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### Introduction

Concern about sustainable has led to increasing interest in the alternatives of fossil resources for chemicals and energy supply.<sup>1</sup> Recently, dehydration of carbohydrates (*e.g.* cellulose, glucose, fructose, sucrose, inulin, and cellobiose) to produce 5-hydroxymethylfurfural (HMF) has attracted much attention because it has been recognized as a platform compound for the production of fine chemicals, polymeric materials, and biofuels.<sup>2</sup>

Although excellent yields of HMF can be achieved from the dehydration of fructose using many methods,<sup>3</sup> the production of HMF from glucose and cellulose would be more attractive because they are much more abundant. However, the preparation of HMF from glucose and cellulose is more difficult and many efforts have been devoted to this topic. Different catalysts have been developed for the dehydration of glucose to produce HMF, such as chromium chlorides,4 stannous chloride,5 lanthanide chlorides,6 boric acid,7 germanium(IV) chloride,8 tantalum compounds,9 chromium(0) nanoparticles.10 But for direct transformation of cellulose into HMF, only a few catalysts were successful, which included CrCl<sub>2</sub>/RuCl<sub>3</sub>,<sup>11</sup> CuCl<sub>2</sub>/CrCl<sub>2</sub>,<sup>12</sup> Brønsted-Lewis-surfactant-combined heteropolyacid,13 and so on. Regardless of these developments, exploration of efficient catalytic system for the dehydration of glucose and cellulose is still very interesting and challenging.

# Efficient conversion of glucose and cellulose to 5-hydroxymethylfurfural in DBU-based ionic liquids

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Development of an efficient catalytic system for the dehydration of carbohydrates to produce 5-hydroxymethylfurfural (HMF), which is a platform molecule for biomass transformation, is a very attractive topic. In this work, three DBU-based ionic liquids (ILs) were prepared and used as the solvent for the conversion of carbohydrates into HMF. It was found that all these new ILs were excellent solvents for the dehydration of glucose, cellulose, fructose, sucrose, inulin, and cellobiose to form HMF using  $CrCl_3 \cdot 6H_2O$  as the catalyst. The effects of temperature, reaction time, catalyst amount, and substrate/solvent weight ratio on the dehydration of glucose in  $CrCl_3 \cdot 6H_2O/Bu-DBUCI$  were studied systematically. It was shown that the yield of HMF could reach 64% from glucose. In addition, the  $CrCl_3 \cdot 6H_2O/Bu-DBUCI$  system could be easily separated from the product, and could be reused five times without considerably decreasing in activity and selectivity.

Solvents have great impact on the activity and selectivity for the dehydration of carbohydrates to form HMF. The dehydration reaction has been carried out in water,<sup>14</sup> traditional organic solvents,15 multiphase systems,16 and in ionic liquids (ILs).17 ILs have received extensive attention in recent years because of their unusual properties, such as negligible vapor pressure, non-flammability, high thermal and chemical stability, and adjustable solvent power for organic and inorganic substances.18 Due to the good solubility of carbohydrates in ILs, transformation of carbohydrates into HMF using ILs as solvents or catalysts is very promising, and there have been many reports on this.<sup>19</sup> For example, Zhao et al. reported that satisfactory yields of HMF could be reached by the dehydration of fructose and glucose in 1-ethyl-3-methylimidazolium chloride ([Emim]-Cl) using chromium(II) chloride as the catalyst.<sup>20</sup> 1-H-3-Methyl imidazolium chloride was used as both solvent and catalyst for the conversion of fructose to HMF with satisfactory yield.21 Furthermore, efficient conversion of fructose and inulin to HMF was studied in choline chloride (ChoCl)-based ILs.17b Qu et al. found 1-hydroxyethyl-3-methylimidazolium that tetrafluoroborate could catalyze the dehydration of glucose to HMF efficiently in DMSO.22 Other ILs, such as triisobutyl(methyl)phosphonium tosylate,23 dicationic ILs24 and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF4),5 could also be used in the dehydration of carbohydrates to generate HMF. Although there have been many reports about the application of ILs in HMF production, it is still highly desirable to develop new and easily prepared ILs as the efficient reaction media for transformation of carbohydrates into HMF.

