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Efficient process for the direct transformation of cellulose and carbohydrates to 5-(hydroxymenthyl)furfural with dual-core sulfonic acid ionic liquids and co-catalysts†

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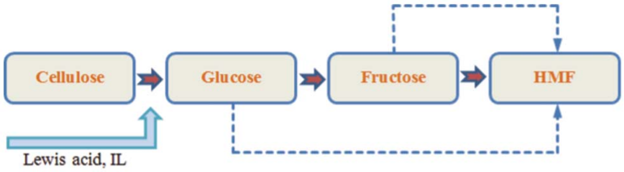
The direct transformation of cellulose and carbohydrates into 5-(hydroxymethyl)furfural (HMF) in the solvent [BMIM]Cl using dual-core sulfonic acid ionic liquids (ILs) as catalysts and metal salts as co-catalysts was investigated, aiming at a more environmentally friendly process not involving chromium. From the high throughput screening of various metal salts, a combination of [bi-C_3SO_3HMIM][CH_3SO_3] (IL-2) and manganese chloride ($MnCl_2$) was found to be the most effective catalyst. HMF was directly afforded from cellulose in 66.5% yield. Thus, synthesis of HMF was successfully performed from cellulose using ILs and $MnCl_2$. Following the principles of green engineering, we recycled the catalyst in our system for cellulose hydrolysis and this catalyst maintained its good performance even after four runs. Furthermore, various sugars and lignocellulosic raw materials could be directly converted into HMF in reasonable yields under these conditions. The mechanism that explains the high activity of ILs in combination with $MnCl_2$ is also proposed.

Introduction

With the rapid development of society, energy demand has increased, and is projected to grow by more than 50% by 2025.[1] However, it is known that fossil fuels cannot be considered as the world's main source of energy for more than another 100 years. As a result, cellulose, which is the most abundant form of biomass, has been the target of intensive research for conversion to other chemicals.[2–4] It has the potential to become a promising alternative to fossil resources for the sustainable production of 5-hydroxymenthylfurfural (HMF), a versatile and key intermediate in the bio-fuel chemistry and petrochemical industries. Cellulose has a highly crystalline structure formed from linear polymer D-an-hydroglucopyranose units joined together in long chains by β-1,4-glycosidic bonds. An extensive network of such polymer chains arranged in ordered alignment *via* hydrogen-bonding[5] and van der Waals forces[6] results in a supramolecular cellulose structure of varying size, crystallinity, and complexity. So it is practically difficult to dissolve cellulose in most common organic solvents because of its stiff molecules and close chain packing *via* numerous intermolecular and intramolecular H-bonds.[7] The tight H-bond network and van der Waals interactions greatly stabilize it, too, which makes it notoriously resistant to hydrolysis.

As is shown in Scheme 1, the first barrier in the conversion of cellulose to HMF is the decrystallization and cleavage of cellulose to glucose. In the past few years, many studies have focused on this pathway, because cellulose itself is too stable for the crystalline structure to be easily broken.[8–12] However, the depolymerization of cellulose into HMF still remains an expensive and poor efficiency process.

So far, the depolymerization of cellulose into HMF has still been a great challenge from either an environmental or an efficiency point of view. Due to the increased interest and demand for industrial applications, substantial efforts have been devoted to the development of appropriate hydrolysis schemes, including catalysis using mineral acids and hetero-



Scheme 1 The chemical pathway of the direct conversion of cellulose into HMF.

