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Commercially available ammonium salt-catalyzed efficient dehydration of fructose to 5-hydroxymethylfurfural in ionic liquid

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ABSTRACT

Some sulfur oxyacid salts with weak acidity or alkalinity, including Na_2SO_4, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_3$ and $Na_2S_2O_3$, were applied to the conversion of fructose to 5-hydroxymethylfurfural. The results indicated that $(NH_4)_2S_2O_3$ had excellent catalytic performance for the conversion of fructose. A desired HMF yield of 81.6% was obtained with only 5 mg $(NH_4)_2S_2O_3$ as the catalyst in [Bmim]Cl at 120 °C for 50 min. Furthermore, the HMF yield remained at 76.6% with 60 wt% water in the IL–water mixture solvent. In addition, the system of $(NH_4)_2S_2O_3$ and [Bmim]Cl exhibited a constant stability and activity, and a good HMF yield was maintained after nine recycles.

1. Introduction

A gradual shift of the application of fossil resources and platform chemicals towards the abundant, renewable biomass and its derivatives has been observed at present [1]. In this context, 5-hydroxymethylfurfural (HMF) and its derivatives, obtained from renewable biomasses, are of great concern to more researchers due to its sustainable supplement to valuable chemical intermediates and fuels [2]. For example, 2,5-furandicarboxylic acid can be produced by the selective oxidation of HMF [3], which is used as a suitable substitute of terephthalic acid or isophthalic acid in the manufacture of polymer [4]. In addition, levulinic acid produced from the hydrolysis of HMF can be transformed into a variety of products, e.g., acrylate polymers and fuel additives such as γ-valerolactone, 2-methyl-tetrahydrofuran, and ethyl levulinate [5].

High yield of HMF from carbohydrates has been reported in aqueous media [6], ionic liquids [7] and high-boiling organic solvents [8]. Water, as a green solvent, may accelerate the rehydration of HMF, thus bringing many unexpected side products and decreasing the selectivity of HMF in the dehydration reaction. In contrast, organic solvents (e.g., DMSO) improve the selectivity of HMF by suppressing the side reaction. However, the efficient separation of HMF from high-boiling organic solvents and the recycling of the reaction media become the barriers to the commercial application. Consequently, ionic liquids appear to be a better choice. Zhao and co-workers first reported that 68–70% yield of HMF was achieved with ionic liquid 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) as the reaction solvent in 2007 [9], and then the utilization of ionic liquid as the solvent for the catalytic dehydration of hexoses is developed. Many types of ionic liquids have been applied including 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) [10], 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) [11], 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl) [12], 1-octyl-3-methylimidazolium chloride ([Omim]Cl) [13] and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) [14]. And satisfactory yields of HMF are obtained.

Certainly, the most important factor for the dehydration of biomass to HMF is the application of catalyst. Different kinds of catalysts, such as liquid acids [15], transition metal ions [16], acidic ionic-exchange resins [17] and H-form zeolites [18], have been applied to the field. Typically, heterogeneous catalysis becomes more attractive than homogeneous catalysis because of the reusability of heterogeneous catalyst after the reaction. Unfortunately, some poor soluble humins and soluble polymers, formed during the dehydration process, may deposit on the surface of heterogeneous catalysts and obstruct the pores of the catalyst, thus lowering the catalytic activity. Therefore, the regeneration of catalyst will be required. On the other hand, homogeneous catalysts are inexpensive and act as highly active catalysts, suggesting that the homogeneous catalysis might be preferable for the dehydration of biomass. Transition metal ions, such as chromium ion, have shown good activity even applying to the dehydration of glucose. However, the toxicity of metal ions may limit its application

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because of not fulfilling the principle of green chemistry. Similarly, satisfactory yield of HMF has been achieved by using liquid acids as the catalyst (e.g., H_2SO_4 and HCl). However, their strong acidity and high corrosiveness result in the pollution of the environment and the corrosion of the equipment. Therefore, it is essential to find a homogeneous catalyst with high catalytic performance and friendly environment.

Thiosulfate anion ($S_2O_3^{2-}$) has a similar structure as sulfate anion (SO_4^{2-}), which can be seen that an oxygen atom in SO_4^{2-} is substituted by a sulfur atom. Inspired by this, homogeneous catalysis of fructose to HMF in ionic liquids (ILs) associated with thiosulfate has been explored, aiming to attain a green homogeneous catalyst with high activity and commercial availability. Herein, a series of sulfur oxyacid salts with weak acidity or weak alkalinity, such as Na_2SO_4, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_3$ and $Na_2S_2O_3$, were applied to the dehydration of fructose to HMF in this paper. Moreover, the influences of various process parameters on HMF yields as well as the recycle of the catalytic system were investigated.

2. Material and methods

2.1. Materials

HMF (99% purity) was purchased from Wutong Spice Co., Ltd. Sodium sulfate anhydrous (Na_2SO_4, A.R. grade), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, A.R. grade), ammonium sulfate ($(NH_4)_2SO_4$, A.R. grade), fructose (B.R. grade), methanol (CH_3OH, L.C. grade), ethyl acetate ($CH_3COOC_2H_5$, A.R. grade), dimethyl sulfoxid ($(CH_3)_2SO$, A.R. grade) and N,N-dimethylformamide ($HCON(CH_3)_2$, A.R. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium thiosulfate ($(NH_4)_2S_2O_3$, 99% purity) was purchased from Aladdin. Potassium hydrogen phthalate ($C_8H_5KO_4$) and sodium tetraborate ($Na_2B_4O_7$) were purchased from Shanghai Rex Co-Perfect Instrument Co., Ltd. 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-octyl-3-methylimidazolium chloride ([Omim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim]PF_6$) were purchased from Shanghai Cheng Jie Chemical Co., Ltd. $[(C_8H_{17})_2N(CH_3)_2]Cl$ (D_8Cl) and $[(C_{12}H_{25})_2N(CH_3)_2]Cl$ ($D_{12}Cl$) were purchased from Xiamen Pioneer Technology Inc. All reagents were used as received without further purification.

