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Microwave-promoted conversion of concentrated fructose into 5-hydroxymethylfurfural in ionic liquids in the absence of catalysts

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ABSTRACT

Under microwave irradiation, concentrated fructose (33–92 wt%) in ionic liquids afforded 5-hydroxymethylfurfural in ca. 97–57% yields without addition of catalysts, within 3 min. *In-situ* ^{13}C NMR and ^{1}H NMR spectra suggest that the transformation of fructose in ionic liquid is a highly selective reaction that proceeds predominantly via the cyclic fructofuransyl intermediate. This method is expected to be valuable in facilitating cost-effective conversion of carbohydrates into biofuels and platform chemicals.

1. Introduction

Studies into cost-effective strategies to produce chemicals and transportation fuels from renewable resources, such as carbohydrates, have currently been increasing worldwide [1]. The platform compound 5-hydroxymethylfurfural (HMF) is a hexose dehydration product that can be further transformed into other chemicals, such as levulinic acid and 2,5-disubstituted furan derivatives, and is considered to be a key intermediate that bridges bio-based carbohydrate chemistry and petroleum based industrial organic chemistry [2]. For example, via selective hydrogenation, HMF could generate 2,5-dimethylfuran, which possesses excellent properties, including high energy density, high boiling point and water resistance, and has been proposed as a novel biofuel molecule [3]. Fructose is a naturally occurring, abundant C_6 sugar. Dehydration of fructose to HMF has received considerable attention, for example, in water, organic solvents, organic/water mixtures, supercritical fluids and ionic liquid (IL) systems [4]. However, additional catalysts are included in most of these processes, which may cause drawbacks in terms of product separation, catalyst recycling, equipment corrosion and environmental impacts, in addition to excessive costs. On the other hand, although many methods for improving HMF production have been published in the years, few of them have attempted the reaction at high substrate concentrations. A representative work by Valente and co-workers reported the dehydration of 10 wt% fructose in IL/organic solvent biphasic

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systems to give an 88% HMF yield and the successful recycling of ILs [5]. In the limited literatures available on high concentration fructose dehydration, moderate yields (54–70%) have been achieved at 20–50 wt% concentrations in two-phase catalytic systems [3,6]. Thus, developing a more efficient, catalyst-free strategy for HMF production from concentrated fructose remains important.

In this paper, we present an efficient strategy for selective production of HMF in ca. 97–57% yields from highly concentrated fructose (33–92 wt%) in ILs under microwave irradiation (MI) without addition of catalysts. This approach is a significant improvement to our efforts on biomass conversion and should be valuable to facilitate cost-effective conversion of biomass into biofuels and bio-based products.

2. Materials and methods

2.1. Materials and instruments

Fructose was purchased from Sigma (St Louis, USA), N-Methylimidazole (99%) was obtained from J&K Chemical Ltd. (Beijing, China). 1-Chlorobutane (98%) was purchased from ABCR Gmbh & Co. (Karlsruhe, Germany) and freshly distilled before use. All other chemicals were purchased from local suppliers and used without further purification. NMR spectra were measured with a Bruker DRX-400 spectrometer (400.3 MHz for ^{1}H, 100.6 MHz for ^{13}C). A WBFY-205 microwave reactor (Rating power 1100 W, rating output power 650 W, maximal input electric current 7.8 cA, working voltage 220 V, microwave frequency 2450 ± 50 MHz, lumen size 290 mm × 295 mm × 190 mm) was purchased from Gongyi City Yuhua Instrument Co. Ltd, China. A JASCO V-530 spectrophotometer was purchased from JASCO Inc., Japan. Quartz glass cells (light path length = 1.0 cm) were used in the spectrometer. The ionic liquids, 1-Butyl-3-methylimidazole chloride ([C_4mim]Cl), 1-butyl-3-methylimidazole bromide ([C_4mim]Br), 1-ethyl-3-methyl-imidazolium bromide ([C_2mim]Br), N-butyl pyridinium chloride ([C_4Py]Cl), 1-allyl-3-methylimidazolium chloride ([Amim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim]BF_4) and 1-butyl-3-methyl imidazolium hexafluorophosphate ([C_4mim]PF_6) were synthesized according to known procedures [7].