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poly acids. However, there are many disadvantages to these processes, such as the use of mineral acids only being efficient at too high a temperature (170–240 °C), the corrosion of equipment, and the generation of large amounts of acidic waste water. The inherent advantages of heteropoly acid hydrolysis are their high catalytic activity, reusability, fewer side reactions, strong Brønsted acidity and so on. Moreover, a remarkably high yield of glucose (82.4%) was obtained,[13] but the disadvantage was the low selectivity of HMF. Therefore, more efficient catalytic systems have been developed recently; the utilization of metal ions in ionic liquids (ILs) was demonstrated as an efficient approach for the conversion of cellulose into HMF. Zhao's group[14] studied the conversion of lignocellulosic biomass into furans in ionic liquids in the presence of $CrCl_3$ under microwave irradiation, and the yield of HMF reached 45%–52%. In 2009, Raines *et al.*[15] reported that *N*,*N*-dimethylacetamide containing lithium chloride was a privileged solvent that enabled the synthesis of HMF in a single step; the yield of HMF obtained from cellulose was 50%. Cho *et al.*[16] found that a combination of $CrCl_2$ and $RuCl_3$ was an effective catalyst; HMF was directly afforded from cellulose in nearly 60% yield in [EMIM]Cl. But as these studies had all used amounts of chromic salts, they failed to conform to the requirement of "green chemistry", although a high yield of HMF had been obtained. Recently, Kerton's group[17] reported a novel route that produced levulinic acid (4-oxopentanoic acid, LA) and HMF from chitosan in water under microwave irradiation. The volume of water used and the loading of $SnCl_4{\cdot}5H_2O$ could be varied to produce either LA or HMF with good selectivity. The results of this study may lead to the possibility of the chemical transformation of non-toxic and cheap biopolymers and yield useful industrial applications.

Along with this research progress, sulfonic acid functionalized ILs are considered as high-efficiency catalysts, especially when combined with metal chloride salts. Tao's group[18,19] investigated the hydrolysis of cellulose using catalytic amounts of $FeCl_2$ and $CoSO_4$ in ILs in the presence of 4-methyl-2-pentanone (MIBK) at 150 °C for 300 min, and HMF yields of 34 wt% and 24 wt% were achieved, respectively. However, the harsh conditions (high temperature and long time) and low yield did not reflect the superiority of sulfonic acid functionalized ILs.

Herein, we investigate the conversion of cellulose to HMF using several acidic ILs and metal salts, especially dual-core sulfonic acid ILs, such as [bi-C_3SO_3HMIM][HSO_4], [bi-C_3SO_3HMIM][CH_3SO_3], which have strong acidity (Fig. 1). Our objective in this work was to combine the ILs with metal ion catalysts and investigate the catalytic effect on the direct conversion of cellulose to HMF. Thus, an imidazolium-based IL ([BMIM]Cl) was used as the solvent together with various IL and metal ion catalysts at the mild temperatures of 100 °C and 120 °C. Additionally, the investigation studied the mechanisms of cellulose degradation to HMF. This process consisted of the hydrolysis of cellulose to β-glucose, isomerization of β-glucose to fructose, and fructose dehydration to HMF. Furthermore, metal ions mainly act as the catalyst for promoting the rapid conversion of α-glucose to β-glucose and the isomerization of β-glucose to fructose,[14] while cellulose hydrolysis and fructose dehydration can be simply achieved under acidic conditions. From the viewpoint of green chemistry, the reuse of the catalyst is investigated in our study of cellulose hydrolysis. Finally, the reaction system was applied to the conversion of hexoses (Fig. 2) and lignocellulosic raw materials to HMF.

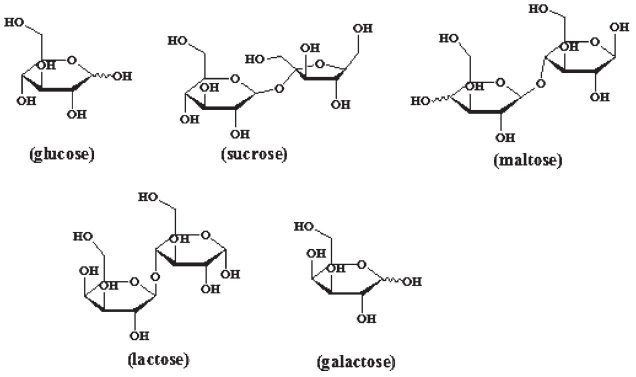
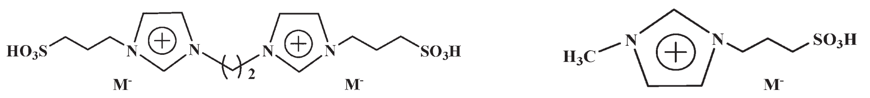


Fig. 2 Mono- and disaccharide precursors for HMF.

