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Conversion of glucose into 5-hydroxymethylfurfural with boric acid in molten mixtures of choline salts and carboxylic acids

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ABSTRACT

The conversion of glucose into a potential platform chemical for fuels and plastics, 5-hydroxymethylfurfural (HMF), has been studied using B(OH)₃ as a promoter in different solvents, namely molten mixtures made of choline salts and carboxylic acids, with the aim of developing an inexpensive and less harmful alternative to Cr/ionic liquid systems. Choline chloride-based molten mixtures afforded poor yields of HMF, whereas the yields were improved by replacing choline chloride with choline dihydrogen citrate. The combination of choline dihydrogen citrate and glycolic acid was the best choice, providing an HMF yield of ~60% at 140 °C within 4 h by adding a small volume of water as a co-solvent.

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1. Introduction

Global concern about dwindling petroleum resources has prompted researchers to seek alternatives. In this context, 5-hydroxymethylfurfural (HMF) has attracted growing interest because it can be produced from biomass feedstocks and further converted into fuels and polymer materials [1,2]. The HMF production is typically based on the high-temperature acid-catalyzed dehydration of fructose, which can be produced by aldose-ketose isomerization of glucose [2,3]. Recent

molecular dynamics simulation studies showed another possible pathway, in which HMF is formed by the direct acid-catalyzed transformation of glucose via a furan aldehyde intermediate without the formation of fructose [4,5]. Glucose is an abundant building block of plant biomass components, e.g., cellulose and starch.

Although fructose can be readily converted into HMF, the direct conversion of glucose in high yields of HMF is difficult [2,3,6]. Recently, Zhao and colleagues have found that CrCl₂ added to an ionic liquid, 1-ethyl-3-methylimidazolium chloride, can serve as a highly and uniquely effective promoter,

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leading to an impressive (~70%) yield of HMF from glucose [7]. The proposed mechanism involves the formation of Cr-glucose intermediate species to facilitate the isomerization of glucose to fructose, followed by the dehydration into HMF. A more recent report pointed out that Cr(II) in the reaction system can readily be oxidized to Cr(III) to be the active species [8]. Chromium/ionic liquid systems can afford a higher (~90%) yield of HMF with the aid of microwave irradiation [9] or simultaneous extraction of the product HMF [10]. Ionic liquids have favorable properties for the glucose conversion, *i.e.*, high boiling point and unique solvating power towards not only ions but also cellulose [6]. The former property is essential for the high-temperature reaction and the latter is promising for the seamless connection of cellulose saccharification and HMF production. However, challenges still remain. Several attempts have been made to develop Cr-free methods as less harmful alternatives, though most of them required heavy metals, *e.g.*, SnCl₄ (61%) [11], ZrO₂ (53%) [12], GeCl₄ (48%) [13], HfCl₄ (35%) [14], and Yb(OTf)₃ (24%) [15], or pyrophoric AlEt₃ (51%) [16] (HMF yield in parentheses). The high cost of ionic liquids is another problem. Examples of alternatives include compressed water-carbon dioxide mixtures, which have recently been applied to the high-temperature autohydrolysis processing of lignocellulosic feedstock [17].

The present study was undertaken to develop an inexpensive and less harmful alternative to Cr/ionic liquid systems. Inexpensive molten mixtures made of choline salts and carboxylic acids were examined as solvents in the present study. In 2004, Abbott and colleagues have reported that simply mixing choline chloride with common carboxylic acids led to deep depression of the melting points, affording liquids which possessed physical properties similar to those of conventional ionic liquids [18]. By replacing carboxylic acids with ZnCl₂ [19] or urea [20], choline chloride-based molten mixtures were applied to the chemical modification of hydroxyl groups of cellulose. The application to the electrolytic coating of metallic materials was also reported [21]. Molten mixtures of these types, however, have not been examined for the conversion of glucose into HMF. As an alternative promoter to Cr salts, B(OH)₃ was employed in the present study. As described above, the proposed mechanism for the Cr-promoted conversion of glucose into HMF involves the formation of Cr-glucose intermediate species, in which a five-membered chelate ring is formed. Sugars are well known to form borate complexes with a similar structure, hence we expected B(OH)₃ to serve as a promoter. Soon after the present study had started, B(OH)₃ in conventional imidazolium-based ionic liquids was reported to provide a moderate (~40%) yield of HMF from glucose [22]. More recently, the yield has been improved to ~50% by the combined use of B(OH)₃ and H₃PW₁₂O₄₀ [23].

