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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<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, were applied to the conversion of fructose to 5-hydroxymethylfurfural. The results indicated that (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> had excellent catalytic performance for the conversion of fructose. A desired HMF yield of 81.6% was obtained with only 5 mg (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and [Bmim]Cl exhibited a constant stability and activity, and a good HMF yield was maintained after nine recycles.

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#### 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  $\gamma$ -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<sub>4</sub>) [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<sub>2</sub>SO<sub>4</sub>,  $(NH_4)_2SO_4$ ,  $(NH_4)_2S_2O_3$  and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 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<sub>2</sub>SO<sub>4</sub>, A.R. grade), sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, A.R. grade), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, A.R. grade), fructose (B.R. grade), methanol (CH<sub>3</sub>OH, L.C. grade), ethyl acetate (CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, A.R. grade), dimethyl sulfoxid ((CH<sub>3</sub>)<sub>2</sub>SO, A.R. grade) and N,N-dimethylformamide (HCON(CH<sub>3</sub>)<sub>2</sub>, A.R. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium thiosulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 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<sub>4</sub>), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF<sub>6</sub>) were purchased from Shanghai Cheng Jie Chemical Co., Ltd.  $[(C_8H_{17})_2N(CH_3)_2]Cl$  (D<sub>8</sub>Cl) and  $[(C_{12}H_{25})_2N(CH_3)_2]Cl$ (D<sub>12</sub>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<sub>2</sub>O 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.

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

## 3. Results and discussion

#### 3.1. Effect of catalyst

First, two sulfate salts  $(Na_2SO_4 \text{ and } (NH_4)_2SO_4)$  and two thiosulfate salts  $(Na_2S_2O_3 \cdot 5H_2O \text{ and } (NH_4)_2S_2O_3)$  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  $(NH_4)_2S_2$ -O<sub>3</sub>. 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 <sup>a</sup> ( <i>T</i> = 293.15 K)	HMF yield (%)
1	none	-	17.2
2	$Na_2SO_4$	7.31	34.3
3	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	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. <sup>a</sup> pH value was measured by PHS-3C precision pH/mV meter. The pH meter standardized with C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub> (pH 4.0, T = 293.15 K) and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (pH 9.0, T = 293.15 K) before using.



Fig. 1. The structure of sulfate ion and thiosulfate anion.

Table 2Effect of catalyst dosage on the HMF yield.

Entry	$(NH_4)_2S_2O_3(mg)$	HMF yield (%)
1	0	17.2
2	1	40.0
3	3	78.8
4	5	81.6
5	7	77.8
6	9	70.2

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



Fig. 2. Temperal HMF yield as function of the reaction time on the different dosages of  $(NH_4)_2S_2O_3$ . Conditions: fructose 0.1 g, [Bmim]Cl 0.5 g, 120 °C.

HMF yield boosted with prolonging the reaction time. When increasing the dosage of catalyst to 5 mg and 9 mg, the HMF yields increased sharply in the initial phase and subsequently decreased smoothly. Notably, the trend was more obvious when the larger amount of catalyst was used. The results might be because of the fact that the side reactions in the catalytic system are also accelerated by the over-using catalysts. Alternatively, the addition of excess catalyst can lead the mass transfer limitations [22].

## 3.3. Effects of reaction temperature and reaction time

The reaction temperature and time of the dehydration reaction were varied to investigate the rate of HMF formation as a function of time. As illustrated in Fig. 3, the increasing reaction temperature was favorable for improving the initial yield of HMF to some extent. More precisely, the higher temperature was, the shorter the time exhausted in reaching peak yield of HMF was. HMF yield of 81.6% was obtained at 120 °C for 50 min, while it only took 30 min to reach HMF peak yield of 82.5% at 130 °C and 78.4% at 140 °C, respectively. The results are attributed to the endothermic nature of fructose dehydration [23] and the increasing rate of dehydration with the increasing temperature [17].

Moreover, a clear relation between the vibrations of HMF yields and the prolonged reaction time at each temperature was observed. At low temperature (100 °C), the HMF yields were quite poor and the change of HMF yields with the prolonged was not obvious. This may arise from the low selectivity of HMF, which is due to the existence of partially dehydrated intermediates in the

![](_page_2_Figure_13.jpeg)

Fig. 3. Temporal HMF as a function of reaction time at different temperatures. Conditions: fructose 0.1 g, catalyst 5 mg, [Bmim]Cl 0.5 g.