Results and discussion

Co-catalyst screening

It is known that metal salts in ILs have been demonstrated to be an efficient catalyst system for the conversion of cellulose to HMF.[14,15] In our study, we initially screened the hydrolysis of cellulose catalyzed with IL-1 by adding a catalytic amount of metal salt at 120 °C for 3 h (the catalyst dosage and molar yield are relative to the number of glucose units in the cellulose,



IL1 [bi-C_3SO_3HMIM][HSO_4]: M^-=HSO_4^-

IL-3 [C_3SO_3HMIM][HSO_4]: M^-=HSO_4^-

IL2 [bi-C_3SO_3HMIM][CH_3SO_3]:M^-=$CH_3SO_3^-$

IL-4 [C_3SO_3HMIM][CH_3SO_3]: M^-=$CH_3SO_3^-$

Fig. 1 Various sulfonic acid ILs used in the study.

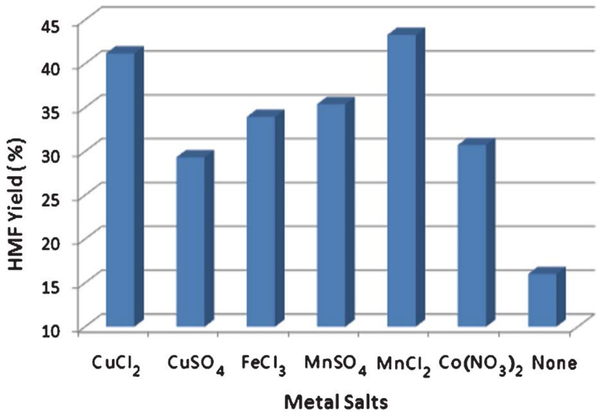


Fig. 3 High throughput screening of various metal catalysts for the direct transformation of cellulose into HMF in [BMIM]Cl. Conditions: each metal catalyst (4 mol% to cellulose), IL-1 (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.2 g), *T* = 120 °C, *t* = 3 h.

which is the same throughout). Fig. 3 shows the results of altering the metal catalyst by using $CuCl_2$, $CuSO_4$, $FeCl_3$, $MnSO_4$, $MnCl_2$ and $Co(NO_3)_2$, which each showed differing yields of HMF from 29.34% to 43.3%, and demonstrates that the presence of a metal salt can improve the yield of HMF significantly compared with the reaction without a catalyst. This is because although ILs can effectively transform cellulose into polysaccharide, disaccharide, and hydrolyze these into glucose, they cannot convert glucose into HMF. However, the metal salts have an excellent ability to hydrolyze glucose into HMF. So, when the two kinds of catalyst are used in concert to catalyze cellulose degradation, they obtain a higher yield of HMF. Compared with other metal salts, the catalytic effect of $MnCl_2$ and $CuCl_2$ is remarkable. The yield of HMF was increased by 27.28% and 25.16%, respectively. In our present system, the reason for the promotional effect of the manganese salt may be due to the Mn^{2+} coordination interaction. In addition, the Mn^{2+} could play an important role in promoting the rapid conversion of α-glucose to β-glucose and the isomerization of β-glucose to fructose, which improves the yield of HMF. In terms of conversion pathways, the direct transformation of cellulose into HMF involves four reactions: (I) the hydrolysis of polymeric microcrystalline cellulose into glucose (the saccharification process), (II) the rapid conversion of α-glucose to β-glucose, (III) the isomerization from the aldose-type sugar (opening the ring of β-glucose) to the 1,2-enediol intermediate which can finally convert into fructose *via* a ring closure, that is, allowing five-membered ring formation, and (IV) the dehydration of fructose to generate the final product, HMF (Scheme 1). In this way, we propose a mechanism in which $MnCl_2$ in IL-1 forms complexes of $[MnCl_2(HSO_4)_n]^{n-}$ and we suggest that these play a role in proton transfer, and facilitating the mutarotation of α-glucose (Fig. 4(a)). The proposed mechanism of the $MnCl_2$ and IL-1 promoted conversion of β-glucose into HMF and other products is shown in Fig. 4(b).

