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Short communication

Alkylation of thiophenic compounds catalyzed by deep eutectic solvents

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ABSTRACT

Deep eutectic solvents (DESs), which were prepared by using $AlCl_3$ and acetamide or urea, show excellent catalytic performance for the olefin alkylation thiophenic sulfur (OATS) in 3-methylthiophene (3-MT) model oil and real gasoline within 40 min at 50 °C. The addition of toluene and benzene increases the conversion of thiophenic compounds and decreases the conversion of olefin. Then the mechanism of OATS with modified catalyst was discussed.

1. Introduction

With the coming new standard of lower sulfur content in the gasoline, methods to remove sulfur compounds in the gasoline completely have received widespread attention. In refineries, catalytic hydrogenation desulfurization (HDS) is widely used. Unfortunately, some intrinsic defects cannot be overcome, such as the decrease of octane number (RON) and high associated capital cost. Many new techniques without hydrogen consumption have been explored [1,2]. As one of these approaches, olefin alkylation thiophenic sulfur (OATS) is an interesting way to remove the heavy alkylated sulfur compounds by further distillation [3]. OATS can be carried out in mild conditions with a minimal decrease of RON, which is a significant advantage for refiners.

The catalysts of OATS proposed by early literatures are solid acidics, i.e. various zeolites (HY, USY, MCM-22 etc.) [4–6] and supported heterogeneous acid [7,8]. In the initial phase of the process, some of these solid catalysts have high catalytic activity and selectivity, but later the formation of carbon deposition will cause rapidly decaying reactivity, especially at high temperature [9]. Later, the desulfurization via the Friedel–Crafts reaction catalyzed by $AlCl_3$ or $AlCl_3$ base liquid at room temperature was investigated [10–12]. The appearance and composition of $AlCl_3$ based liquid are similar to traditional chloroaluminate ionic liquids, which have been investigated for isobutane/2-butene and benzene/dodecene alkylation at room temperature [13,14].

As an alternative to ILs, DESs are defined as a mixture of two or more compounds with a melting point significantly lower than those of the constituting compounds [15]. DESs share most remarkable qualities of traditional ILs (e.g., special solubility, negligible vapor tension, tenability and mild condition) while conquering several limitations compared with ILs. Especially, DESs are cheap and simple to prepare. As catalyst, DESs have been used for various applications in Diels–Alder and N-alkylation [16–19]. According to these previous researches, they could provide a potential application in the alkylation of thiophenic compounds.

In our previous work, arenium ion DESs were synthesized and used as extraction for thiophenic compounds [20]. In this work, we added urea or amide to $AlCl_3$ to form DESs and investigated the catalytic performance for alkylation of thiophenic compounds in model oil (3-MT) and real gasoline. The acidity of the DESs was adjusted by varying the molar fraction of aluminum chloride and adding benzene derivative. The mechanism of OATS catalyzed by DESs was also studied.

2. Experimental section

2.1. Materials

3-MT (>99%), n-heptane (GC, >99%), n-decane (GC, >99%) and $AlCl_3$ (>99%) were bought from Shanghai Aladdin reagent Co. Ltd. Acetamide and urea were purchased from Chengdu Kelong Fine Chemical Industry. Real gasoline was supplied by PetroChina Wuxi Petrochemical Comp.

2.2. Synthesis and characterization of DESs

The DESs were prepared by simple mechanical mixing [20]. The detailed preparation methods and characterization results of two kinds of DESs were shown in the Supporting Information.

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2.3. Catalytic test

The composition of model oil used was 3-MT (0.32 wt.%, 1000 ppm), 1-hexene (3.2 wt.%) and n-heptane (96.48 wt.%). The activity test was conducted by adding the 6% DESs to the model oil or real oil in a 100 mL stirred batch reactor for 40 min at 50 °C. For model oil, the product was analyzed by a GC-FID (Beijing Fuli 9790II, with a KB-1 column, 60 m × 0.25 mm × 0.25 μm; constant temperature: 140 °C). For real gasoline, the sulfur compound distribution was analyzed by GC-SCD (Agilent 7890A, with a varian 3800 column, 30 m × 0.32 mm × 0.2 μm; temperature program: 50 °C for 1 min-temperature rising 5 °C/min to 280 °C), and sulfur content was determined by sulfur and chlorine analyzer (Taizhou Guochang Analytical Instruments Co. Ltd.). The sulfur compound distribution in oil and DES phase was analyzed by HPLC (Shimadzu LC-20A, wavelength 242 nm for 3-MT; CH_3OH: H_2O = 6:4; flow rate = 1 ml/min).

3. Results and discussion

3.1. Factors influencing the conversion of 3-MT

The molar ratio of $AlCl_3$ to acetamide and urea, mass ratios, reaction time and temperature, were discussed.

The effect of molar ratio of $AlCl_3$ to acetamide or urea is illustrated in Fig. 1a. The conversion of 3-MT was increased with the $AlCl_3$ ratio increasing at the beginning and then trend to flat. But the conversion of 1-hexene keeps the increasing trend. The highest conversation of 3-MT were 97.31% and 93.69% respectively at $AlCl_3$/acetamide or urea ratio of 1.8. So a suitable molar ratio of $AlCl_3$ to acetamide or urea is suggested to be 1.8:1.