In this work, we synthesized three new DBU-based ILs. The main advantages of the DBU-based ILs are facile synthesis from

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commercially available and relatively inexpensive starting materials, excellent air/water and thermal stability. More importantly, the tertiary nitrogen existed in the cations affords Lewis basic property to the ILs, which could improve the dehydration of carbohydrates to produce HMF through a hydrogen bond formed in situ between the hydroxy groups of carbohydrate and the tertiary nitrogen atom of the ILs. Indeed, we found that the DBU-based ILs were excellent solvents for the dehydration of glucose and cellulose to produce HMF using CrCl<sub>3</sub>·6H<sub>2</sub>O as the catalyst. In addition, the DBU-based IL/ CrCl<sub>3</sub>·6H<sub>2</sub>O catalytic system was also suitable to the conversion of other sugars such as fructose, sucrose, inulin and cellobiose. To the best of our knowledge, this is the first application of DBU-based ILs to produce HMF from carbohydrates.

### **Results and discussion**

#### Synthesis of the ILs

The routes to synthesize the DBU-based ILs and their structures are presented in Scheme 1, and the synthetic procedures and the characterization are discussed in detailed in the Experimental section.

#### Catalytic performance of different catalysts on dehydration of glucose in Bu-DBUCl

The activity of various catalysts for the dehydration of glucose to produce HMF (Scheme 2) was tested at 100 °C in Bu-DBUCl, and the results are summarized in Table 1. It can be seen from Table 1 that no product was detected without catalyst (entry 1). Some Lewis acids (entries 4-8) and H<sub>3</sub>BO<sub>3</sub> (entry 3) could catalyze the dehydration of glucose in the IL. Among the catalysts we tested,  $CrCl_3 \cdot 6H_2O$  (entry 8) had the best activity for the reaction and the yield of HMF could reach 64%, which was comparable to the results obtained by Zhao et al.20 using catalytic system CrCl<sub>2</sub>/ [Emim]Cl. In addition, some results of typical catalytic systems used in the production of HMF from glucose were also given in Table 1. It can be known that the catalytic system of this work was very efficient. Based on the results discussed above, we chose CrCl<sub>3</sub>·6H<sub>2</sub>O as the dehydration catalyst to study effect of reaction parameters on the reaction in Bu-DBUCl.



Scheme 1 Synthesis of the DBU-based ILs.



Scheme 2 Dehydration of glucose to produce HMF in Bu-DBUCI

Table 1 Dehydration of glucose catalyzed by various catalysts<sup>a</sup>

Entry	Catalyst	Solvent	$\operatorname{Yield}^{b}(\%)$	Ref.
1	None	Bu-DBUC	0	
2	LaCl <sub>2</sub> ·6H <sub>2</sub> O	Bu-DBUCI	0	
3	H <sub>3</sub> BO <sub>3</sub>	Bu-DBUCl	1	
4	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	Bu-DBUCl	6	
5	SnCl <sub>4</sub> ·5H <sub>2</sub> O	Bu-DBUCl	27	
6	$Cr(NO_3)_3 \cdot 9H_2O$	Bu-DBUCl	54	
7	CrCl <sub>2</sub>	Bu-DBUCl	63	
8	$CrCl_3 \cdot 6H_2O$	Bu-DBUCl	64	
9	$SnCl_4 \cdot 5H_2O$	[Emim]BF4	61	5
10	YbCl <sub>3</sub> or Yb(OTf) <sub>3</sub>	[Bmim]Cl	24	6
11	$H_3BO_3$	[Emim]Cl	41	7
12	$\text{GeCl}_4$	[Bmim]Cl	48	8
13	$CrCl_2$	[Emim]Cl	70	20

<sup>a</sup> Reaction conditions of this work: 0.1 g glucose, 10 mg catalyst, 1 g Bu-DBUCl, reaction time 3 h, reaction temperature 100 °C. <sup>b</sup> Yields were determined by HPLC.

#### Effect of catalyst amount

Effect of the amount of CrCl<sub>3</sub>·6H<sub>2</sub>O on the dehydration of glucose to produce HMF was examined in Bu-DBUCl at 100 °C with a reaction time of 3 h, and the results are given in Fig. 1. It can be known from the figure that the yield of HMF increased to a maximum of 64% with an increase in the amount of  $CrCl_3 \cdot 6H_2O$  from 0 to 10 mg and then slowly decreased to 55% with further increase in the amount of  $CrCl_3 \cdot 6H_2O$  from 10 to 30 mg. These results indicated that lower catalyst amount resulted in a slow reaction rate and excess catalyst could cause the side reactions such as polymerization and rehydration of



Fig. 1 Effect of catalyst amount on the reaction. Reaction conditions: 0.1 g glucose, 1 g Bu-DBUCl, reaction time 3 h, reaction temperature 100 °C.