The effect of reaction time on the direct transformation of cellulose into HMF

The reaction time is a key parameter determining the conversion of cellulose and the yield of HMF. The results of the investigation into the effect of time are presented in Fig. 5. When reactions were carried out at 120 °C in [BMIM]Cl using $MnCl_2$ and an acidic ionic liquid as the co-catalyst, a maximum HMF yield of 45.62% was achieved after 2 h followed by a sharp decrease. Obviously, the hydrolysis rate at 120 °C was higher than the rate at 100 °C, when only a 34.95% yield of HMF was obtained after 2 h. As can be seen in Fig. 5, it would improve the yield of HMF if a high reaction temperature and long reaction time were used as this enhances the catalytic activity in the hydrolysis and dehydration steps, so for future reactions we used a temperature of 120 °C, although this is above the boiling point of water.

The effects of the (co-)catalyst and H_2O on the reaction

As mentioned by Shimizu *et al.*,[20] an acid catalyst with stronger Brønsted acidity could result in a higher relative rate of acid-catalyzed cellulose hydrolysis, thus the effect of the acidic ionic liquid dosage on the hydrolysis of cellulose should be studied. As shown in Fig. 6, the conversion of cellulose to HMF could be promoted by using acid catalysts in a reasonable dosage range. The amount of IL-1 used was 5 mol%, 9 mol%, 18 mol% and 54 mol%, respectively. When the dosage of IL-1 was increased from 5 mol% to 9 mol%, the yield of HMF increased obviously, from 15.78% to 51.98% after 1 h. However, when the amount of IL-1was increased from 9 mol% to 18 mol%, the yield of HMF after 1 h decreased to 48.01%, and when the dosage of IL-1 reached 54 mol%, only 15.3% of HMF was obtained after 1 h and the yield decreased sharply. It also showed that time become more critical when the dosage of IL-1 increased: (1) with increasing catalytic dosage, the reaction rate was accelerated; a maximum HMF yield of 22.19% was achieved with 5 mol% IL-1 after 2 h, but it only took about 1 h to reach the highest level (51.98%) with 9 mol% IL-1, and 0.5 h (50.09%) for 54 mol%, (2) when the amount of acidic ionic liquid was in excess (54 mol%), the yield of HMF declined markedly to only 4.93% after 2 h. In summary, the HMF yield decreased as the dosage of IL-1 increased (above 9 mol%), and longer reaction times lead to a decrease in HMF yield due to an increase in the dehydration rate of the HMF monomer.

Shimizu *et al.*[20] found that in the conversion of fructose to HMF under acidic conditions, the complete removal of water decreased the HMF yield while mild evacuation could improve the HMF yield. Considering that water dosage may affect the conversion of cellulose to HMF, in this study several special experiments were designed in order to investigate the influence of water on the conversion of cellulose to HMF. The experiment was carried out at 120 °C for 1 h and 2 h. As shown in Fig. 7, the reaction time had a relatively minor influence on the yield of HMF, except when the dosage of H_2O was 0.1 g. In our study, the optimal dosage of H_2O was found to be 0.1 g, when we obtained the maximum yield of HMF of 59.89% after 1 h. When the dosage of H_2O was 0.3 g, the yield of HMF was only 14.41% after 1 h and 15.13% after 2 h. The

