Green Chemistry

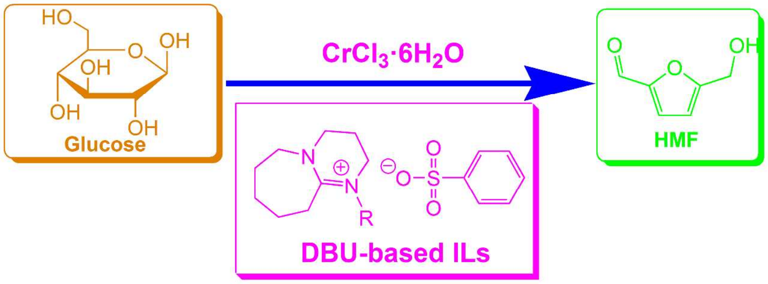
Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Graphical abstract

DBU-based ionic liquids with benzenesulfonate anion were excellent solvents for dehydration of glucose to HMF with high yield of 83.4%.



Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Very efficient conversion of glucose to 5-hydroxymethylfurfural in DBU-based ionic liquids with benzenesulfonate anion

Lingqiao Wu, Jinliang Song,* Binbin Zhang, Baowen Zhou, Huacong Zhou, Honglei Fan, Yingying Yang, Buxing Han*

Efficient conversion of glucose to 5-hydroxymethylfurfural (HMF), an important platform molecular for fuels and chemicals, is a promising topic in green chemistry. In this work, several new DBU-based (DBU=1,8-diazabicyclo[5.4.0] undec-7-ene) ionic liquids (ILs) with benzene sulfonate (BS) anion were synthesized and used as the solvents for the dehydration of glucose to HMF. It was found that all the ILs were excellent solvents for the dehydration of glucose to form HMF using $CrCl_3$ as the catalyst. The effects of various factors, such as kinds of catalysts, catalyst amount, reaction time and reaction temperature, on the yields of HMF were studied systematically in Et-DBUBS/$CrCl_3$ catalytic system. The yield of HMF from glucose could reach 83.4% under the optimized reaction conditions, and the reasons for the high yield were investigated on the basis of control experiments. The Et-DBUBS/$CrCl_3$ system could be reused at least five times without considerable reduction in the efficiency. Further study indicated that the catalytic system was also very efficient for transformation of fructose, inulin, and cellobiose to HMF.

Introduction

Diminishing fossil fuel reserves and growing concerns about global warming have led to increasing interest in searching sustainable alternatives of fossil resources for chemicals and energy supply.[1] Much attention has been paid to the conversion of biomass into various valuable chemicals in recent years.[2] Dehydration of carbohydrates (*e. g.* glucose, fructose, inulin, cellobiose and cellulose) into 5-hydroxymethylfurfural (HMF) is one of the most promising and successful routes because HMF is considered as an important platform chemical derived from biomass[3] and can be used to produce fine chemicals, liquid fuels and materials, which are mainly derived from petroleum currently.[4]

Although high yields of HMF could be easily obtained from dehydration of fructose using various catalytic systems,[5] the production of HMF from glucose is more attractive because glucose could be easily obtained through the hydrolysis of cellulose, which is inedible and the amount produced is very large. However, dehydration of glucose to produce HMF is more difficult than fructose and much effort has been devoted to the transformation of glucose into HMF. Up to now, various catalysts have been developed for the production of HMF from dehydration of glucose, including Lewis acid catalysts,[6] tantalum compounds,[7] boric acid,[8] ionic liquids (ILs),[9] ion exchange resins,[10] zeolites,[11] chromium(0) nanoparticles,[12]Sn-Mont catalyst,[13]bifunctional SO_4^{2-}/ZrO_2 catalysts,[14]mesoporous tantalum phosphate,[15] and so on.

Among the above catalysts, Lewis acid catalysts are an important type of catalyst for the dehydration of glucose to produce HMF. For example, it has been reported that chromium(II) chloride could catalyze dehydration of glucose to HMF with good yields of about 70% using 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as reaction solvent.[16] Hu *et al.* reported that 62% yield of HMF was achieved from glucose in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) catalyzed by $SnCl_4$.[17] Furthermore, germanium(IV) chloride was found to be effective catalyst for the production of HMF from glucose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with a yield of 48.4%.[18] Other Lewis acids, such as lanthanide chlorides,[19] hafnium(IV) chloride,[20] scandium chloride,[21] aluminum chloride,[22] aluminum alkyls and alkoxides,[23] could also be used to catalyze the dehydration of glucose to form HMF in various reaction solvents. Although excellent results have been obtained, development of efficient catalytic systems to enhance the efficiency and yield of the reaction is still highly desirable.

