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Short Communication

Triflic acid catalyzed isobutane alkylation with trifluoroethanol as a promoter

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ABSTRACT

The alkylation of isobutane and butene (C_4 cut from industrial alkylation feed) catalyzed by triflic acid (TFSA)/trifluoroethanol (TFEA), has been systematically investigated in a batch autoclave. High selectivity of trimethylpentane (TMP, 80.1%) and high research octane number (RON, 97.2) were achieved with 30 vol.% TFEA in TFSA/TFEA catalytic system at 8 °C. Moreover, the TFSA/TFEA system can be recycled several times without significant loss of activity.

1. Introduction

The alkylation of isobutane and C_3–C_5 alkenes is an important unit in petroleum refineries to produce highest-quality blending component for the gasoline pool with low sulfur and without alkenes or aromatics [1]. However, sulfuric acid and anhydrous hydrofluoric acid are exclusively used in the commercial alkylation processes today, which has caused significant concerns about safety and environmental pollution. For example, large amounts of spent acid are produced in the sulfuric acid process, which are difficult to be treated harmlessly [2]. For HF process, HF is highly toxic and volatile, which would lead to disastrous destruction to our living environment in case of leakage [3]. Thereafter, much attention has been given to develop greener, more efficient and cost-effective alternatives to the commercial catalysts. Solid acids are highly desirable as they are non-toxic, non-corrosive and environmentally friendly [4–6]. However, solid acids usually deactivate quickly. It is a challenge to find economic and efficient methods to regenerate the deactivated solid acids, which is a "bottle-neck" for the success of its industrialization.

Recently, room temperature ionic liquids (RTILs) have been extensively investigated as catalysts for the alkylation [7–13], and most investigations concentrated on chloroaluminate-based ionic liquids. However, the acidity of chloroaluminate ionic liquids is difficult to control due to its extreme oxophilicity [14], which resulted in low-quality alkylate. Recently the mixtures of ionic liquids and mineral acids were reported to catalyze the alkylation of isobutane and 1-butene [15]. The physical–chemical properties of the catalytic systems, such as the acidity, solubility, density, viscosity, interfacial properties and so on, could be tuned effectively by choosing the ionic liquids and the acids. However, the best selectivity of C_8 was only 75.8% with TMP/DMH ratio of 6.8 for the mixture of imidazolium-based ionic liquid and TFSA—a small improvement over H_2SO_4 alone. Trifluoroacetic acid or water were also added as promoters in TFSA for the alkylation, but the selectivity of TMP (50.2% and 56.0% for trifluoroacetic acid and water respectively) and RON (89.1 and 91.3 for trifluoroacetic acid and water respectively) were still low [16].

Trifluoroethanol (TFEA) has been widely used as a solvent, a cosolvent, a catalyst or an additive in biochemistry, polymerization and alkylation due to its strong ionization power and good recoverability [17–19]. Recently, TFEA was reported to be able to coordinate boron trifluoride (BF_3) and form a stable composition with a acidity between that of H_2SO_4 and triflic acid [20], which showed excellent catalytic performance in C_4 alkylation [21].

Herein, the TFSA/TFEA catalyst has been systematically investigated to catalyze the isobutane–butene (C_4 cut from industrial alkylation feed) alkylation. The ratio of TFSA and TFEA, the acid/hydrocarbon ratio and other reaction conditions were optimized for the alkylation and the reusability of TFSA/TFEA was also investigated in this study.

2. Experimental section

2.1. Materials and reagents

TFSA (>99.9% in purity) was purchased from 718th Research Institute of China Shipbuilding Industry Corporation. TFEA (>99.9% in

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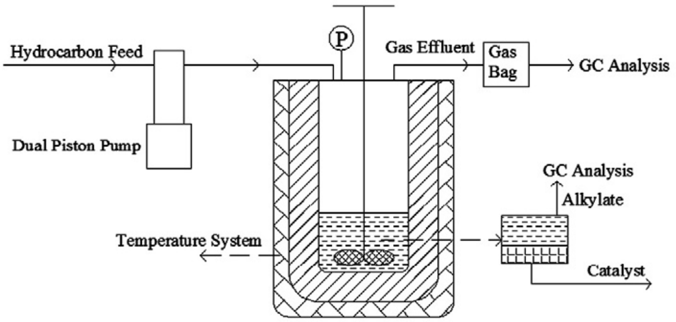

Fig. 1. Schematic of alkylation apparatus.

purity) was purchased from Chemical Development Institute of Weihai Yunqing. Tetramethylsilane (99.9% in purity) and Mesityloxide (>90% in purity) were purchased from Alfa Aesar and kept in a vacuumed desiccator. All reagents were used as received without further purification. Isobutane (>99.7% in purity) was obtained from Linggas, ltd. Butene (C_4 cut from industrial alkylation feed) was supplied by Sinopec Beijing Yanshan Company, the composition of which was shown in Table 1.

The C_4 hydrocarbon feeds with I(isobutane)/O(olefin) ratio of 10:1 were premixed in a storage vessel as shown in Table 2.