Fig. 2 Effect of reaction time on the yield of HMF. Reaction conditions: 0.1 g glucose, 1 g Bu-DBUCl, 10 mg CrCl<sub>3</sub>·6H<sub>2</sub>O, reaction temperature 100 °C

the products. Therefore, 10 mg of the catalyst would be an appropriate amount at the reaction conditions.

#### Effect of reaction time

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The dependence of HMF yield on reaction time is presented in Fig. 2. The reaction was performed in the presence of 10 mg CrCl<sub>3</sub>·6H<sub>2</sub>O at 100 °C in Bu-DBUCl. The yield of HMF increased sharply at beginning, and slowly from 50 min to 180 min, and a vield of 64% could be achieved at 180 min. No increase in the yield of HMF was observed with further prolonged reaction time. Therefore, the reaction time of 3 h was suitable for this system.

#### Effect of reaction temperature

Fig. 3 shows the effect of reaction temperature on the dehydration of glucose to produce HMF in Bu-DBUCl catalyzed by CrCl<sub>3</sub>·6H<sub>2</sub>O in the temperature range of 80-120 °C with a reaction time of 3 h. The maximum yield occurred at 100 °C at the reaction conditions. In the reaction system, reaction temperature affected the reaction in two opposite ways. Firstly, the dehydration of glucose was accelerated by increasing temperature, which was favorable to obtaining high HMF yield. Secondly, the side reactions, such as polymerization and rehydration of HMF, were also accelerated by rising temperature.



Fig. 3 Effect of reaction temperature on the yield of HMF. Reaction conditions: 0.1 g glucose, 1 g Bu-DBUCl, 10 mg CrCl<sub>3</sub>·6H<sub>2</sub>O, reaction time 3 h.



Fig. 4 Influence of substrate/solvent weight ratio on the reaction. Reaction conditions: reaction temperature 100 °C, reaction time 3 h.

The competition of the two opposite factors resulted in the highest yield at 100 °C.

#### Influence of substrate/solvent weight ratio

The substrate/solvent weight ratio was also important for the overall efficiency of the reaction system (Fig. 4). The weight ratio of glucose/CrCl<sub>3</sub>·6H<sub>2</sub>O was fixed at 10 : 1. It can be seen from Fig. 4 that the HMF vield decreased gradually from 69% to 48% when the glucose/Bu-DBUCl weight ratio was increased from 0.05 : 1 to 0.3 : 1. This may result mainly from the increasing concentration of CrCl<sub>3</sub>·6H<sub>2</sub>O in Bu-DBUCl, which could increase the side reactions such as polymerization and rehydration of products.

#### The reusability of the catalyst system CrCl<sub>3</sub>·6H<sub>2</sub>O/Bu-DBUCl

The reusability of the CrCl<sub>3</sub>·6H<sub>2</sub>O/Bu-DBUCl catalytic system was studied in this work. After the reaction, the product was extracted by diethyl ether, and the catalytic system was used directly for the next run after drying, as described in the Experimental section. The results were shown in Fig. 5. It can be known from the figure that the decrease of the activity of the catalyst system was not considerable after reused five times.



Fig. 5 Reusability of CrCl<sub>3</sub>·6H<sub>2</sub>O/Bu-DBUCl catalytic system. Reaction condition: 0.1 g glucose, 1 g Bu-DBUCl, 10 mg CrCl<sub>3</sub>·6H<sub>2</sub>O, reaction temperature 100 °C, reaction time 3 h.

Table 2 Synthesis of HMF from cellulose catalyzed by CrCl<sub>3</sub>·6H<sub>2</sub>O in Bu-DBUCl<sup>a</sup>

Entry	Amount of catalyst (mg)	Amount of cellulose (mg)	Time (h)	Temperature (°C)	Yield <sup>b</sup> (%)
1	10	100	1	120	27
2	10	100	2	120	34
3	10	100	3	120	41
4	10	100	4	120	40
5	10	100	1	130	39
6	10	100	2	130	41
7	10	100	3	130	41
8	10	100	4	130	40
9	5	100	2	130	40
10	15	100	2	130	40
11	5	50	2	130	37
12	15	150	2	130	38

#### Synthesis of HMF from cellulose in Bu-DBUCl

It is well known that glucose can be obtained by hydrolysis of cellulose. In this work, the direct conversion of cellulose into HMF was also studied in the  $CrCl_3 \cdot 6H_2O/Bu-DBUCl$  catalytic system, and the influence of reaction time and reaction temperatures on the yield of HMF from cellulose were examined (entries 1–8, Table 2). The best yield was obtained in 3 h at 120 °C (entry 3) or in 2 h at 130 °C (entry 6), which were both 41%. At the higher temperature the maximum yield could be obtained in a shorter time. In addition, the amount of cellulose was also studied (entries 6, 11 and 12) and 10 wt% cellulose based on the IL showed the highest HMF yield.