Additionally, solvents have an important effect on the activity and selectivity for the formation of HMF from the dehydration of glucose. The dehydration of glucose has been conducted in traditional organic solvents,[24] water,[25] multiphase systems[26] and ILs[27]. Among these solvents, ILs are very attractive for the dehydration reaction because of their unusual properties, such as high thermal and chemical stability, non-flammability, negligible vapor pressure, adjustable functions.[28] Up to now, some ILs have been successfully used as the reaction solvents for the dehydration of glucose to produce HMF, including [EMIM]Cl,[16] [BMIM]Cl,[29] [EMIM]BF_4,[17] Bu-DBUCl,[30] etc. However, the type of ILs for the reaction is limited and enhancing the yield of the product is of great importance. Therefore, it is still highly desirable to develop new and easily prepared ILs as the efficient reaction media for transformation of glucose into HMF.

In this work, we synthesized several DBU-based (DBU=1,8-diazabicyclo[5.4.0] undec-7-ene) ILs with benzene sulfonate (BS) anion (Scheme 1). Interest in these ILs stems from their facile synthesis from commercially available and relatively inexpensive starting materials, excellent air/water and thermal stability. More importantly, the existence of BS anion may increase the activity and selectivity of the reaction through the formation of hydrogen bond between BS and glucose. Indeed, it was found that these DBU-based ILs could be used as very efficient reaction media for the dehydration of glucose to form HMF catalyzed by $CrCl_3$ $6H_2O$ (abbreviated as $CrCl_3$ in the following). Furthermore, the DBU-based ILs/$CrCl_3$ catalytic system could be also used in the production of HMF from other carbohydrates, such as fructose, inulin, and cellobiose. To the best of our knowledge, this is the first application of DBU-based ILs with BS anion in conversion of carbohydrates into HMF, and the HMF yield from glucose obtained in our catalytic systems was very high, which could reach up to 83.4%.

Experimental section

Materials

Fructose (99%), cellobiose (98+%), cellulose (microcrystalline), starch (soluble), (1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (98%), $AlCl_3$, $CrCl_3$ $6H_2O$ (98%) and $CrCl_2$ (98%) were purchased from Alfa Aesar. Glucose (99%) and inulin (95%) was provide by J&K Scientific Ltd. Benzyl chloride, $MnCl_2$ $4H_2O$, $NiCl_2$ $6H_2O$, $SnCl_4$ $5H_2O$, acetonitrile, ethyl acetate, KOH, benzenesulfonic acid (70% water solution) and diethyl ether were A. R. grade and were provided by Sinopharm Chemical Reagent Beijing Co., Ltd. Bromoethane, allyl bromide and butyl bromide with C. P. grade were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All chemicals were used as received. Potassium benzene sulfonate was synthesized through the reaction between KOH and benzenesulfonic acid.

Synthesis of ILs with BS anion

To synthesize ILs with BS anion, the corresponding ILs with halogen anion (Cl or Br) were firstly synthesized. 0.5 mol of DBU and 0.8 mol of halohydrocarbon were added to 500 mL ethyl acetate in a flask of 1000 mL. The reaction mixture was stirred at room temperature for 48 h. After the reaction, the ILs with halogen anion were obtained by filtering, washing with diethyl ether, and drying at 40 °C for 24 h under vacuum.

Then, the ILs with halogen anion (Cl or Br) obtained above (0.3 mol) and potassium benzene sulfonate (0.35 mol) were added to acetonitrile (800 mL) in a beaker of 1000 mL equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature under 48 h. After the reaction, the reaction mixture was filtered to remove the solid salts. Then, the filtrate was heated at 80 °C under vacuum to remove acetonitrile to get the ILs with BS anion. The synthesized ILs were characterized as follows.

Et-DBUBS. White solid; ^{1}H NMR (D_2O, 300 MHz) δ (ppm) 7.81-7.54 (m, 5H), 3.57-3.40 (m, 8H), 2.79-2.76 (m, 2H), 2.04-1.94 (m, 2H), 1.70-1.68 (m, 6H), 1.20-1.16 (m, 3H); ^{13}C NMR δ (ppm) 166.1, 142.3, 131.5, 129.0, 125.3, 54.4, 48.6, 48.4, 46.0, 28.4, 28.0, 27.5, 25.5, 23.2, 19.6, 12.8.

