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Short communication

Green process for production of 5-hydroxymethylfurfural from carbohydrates with high purity in deep eutectic solvents

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ABSTRACT

5-Hydroxymethylfurfural (5-HMF) is one of the most important platform chemicals in biorefinery. In this work, an effective and green route for 5-HMF production in deep eutectic solvents (DESs) was demonstrated using extremely low concentration of hydrochloric acid as the catalyst. Moreover, the DES/acetonitrile (MeCN) biphasic reaction system adopted in this research showed excellent recyclability, which could be directly reused for multiple times without downgrading of the 5-HMF yield.

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1. Introduction

With the increasing concerns about energy crisis and environmental deterioration, it is imperative to find renewable alternatives to reduce the heavy reliance on fossil resources. Due to the renewability, extensive distribution and accessibility, biomass-derived carbohydrates have been studied as promising substitutes of fossil resources producing carbon-based fuels and chemicals (Huber et al., 2006; Stephanopoulos, 2007). Catalytic conversion of bio-based sugars into platform molecules is acknowledged as an effective way of utilizing biomass resource (Chheda et al., 2007; Cortright et al., 2002; Hu et al., 2012b). 5-Hydroxymethylfurfural (5-HMF), one of the most promising platform compounds, has been extensively studied for the synthesis of downstream furan derivates, levulinic acid (LA) and other value-added chemicals such as polymeric monomers and pharmaceutical intermediates (Girisuta et al., 2006b; Román-Leshkov et al., 2007; Zhao et al., 2007).

Currently, much efforts have been devoted to the efficient preparation of 5-HMF (Liu et al., 2015; Utami and Amin, 2013; Zhang et al., 2015). Fructose has been proved as an ideal feedstock for the synthesis of 5-HMF among all kinds of carbohydrates (Galkin et al., 2016; Moreau et al., 2006; Román-Leshkov et al., 2007, 2006), which can be dehydrated in monophasic or biphasic solvent systems catalyzed by homogeneous and heterogeneous Brönsted acids (Table S1). However, solvent systems inevitably have negative effects on the 5-HMF synthesis from fructose. Although water has been widely applied in the production of 5-HMF, it undesirably promotes the further conversion of 5-HMF to LA (Carniti et al., 2011; Girisuta et al., 2006a; Karimi and Mirzaei, 2013; Li et al., 2013; Sun et al., 2015). Polar non-proton organic solvent such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) effectively inhibit the further dehydration of 5-HMF to LA, while it bring difficulties for the isolation and purification of 5-HMF product (Girisuta et al., 2007; Liu et al., 2015; Musau and Munavu, 1987; Mushrif et al., 2012). Ionic liquid provide excellent reaction performance, however its application is limited by the economic inefficiency and difficult reutilization (Chinnappan et al., 2015; Hu et al., 2013; Rogers and Seddon, 2003).

Deep eutectic solvent (DES) is known as a liquid mixture formed by hydrogen-bond donors (HBD) and hydrogen-bond acceptors (HBA) (Abbott et al., 2004; Gorke et al., 2008; Smith et al., 2014; Zhang et al., 2012), which has attracted much attention owing to its superior physical and chemical properties. Thus, DES has been adopted in many cases for the conversion of carbohydrates. Ilgen et al. (2009) reported that fructose was capable of forming DES with Choline chloride (ChCl), which is a biodegradable quaternary ammonium salt. Liu et al. (2013) demonstrated that ChCl has a good capture capacity of CO_2, leading to the generation carbonic acid which further catalyzed the dehydration of fructose to 5-HMF with a yield of 72%. Hu et al. (2008) obtained a 90% yield of 5-HMF from fructose in a DES mixture formed by citric acid and ChCl.

Herein, we perform that extremely low content of inorganic acids can effectively promote the dehydration of fructose in DES

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Table 1
Catalytic performance of various acid catalysts for the conversion of fructose to 5-HMF in DES.

Entry	Catalyst	Fructose conversion(%)	5-HMF yield (%)	Main by-product
1	HCl (24 mol% of fructose)	99	45.2	5-CMF, LA
2	H_2SO_4 (24 mol% of fructose)	99	43.6	LA
3	$AlCl_3$	23	9.1	–
4	$ZnCl_2$	5	2.2	–
5	$CrCl_3$	99	75.0	Humins
6	$H_3PW_{12}O_{40}$	98	78.2	LA
7	$H_3P_4MO_{12}O_{40}$	72	45.5	LA
8	Extremely-low HCl (1.2 mol% of fructose)	99	90.3	Humins
9	Extremely-low H_2SO_4 (1.2 mol% of fructose)	97	82.8	Humins

Reaction conditions: fructose 0.9 g, ChCl 3.6 g, 100 °C, 4 h, catalyst mass ratio: 20 wt%.

mixture consist of fructose and ChCl. Moreover, in a biphasic reaction system formed by DES and MeCN, we present a promising integrated process for the conversion and in-situ extraction of fructose into 5-HMF. This biphasic system shows excellent recyclability, which could be reused for multiple times without any regeneration process.