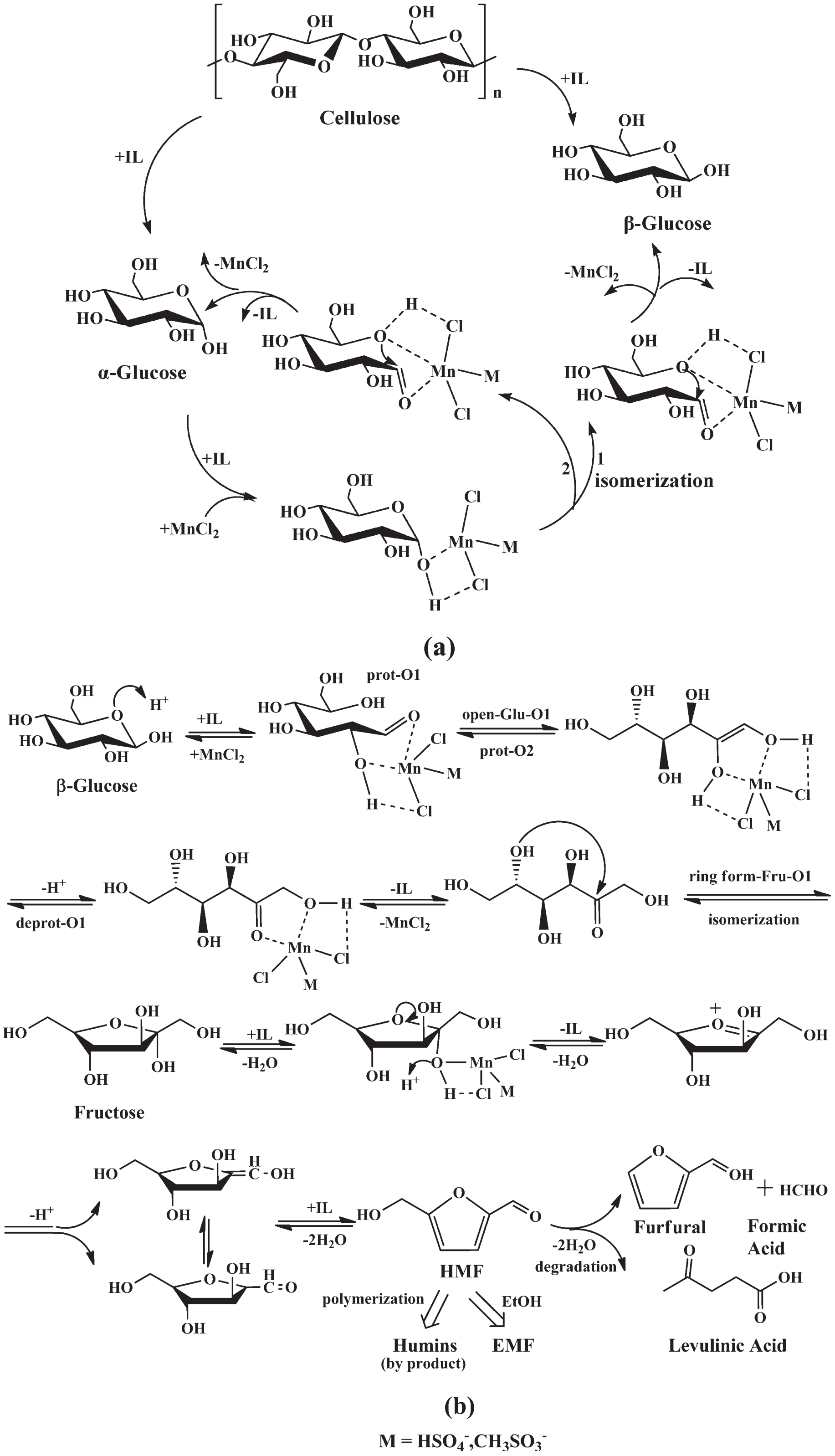


Fig. 4 (a) Proposed mechanism of $MnCl_2$ and IL promoted conversion of cellulose into β-glucose. (b) Proposed mechanism of $MnCl_2$ and IL promoted conversion of β-glucose into HMF and the other products.

results confirm that the presence of a small amount of water in the reaction system does promote the reaction, but more water had a negative effect on the conversion of cellulose to HMF and results in the decomposition of HMF to levulinic acid, which is consistent with a previous report by Hu *et al.*[21] In addition, when the water content continued to increase, the

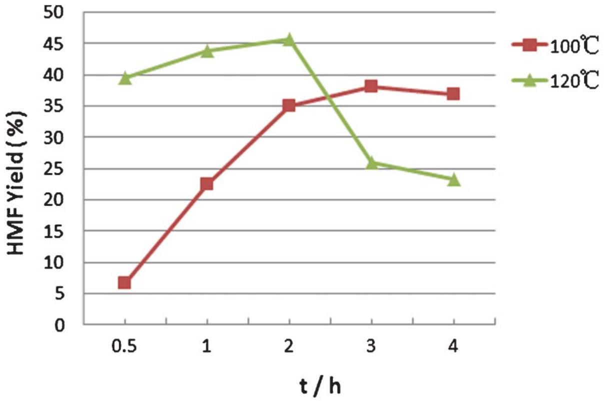


Fig. 5 Results of the experiment into the reaction time for the direct transformation of cellulose into HMF using $MnCl_2$/IL-1 in [BMIM]Cl. Conditions: $MnCl_2$ (4 mol% to cellulose), IL-1 (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.2 g), red line: 100 °C, green line: 120 °C.