Al-DBUBS. Light yellow solid; ^{1}H NMR (D_2O, 300 MHz) δ (ppm) 7.82-7.51 (m, 5H), 5.88-5.77 (m, 1H), 5.26 (q, J=9.0Hz, 2H), 4.10-4.07 (m, 2H), 3.58-3.36 (m, 6H), 2.71-2.68 (m, 2H), 2.05-1.97 (m, 2H), 1.70-1.60 (m, 6H). ^{13}C NMR δ (ppm) 166.9, 142.5, 131.5, 130.9, 128.9, 125.3, 116.9, 54.9, 54.7, 48.7, 46.7, 28.0, 27.9, 25.5, 22.5, 19.5.

Bu-DBUBS. Light yellow oil; ^{1}H NMR (D_2O, 300 MHz) δ (ppm) 7.80-7.51 (m, 5H), 3.54-3.52 (m, 2H), 3.45-3.37 (m, 6H), 2.76 (d, J=9.01Hz, 2H), 2.05-1.93 (m, 2H), 1.71-1.35 (m, 8H), 1.35-1.22 (m, 2H), 0.90 (t, J=5.7 Hz, 3H); ^{13}C NMR δ (ppm) 166.2, 142.6, 131.5, 128.9, 125.3, 54.4, 53.2,48.6, 46.7, 30.0, 28.0, 27.6, 25.5, 22.7, 19.5, 19.1, 13.0.

Bn-DBUBS. Transparent oil; ^{1}H NMR (D_2O, 300 MHz) δ (ppm) 7.82-7.77 (m, 2H), 7.51-7.34 (m, 6H), 7.23 (d, J=6.90 Hz, 2H), 4.69 (s, 2H), 3.58-3.39 (m, 6H), 2.70 (t, J=5.40, 2H), 2.05-1.97 (m, 2H), 1.63 (d, J=2.70, 4H), 1.47 (d, J=5.10, 2H); ^{13}C NMR δ (ppm) 167.1, 142.6, 135.1, 131.4, 129.1, 128.9, 128.1, 126.4, 125.3, 56.0, 54.8, 48.8, 47.4, 28.2, 27.9, 25.4, 22.2, 19.5.

General procedures of the reaction for HMF generation

All the experiments were carried out in a flask of 5 mL in an oil bath. Only the procedures for the synthesis of HMF from glucose in an IL are discussed because those for other sugars were similar. Typically, desired amounts of glucose and catalyst were added to the preheated Et-DBUBS in the flask sealed with a glass stopper. The reaction mixture was stirred at desired temperature. After a suitable reaction time, the mixture was cooled to room temperature immediately. Then, all the samples were analyzed by HPLC to obtain the HMF yields. Each reaction was repeated at least two times, and average yield was reported. In the experiment to test the reusability, 0.5 mL of deionized water was added into the reaction system after the reaction. Then the produced HMF was extracted with diethyl ether. After extraction, the Et-DBUBS/$CrCl_3$ system was heated to 80 °C to remove the water under vacuum. Then, the Et-DBUBS/$CrCl_3$ system was directly used for the next run by adding new glucose.

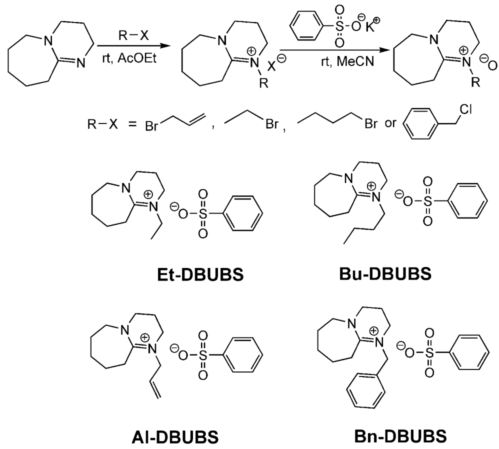
HMF analysis

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 5 ìm column at 35 °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 a flow rate of 0.8 mL/min.

Results and discussion

Synthesis of the ILs with BS anion

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



Scheme 1. Synthesis of the DBU-based ILs with BS anion and their structures.

Catalyst screening in Et-DBUBS

Some metal salts in ILs have been demonstrated to be efficient catalysts for the conversion of glucose to HMF.[16] In our study, activity of various catalysts for the conversion of glucose to HMF was tested at 100 °C for 3 h in Et-DBUBS, and the results are summarized in Table 1. Among the catalysts tested, $CrCl_3$ (entry 1), $SnCl_4\ 5H_2O$ (entry 2) and $CrCl_2$ (entry 3) had high activity for the reaction and $CrCl_3$ was the best for the reaction. The yield of HMF could reach 78.6% in the presence of $CrCl_3$ in IL Et-DBUBS. In addition, some results of typical catalytic systems used in the production of HMF from glucose were also given in Table 1 (entries 6-9). It can be known that the catalytic system of this work was very efficient. Based on the results discussed above, we chose $CrCl_3$ as the dehydration catalyst to study effect of reaction parameters on the reaction in Et-DBUBS.