2.2. Experimental methods

2.2.1. Typical procedure

Fructose (0.1 g) and ionic liquid (0.5 g) were put into the reaction bulb and heated in a phase at reaction temperature. Then, adding a given amount of catalysts into the mixture, the reaction started with a magnetic stirrer. After the desired time, the mixture was cooled quickly and diluted using pure water. The solution was filtered through a syringe filter before HPLC analysis.

2.2.2. Analysis

The sample was analyzed by means of high performance liquid chromatography (HPLC). The HPLC setup was equipped with two Varian ProStar210 pumps, an Agilent TC-C (18) column, and a Varian ProStar325 UV–Vis detector. The measured absorbance wavelength was 283 nm. A solution of methanol and H_2O in the ratio 50:50 (v/v) was used as the mobile phase at 0.8 mL/min flow rate. The column oven temperature was 35 °C. The amount of HMF was calculated by using an external standard method.

For fructose, HMF yield was defined as follows:

$$\text{Yeild} = \frac{n_{\text{HMF}}}{n_{\text{fructose}}} \times 100\% = \frac{m_{\text{HMF}} \times M_{\text{fructose}}}{M_{\text{HMF}} \times m_{\text{fructose}}} \times 100\%$$

where n_{HMF} was the moles of HMF; n_{fructose} was the initial moles of fructose; M_{HMF} and M_{fructose} were the mole mass of HMF and fructose, respectively. m_{HMF} was the mass of HMF calculated by HPLC; m_{fructose} was the initial mass of fructose.

3. Results and discussion

3.1. Effect of catalyst

First, two sulfate salts (Na_2SO_4 and $(NH_4)_2SO_4$) and two thiosulfate salts ($Na_2S_2O_3 \cdot 5H_2O$ and $(NH_4)_2S_2O_3$) were applied to the production of HMF from fructose in [Bmim]Cl. The results are listed in Table 1. As seen from Table 1, the HMF yields were depended on the catalyst largely. In the absence of catalyst, only 17.2% yield of HMF was obtained, indicating that the auto-catalysis of [Bmim]Cl for the dehydration of fructose was quite poor. An desired yield of 81.6% was achieved when $(NH_4)_2S_2O_3$ was employed whereas only moderate yield was obtained with $(NH_4)_2SO_4$. Notably, when $Na_2S_2O_3 \cdot 5H_2O$ were used as the catalyst, the HMF yield was even lower than that without catalyst.

A clear relationship between the nature of the catalysts and the HMF yields is observed. Compared with the sodium salts (entries 2 and 3), the ammonium salts (entries 4 and 5) with stronger acidity favored the conversion of fructose to HMF because that the dehydration of fructose to HMF was an acid-catalyzed process. Interestingly, though the acidity of $(NH_4)_2SO_4$ was stronger than $(NH_4)_2S_2O_3$, the catalytic performance of $(NH_4)_2S_2O_3$ was even higher. As observed in Fig. 1, $S_2O_3^{2-}$ has the similar structure as SO_4^{2-}, but it was reported that the sulfate anion could shift the pyranose-furanose equilibrium, thus hindering the dehydration reaction [19]. Therefore, $(NH_4)_2S_2O_3$ was chosen as the catalyst for the conversion of fructose to HMF and the reaction conditions were further optimized.

3.2. Effect of catalyst dosage

Table 2 shows the effect of catalyst dosage on the HMF yield. Only 17.2% yield of HMF was obtained in the absence of $(NH_4)_2S_2O_3$. Nevertheless the yield of HMF increased to 40.0% when 1 mg $(NH_4)_2S_2O_3$ was added. The result confirms the addition of $(NH_4)_2S_2O_3$ can promote the conversion of fructose to HMF. When the amount of $(NH_4)_2S_2O_3$ increased to 5 mg, the HMF yield boosted to 81.6%. The high catalyst dosage facilitated the production of HMF from fructose, possibly because the kinetic of fructose dehydration was faster in the case of higher catalyst dosage [20]. However, the yields of HMF dropped off when the amount of catalyst was further increased. The decrease might be ascribed to the fact that the over-using catalyst accelerated the side reactions such as the rehydration and condensation of HMF [21]. Thus, $(NH_4)_2S_2O_3$ of 5 mg was chosen for subsequent experiments.

Fig. 2 depicts the effect of the dosages of $(NH_4)_2S_2O_3$ on the HMF yields with reaction running. At low dosage (1 mg) of catalyst, the

Table 1
Effect of catalyst on the HMF yield.

Entry	Catalyst	pH[a] (T = 293.15 K)	HMF yield (%)
1	none	–	17.2
2	Na_2SO_4	7.31	34.3
3	$Na_2S_2O_3 \cdot 5H_2O$	7.80	2.3
4	$(NH_4)_2SO_4$	4.97	59.0
5	$(NH_4)_2S_2O_3$	5.54	81.6

Conditions: fructose 0.1 g, Catalyst 0.034 mmol, [Bmim]Cl 0.5 g, 120 °C, 50 min.

[a] pH value was measured by PHS-3C precision pH/mV meter. The pH meter standardized with $C_8H_5KO_4$ (pH 4.0, T = 293.15 K) and $Na_2B_4O_7$ (pH 9.0, T = 293.15 K) before using.