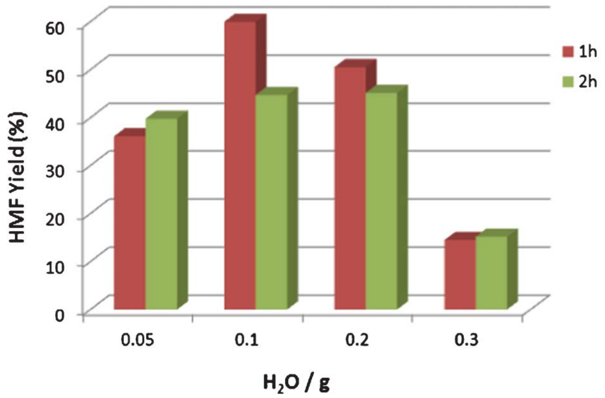


Fig. 7 Results of the experiment into the dosage of H_2O on the direct transformation of cellulose into HMF using $MnCl_2$/IL-1 in [BMIM]Cl. Conditions: $MnCl_2$ (4 mol% to cellulose), IL-1 (9 mol%), cellulose (150 mg), [BMIM]Cl (3 mL), T = 120 °C, red bars: 1 h, green bars: 2 h.

selectivity of HMF declined, which is also in a good agreement with previous reported by Hu *et al.*[22]

Based on the above results, we found that the direct transformation of cellulose into HMF in the absence of metal salts was unable to afford a yield over 17%. So the concentration of the metal salt had a significant effect on the HMF yield in [BMIM]Cl,[23] further signifying differences between the catalytic systems (Fig. 8).

Thus, the effect of the molar ratio of $MnCl_2$ and IL-1 was investigated. A series of molar ratios from 1 : 9 ($MnCl_2$: IL-1) to 9 : 9 were screened. The reactions were carried out at 120 °C for 1 h. It can be seen that the HMF yield increased first, and then decreased as the concentration of Mn^{2+} increased. A molar ratio of $MnCl_2$ less than 5 : 9 ($MnCl_2$: IL-1) was required (HMF yield 57.11%) for the efficient transformation of cellulose into HMF, and a molar ratio of 3 : 9 showed the best catalytic performance (62.63%). In effect, from an environmental point of view, the molar ratio can be reduced to 2 : 9, at which HMF was still obtained with over 50% yield (50.02%).

When it came to investigating the influence of impurities in the solvent, [BMIM]Cl, we found that impurities can impair the dissolution capacity of the IL. Considering the synthesis process and the hygroscopicity of [BMIM]Cl, impurities in [BMIM]Cl can be residue reactants, the products of side-reactions or water. As is known from the results, the β-1,4-glycosidic bonds of carbohydrates dissolved in the IL could easily be attacked by the sulfonic acid groups of the acidic ionic liquids and metal salts, which promotes the hydrolysis of cellulose. However, if there were amounts of H_2O in the [BMIM]Cl solvent, the water molecules may affect and even block the dissolution of the cellulose. From our research, we found that the water in [BMIM]Cl hampered the dissolution of cellulose in [BMIM]Cl, and it has been shown that 1 wt% of water in [BMIM]Cl is sufficient to prevent cellulose dissolution.[24] Moreover, with an increase in the amount of deionized water added into [BMIM]Cl, the HMF yield declined sharply

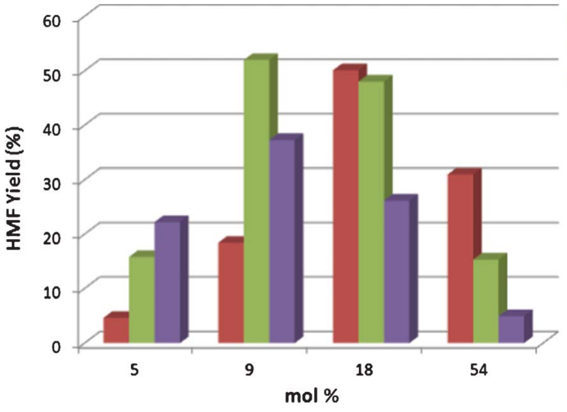


Fig. 6 Results of the experiment into the dosage of IL-1 on the direct transformation of cellulose into HMF using $MnCl_2$/IL-1 in [BMIM]Cl. Conditions: $MnCl_2$ (4 mol% to cellulose), cellulose (150 mg) [BMIM]Cl (3 mL), H_2O (0.2 g), T = 120 °C, red bars: 0.5 h, green bars: 1 h, purple bars: 2 h.