Table 1. Catalytic activity of different metal catalysts in Et-DBUBS.[a]

Entry	Catalyst	Solvent	Temperature (°C)	Yield (%)[b]	Selectivity (%)
1	$CrCl_3$	Et-DBUBS	100	78.6	84.2
2	$SnCl_4\ 5H_2O$	Et-DBUBS	100	69.1	69.6
3	$CrCl_2$	Et-DBUBS	100	62.2	63.4
4	$AlCl_3$	Et-DBUBS	100	47.4	52.3
5	$NiCl_2\ 6H_2O$	Et-DBUBS	100	1.2	--
6	$MnCl_2\ 4H_2O$	Et-DBUBS	100	0	--
7[c]	$CrCl_3\ 6H_2O$	Bu-DBUCl	100	64	--
8[d]	$CrCl_2$	[EMIM]Cl	100	71	--
9[e]	$SnCl_4$	$[EMIM]BF_4$	100	61	--
10[f]	FPILs	DMSO	150	34.2	--

[a]Reaction conditions: 1 g Et-DBUBS, 0.1 g glucose, 10 mol% (based on glucose) catalyst, reaction time 3 h. [b]HMF yields were determined by HPLC. [c]The data was obtained from reference 30. [d]The data was obtained from reference 16. [e]The data was obtained from reference 17. [f]The data was obtained from reference 31.

Influence of catalyst amount

In order to investigate the appropriate amount of catalyst, the influence of amount of $CrCl_3$ on the dehydration of glucose into HMF was examined in Et-DBUBS at 100 °C with a reaction time of 3 h, and the results are given in Figure 1. It can be seen that the yield of HMF reached a maximum as the amount of the catalyst was 10 mol%. Further increasing the amount of catalyst resulted in slight decrease of HMF yield. These results demonstrated that less catalyst amount led to a relatively slow reaction, and excess catalyst amount could cause the side reactions to humins or other compounds.[22] Therefore, 10 mol% amount of catalyst based on glucose was the optimal catalyst amount for the reaction at our reaction conditions.

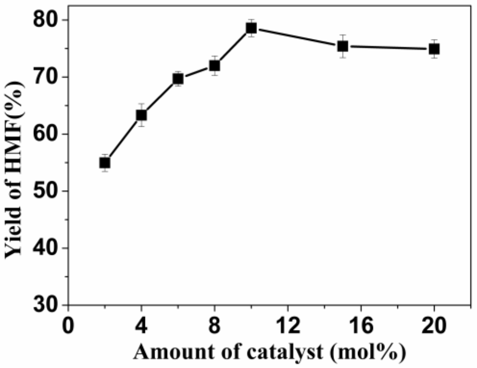


Figure 1. Influence of the amount of catalyst on HMF yield. Reaction conditions: 1 g Et-DBUBS, 0.1 g glucose, reaction temperature 100 °C, reaction time 3 h.

Effect of reaction temperature

We studied the effect of reaction temperature on the dehydration of glucose to HMF in Et-DBUBS/$CrCl_3$ system with a reaction time of 3 h and the results are shown in Figure 2. The yield of HMF reached 82.2 % when the temperature increased from 80 °C to 110 °C and then slowly decreased to 80.7 % when the reaction temperature increased to 120 °C. 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,[15] were also accelerated by rising temperature. The competition of the two opposite factors resulted in the highest yield at 110 °C.

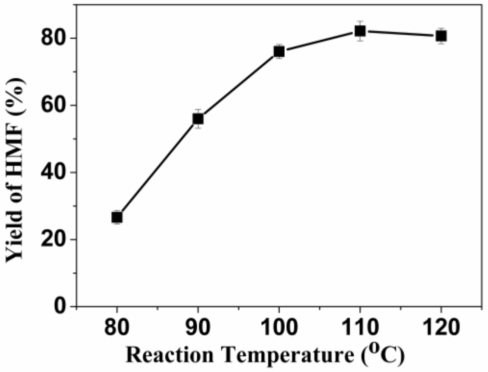


Figure 2. Effect of reaction temperature on the conversion of glucose to HMF in Et-DBUBS/$CrCl_3$ system. Reaction conditions: 1 g Et-DBUBS, 0.1 g glucose, 10 mol% $CrCl_3$ (based on glucose), reaction time 3 h.