#### Dehydration of other carbohydrates

In the light of the good dehydration results obtained with glucose and cellulose, the  $CrCl_3 \cdot 6H_2O/Bu-DBUCl$  catalytic system was also used to catalyze the dehydration of other carbohydrates, and the results are illustrated in Fig. 6. As expected, fructose and sucrose gave higher HMF yield of 69% and 63%, respectively. Inulin and cellobiose only gave moderate yields, which were 46% and 39%, respectively. Reaction times for obtaining the



**Fig. 6** Dehydration of different carbohydrates. *Reaction conditions*: 0.1 g substrate, 1 g Bu-DBUCI, 10 mg CrCl<sub>3</sub>·6H<sub>2</sub>O, reaction temperature 100 °C.

 Table 3
 Effect of DBU-based ILs on HMF yield from different substrates<sup>a</sup>

				Yield <sup><math>b</math></sup> (%)				
Entry	Substrate	Temperature (°C)	Time (h)	Bu-DBUCl	Oc-DBUCl	HEOE- DBUCl		
1	Fructose	100	1.5	69	68	67		
2	Glucose	100	3	64	63	62		
3	Sucrose	100	2	63	60	61		
4	Inulin	100	2	46	42	42		
5	Cellobiose	100	3	39	37	45		
6	Cellulose	130	2	41	42	24		
<sup><i>a</i></sup> Reaction conditions: ionic liquids 1 g, substrate 0.1 g, $CrCl_3 \cdot 6H_2O$ 10 mg. <sup><i>b</i></sup> Yields were determined by HPLC.								

maximum HMF yield were 1.5 h, 2 h, 2 h, and 3 h, respectively for fructose, sucrose, inulin, and cellobiose. It can also be seen that the catalytic system was very effective for transformation of fructose, and the yield could reach 65% in 15 min.

#### Effect of the DBU-based ILs

The conversion of various carbohydrates in the other two ILs synthesized in this work was also studied using  $CrCl_3 \cdot 6H_2O$  as the catalyst, and the results are listed in Table 3. In general, the yields of HMF from the carbohydrates were similar. The lower yield of HMF from cellulose in HEOE-DBUCl could be caused by the functional group in the side chain on DBU.

#### Conclusions

Three DBU-based ILs, Bu-DBUCl, Oc-DBUCl, and HEOE-DBUCl have been synthesized. The ILs can be used as efficient solvent for the dehydration of different carbohydrates to produce HMF in the presence of  $CrCl_3 \cdot 6H_2O$  catalyst. In the catalytic system  $CrCl_3 \cdot 6H_2O/Bu-DBUCl$ , a HMF yield of 64% can be achieved from the dehydration of glucose at 100 °C with a reaction time of 3 h. The catalytic system is easily recovered and can be reused five times without considerable reduction of the reaction activity and selectivity. In addition, the catalytic system can also catalyze the dehydration of cellulose to produce HMF efficiently and a yield of 41% was achieved at 130 °C with a reaction time of 2 h. We believe that the simple, efficient, and easily recyclable ILs has great potential of application for producing HMF from the dehydration of carbohydrates.

#### Experimental section

#### Materials

Fructose, sucrose, inulin, glucose, cellobiose, cellulose, 1chlorobutane, 1-chlorooctane, 2-(2-chloroethoxy)ethanol, 1,8diazabicyclo[5.4.0]undec-7-ene (DBU),  $CrCl_3 \cdot 6H_2O$  and  $CrCl_2$ were purchased from Alfa Aesar.  $LaCl_3 \cdot 6H_2O$ ,  $H_3BO_3$ ,  $Cr(NO_3)_3 \cdot 9H_2O$ ,  $ZrOCl_2 \cdot 8H_2O$ ,  $SnCl_4 \cdot 5H_2O$ , acetonitrile, ethyl acetate, and diethyl ether were all analytical grade and were provided from Beijing Chemical Reagent Company. All chemicals were used as received.

