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## Preparation of alkylate gasoline in polyether-based acidic ionic liquids

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### ABSTRACT

A series of novel polyether-based Brønsted acidic ionic liquids (ILs) have been synthesized, which contain both a polyoxyethylene (POE) chain and a sulfonic group ( $-\text{SO}_3\text{H}$ ). The prepared ILs can well dissolve trifluoromethanesulfonic acid (TfOH), and IL/TfOH mixture has good intermiscibility with the reactants of isobutane and isobutene. Then, a new IL/TfOH catalytic system for the preparation of alkylate gasoline has been developed. The advantages of the new catalytic system are high selectivity for  $\text{C}_8$ -alkylate product and the recyclability of TfOH catalyst. Under the optimal catalytic conditions (using the IL with the polymerization degree  $n = 75$ , IL/TfOH(v/v) = 5, reaction temperature  $60^\circ\text{C}$ , reaction time 30 min, and stirring rate 800 rpm), the  $\text{C}_8$ -selectivity can reach 80%, and above 95% of  $\text{C}_8$ -alkylate product is trimethylpentane (TMP). Therefore, the new IL/TfOH catalytic system can afford high-quality alkylate gasoline. In addition, the conversion of isobutene and  $\text{C}_8$ -selectivity both have gradually a little drop during 6 recycles, which should attribute to a little loss of TfOH in every recycle.

### 1. Introduction

Alkylate gasoline is a mixture of highly branched-chain alkanes, especially  $\text{C}_8$ -alkanes. Alkylate gasoline is commonly used as a superior additive in global gasoline pool due to its many advantages such as high octane number, low Reid vapor pressure, low octane sensitivity, no aromatics and very low content of sulfur, nitrogen, and alkenes [1–3]. Among total global gasoline consumption, alkylate gasoline accounts for approximately 15%, and world production of alkylate gasoline is about 100 million tons/year. However, with the increase of private vehicles and the ever growing environmental requirements of motor gasoline, it is an inevitable trend for more alkylate gasoline.

Alkylation of isobutane with  $\text{C}_3 \sim \text{C}_5$  olefins under the acidic catalyst is mainly used for the production of alkylate gasoline in the petroleum industry. To date, the generally used acid catalyst is still the traditional concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or hydrofluoric acid (HF) [4–6]. It is obvious that both catalysts are “non-green” because of large discharge of waste acid, highly corrosion and environmentally detrimental effects. In addition, there are two problems. On the one hand, the catalyst is one-off consumption and it is uneconomic, because it is very costly to regenerate the waste acid from the acid soluble oil (ASO). On the other hand, the selectivity of alkylation for  $\text{C}_8$ -product is not high ( $< 50\%$ ) because of strong acidity of  $\text{H}_2\text{SO}_4$  or HF resulting in many side reactions. Therefore, there is an urgent need to develop a

green, economic, and high selectivity catalyst for the production of alkylate gasoline. During recent decades, many solid acid catalysts have been developed and utilized in alkylation process [7–11]. The solid acid catalysts show good catalytic activity and selectivity for alkylate product under certain conditions. However, there are some inherent drawbacks such as rapid deactivation of catalyst, low reaction rate, and etc.

In recent years, ionic liquids (ILs) with superior properties such as non-volatility, thermal and structure stability, and easy separability, are intensively discussed as environmentally friendly solvents or catalysts in chemical industry [12–14]. Acidic IL with adjustable acidity is thought to be a potential alternative to replace the traditional inorganic/organic acid in catalyzed alkylation process. A large number of Lewis acidic ILs mainly including chloroaluminate-based ILs have been applied for isobutane/butene alkylation, and the promising results are obtained [15–21]. However, these Lewis acidic ILs are usually sensitive to air and moisture, so the reusability is not good. In addition, some additives such as water, CuCl, or acidic exchange resin are usually needed to improve the selectivity of the reaction. Recently, Brønsted acidic ILs with high stability are also used in the alkylation of isobutene with butane. However, Brønsted acidic ILs because of low acidity are usually coupled with other strong acid such as  $\text{H}_2\text{SO}_4$  or trifluoromethanesulfonic acid (TfOH) as the catalyst of alkylation [22–27].