Effect of reaction time

We studied the influence of reaction time at different reaction temperature (Figure 3). From Figure 3, we can see that when the reaction was conducted at 110 ^{o}C, the yield increased dramatically with time at the beginning, and reached the maximum 83.4% at 2 hrs. The yield was unchanged as the reaction time increased from 2 h to 3 h.

Possible reason for the high yield in Et-DBUBS

[BMIM]Cl/$CrCl_3$ is a very efficient catalytic system with high HMF yield.[16,32] We believe that the reaction pathway of the reaction in our reaction system is the same as that reported by Zhao and co-workers.[16] In order to study the possible reason for the high yield in Et-DBUBS/$CrCl_3$ catalytic system, we also carried out the reaction in [BMIM]Cl/$CrCl_3$, and the results obtained in this work were consistent with that reported by Zhao and co-workers.[16] The yields of HMF in the two catalytic systems at the same reaction conditions are compared in Figure 3. Three main factors affected the maximum yield of HMF, *i.e.*, the rate to generate the product HMF, the rate to form by-products directly from the reactant (glucose), and the rate for the conversion of HMF to by-products. To elucidate the effect of the conversion of HMF to by-products on the yield, we studied the transformation of HMF (10 wt%) in Et-DBUBS/$CrCl_3$ and [BMIM]Cl/$CrCl_3$ at the same conditions shown in Figure 3. The results demonstrated that conversion of HMF was negligible at the condition in 2 h. These control experiments indicated that the third factor above was not the reason for the higher yield of HMF in our catalytic system. Figure 3 shows that the maximum yield in both systems occurred at 2 h. Meanwhile, our experiments showed that the times for the complete conversion of glucose in the two ILs were the same. Therefore, it can be deduced that the rate to form by-products directly from glucose in Et-DBUBS/$CrCl_3$ was slower, which was the main reason for the very high yield of HMF in the system.

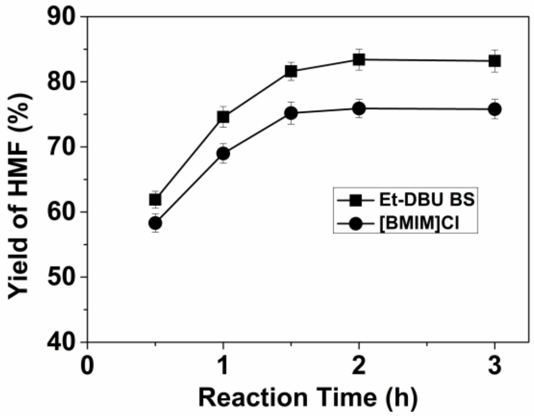


Figure 3. Effect of reaction time on dehydration of glucose to the HMF in ILs/$CrCl_3$ catalytic system. Reaction conditions: 1 g solvent, 0.1 g glucose, 10 mol% (based on glucose) $CrCl_3$, reaction temperature 110 ^{o}C.

Effect of amount of glucose

The effect of the amount of glucose on the HMF yield was investigated as the amount of $CrCl_3$ was fixed at 10 mol% (based on glucose). As shown in Figure 4, HMF yield decreased from 84.4% to 68.4% when the amount of glucose increased from 50 mg to 200 mg. This may result mainly from the increasing concentration of $CrCl_3$ and glucose in Et-DBUBS, which could increase the side reactions such as polymerization and rehydration of products, and humin was the main by-product.[22]

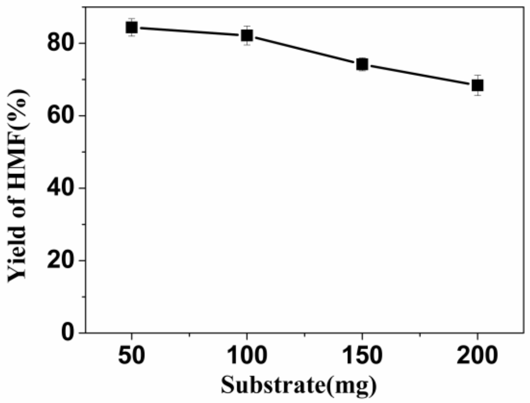


Figure 4. Effect of different mass of glucose on the HMF yield. Reaction conditions: 1 g Et-DBUBS, 10 mol% (based on glucose) $CrCl_3$, reaction temperature 110 ^{o}C, reaction time 2 h.