#### Synthesis of the ILs

To synthesize a IL, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.1 mol) and chloroalkane (0.12 mol) were added to acetonitrile (50 mL) in a round-bottomed flask of 250 mL equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was stirred at 75  $^\circ \mathrm{C}$  under  $N_2$  for 24 h. After the reaction, the volatile substances were removed from the resulting solution under reduced pressure. For the IL formed from DBU with 1-chlorobutane (Bu-DBUCl) or 1-chlorooctane (Oc-DBUCl), the remaining oil was re-dissolved in acetonitrile (25 mL) and recrystallized by adding 500 mL of diethyl ether. The IL was filtered, washed thoroughly with diethyl ether, and dried in vacuum at 40 °C for 24 h. For the IL formed by DBU and 2-(2-chloroethoxy)ethanol (HEOE-DBUCl), the remaining oil was washed by diethyl ether (100 mL  $\times$  10) to removed unreacted DBU and 2-(2-chloroethoxy)ethanol. Then, the oil was heated at 60 °C under vacuum to removed diethyl ether to get the IL HEOE-DBUCl. The purity of all the ILs prepared in this work was >99%. The synthesized ILs were characterized as follows.

**Bu-DBUCI.** White solid (purity >99%); <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$  (ppm) 3.58–3.61 (m, 2H), 3.44–3.49 (m, 6H), 2.82 (d, J = 9.6 Hz, 2H), 2.01–2.07 (m, 2H), 1.68–1.75 (m, 6H), 1.58–1.64 (m, 2H), 1.27–1.37 (m, 2H), 0.91 (t, J = 7.6 Hz, 3H). Elemental analysis calcd (%) for Bu-DBUCl (244.81): C 63.78, H 10.30, N 11.44; found: C 63.65, H 10.23, N 11.56%.

**Oc-DBUCI.** White solid (purity >99%); <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$  (ppm) 3.58–3.61 (m, 2H), 3.44–3.51 (m, 6H), 2.82 (d, J = 9.6 Hz, 2H), 2.01–2.07 (m, 2H), 1.68–1.75 (m, 6H), 1.61–1.64 (m, 2H), 1.27–1.31 (m, 10H), 0.85 (t, J = 6.4 Hz, 3H). Elemental analysis calcd (%) for Oc-DBUCI (300.92): C 67.85, H 11.06, N 9.31; found: C 66.43, H 10.90, N 9.49%.

**HEOE-DBUCI.** Light yellow oil (purity >99%); <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$  (ppm) 3.71–3.78 (m, 6H), 3.62–3.64 (m, 2H), 3.51–3.57 (m, 6H), 2.87 (d, J = 10 Hz, 2H), 2.05–2.10 (m, 2H), 1.70–1.73 (m, 6H). Elemental analysis calcd (%) for HEOE-DBUCI (276.81): C 56.41, H 10.29, N 10.12; found: C 56.23, H 10.35, N 9.96%.

#### Catalytic reaction

Only the procedures to convert glucose into HMF in Bu-DBUCl catalyzed by CrCl<sub>3</sub>·6H<sub>2</sub>O are discussed because those for other sugars in different ILs were the same except that the materials used were different. In a typical experiment, desired amounts of glucose and catalyst were dissolved in Bu-DBUCl in a flask of 10 mL sealed with a glass stopper. The mixture was stirred at 100 °C for a desired time. Then, the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields. Each reaction was repeated at least two times. In the experiments to test the reusability, 1 mL of water was added into the reaction system after the reaction. Then the mixture was extracted with diethyl ether to remove the HMF produced. After extraction, the water in the CrCl<sub>3</sub>·6H<sub>2</sub>O/Bu-DBUCl mixture was removed under reduced pressure at 80 °C. The CrCl<sub>3</sub>·6H<sub>2</sub>O/Bu-DBUCl system was then used directly for the next run by adding new glucose.

#### Analysis methods for product

The amount of HMF was analyzed by HPLC with Shimadzu LC-15C pump, Shimadzu UV-Vis SPD-15C detector at 282.0 nm, and a Supelcosil LC-18 5ìm column at 30 °C. Before analyzed, the reaction mixture was diluted to 1000 mL. Methanol/water solution (50/50 v/v) was used as the mobile phase at flow rate of 0.8 mL min<sup>-1</sup>.

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