

Structure-Activity Relationship Studies on Ionic Liquids Catalyzed Cyclotrimerization of Propanal

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Brønsted acidic ionic liquids (BAILs) are excellent catalysts for the cyclotrimerization of propanal. In order to explore the actual rule of the ionic liquids catalysts, the interactions between propanal molecule and three BAILs from molecule level by means of density functional theory were carried out. It is interesting to find that the stronger of the interaction, the easier for propanal to be activated.

Introduction

Cyclotrimerization of aldehydes is generally catalyzed by Brønsted or Lewis acids and other catalysts such as heteropolyacids, etc. However, many of these catalysts suffer from one or more limitations such as corrosion of equipment, tedious isolation of catalyst-product. Hence, the development of highly efficient and environmental friendly catalysts for the reaction is still highly desired. Recently, Brønsted acidic ionic liquids (BAILs) have been exploited successfully as catalysts for cyclotrimerization reactions and have received effective results [1,2]. Based on our previous studies on cyclotrimerization of aldehydes catalyzed by BAILs, in order to better understand the behavior of BAILs, herein the structure-activity relationship and the interactions between propanal molecule and ionic pairs of three BAILs were explored.

Experimental

The BAILs used in this article (Fig. 1) were synthesized according to the method described in the literature [3-5]. The structures and purities were all characterized by NMR and FT-IR.

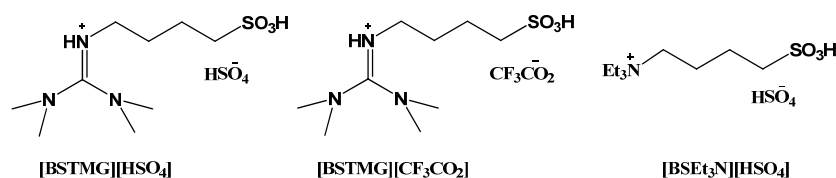


Fig.1. Structures of ionic liquids used in this study.

The cyclotrimerization reaction was carried out in a glass flask equipped with stirrer and temperature controller. A small amount of samples were taken out from the reactor at regular intervals and analyzed with 7890 GC analyzer (Agilent) equipped with a FID detector.

All calculations in our study were performed using the Gaussian 09 program [6]. All the geometries were optimized at B3LYP/6-31G (d,p) level.

Results and discussion

Fig. 2 A shows the effects of different BAILs catalysts on the initial reaction rate. As high as 80% propanal conversion was obtained in the 100 min for [BSEt₃N][HSO₄]. [BSTMG][HSO₄] gave a moderate conversion of 60% in the same time. However the activity of [BSTMG][CF₃CO₂] was very poor.

It is well known that the activity of an acidic catalyst relies heavily on its acidity. As reported in the literature [7], using pyridine as a probe molecule the Brønsted acidity of an ionic liquid could be characterized. Judged by the intensity of the absorption peak at 1540 cm⁻¹, we can conclude from Fig.2 B that the Brønsted acid amounts of BAILs follow the trend:

$[\text{BSEt}_3\text{N}][\text{HSO}_4] > [\text{BSTMG}][\text{HSO}_4] > [\text{BSTMG}][\text{CF}_3\text{CO}_2]$, which is in good agreement with their catalytic activities in cyclotrimerization of propanal.

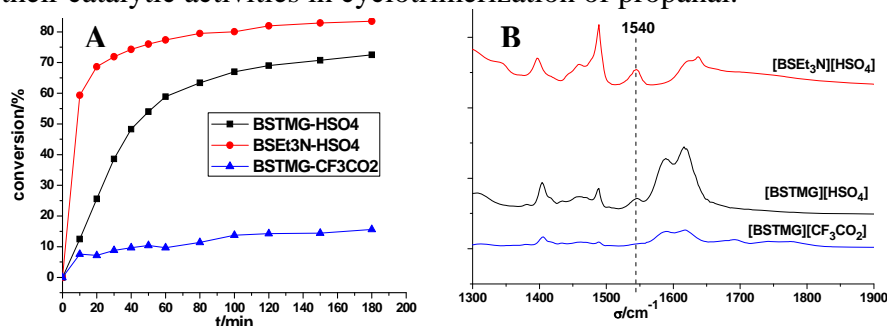


Fig. 2. A) Cyclotrimerization of propanal to compare the efficiency of different BAILs; B) FT-IR spectra of ionic liquids with pyridine as probe molecule.

The catalytic activity of BAILs was theoretically studied by computing the interaction between the three BAILs and propanal. Fig. 3 shows the optimized geometries for the BAILs-propanal complexes. It could be found that the interactions between $[\text{BSTMG}][\text{CF}_3\text{CO}_2]$ and propanal are very weak with the longer distance between acidic H1 and O13. So it is hard for propanal to be activated by $[\text{BSTMG}][\text{CF}_3\text{CO}_2]$. The carbonyl group of propanal strongly interacts with the acid protons of $[\text{BSTMG}][\text{HSO}_4]$ and $[\text{BSEt}_3\text{N}][\text{HSO}_4]$ with $\text{H4}\cdots\text{O13}$ of 1.676 Å and $\text{H3}\cdots\text{O13}$ of 1.587 Å respectively, which reveals that $[\text{BSTMG}][\text{HSO}_4]$ and $[\text{BSEt}_3\text{N}][\text{HSO}_4]$ can transfer H to propanal to form the active carbonium ion.

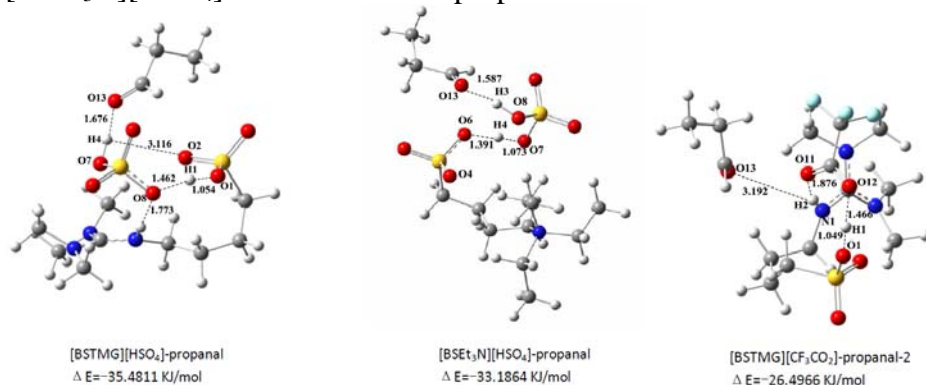


Fig. 3. Optimized geometries for the BAILs-propanal complexes.

Conclusions

With the aid of FT-IR and DFT, we explored the structure-activity relationship of three BAILs in cyclotrimerization of propanal and we found that the activities of BAILs and their structures, acidities and interactions are highly correlative.

Acknowledgements

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