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Isobutane alkylation with 2-butene catalyzed by amide- AlCl_3 -based ionic liquid analogues

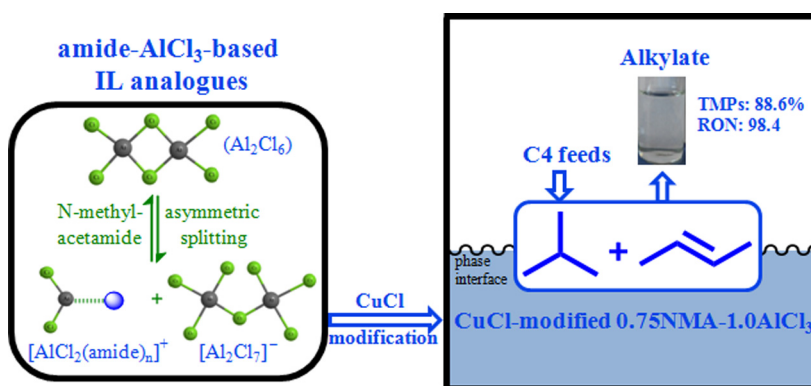
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HIGHLIGHTS

- 0.75NMA-1.0 AlCl_3 IL analogue was an efficient catalyst for isobutane alkylation.
- CuCl modification improved greatly both the catalytic performance and the quality of alkylate.
- C8 selectivity, TMPs/DMHs ratio and RON in semicontinuous mode reached 94.65 wt%, 14.98 and 98.40, respectively.
- C8 selectivity, TMPs/DMHs ratio and RON in batch mode reached 84.10 wt%, 14.86 and 96.54, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkylate is an ideal blending component for motor gasoline. The alkylation of isobutane with 2-butene to produce high-quality alkylate was catalyzed by several amide- AlCl_3 -based ionic liquid (IL) analogues with different structures and CuCl modification. The influences of the amide structure, amide/ AlCl_3 molar ratio, and CuCl modification on the catalytic performance were investigated in an autoclave operated in semicontinuous mode. Results showed that the *N*-methylacetamide- AlCl_3 -based IL analogue (molar ratio of *N*-methylacetamide to AlCl_3 was 0.75, marked as 0.75NMA-1.0 AlCl_3) with bidentate coordination and low viscosity was an efficient catalyst for isobutane alkylation. Furthermore, CuCl modification further enhanced the catalytic performance of 0.75NMA-1.0 AlCl_3 . The selectivity of C8 increased from 76.18 wt% to 94.65 wt%, in which the molar ratio of trimethylpentanes to dimethylhexanes (TMPs/DMHs ratio) and the research octane number (RON) of alkylate reached up to 14.98 and 98.40, respectively. The effects of reaction conditions on the alkylation performance were investigated in an autoclave operated in batch mode. The results indicated that the alkylation of isobutane with 2-butene catalyzed by CuCl-modified 0.75NMA-1.0 AlCl_3 was a short-time and fast reaction. The optimal reaction temperature, reaction time, stirrer speed, and isobutane/2-butene molar ratio were 15 °C, 30 s, 1500 r/min, and 100:1, respectively. Under these optimal reaction conditions, the selectivity of C8, TMPs/DMHs ratio, and RON were 84.10 wt%, 14.86, and 96.54, respectively.

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1. Introduction

Gasoline quality upgrading is a hot topic today as environmental protection has attracted more attention. The alkylate obtained from isobutane alkylation has the characteristics of high octane number, low vapor pressure, and low contents of sulfur, olefins, and aromatics, which are excellent blending components for clean motor gasoline [1,2]. Concentrated sulfuric acid and hydrofluoric acid are widely used for commercial isobutane alkylation. However, severe corrosion, difficult acid sludge treatments, and difficult safety protection restrict their potential development [3,4]. Therefore, many studies are now focused on the development of catalysts that are less hazardous, more effective, and environment-friendly. Solid acid catalysts with good catalytic activity and selectivity are considered to be potential alternatives to eliminate the aforementioned drawbacks associated with the traditional alkylation of catalysts. However, solid catalysts have still not caught on as alkylation catalysts because of the fast catalyst decay and high capital cost for regeneration [5,6].

Lewis acidic chloroaluminate ionic liquids (ILs) in the homogeneous biphasic regime were used as a more sustainable alternative for isobutane alkylation because of the possibility of acidity control and the unique physicochemical properties [7,8]. Chauvin et al. [9] reported isobutane alkylation with 2-butene catalyzed by the imidazolium chloroaluminate IL, and determined that the conversion of 2-butene reached 91.0%, the selectivity of C8 was 50.5%, and the selectivity of trimethylpentanes (TMPs) was less than 10%. Subsequently, various imidazolium and pyridinium ILs have been investigated as catalysts for isobutane alkylation by Tang et al. [10], Yoo et al. [11], Kumar et al. [12], and Bui et al. [13]. Our research group developed a composite IL, which was a kind of chloroaluminate IL modified with CuCl that showed excellent catalytic performance, to improve the selectivity of C8 and TMPs further [7]. Moreover, Huang et al. [14] reported that the imidazolium ILs with SbF_6 anion as buffer agents could significantly improve the catalytic lifetime of concentrated sulfuric acid twofold. Although the recycling of ILs is implemented, traditional imidazolium and pyridinium chloroaluminate ILs are unsuitable for large-scale applications because of their high cost, poor biodegradability, and complex preparation.