The present paper describes a higher (~60%)-yield conversion of glucose into HMF by the sole use of a B(OH)₃ promoter in a choline salt-based molten mixture as an inexpensive and less harmful alternative to Cr/ionic liquid systems. For preparing the molten mixtures, choline chloride was used at the beginning of the present study but eventually replaced by choline dihydrogen citrate, as described later (Section 3.1). Although inexpensive and commercially available, choline dihydrogen citrate has not been examined for the preparation

of choline salt-based molten mixtures, and thus for the conversion of glucose into HMF, so far.

2. Materials and methods

Boric acid, benzoic acid, DL-malic acid, oxalic acid, salicylic acid, and methanesulfonic acid were purchased from Wako Jun-yaku (Osaka, Japan). Succinic acid and urea were purchased from Kishida Kagaku (Osaka, Japan). Glycolic acid, DL-mandelic acid, choline chloride, choline dihydrogen citrate, and choline bitartrate were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). These materials were dried at 140 °C for 90 min before use, except for urea (dried at 130 °C to prevent the decomposition). D-Glucose, D-fructose, and 5-hydroxymethylfurfural were purchased from Tokyo Kasei Kogyo. Ethylene glycol and dimethyl sulfoxide were purchased from Wako Jun-yaku. Water was purified with a Millipore (Billerica, MA, USA) Direct-Q 3 UV system.

A typical procedure (Entry 10 in Table 1) was as follows: Choline dihydrogen citrate (2.5 mmol, 738 mg), glycolic acid (2.5 mmol, 190 mg), and B(OH)₃ (2.0 mmol, 124 mg) were mixed in a test tube and heated on a dry bath at 140 °C to make the mixture melt. After cooling with running water, glucose (0.2 mmol, 36 mg) was added to the tube, which was subsequently capped with a stopper and heated on a dry bath at 140 °C for 2 h. In order to determine the HMF yield by high-performance liquid chromatography (HPLC), the tube was cooled with running water and the whole contents were diluted to 5.0 cm³ with water [with ultrasonic irradiation (38 kHz, 12 W), if a precipitate occurred]. Because of the high sensitivity, the solution was further (*e.g.*, 500-fold) diluted with water for the analysis by HPLC. The HPLC separation was performed on an Imtakt Unison UK-C18 column (75 mm × 2 mm) using water as an eluent. The spectrophotometric detection was made at 283 nm. A calibration graph was prepared using aqueous HMF solutions at μg cm⁻³ levels. For the determination of glucose and fructose, an Imtakt Unison UK-Amino column (250 mm × 3 mm) was used with an aqueous 80% (v/v) acetonitrile eluent. The sample to be injected was diluted 5-fold with acetonitrile and the detection was made by differential refractometry.

3. Results and discussion

3.1. Choice of choline salt and carboxylic acid

As described in Section 1, the present study started with the application of choline chloride-based molten mixtures as solvents. The HMF yields are summarized in Table 1. Although choline chloride (melting point, 305 °C) was completely melted even at 140 °C by mixing with carboxylic acids (except for benzoic acid), the HMF yields were disappointing (Entries 1–6). The reaction mixtures were strongly turbid and colored dark brown, which indicates the formation of humin. When the stopper was removed and a wet pH-test strip was placed on the top of the tube, the color of the strip changed sharply to indicate the presence of a strong acid, probably HCl. A large excess of the strong acid might induce the formation of

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