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In our laboratory, some task-specific, polyether-based ILs with polyoxyethylene (POE) chain, have been synthesized and as catalysts used in C–C coupling reaction and oxidation reaction [28–30]. The POE chain endows the IL an unique solubility even or a typical thermoregulation in the catalytic system. The thermoregulation is that the IL catalyst can completely dissolve in the reagents at the higher reaction temperature, and then automatically separate from the product at the room temperature after the reaction. So, the homogeneous catalysis and the heterogeneous separation can be well integrated.

In this paper, a series of novel polyether-based Brønsted acidic ILs have been synthesized, which contain both a POE chain and a sulfonic group (–SO<sub>3</sub>H). When the prepared IL is used for catalyzing the alkylation of isobutane with isobutene, there is no desired catalytic activity because of the IL having no enough acidity. However, strong acid TfOH can be well dissolved in the prepared IL, and IL/TfOH has well intermiscibility with the reactants of isobutane and isobutene. The acidity of the IL/TfOH mixture can be fine-tuned by adjusting the amount of TfOH. So, the new IL/TfOH catalytic system exhibits a good catalytic activity, especially a high selectivity for C<sub>8</sub>-alkylate product, which is obviously superior to that of pure strong acid catalyst. In addition, TfOH in the IL can be well separated from the produced alkylate gasoline, and exhibits excellent recycling performance.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals were used as purchased, and solvents were dried by known procedures and used freshly distilled. The mixed feedstock of isobutane (90.93 wt%) and isobutene (9.07 wt%) with 1.0 MPa nitrogen was obtained from Dalian Airichem Specialty Gases & Chemicals Co. Ltd in China. Infrared (IR) spectrum of the product was recorded using a Nicolet-510P IR spectrometer. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum was recorded on a Bruker AV 500 MHz spectrometer with tetramethylsilane as the standard. The viscosity of the prepared IL was measured using a NDJ-5S rotational viscometer. Gas chromatography/Mass spectrometry (GC9790/MS) with a capillary column (HP-PONA, 50 m × 0.25 mm × 0.25 μm) was used for qualitative analysis of the alkylation product. The quantitative analysis was determined by Gas chromatography (GC9790) with the same capillary column (HP-PONA, 50 m × 0.25 mm × 0.25 μm).

### 2.2. Synthesis of polyether-based acidic ILs

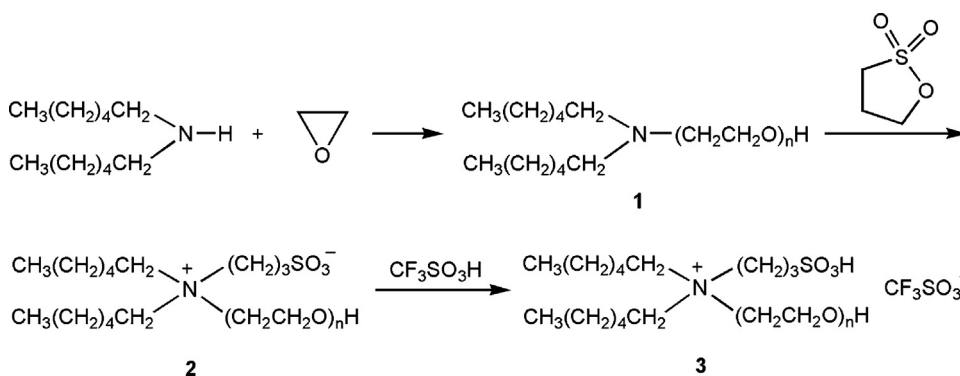
The synthesis route of polyether-based acidic ammonium ILs was outlined in Scheme 1. 15 mL (0.30 mol), 25 mL (0.50 mol), 40 mL (0.79 mol), 50 mL (0.99 mol), 60 mL (1.19 mol) of ethylene oxide were respectively added to di-*n*-hexylamine (0.01 mol) in 10 mL absolute ethyl alcohol in a high-pressure reaction kettle. The autoclave was sealed and excluded the air by 3.0 MPa nitrogen for five times. After that, the reaction was kept at room temperature for 2 h under stirring,