The reusability of $CrCl_3$ $6H_2O$/Et-DBUBS system

In this work, we also investigated the reusability of the Et-DBUBS/$CrCl_3$ catalytic system. 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. It can be seen from Figure 5 that Et-DBUBS/$CrCl_3$ system could be reused at least five times without considerable reduction in reaction efficiency.

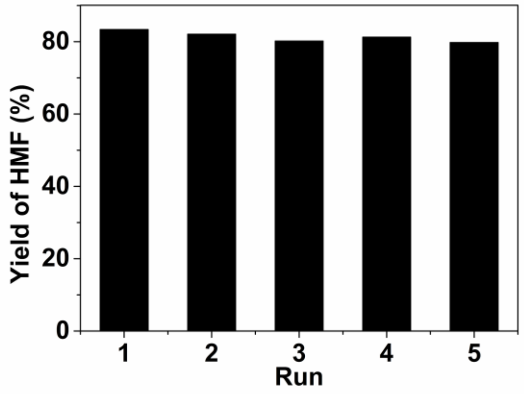


Figure 5. Reusability of Et-DBUBS/$CrCl_3$ system. Reaction conditions: 1 g Et-DBUBS, 0.1 g glucose, 10 mol% (based on glucose) $CrCl_3$, reaction temperature 110 ^{o}C, reaction time 2 h.

Effect of various DBU-based ILs with BS anion

Table 2 shows the results of synthesis of HMF from glucose catalyzed by $CrCl_3$ in various new ILs prepared (shown in Scheme 1) as reaction solvents. The four ILs were all effective solvents for the production of HMF from glucose (entries 1-4) and Et-DBUBS generated the best result with 83.4% HMF yield (entry 1), which was higher than the typical results reported in the literature (entries 6-9, Table 1). From Table 2, we can also know that the yield of HMF decreased with increasing chain length on the nitrogen atom of DBU in the ILs (entries 1 and 3). The low efficiency in Bn-DBUBS may results from the steric hindrance due to the existence of benzyl group, which may affect the isomerization of glucose. From entries 3 and 7, it can be known that the ILs with BS anion gave higher HMF yields than ILs with Cl anion. In addition, Et-DBUBS could give a higher HMF yield than [EMIM]Br and [EMIM]BF_4 (entries 5 and 6).

Table 2. Effect of different solvents for the conversion of glucose to HMF.[a]

Entry	Solvent	Time (h)	Temperature (°C)	Yield (%)[b]	Selectivity (%)
1	Et-DBUBS	2	110	83.4	83.7
2	Al-DBUBS	2	110	78.5	80.4
3	Bu-DBUBS	2	110	70.1	74.0
4	Bn-DBUBS	2	110	72.4	72.6
5	[EMIM]Br	2	110	52.3	52.4
6	[EMIM]BF_4	2	110	1.3	1.3
7[c]	Bu-DBUCl	3	100	64.0	--

[a]Reaction conditions: 1 g solvent, 0.1 g glucose,10 mol% (based on glucose) $CrCl_3$. [b]HMF yields were determined by HPLC. [c]The data was obtained from reference 30.

Dehydration of different substrates

Based on the results obtained from the dehydration of glucose, transformation of other carbohydrates into HMF was also studied in the Et-DBUBS/$CrCl_3$ system at suitable conditions and the results were shown in Table 3. As expected, fructose gave the best result with a HMF yield of 91.3% (entry 1) in our catalytic system. Except for fructose, inulin and cellobiose also gained good HMF yield of 77.9% and 68.3%, respectively (entries 3 and 4).

Table 3. Dehydration of different substrates in Et-DBUBS catalyzed by $CrCl_3$.[a]

Entry	Substrate	Time (h)	Temperature (°C)	Yield (%)[b]
1	Fructose	2	110	91.3
2	Glucose	2	110	83.4
3	Inulin	2	110	77.9
4	Inulin	4	110	87.5
5	Cellobiose	2	110	68.3
6	Cellobiose	4	110	74.8
7	Starch	2	110	1.4
8	Cellulose	2	110	0.3

[a]Reaction conditions: 1 g Et-DBUBS, 0.1 g substrate, 10 mol% (based on hexose unit) $CrCl_3$. [b]HMF yield is determined by HPLC.