The effects of different $AlCl_3$ molar ratios on the catalytic performance of the DESs are shown in Fig. 2, the acidity of DESs with different $AlCl_3$ molar ratio was determined by FI-IR using acetonitrile as probe molecules [21]. Pure acetonitrile has two characteristic CN stretching bands at 2252 cm^{-1} (band 1) and 2291 cm^{-1} (band 2). Acetonitrile added with DESs has a new band (band 3) appearing at about 2300 cm^{-1}, which proves that the DESs is Lewis acid [21]. When the molar ratio of $AlCl_3$ to acetamide is 1:1 (1.0$AlCl_3/CH_3CONH_2$), $AlCl_4^-$ is the main Al species and there is no Lewis acidity due to the absence of band 3 [22]. Increasing the molar ratio of DESs led that bands 1, 2, and 3 all shifted to higher wavenumbers, especially for the band 2. Because the strong acid $Al_2Cl_7^-$, was formed to improve activity of the catalyst. Similar shifts were also observed for the urea based liquid.

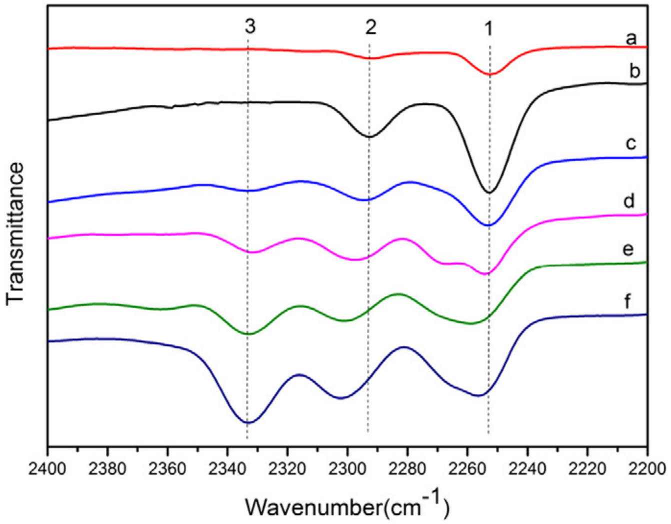

Fig. 2. FT-IR spectra of $AlCl_3/CH_3CONH_2$ using acetonitrile as an acidity probe: (a) pure acetonitrile, (b) 1.0$AlCl_3/CH_3CONH_2$, (c) 1.4$AlCl_3/CH_3CONH_2$, (d) 1.8$AlCl_3/CH_3CONH_2$, (e) 2.0$AlCl_3/CH_3CONH$, (f) 2.2$AlCl_3/CH_3CONH$.

Fig. 1b shows that 3-MT conversion increases with catalyst amount until 6%. From Fig. 1c, it is indicated that the conversion of 3-MT reach the highest with the time increasing to 40 min. From Fig. 1d, it can be

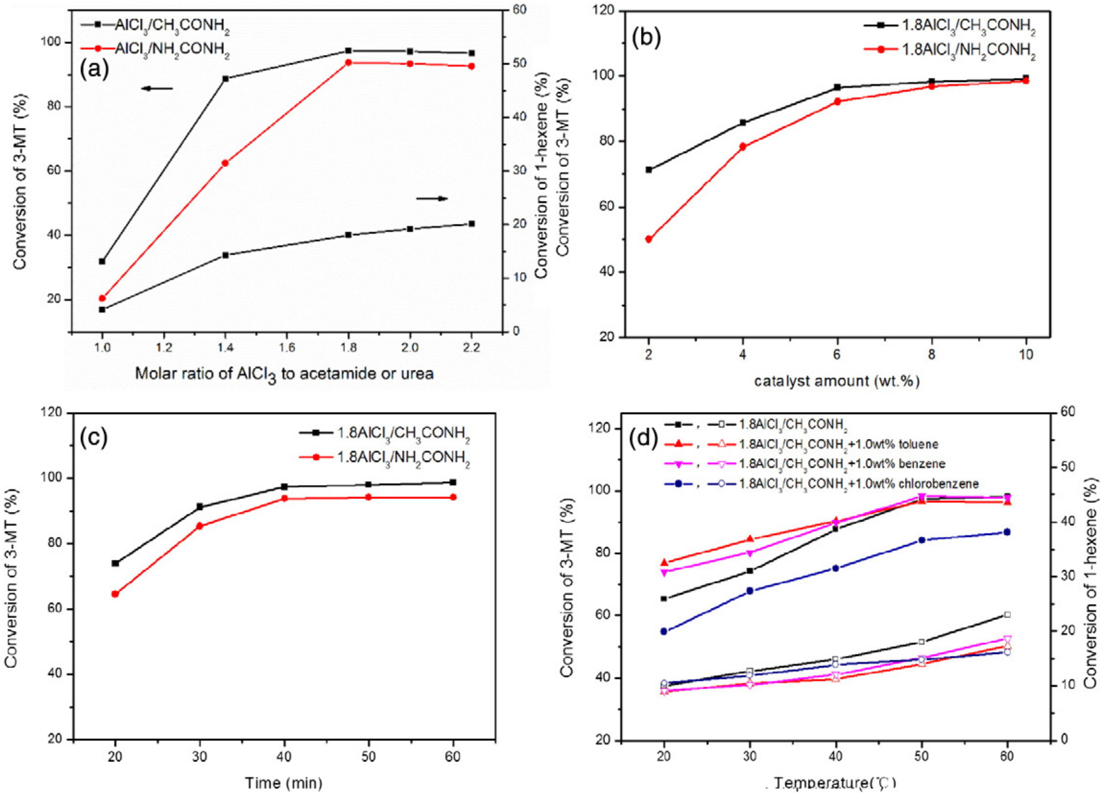

Fig. 1. The effect of (a) molar of $AlCl_3$, (b) catalyst amount, (c) reaction time, (d) temperature. Typical reaction conditions: 1.8$AlCl_3/CH_3CONH_2$ and 1.8$AlCl_3/NH_2CONH_2$, 6 wt.%, 50 °C, 40 min.