dehydration of fructose at lower temperature [24]. When the temperature increased to 110 °C, the HMF yield increased smoothly in the first 50 min but sharply in the following 20 min. The result shows that the extension of the reaction time at a lower temperature is favorable for the yields of HMF [23]. When the reaction temperature was increased further (120 °C and 130 °C), HMF yield boosted firstly and then decreased with the extending reaction time. Maybe the increasing temperature not only accelerates the dehydration of fructose to HMF, but also speeds up the formation of some insoluble humins and soluble polymers by the polymerization of HMF [20]. This demonstrates that HMF is no longer the favored product. Meanwhile, with the formation of H<sub>2</sub>O in the process of the dehydration inevitably, the alternation of the solvent from [Bmim]Cl to [Bmim]Cl/H<sub>2</sub>O mixture solvent accelerates the rehydration of the HMF. leading to the generation of levulinic acid [25]. Notably, the highest yield of HMF at 140 °C was 78.4%, which was lower than that at 120 °C (81.6%). This proves that an over high temperature is undesirable for the fructose dehydration again. Thus, from the point of environment and commercialization, 120 °C and 50 min were considered as the appropriate reaction temperature and the reaction time for the dehydration of fructose, respectively.

# 3.4. Effect of solvent

Two kind of organic solvents (DMSO and DMF), two kind of ammonium ionic liquids ( $D_8Cl$  and  $D_{12}Cl$ ) and four kind of imidazolium ionic liquids ([Bmim]BF<sub>4</sub>, [Bmim]PF<sub>6</sub>, [Bmim]Cl and [Omim]Cl) were carried out to investigate the effect of the solvent on the fructose dehydration. Eight control experiments were conducted without (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in order to test the activity of solvents alone. As shown in Fig. 4, eight reaction solvents all showed a certain degree catalytic performance on the dehydration reaction at 120 °C.

Interestingly, DMSO and DMF presented moderate yields of 61.3% and 69.4% without adding  $(NH_4)_2S_2O_3$ , respectively. As reported in the literatures, DMSO served as the catalyst for the dehydration of fructose to HMF without adding mineral or Lewis acid catalyst at a higher temperature [26]. Additionally, DMSO acted as both an electron accepter and an electron donator to improve the dehydration of fructose [27]. Similarly, DMF might work like DMSO in the dehydration reaction due to its strong electron pair donating and accepting ability [28] and had been proved to be preferable in the fructose dehydration in the previous study [29]. However, DMSO and DMF, as aprotic solvents, might bind the free H<sup>+</sup> in the solvent and absorb on the acid sites of the catalyst to inhibit or block the reaction [27], resulting in slight reduction of HMF yields when adding a minute quantity of  $(NH_4)_2S_2O_3$ .

![](_page_3_Figure_1.jpeg)

**Fig. 4.** Effect of solvent on the HMF yield. Conditions without catalyst: fructose 0.1 g, solvent 0.5 g, 120 °C, 50 min. Conditions with catalyst:  $(NH_4)_2S_2O_3$  5 mg, fructose 0.1 g, solvent 0.5 g, 120 °C, 50 min.

Notably, the best HMF yield (81.6%) was achieved in [Bmim]Cl with  $(NH_4)_2S_2O_3$  as a catalyst, whereas [Bmim]Cl presented a quite poor HMF yield of 17.2% in the control experiment. However, very poor HMF yields were obtained even with adding  $(NH_4)_2S_2O_3$  when [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub> were employed as the solvent, respectively. The result is ascribed to that Cl<sup>-</sup> prefers to form strong hydrogen bonds with fructose in comparison with BF<sub>4</sub> and PF<sub>6</sub>, accelerating the dehydration of fructose to HMF [30]. Furthermore, [Bmim]Cl, acting as both Brønsted acid and nucleophile, can trigger the conversion of fructose, which is in accordance with the result reported by Ryu and Choi [31].

 $D_8Cl$ ,  $D_{12}Cl$ , [Bmim]Cl and [Omim]Cl with the same anion (chloride ion) owned different cations. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> showed higher activity in imidazolium ionic liquids than in ammonium ionic liquids. Moreover, the HMF yields significantly decreased in the ionic liquids with longer alkyl chains of the cations, which was in agreement with the result reported by Shi and Zhao [30]. The longer the alkyl groups in the ionic liquids cations are, the stronger the aggregations effect is. It may be an obstacle to the transfer of electrons and protons in the molecular interior, hindering the fructose dehydration.

#### 3.5. Effects of initial fructose concentration

A high substrate concentration is crucial for the industrial production of HMF, thus, different initial concentrations of fructose varied from 9.1 wt% to 50.0 wt% were studied. As shown in Table 3, with the initial fructose concentration adding up, the HMF yield firstly increased, and then dropped off. When the initial fructose concentration increased from 9.1 wt% to 28.6 wt%, the HMF yields changed quickly from 48.3% to 83.8%. However, a significant loss of HMF yield was been obtained when the initial fructose concentration further increased to 50.0 wt%. The partial loss of HMF with high fructose concentration is due to the increasing collision probability of fructose and generated HMF, leading to the self- or crosspolymerization between them and the formation of humins [8,20]. A HMF yield of 81.4% was still achieved at the initial fructose concentration of 37.5 wt% (0.30 g) at 120 °C for 50 min, suggesting the high efficiency of the catalytic system.