Less investigated alternatives are IL analogues prepared by metal halides with donor molecules. As a new type of liquid catalyst, IL analogues have attracted significant research attention because of their tunable Lewis acidity and high catalytic activity. Abbott et al. [15–17] reported that AlCl_3 underwent asymmetric splitting to form IL analogues with metal-containing anions and cations in the presence of amides. Subsequently, Coleman et al. [18] determined that amide- AlCl_3 -based IL analogues were a mixture of anionic, cationic, and neutral complexes in equilibrium through Raman and NMR spectroscopies. Matuszek et al. [19] and Hogg et al. [20] determined that amide- AlCl_3 -based IL analogues with the same amide/ AlCl_3 molar ratio exhibited better activity and selectivity than traditional chloroaluminate ILs in the oligomerization of α -olefins and the Friedel-Crafts alkylation of benzene.

Our research group observed that the amide structure and amide/ AlCl_3 molar ratio influenced the asymmetric splitting degree of AlCl_3 and that the acidity of amide- AlCl_3 -based IL analogues depends on the amide structure and the amide/ AlCl_3 molar ratio [21]. By contrast, the active Lewis acidic species in chloroaluminate ILs is only Al_2Cl_7 , and only its concentration can be adjusted. Therefore, amide- AlCl_3 -based IL analogues provide a greater scope for adjusting acidity compared with chloroaluminate ILs [22]. Furthermore, amide- AlCl_3 -based IL analogues not only have the characteristics and properties that are similar to ILs but are also superior to traditional chloroaluminate ILs given their low cost, easy preparation, and less moisture sensitivity [23].

Amide- AlCl_3 -based IL analogues were applied as catalysts in isobutane alkylation with 2-butene to explore the applications of amide- AlCl_3 -based IL analogues in catalysis reaction further. In the current study, several amide- AlCl_3 -based IL analogues with different structures and CuCl modification were used as safer and economical catalysts, and their catalytic performances were compared with those of traditional chloroaluminate ILs. The influences of the amide structure, amide/ AlCl_3 molar ratio, and CuCl modification on the catalytic process were investigated together with the influence of reaction conditions on the catalytic performance.

2. Experimental

2.1. Materials and instruments

All reagents were used as received without further treatment unless stated otherwise. Acetamide (AA; 99.5%), *N*-methylacetamide (NMA; 99.5%), *N,N*-dimethylacetamide (DMA; 99.5%), *N*-methylformamide (NMF; 99.5%), triethylamine hydrochloride (Et_3NHCl ; 99.5%), anhydrous AlCl_3 (99.5%), and CuCl (99.5%) were purchased from Aladdin Chemistry Company. Isobutane and 2-butene were obtained from a commercial alkylation unit. The feedstock in the alkylation experiments was obtained by blending isobutane and 2-butene at various molar ratios. Then, the feedstock was dried by a molecular sieve to ensure that the water content was less than 10 mg/L. The composition of the feedstocks at different isobutane/2-butene molar ratios (I/O molar ratios) are shown in Table S1. Gas chromatography (GC) spectra were recorded on an Agilent 7890B Gas Chromatograph with PONA capillary column ($50\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The qualitative analysis was conducted based on the holding time of the peak, whereas the quantitative analysis was conducted through the area normalization method.

2.2. Synthesis of IL analogues

IL analogues with different amide/ AlCl_3 molar ratios were prepared in a glovebox under N_2 protection. The synthesis of 0.65AA-1.0 AlCl_3 was used to describe the general procedure for the synthesis of the amide- AlCl_3 -based IL analogues. 0.65AA-1.0 AlCl_3 was synthesized in a 250 mL two-necked flask placed in a thermostatic oil bath equipped with a stirrer. Anhydrous AlCl_3 (26.68 g, 0.2 mol) was placed in the flask; then, AA (7.68 g, 0.13 mol) was added slowly while stirring for 30 min. The mixture was then heated to 80 °C and maintained at that temperature until all solids “dissolved” (approximately 4 h). The method used to modify the structure of amide- AlCl_3 -based IL analogues with CuCl was similar to the patent application US20040133056A1 [24]. The viscosity range of different amide- AlCl_3 -based IL analogues was between 60 cp and 150 cp at temperature of 15–30 °C. All amide- AlCl_3 -based IL analogues were maintained free from moisture.

2.3. Alkylation apparatus and procedure

Isobutane alkylation with 2-butene was conducted in a 600 mL stirred autoclave, as shown in Fig. 1. The experiments for the selection of amide- AlCl_3 -based IL analogues was conducted in semicontinuous mode. The semicontinuous mode procedure was as follows: the autoclave with the added amide- AlCl_3 -based IL analogues (150 mL) was sealed and controlled to a set temperature, after which the stirrer was started. Approximately 400 mL of feedstock was directly pumped into the autoclave at a flow rate of 750 mL/h. After completion of the pumping feedstock, the stirring was stopped. The alkylate was instantly collected using the sam-

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