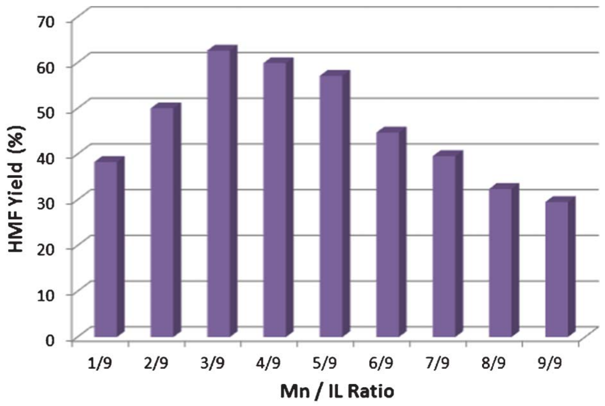


Fig. 8 HMF yields according to the molar ratio of $MnCl_2$ and IL-1. Conditions: IL-1 (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.1 g), T = 120 °C, t = 1 h.

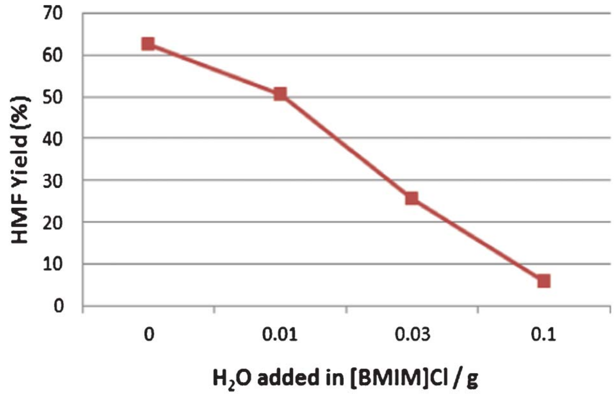


Fig. 9 The effect of the addition of H_2O to [BMIM]Cl on the hydrolysis of cellulose catalyzed by $MnCl_2$/IL-1. Conditions: $MnCl_2$ (3 mol% to cellulose), IL-1 (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.1 g), *T* = 120 °C, *t* = 1 h.

(Fig. 9). We also noted that an amount of deionized water (3.3 wt%) was added to [BMIM]Cl and then put into a reactor with cellulose, a kind of intractable gel formed. The trouble was that the gel was difficult to remove, and a similar phenomenon was also found by Xia *et al.*[25] and Binder *et al.*[15] Therefore, we concluded that strict purification procedures for [BMIM]Cl were required to ensure the effective hydrolysis of cellulose to HMF.

Next, the results of the conversion of cellulose to HMF by various acidic IL catalysts (9 mol%) with $MnCl_2$ (3 mol%) as co-catalyst are shown in Fig. 10. It can be seen that with various acidic ILs as the catalyst, the present system was effective in the conversion of cellulose to HMF. Higher yields of HMF were obtained in the presence of IL-1 and IL-2, the yield was 62.63% and 66.5%, respectively. However, in case of IL-3 and IL-4, the yield of HMF was 52.46% and 54.51%, respectively. It should be noted that the dual-core sulfonic acid ionic liquids (IL-1 and IL-2) were more efficient for the conversion of cellulose to HMF compared to the single-core sulfonic acid ionic liquids (IL-3 and IL-4). Moreover, the ILs had the same cation but those containing the $CH_3SO_3^-$ anion exhibited better catalytic performance than those containing the HSO_4^- group. But this condition seemed to have less effect on the yield of HMF.