then 60 °C for 4 ~ 6 h. After reaction, the reaction mixture was transferred into a round-bottom flask, and the solvent and the unreacted ethylene oxide were removed by vacuum distillation to give the tertiary amine **1** with a POE chain. The average polymerization degree (*n* value) of POE chain was calculated by the increment of mass. The relationship between the average polymerization degree and the dosage of ethylene oxide was shown in Fig. S1. **1**, 3-Propane sultone (0.01 mol) was first dissolved in ethyl acetate in a three-necked and round-bottomed flask. The intermediate **1** (0.01 mol) was then dropped to the flask. After the dropping, the reaction was performed for 5 h at 50 °C under stirring. Subsequently, the solvent was distilled off in vacuum to afford the intermediate **2**. The obtained intermediate **2** (0.01 mol) was first dissolved in 10 mL distilled water. Then, a 10 mL aqueous solution of TfOH (0.01 mol) was dropped. The mixture was stirred at room temperature for 12 h. Water was removed by the distillation under vacuum to give the target product, the polyether-based acidic IL **3**. The IL **3** was directly used in the catalysis without any purification.

For the synthesized IL **3** with an average polymerization degree (*n* = 75), the viscosity and the density at 20 °C are 20.75 mPa·s and 1.0710 g/mL, respectively. The typical IR and <sup>1</sup>H NMR spectral data of **3** (*n* = 75) are listed here (see Fig. S2 and Fig. S3). IR (KBr):  $\nu = 3417 \text{ cm}^{-1}$  (–OH),  $2871 \text{ cm}^{-1}$  (C–H),  $1455 \text{ cm}^{-1}$  (S=O),  $1251 \text{ cm}^{-1}$  (C–N),  $1121 \text{ cm}^{-1}$  (C–O–C),  $1068 \text{ cm}^{-1}$  (S–O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.81$  (t, *J* = 8.0 Hz, 3H),  $0.88$  (t, *J* = 8.0 Hz, 3H),  $1.10 \sim 1.23$  (m, 18H, CH<sub>2</sub>),  $3.42 \sim 3.64$  (m, 308H, CH<sub>2</sub>).

### 2.3. Procedure of alkylation

Fig. 1 showed the alkylation apparatus. In all the experiments, a certain amount of IL and/or TfOH were added into a 75 mL autoclave equipped with a mechanical stirring. The autoclave was sealed and excluded the air by high-pure nitrogen for five times. After that, a certain mass ratio of isobutane to olefin (isobutene) (I/O) in the feed storage tank was pumped into the autoclave under 2.0 MPa N<sub>2</sub> with a velocity of 10 mL/min. Subsequently, the alkylation reaction proceeded at a setting temperature for a determined time with a certain stirring rate. After the determined time, the autoclave was cooled in the ice water bath. Then all the gas phase in the autoclave was collected into a gasbag to detect isobutene conversion by GC. The liquid phase in the autoclave was separated into two phases because of insolubilization between the hydrocarbon product and the IL. The upper hydrocarbon layer was the produced alkylate gasoline, which was separated from the below IL phase by decantation. The alkylate gasoline was washed 3 times with deionized water and dried, and then analyzed by GC. The IL phase with TfOH in the autoclave was reused directly in the recycle experiments.



Scheme 1. Synthesis of polyether-based acidic ILs.

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