2.2. Isobutane–butene alkylation procedures

Alkylations were performed in a 200 ml stirred batch autoclave equipped with a cooling groove (DC 2006-II, ethanol as circulating chiller) as shown in Fig. 1. The autoclave was charged with a given amount of catalyst, pressured with argon to 0.5 MPa, and then equilibrated to a given temperature. Then 50 ml C_4 feeds were pumped into the reactor at a flow rate of 500 ml/h while stirring at a speed of 1000 rpm, and the reaction was continued for 10 min. After the reaction was finished, the autoclave was depressurized to release the gasses slowly, which was collected with a gas bag and analyzed by gas chromatography (SP 6890) offline with a capillary column (HP-PLOT Al_2O_3 S, 50 m × 0.53 mm). The alkylate was separated from the acid, washed 3 times with deionized water, and then analyzed immediately by gas chromatography (SHIMADZU GC2014) with a capillary column (DB-petro 100 m × 0.25 mm). And the alkylate components were identified using a HP 6890/5975 gas chromatography/mass spectrometry (GC/MS) system. For recycling studies, the catalyst was recovered back into the reactor and charged with fresh C_4 feed, and then the procedures were repeated.

2.3. Acidity determination of the TFSA/TFEA catalysts by ^{13}C NMR

We determined H_0 acid scale of the TFSA/TFEA catalysts by ^{13}C NMR with mesityloxide, α, β-unsaturated ketone, as an acidity indicator according to the literature [22–24]. In a typical procedure, three samples of the given TFSA/TFEA catalysts (ca. 2 ml) were weighed into 10 ml vials respectively. Then given amounts of mesityloxide were added into the above vials, and the resulted concentration varied between 0.05 and 0.8 mol/l. All the liquids were carefully shook to ensure a full dissolution of the indicators.

Table 1
The composition (wt.%) of butene.

Item	Isobutane	1-Butane	Trans-2-butene	1-Butene	Isobutene	Cis-2-butene
wt.%	53.6	9.0	16.2	8.6	3.0	9.6

Table 2
The composition (wt.%) of the hydrocarbon feed.

Item	Isobutane	1-Butane	Trans-2-butene	1-butene	Isobutene	Cis-2-butene
wt.%	88.6	2.5	3.9	2.0	0.7	2.3

Subsequently, the sample was loaded into a NMR tube assembled with another coaxial tube, which was filled with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were acquired at 300 K on a Bruker Avance III 600 MHz spectrometer. The chemical shift differences of $C_ß$ and C_α ($\Delta\delta$) in the mesityloxide molecular at three varied concentrations were used to determine the infinite dilution ($\Delta\delta^0$) by exploration. And the Hammett acidity (H_0) can be calculated through the equations as reported in literature [22]. We firstly determined the H_0 acidity scale of 95–98% H_2SO_4 using the above methods, which agrees well with the reported value by Dan F rcasiu [23–24] (the details shown in Table 5 in the supporting information).

3. Results and discussion

3.1. Effect of the TFEA content in catalyst on the alkylate composition

As well known, the acidity and the composition of the catalyst are probably the most important parameters affecting alkylation [16]. Therefore, we firstly studied the effect of the TFEA content on the acidity of TFSA/TFEA catalyst and the alkylate composition. The effect of varied TFEA content in catalyst from 10 vol.% to 50 vol.% was investigated, and the results were shown in Table 3 and Fig. 2 respectively. High selectivity of TMP (up to 80.1%) and RON (up to 97.2) was obtained with 30 vol.% TFEA in the TFSA/TFEA catalyst. The above catalyst was also of the most suitable acidity ($H_0 = -9.6$), which was determined by ^{13}C-NMR spectroscopy as reported in literature [22–24]. The acidity of TFSA/TFEA catalyst with only 10 vol.% TFEA was too high ($H_0 = -13.1$), which promoted the side cracking reaction, and resulted in higher selectivity of light ends (C_5–$C_{7,}$ 27.6%) and lower

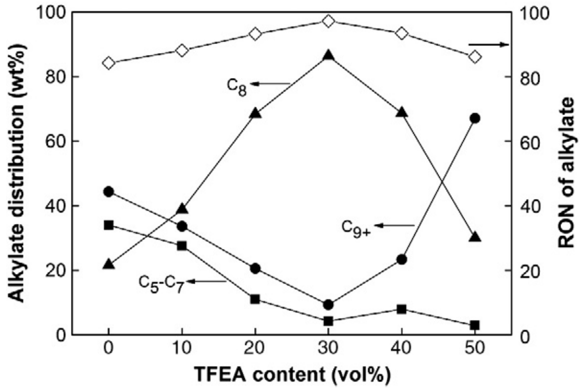

Fig. 2. Effect of TFEA content on the alkylate composition. Conditions: 8 °C; 0.5 MPa; 10 min; 1000 rpm; 20 ml catalyst (TFEA: 10 to 50 vol.%); 50 ml C_4 feed.