2. Experimental

2.1. Raw materials

5-HMF (99%) was supplied by Sigma-Aldrich Co. Ltd. (St. Louis, USA). Phosphotungstic acid ($H_3PW_{12}O_{40}$), phosphomolybdic acid ($H_3P_4Mo_{12}O_{40}$), Choline Chloride (ChCl), Chlormequat Chloride (CCC), [BMIM]Cl, [BMIM]BF_4, [BMIM]Ac, [BMPD]Cl, [B(SO_3H)MIM]OTf, fructose and other carbohydrates were purchased from Aladdin Chemical Technology Co. Ltd. (Shanghai, China). All other analytical grade chemicals used in this work were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Typical process for the conversion of fructose into 5-HMF

In a typical run, the conversion of fructose into 5-HMF was conducted in a glass flask (100 ml) with a condenser in oil bath. The DES system was formed with 0.9 g fructose and 3.6 g ChCl. 1.2 mol% HCl (0.06 mmol) was added as the catalyst. The flask was then placed in oil bath and heated with vigorous stirring. After reaction, 5-HMF was extracted by hot EtOAc (60 °C, 30 ml*3 times). The organic phase was then neutralized with saturated $NaHCO_3$ solvent and stored for later analysis. The residual was dissolved in deionized water, and the conversion of fructose was analyzed by HPLC. In a biphasic reaction system, 30 ml MeCN was added in the reactor as in-situ extracting solvent.

2.3. Products analysis

Considering that ChCl can damage the HPLC instrument, the quantification of 5-HMF yield was carried out by a Thermo-Fisher Trace 1300 & ISQ LT GC–MS instrument equipped with a TR- 5MS column (15.0 m × 250 μm × 0.25 μm). The following program was applied: 323 K (1 min) – 8 K/min – 423 K (1 min). He was used as carrier gas with a split ratio of 1:50 and a flow rate of 1.2 ml min^{-1}. The mass spectra were obtained by electron impact ionization (EI), with a 25 μA emission current and electron energy of 70 eV. The 5-HMF yield was calculated as following:

$$\text{5-HMF Yield (\%)} = \frac{n_{5-HMF}}{n_{initial\ fructose}} \times 100\%$$

The amount of unreacted fructose was analyzed by HPLC method on a Waters 2695 instrument equipped with a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) and a refractive index detector. The mobile phase was 0.005 M H_2SO_4 with a flow rate of 0.6 ml min^{-1} at 60 °C. Then the fructose conversion was calculated with the follow formula:

$$\text{Fructose conversion (\%)} = \left(1 - \frac{\text{Mole of fructose in solvent}}{\text{Initial mole of fructose}}\right) \times 100\%$$

3. Result and discussion

3.1. Screening of catalyst in the synthesis of 5-HMF

The DES system adopted in this research was composed of fructose and ChCl (Ilgen et al., 2009; Zuo et al., 2016). Various Brönsted acids, Lewis acids, and heteropoly acids were tested in the reaction. As shown in Table 1, the yields of 5-HMF were rather low with high concentrations of HCl or H_2SO_4 (Entry 1&2), which was attributed to the subsequent conversion of 5-HMF to other chemicals (Mascal and Dutta, 2011; Mascal and Nikitin, 2008). Phosphotungstic acid ($H_3PW_{12}O_{40}$) provided a 5-HMF yield of 78.2% in DES reaction system (Entry 6). $CrCl_3$ showed favorable catalytic performance and a 75.0% 5-HMF yield was obtained (Entry 5). However, $ZnCl_2$ and $AlCl_3$ were ineffective for this reaction due to the low Lewis acidity. Among all catalyst tested, the extremely low concentration of inorganic acid was most effective for the dehydration of fructose to 5-HMF without other byproducts (Fig. S1).

3.2. Optimization of the reaction conditions in the 5-HMF synthesis

Various catalyst loading was studied with 50% or 20% mass ratio of fructose in DES (Fig. 1a). The conversion of fructose and 5-HMF yield were strongly affected by the dosage of HCl. Lower amount of HCl resulted in uncompleted conversion of fructose while overmuch HCl led to the formation of byproducts such as LA and 5-CMF (Mascal, 2015; Mascal and Dutta, 2011). The maximum 5-HMF yield of 90.3% was obtained with 1.2 mol% of HCl. The effects of reaction temperature and time were illustrated in Fig. 1b and c. With a temperature of 100 °C and reaction time of 4 h, a 5-HMF yield up to 90.3% was achieved. Besides, the mass ratio of fructose and ChCl also significantly influenced reaction (Fig. 1d), and a 20 wt% of fructose content (related to the weight of DES) was preferred.

The initial water concentration in the DES system has been acknowledged as a key parameter (Passos et al., 2016). It was reported that water could promote the dehydration of 5-HMF especially under acidic conditions (Galkin et al., 2016; Hu et al., 2015; Saha and Abu-Omar, 2014). However, as illustrated in Fig. 1e, the yield of 5-HMF change slightly with increasing water content from 10 wt% to 40 wt% in the DES system. Interestingly, once the reaction was carried out with a vacuum pump to *in-situ* evaporate water (Fig. S2), the 5-HMF yield decreased to 72.1%. It was supposed that

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