## 3.6. Effect of water content

Water is the most economically and environmentally acceptable solvent, thus, different amounts of water were added to replace the ionic liquid [Bmim]Cl and the influence of water addition on fructose conversion to HMF is plotted in Fig. 5. The HMF yields decreased smoothly with the increased water content in

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Effect of different initial fructose concentration on the yield of the reaction.

Entry	Initial fructose concentration (wt%) <sup>a</sup>	Initial fructose loading (g)	HMF yield (%)
1	9.1	0.05	48.3
2	16.7	0.10	81.6
3	28.6	0.20	83.8
4	37.5	0.30	81.4
5	44.4	0.40	65.2
6	50.0	0.50	53.9

Conditions: (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 5 mg, [Bmim]Cl 0.5 g, 120 °C, 50 min.

<sup>a</sup> Fructose concentration was based on the total mass of fructose and reaction solvent.

![](_page_3_Figure_14.jpeg)

**Fig. 5.** Effect of initial water content on the HMF yield. Conditions:  $(NH_4)_2S_2O_3$  5 mg, fructose 0.1 g, total weight of solvent 0.5 g, 120 °C, 50 min. Water content is based on the total weight of solvent.

![](_page_3_Figure_16.jpeg)

Fig. 6. HMF yields of recycling test in  $(NH_4)_2S_2O_3/[Bmim]Cl$  system. Conditions:  $(NH_4)_2S_2O_3$  5 mg, fructose 0.1 g, [Bmim]Cl 0.5 g, 120 °C, 50 min.

the mixed solvent. When the water percentage in the solvent mixture increased to 60 wt%, the HMF yield remained at 76.6% and only decreased 6% in comparison with that without adding water. The result indicates that the system of  $(NH_4)_2S_2O_3/[Bmim]Cl$  has a good containment for water although the conversion of fructose to HMF is a dehydration reaction. This is because of the fact that the mass transfer is enhanced with the reducing viscosity of solvent by adding water [12] and the solubility of  $(NH_4)_2S_2O_3$  in the solvent also increases with the increased water content. Further, the interaction between fructose and fructofuranosyl cations, a direct precursor of HMF, can be weakened in a moisture system, inhibiting the formation of soluble polymers and solid humins [32]. However, the HMF yield declined to 69.8% obviously when the water percentage in the solvent mixture increased to 70 wt%. With the further increase of the initial water content, the yields of HMF plunged. It is attributed to that the addition of water to the ionic liquid accelerates the rehydration of HMF and lowers the selectivity of HMF in the dehydration of carbohydrates at the same time [14]. Besides, the successive addition of water to the ionic liquid lowers the dielectric constant of the reaction media and reduces catalytic activity, thus impeding the sugar conversion [12]. The above results indicate that the system of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>/[Bmim]Cl has a good tolerance for water, but the capacity is limited.

## 3.7. Recycling of [Bmim]Cl and catalyst

Long-term recyclability is of great significance for employing a catalyst in industrial process. In this work, the reuse of  $(NH_4)_2S_2O_3$ and the ionic liquid [Bmim]Cl was carried out to investigate the stability and activity of the system. After the first reaction run, 1 mL of deionized water was added to the mixture to decrease the viscosity of the ionic liquid and facilitate the extraction of HMF. Then, HMF was separated from the reaction mixture by 20 extractions, each with 5 mL of ethyl acetate as extracting agent. The extracted liquid was examined by UV-Vis detector in an external standard to attain the amount of HMF. The mixture after the extraction was heated at 60 °C overnight to remove the water and residual ethyl acetate. Then the dried [Bmim]Cl solvent with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> catalyst was utilized directly in the next run by adding 0.1 g fructose under the same reaction conditions. As shown in the Fig. 6, the decrease of the catalytic activity was negligible after 9th run, demonstrating that the system of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>/[Bmim]Cl exhibited an excellent stability for the fructose dehydration to HMF. However, the yield of HMF in some recycling tests was even higher than that in the 1st run, which might be due to the retention of HMF and unreacted feedstock in the previous runs [33,34].

#### 4. Conclusion

This study is the first to demonstrate that (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and [Bmim]Cl was an excellent combination for fructose dehydration to HMF. With an initial fructose concentration of 37.5 wt% and a water percentage in the IL-water mixture solvent of 60 wt%, the HMF yields maintained at 81.4% and 76.7%, respectively. Meanwhile, the system with  $(NH_4)_2S_2O_3$  as catalyst and [Bmim]Cl as solvent was efficiently reused and the catalytic activity retained steadily after nine recycling tests. Combined with desirable catalytic performance, low corrosiveness, low acidity and commercial availability,  $(NH_4)_2S_2O_3$  is a very attractive alternative to the reported homogeneous catalysts.

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