



Short Communication

Dual catalytic function of 1,3-dialkylimidazolium halide ionic liquid on the dehydration of fructose to 5-hydroxymethylfurfural

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ABSTRACT

In the fructose dehydration to 5-hydroxymethylfurfural (HMF) in dimethyl sulfoxide, the catalytic function of 1,3-dialkylimidazolium-based ionic liquids with different counter-anions was investigated. It was found that the effects of alkyl chain length and additional alkyl group in Cl-containing ionic liquids were negligible whereas the activity of 1-butyl-3-methylimidazolium-based ionic liquids was considerably changed by varying the anion (particularly, halide ions). The latter finding was confirmed by the control experiment result that the addition of KBr or Ca(CH₃COO)₂ dramatically tuned the catalytic activity of 1-butyl-3-methylimidazolium chloride. From these results and the proposed reaction pathway, it was consequently believed that 1,3-dialkylimidazolium halide contained the dual catalytic function to act as both Brønsted acid and nucleophile for the fructose dehydration to HMF.

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1. Introduction

In order to reduce the dependence of fossil fuels as well as to limit global warming caused by emission of greenhouse gasses, it is worthwhile developing highly energy-efficient conversion of cellulosic biomass into renewable liquid fuels and chemicals [1–3]. Among a variety of biomass-derived chemicals, 5-hydroxymethylfurfural (HMF) is a key intermediate to produce high energy-content fuels (e.g., 2,5-dimethylfuran) [4] and chemicals (e.g., 2,5-furandicarboxylic acid as a replacement of terephthalic, isophthalic and adipic acids) [5]. Thus, a great deal of attention has been paid to the dehydration of fructose using efficient catalytic systems coupled with a downstream separation process [6–9].

Since the dehydration reaction proceeds under an acidic condition, common mineral acids (H₂SO₄, H₃PO₄ and HCl) and solid acids (ion-exchange resins, sulfated zirconia, etc.) are used in many previous studies [6]. In recent years, various ionic liquids (ILs) have been applied for the dehydration of sugars, where ILs are utilized as a small amount of catalyst and/or a reaction medium [10–16]. Furthermore, the report of Zhang and coworkers [17] stimulated numerous studies to address ILs' potential for the production of HMF, and also opened the attempt to search for new solvents that can replace ILs due to their high cost. As an example, Binder and Raines [16] reported that

N,N-dimethylacetamide (DMA) containing LiCl (DMA–LiCl) was as effective as 1-ethyl-3-methylimidazolium chloride for HMF synthesis.

Taking a glance at recent results regarding the conversion of fructose to HMF, we wondered the detailed reaction pathway on the fructose-to-HMF conversion using imidazolium-based ILs as a catalyst. As an acidic contribution to the reaction, the proton in imidazolium cations has a well-known Brønsted acidity. Nevertheless, several ILs with more and/or higher acidic characters have been developed in order to increase the reaction rate; for example, Moreau et al. [18] reported that 1-H-3-methylimidazolium chloride produced HMF in a yield of 92% within 15–45 min. On the other hand, previous studies were also conducted to vary ILs' anionic counterpart, where its nucleophilicity was adjusted or additional acidity was introduced. In the report by Binder and Raines [16], the effect of halide ions on the synthesis of HMF from fructose was intensively investigated with H₂SO₄ and imidazolium-based ILs being the catalyst and the additive, respectively. Despite these abundant results, alkylimidazolium-based ionic liquids may have intrinsic dehydration activities. In other words, ILs' constituents, cation and anion, may have each specific contribution to the fructose dehydration reaction.

Thus, the present work has been focused on revealing the catalytic capability of imidazolium-based ionic liquids on the dehydration of fructose to HMF. For comparison, Nafion NR50, acetic acid and CaCl₂ were used as a catalyst. Then, the effect of chloride-containing cations with different hydrocarbon substituents attached to the imidazolium ring was investigated for the reaction. In addition, the effect of the anion of imidazolium-based ILs was determined with Cl[−], Br[−], BF₄[−], PF₆[−], CH₃SO₄[−] and acetate (OAc[−]). To confirm the anion's effect, the

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