

## Interfacial Behaviors of Isobutane Alkylation with 2-butene Catalyzed by Sulfuric Acid/Sulfonic-acid-functionalized Ionic Liquid

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### Highlights

- Effects of the concentration of SFIL on interfacial behaviors were investigated.
- Solubility of reactants at interface was improved by SFIL with increased concentration.
- Stronger self-aggregation of the cations at interface with increased concentration of SFIL.
- The optimal mass ratio of SFIL to catalysts is 10 %.

### 1. Introduction

Ionic liquids (ILs), also called room temperature ionic liquids (RTILs), are a class of organic salts that are liquid at near room temperature. Recently, ILs have attracted significant attention because of their unique properties, such as negligible vapor pressure, high chemical, thermal, and photocatalytic stability, nonflammability, and thus become good alternatives to traditional liquid solvents and catalysts.<sup>1</sup> In particular, the ILs have been widely investigated in the C4 alkylation, because the alkylate, produced by the C4 alkylation, a desirable blending component for high quality gasoline.<sup>2</sup> Currently, the alkylation processes for commercial importance still rely heavily on either sulfuric or hydrofluoric acid as catalyst, although the 120 kt/a composite ionic liquid alkylation (CILA) unit has realized industrialization in China. However, the equipment corrosion, high acid consumption, safety, and environmental issues related to the disposal of spent acid are still challenges to overcome.<sup>3</sup> To cope with these problems, the sulfonic acid functionalized BILs (SFILs) was used to improve the catalytic activities, as well as the stability of the sulfuric acid, which showed an excellent catalytic performance with the selectivity of C8-alkylate more than 75.7%, the RON up to 95.66 and, more importantly, the reusability up to 24 runs, outclassing the pure H<sub>2</sub>SO<sub>4</sub>. Actually, the SFIL acts as a surfactant which can improve the acid/hydrocarbon interfacial properties and further enhance the catalytic activities of sulfuric acid, due to the fact that the C4 alkylation catalyzed by sulfuric acid is a typical liquid/liquid interfacial reaction.<sup>4</sup> However, there is still little information about the interfacial properties between the reactant hydrocarbons and the binary catalyst mixtures, especially the effect of the concentration of SFIL. So, in this work, the molecular dynamics simulation was used to probe the interfacial behaviors involving the SFIL/H<sub>2</sub>SO<sub>4</sub>-catalyzed C4 alkylation.

### 2. Methods

Molecular dynamics (MD) simulation was conducted at 300 K and 1 atm using GROMCS software with the OPLS-AA force field describing the interaction between different species. The simulation boxes were built with the reactant mixtures placed in both sides and the sulfuric acid in the middle, and the SFIL, [C<sub>8</sub>PSIm][HSO<sub>4</sub>] was located at the gap between the reactants and sulfuric acid, as shown in Figure 1. The 40 ns NPT was run to equilibrate these boxes and the last 5 ns was used for collecting data.

### 3. Results and discussion

From Figure 2, it is clear that SFIL shows no obvious improvement on the dissolution of reactants in the sulfuric acid, when its mass fraction increases from 2 % to 6 %. However, the dissolution of reactants in H<sub>2</sub>SO<sub>4</sub> can be obviously facilitated by the increasing mass fraction of SFIL from 6 % to 15 %. Moreover, the cations of the SFIL tend to self-aggregate at the interface between the hydrocarbons and H<sub>2</sub>SO<sub>4</sub>. The self-aggregation of the cations is beneficial for the catalytic activity of the H<sub>2</sub>SO<sub>4</sub>. From Figure 3, the alkylation experimental results show that the optimal mass ratio of [MPSIm][HSO<sub>4</sub>] to catalysts is 10 % since the

selectivity of C8 and RON reach the highest value, which agrees well with the solubility trend in Figure 2. It should be noted that when the mass fraction of SFIL in the  $H_2SO_4$  is more than 10 %, and the acidity of  $H_2SO_4$  will be probably too low to obtain the high quality of the alkylate.

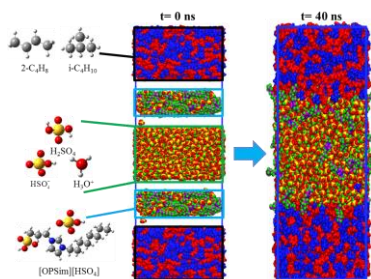


Figure 1. Optimized molecular structures and simulated systems.

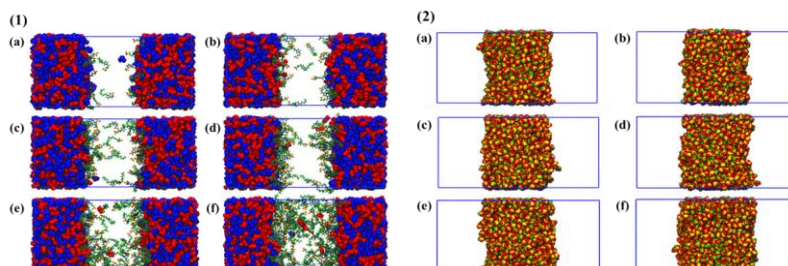


Figure 2. Equilibrated snapshots of MD simulation. Mass fraction of SFIL to catalysts: (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10%, (f) 15%. Where (1) represents  $2C_4$ ,  $iC_4$ , and cations; (2) represents  $H_2SO_4$ .

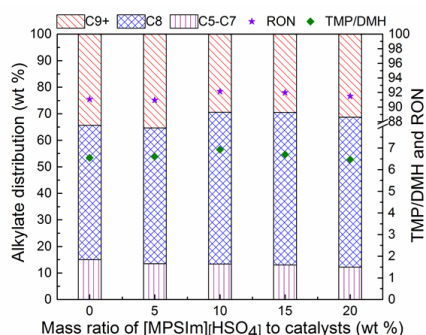


Figure 3. Effect of the mass ratio of  $[MPSIm][HSO_4]$  to catalysts on the alkylate products.

#### 4. Conclusions

From the MD simulation, the increasing mass fraction of SFIL can obviously enhance the dissolution of reactants both in the bulk and at interface, which agrees well with the experimental result. There is a significant density enrichment for both of the cations and the alkyl groups at the interface, indicating a strong self-aggregation of the cations at interface. This self-aggregation of the cations is beneficial for the dissolution of the reactants. The useful information that the MD simulation provides can be used in better design and optimization of the alkylation processes.

#### References

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#### Keywords

C4 alkylation; SFIL; Molecular dynamic simulation; Interfacial properties.

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