Conclusion

Several DBU-based new ILs, Et-DBUBS, Al-DBUBS, Bu-DBUBS and Bn-DBUBS, have been synthesized, and used as solvents in the synthesis of HMF from dehydration of glucose catalyzed by $CrCl_3$. In Et-DBUBS/$CrCl_3$ catalytic system, the HMF yield can be as high as 83.4%. One of the main reasons for the very high yield of the product is that the rate to generate by-products directly from glucose in Et-DBUBS/$CrCl_3$ was slow. The Et-DBUBS/$CrCl_3$ catalytic system can be reused at least five times without considerable reduction in HMF yield. In addition, satisfactory results were also obtained when fructose, inulin and cellobiose were used as the feedstocks to produce HMF. The efficient, simple, cheaper and reusable catalytic system has great potential application for producing HMF from the dehydration of carbohydrates.

Acknowledgements

The authors thank the National Natural Science Foundation of China. This work was supported by National Natural Science Foundation of China (21173234, 21133009, U1232203, 21021003), and Chinese Academy of Sciences (KJCX2.YW.H30).

Notes and references

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
Tel/fax: 86-10-62562821. E-mail address: Hanbx@iccas.ac.cn, songjl@iccas.ac.cn.

1 (a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.*, 2006, **106**, 4044-4098; (b) Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature*, 2007, **447**, 982-985; (c) A. Corma, S. Iborra, A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502; (d) H. de Lasa, E. Salaices, J. Mazumder, R. Lucky, *Chem. Rev.*, 2011, **111**, 5404-5433; (e) V. V. Ordomsky, V. L. Sushkevich, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, *J. Catal.*, 2013, **300**, 37-46.

2 (a) F. W. Lichtenthaler, *Acc.Chem.Res.*, 2002, **35**, 728-737; (b) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075-8098; (c) C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science*, 2012, **337**, 695-699; (d) L. Bui, H. Luo, W. R. Gunther, Y. Román-Leshkov, *Angew. Chem. Int. Ed.*, 2013, **52**, 8022-8025; (e) M. Y.He, Y. H. Sun, B. X. Han, *Angew. Chem. Int. Ed.*, 2013, **52**, 9620-9633; (f) J. L. Song, H. L. Fan, J. Ma, B. X. Han, *Green Chem.*, 2013, **15**, 2619-2635; (g) T. Wang, M. W. Nolte, B. H. Shanks, *Green Chem.*, 2014, **16**, 548-572.

3 (a) M. Bicker, S. Endres, L. Ott, H. Vogel, *J. Mol. Catal. A: Chem.*, 2005, **239**, 151-157; (b) J. N. Chheda, G.W. Huber, J.A. Dumesic, *Angew. Chem. Int. Ed.*, 2007,**46**, 7164-7183; (c) M. E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, *Chem. Rev.*, 2011, **111**, 397-417; (d) S. Subbiah, S. P. Simeonov, J. M. S. S. Esperança, L. P. N. Rebelo, C. A. M. Afonso, *Green Chem.*, 2013, **15**, 2849-2853.

4 (a) H. Rasmussen, H. R. Sørensen, A. S. Meyer, *Carbohydr.Res.*, 2014, **385**, 45-57 (b) Y. Román-Leshkov, M. Moliner, J. A. Labinger, M. E. Davis, *Angew. Chem. Int. Ed.*, 2010, **49**, 8954-8957; (c) H. Ning, J. L. Song, M. Q. Hou, D. Z. Yang, H. L. Fan, B. X. Han, *Sci. China Chem.*, 2013, **56**, 1578-1585; (d) R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499-1597.

5 (a) C. Moreau, A. Finiels, L. Vanoye,*J. Mol. Catal. A: Chem.*, 2006, **253**, 165-169 ; (b) T. S. Hansen, J. Mielby, A. Riisager, *Green Chem.*, 2011, **13**,109-114; (c) A. J. Crisci, M. H. Tucker, M. Y. Lee, S. G. Jang, J. A. Dumesic, S. L. Scott, *ACS Catal.*, 2011, **1**, 719-728; (d) H. Xie, Z. K. Zhao, Q. Wang, *ChemSusChem*, 2012, **5**, 901-905; (e) X. Qi, H. Guo, L. Li, R. L. Smith, *ChemSusChem*, 2012, **5**, 2215-2220;

(f) J. L. Song, B. B. Zhang, J. H. Shi, J. Ma, G. Y. Yang, B. X. Han, *Chin. J. Chem.*, 2012, **30**, 2079-2084; (g) R. Liu, J. Chen, X. Huang, L. Chen, L. Ma, X. Li, *Green Chem.*, 2013, **15**, 2895-2903.

