

Mesoscale Modeling of Interfacial Behaviors between Hydrocarbons and Catalyst: Alkylation of Isobutane with 2-butene Catalyzed by Sulfuric Acid/Brønsted Acidic Ionic Liquid

Weizhong Zheng, Ling Zhao, Weizhen Sun*

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

*Corresponding author: sunwz@ecust.edu.cn

Highlights

- Interfacial behaviors of BILs enhanced C4 alkylation were studied.
- Solubility of reactants at interface was enhanced by BILs with longer alkyl groups.
- There is a significant self-aggregation of the cations at the interface.
- The interfacial diffusion of reactants decreases with the prolonged alkyl groups.

1. Introduction

Automotive exhaust emissions become significant sources of air pollution, which has aroused concerns worldwide. Accordingly, the gasoline upgrading is forced to develop into a more clean-burning direction, such as elimination of lead, limited amount of olefins and sulfur, reduced content of aromatics and increase of oxygenates. Due to the advantages of high octane number, low vapor pressure, and zero content of olefins and sulfur, the alkylate produced by the alkylation of isobutane with C4 olefins is a desirable blending component for high quality gasoline.¹ Although the alkylation processes for commercial importance use either sulfuric or hydrofluoric acid as catalyst, both of them suffer from fatal drawbacks.²

In recent years, ionic liquids (ILs) have drawn considerable attentions for their applications in C4 alkylation owing to their chemical stability, negligibly low vapor pressure, and Brønsted and Lewis acidity.³ As a dual solvent-catalyst, Brønsted acidic ionic liquids (BILs) can enhance obviously the catalytic activities of sulfuric acid, when used as a co-catalyst with the sulfuric acid.⁴ In particular, the sulfonic acid functionalized BILs (SFILs) not only can improve the catalytic activities, but also can enhance greatly the stability of the sulfuric acid. Actually, the BILs act as a surfactant which can improve the acid/hydrocarbon interfacial properties and further enhance the catalytic activities of sulfuric acid, because C4 alkylation catalyzed by sulfuric acid is a typical liquid/liquid interfacial reaction. However, it is difficult to detect the interfacial properties using experimental methods. Alternatively, the molecular dynamics simulation is proved to be a proper tool to probe the interfacial behaviors involving the C4 alkylation.

2. Methods

Molecular dynamics 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. The BILs, including sulfonic-acid functionalized ILs ($[C_nPSIm][HSO_4]$ ($n=4, 6, \text{ and } 8$)) and non-functionalized ILs ($[C_nMIm][HSO_4]$ ($n=3, 4, 6, \text{ and } 8$)) with different length in alkyl chains, were located at the gap between the reactants and sulfuric acid. 30 ns NPT was run to equilibrate these boxes and the last 5ns was used for collecting data.

3. Results and discussion

From Figure 1, it is clear that BILs can obviously facilitate the dissolution of reactants in the sulfuric acid. Moreover, the BILs with the longer alkyl groups can enhance the higher solubility of reactants than that with the shorter alkyl groups, which is beneficial for the catalytic activity of H_2SO_4 . From Figure 2, the mole fractions of the reactants in the bulk and at the interface increase as the length of alkyl groups increases,

which agree well with the solubility trend in Figure 1. However, as shown in Figure 3, the interfacial diffusion of reactants decreases with the prolonged alkyl groups which is unfavorable for the C4 alkylation.

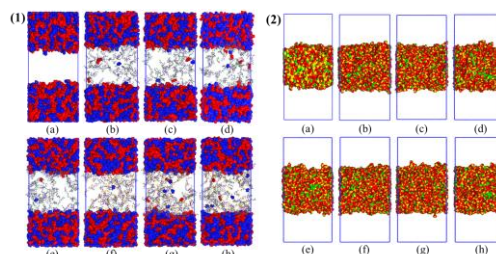


Figure 1. Equilibrated snapshots of MD simulation. (a) H_2SO_4 , (b) [PM.], (c) [BM.], (d) [HM.], (e) [OM.], (f) [PSM.], (g) [OSM.], (h) [OPS.].

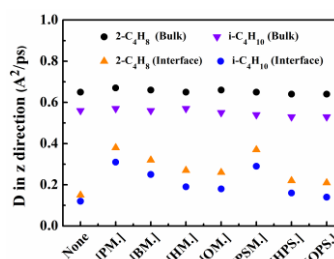
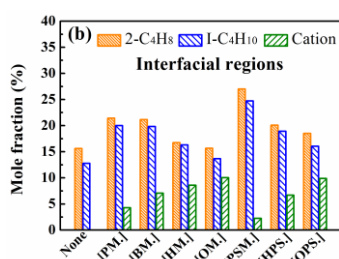


Figure 2. Bulk and interfacial composition of different systems.

Figure 3. interfacial diffusion of reactants in different systems

4. Conclusions

The BILs with longer alkyl groups can obviously enhance the dissolution of reactants both in the bulk and at interface, and the longer alkyl groups of the cations are responsible for the enhanced dissolution behavior. 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. In addition, the interfacial diffusion of reactants decreases with the prolonged alkyl groups. The useful information that the MD simulation provides can be used in better design and optimization of the alkylation processes.

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Keywords

C4 alkylation; Brønsted acidic ionic liquids; Molecular dynamic simulation; Interfacial properties.

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