2.2. Typical procedure for fructose dehydration

A given amount of fructose was dissolved in [C_4mim]Cl (1.0 g) at 80 °C, the reaction mixture was then immediately subjected to microwave irradiation in a reactor at an appropriate power for a specific reaction time. Samples were withdrawn at the specified time, weighed (recorded as M_1, usually ca. 50 mg), quenched with cold water and subjected to HMF analysis. The HMF concentration was measured by absorbance at 282 nm using a standard curve method [8] (see in ESI). Alternatively, the entire reaction mixture was mixed with a minimal amount of silica gel, and purified by column chromatography (ethyl acetate: petroleum ether = 1: 10 to 1: 1) to afford HMF as a yellow oil-liquid, which was transformed to a yellow solid state upon storage at −20 °C ^{1}H NMR (400 Hz, $CDCl_3$): δ 9.70 (s, 1H), 7.35 (d, J = 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 4.84 (s, 2H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 178.2, 161.2, 152.8, 123.4, 110.5, 58.0. (Fig S2,S3) The isolated yields were in good agreement with those obtained spectrophotometrically at 282 nm.

2.3. In-situ NMR spectra detection

After 0.5 g fructose was dissolved in 1.0 g [C_4mim]Cl at 80 °C, the reaction mixture was transferred into an NMR tube (5 mm × 18 cm, NEW ERA) and heated in-situ to 130 °C for NMR detection. All the solution NMR spectroscopy experiments were performed using a DMSO capillary for the lock. ^{1}H and ^{13}C NMR spectra were acquired at 400.1 and 100.6 MHz, respectively. Their chemical shifts were referenced to tetramethylsilane (TMS).

3. Results and discussion

3.1. Preliminary study on fructose dehydration in IL under MI

Fig. 1 shows the preliminary results of fructose dehydration in ionic liquid [C_4mim]Cl under MI. After 0.1 g fructose was dissolved in 1.0 g [C_4mim]Cl at 80 °C, and the reaction mixture was irradiated at 80 W for up to 120 min. However, no HMF was detected based on spectrophotometric analysis at 282 nm, indicating that no reaction occurred (line 5). When the reaction was irradiated at 240 W for 6 min, the HMF yield reached 98% (line 4). A further increase in irradiation power to 400 W completed the reaction within 1 min with a similar HMF yield (line 3). In this case, the temperature of the reaction mixture reached 155 °C. If the irradiation power was higher than 400 W, an even faster fructose consumption, but lower HMF yield was obtained in addition to the formation of black humins (lines 1 and 2; both the conversion data are over

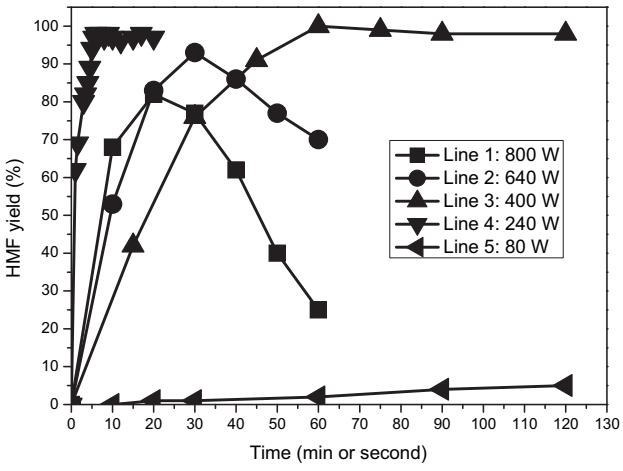

Fig. 1 – Influence of irradiation power on dehydration of fructose. Conditions: 0.1 g of fructose dissolved in 1.0 g of [C_4mim]Cl at 80 °C, then immediately submitted to microwave irradiation. For the reactions at 240 W and 80 W, time units are in minutes, for other reactions, time units are in seconds.