6 J. B. Binder, R. T. Raones, *J. Am. Chem. Soc.*, 2009, **131**, 1979-1985.

7 F. Yang, Q. Liu, M. Yue, X. Bai, Y. Du, *Chem. Commun.*, 2011, **47**, 4469-4471.

8 T. Ståhlberg, S. Rodriguez-Rodriguez, P. Fristrup, A. Riisager, *Chem. Eur. J.*, 2011, **17**, 1456-1464.

9 Y. Qu, C. Huang, Y. Song, J. Zhang, B. Chen, *Bioresour. Technol.*, 2012, **121**, 462-466.

10 V. Heguaburu, J. Franco, L. Reina, C. Tabarez, G. Moyna, P. Moyna, *Catal. Commun.*, 2012, **27**, 88-91.

11 (a) I. Jiménez-Morales, J. Santamaría-González, A. Jiménez-López, P. Maireles-Torres, *Fuel*, 2014, **118**, 265-271; (b) M. Moliner, Y. Román-Leshkov, M.E. Davis, *Proc. Natl. Acad. Sci. USA*, 2010, **107**, 6164-6168; (c) J. S. Kruger, V. Nikolakis, D. G. Vlachos, *Appl. Catal. A: Gen.*, 2014, **469**, 116-123.

12 J. He, Y. Zhang, E. Y.-X. Chen, *ChemSusChem*, 2013, **6**, 61-64.

13 J. J. Wang, J. W. Ren, X. H. Liu, J. X. Xi, Q. N. Xia, Y. H. Zu, G. Z. Lu, Y. Q. Wang, *Green Chem.*, 2012, **14**, 2506-2512.

14 A. Osatiashtiani, A. F. Lee, D. R. Brown, J. A. Melero, G. Morales, K. Wilson, *Catal. Sci. Technol.*, 2014, **4**, 333-342.

15 I. Jiménez-Morales, A. Teckchandani-Ortiz, J. Santamaría-González, P. Maireles-Torres, A. Jiménez-López, *Appl. Catal. B: Environ.*, 2014, **144**, 22-28.

16. H.Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science*, 2007, **316**, 1597-1600.

17 S. Q. Hu, Z. F. Zhang, J. L. Song, Y. X. Zhou, B. X. Han,*Green Chem.*, 2009, **11**, 1746-1749.

18 Z. Zhang, Q. Wang, H. Xie, W. Liu, Z. K. Zhao, *ChemSusChem*, 2011, **4**, 131-138.

19 T. Ståhlberg, M. G. Sørensen, A. Riisager, *Green Chem.*, 2010, **12**, 321-325.

20 L. Hu, Y. Sun, L. Lin, S. J. Liu, *Biomass Bioenergy*, 2012, **47**, 289-294.

21 X. Zhou, Z. Zhang, B. Liu, Z. Xu, K. Deng, *Carbohydr. Res.*, 2013, **375**, 68-72.

22 Y. Yang, C. W. Hu, M. M. Abu-Omar, *J. Mol. Catal. A: Chem.*, 2013, **376**, 98-102

23 D. Liu, E.Y.-X. Chen, *Appl. Catal. A: Gen.*, 2012, **435-436**, 78-85.

24 J. J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, *Green Chem.*, 2011, **13**, 2678-2681.

25 (a) T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou, Y. Zhu, *Chem. Commun.*, 2012, **48**, 5494-5496; (b) S. De, S. Dutta, B. Saha, *Green Chem.*, 2011, **13**, 2859-2868.

26 (a) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science*, 2006, **312**, 1933-1937; (b) Z. Zhang, B. Du, L. J. Zhang, Y. X. Da, Z. J. Quan, L. J. Yang, X. C. Wang, *RSC Adv.*, 2013, **3**, 9201-9205; (c) B. Saha, M. M. Abu-Omar, *Green Chem.*, 2014, **16**, 24-38.

27 (a) W. Liu, J. Holladay, *Catal. Today*, 2013, **200**, 106-116; (b) J. Shi, H. Gao, Y. Xia, W. Li, H. Wang, C. Zheng, *RSC Adv.*, 2013, **3**, 7782-7790.

28 J. P. Hallett, T. Welton, *Chem. Rev.*, 2011, **111**, 3508-3576.

29 B. Saha, S. De, M. Fan, *Fuel*, 2013, **111**, 598-605.

30 J. L. Song, B. B. Zhang, J. H. Shi, H. L. Fan, J. Ma, Y. Y. Yang, B. X. Han, *RSC Adv.*, 2013, **3**, 20085-20090.

31 H. Li, Q. Zhang, X. Liu, F. Chang, Y. Zhang, W. Xue, S. Yang, *Bioresour. Technol.*, 2013, **144**, 21-27.

32 G. Yong, Y. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.*, 2008, **47**, 9345-9348.