization of the resulting ionic liquid.

### 2.2. Characterization of ionic liquids

Acidity characterizations were carried out by infrared spectroscopy using pyridine as the acid probe at room temperature, along with a Bio-Rad high-resolution FTIR spectrometer (FTS-40). All spectra were manipulated by Bio-Rad Win-IR software. The samples were prepared by mixing pyridine and IL in a volume ratio of 5:1, and smeared into liquid films on KBr windows.

The <sup>27</sup>Al NMR measurements were carried out on a Bruker WB-400 AMX spectrometer to investigate the difference of anions. The spectra were obtained at 130.32 MHz with a preacquisition delay time of 0.5 s. The <sup>27</sup>Al NMR chemical shifts were referenced to an external Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> standard.

Characterization of the IL anions was achieved using a negative mode of electrospray ionization mass spectrometry (ESI-MS). ESI-MS was recorded on a Thermo Finnigan LCQDeca XP Plus quadrupole ion trap instrument on samples dissolved in methanol.

### 2.3. Procedure and analysis

Isobutane and 2-butene were commercial products from China National Petroleum Corporation (CNPC) with 99% purity and used without further purification. Alkylation reactions were carried out in a liquid-phase pressure vessel (100 mL) with a liquid inlet. A mechanical stirrer with a fixed impeller on the shaft provided agitation at 1200 r/min. The catalyst (e.g., 15 mL) was put into the reactor at first. After stirring, the liquid feed (a mixture of isobutane/2-butene in a 7.5:1 molar ratio) was charged into the reactor by means of a plunger pump at a rate of 500 mL/h. The reaction temperature was controlled at 298 K by a water bath with temperature controller. When the pressure of the reactor was higher than 0.4 MPa, we stopped the pump and stirrer. The total reaction time was about 30 min. The product and catalyst were decanted from the reactor and settled for 30 min. The product was fractionated to remove isobutane and distilled in a Claisen flask. Aliquots of the hydrocarbon phase were withdrawn for analysis.

The investigation for the isobutane-to-olefin (I/O) molar ratio of isobutane/2-butene feed in the toluene–CuAlCl<sub>4</sub> system was also performed in the alkylation reactor. In a typical experiment, the toluene–CuAlCl<sub>4</sub> (15 mL) mixture was introduced into the reactor at room temperature. A mixture of isobutane/2-butene (initial I/O=7.5) from the feed vessel was pumped into the stirred (1200 r/min) reactor. The agitation was continued for 30 min, and then the liquid outlet at reactor was opened. The excess isobutane/2-butene mixture was vented at room temperature for analyzing the final molar ratio of isobutane to 2-butene.

The alkylate samples were sent to a gas chromatograph (Hewlett-Packard, 6890). The GC column used for separation was a Supelco Petrocol DH capillary column (50 m × 0.1 mm × 0.1 mm). Initial qualitative identifications of the products were accomplished with the help of a gas chromatograph (Hewlett-Packard, 5890 Series II) equipped with a mass spectrometer (Hewlett-Packard, 5972 Series II column). The research octane number (RON) of alkylate was calculated, according to the method applied in Ref. [7,11]. The gas samples of isobutane/2-butene were also sent to the Hewlett-Packard 6890 GC for investigating the change of I/O ratio of feed. Except the injection mode, the analysis conditions of gas samples were as the same as the alkylate samples.

## 3. Results and discussion

### 3.1. Alkylation reactions under identical conditions

The reaction mechanism of acid catalyzed isobutane/2-butene alkylation is a chain process occurring through carbocation intermediates [19]. The protonation of 2-butene can form *t*-butyl cations (*t*-C<sub>4</sub><sup>+</sup>), which initiate the alkylation reaction. A *t*-C<sub>4</sub><sup>+</sup> cation is added to a 2-butene molecule to form a 2,2,3-trimethylpentane carbocation (2,2,3-TMP<sup>+</sup>). Some of 2,2,3-TMP<sup>+</sup> cations will isomerize to the corresponding 2,2,4-trimethylpentane carbocations (2,2,4-TMP<sup>+</sup>). The desired product 2,2,4-trimethylpentane (2,2,4-TMP) is mainly obtained by intermolecular hydride transfer between isobutane and 2,2,4-TMP<sup>+</sup>. The hydride transfer also generates a new *t*-butyl cation that will react with another 2-butene molecule.

Many side reactions that lead to forming low RON products are always accompanying with the main reaction. The intermediate TMP<sup>+</sup> cation often competes with *t*-C<sub>4</sub><sup>+</sup> cation in the hydrocarbon-phase and adds to another 2-butene molecule forming *i*-C<sub>12</sub><sup>+</sup>, *i*-

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