Recycling the solvent and catalyst for the hydrolysis of MCC

From the principles of green engineering, it is essential to examine recycling of both the solvent and catalyst. In the present hydrolysis system, after the first reaction run for cellulose hydrolysis, the reaction mixture containing spent IL-1 catalyst and solvent [BMIM]Cl was reused for a second run after separation from HMF by 4 lots of extraction with ethyl acetate (× 5 ml) after 3.0 g of water was added. We examined the amount of 5-HMF in the ethyl acetate which represented the total amount of 5-HMF obtained after separation. After extraction, $MnCl_2$ was still in the aqueous phase, and the solution was heated to 80 °C in a vacuum drier until water and residual ethyl acetate were completely removed. Then the catalytic activity of the spent reaction mixture was tested by adding fresh cellulose into the reaction mixture. In a similar fashion, the spent reaction mixture was reused for four catalytic cycles. As can been seen in Fig. 11, the results showed a minimal loss of activity of the spent catalyst, in terms of HMF yield, the loss was only 8.45% after four cycles. This suggests that the homogeneous catalysts can be recycled for HMF synthesis from cellulose.

HMF synthesis from various substrates

The conversion of sugars and lignocellulosic biomass with IL-1 catalyst and co-catalyst $MnCl_2$ were carried out in solvent at 120 °C. The results are listed in Table 1 and Table 2. It can be seen that both sugars (including fructose, glucose, sucrose and maltose) and lignocellulosic biomass (such as straw, reed and filter paper) can be efficiently converted to HMF in the present experimental system.

Table 1 shows the results of experiments on sugar activity. Among these results, 88.21% and 76.67% yields of HMF were obtained in [BMIM]Cl from sucrose and maltose, respectively. Fructose revealed the highest yield of HMF, which was 91.2%. This result is an improvement over previous results.[21,26]

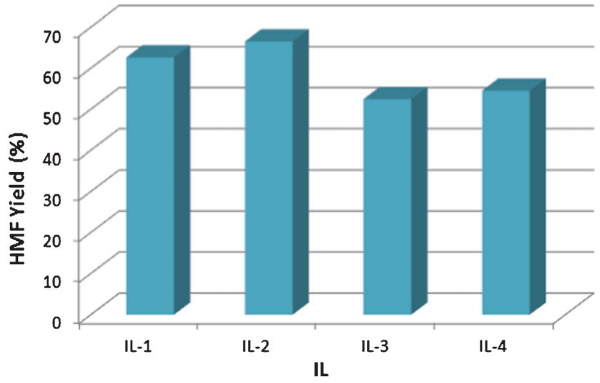


Fig. 10 The hydrolysis of cellulose catalyzed by IL-1, IL-2, IL-3 and IL-4, respectively. Conditions: $MnCl_2$ (3 mol% to cellulose), IL (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.1 g), *T* = 120 °C, *t* = 1 h.

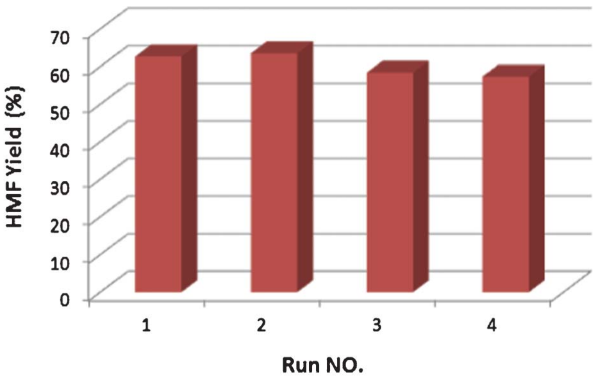


Fig. 11 Reuse of the $MnCl_2$/IL-1/[BMIM]Cl catalytic system for the transformation of cellulose into HMF. Conditions: $MnCl_2$ (3 mol% to cellulose), IL (9 mol% to cellulose), cellulose (150 mg), [BMIM]Cl (3 mL), H_2O (0.1 g), *T* = 120 °C, *t* = 1 h.

Table 1 Results of the direct transformation of various sugars into HMF with IL-1 catalyst and co-catalyst $MnCl_2$ in solvent[a]

Entry	Solvent	Sugar	Time (h)	HMF yield (%)
1[b]	[BMIM]Cl	Fructose	1/6	91.2
2	[BMIM]Cl	D-(+)-Glucose	1.0	35.35
3	[BMIM]Cl	D-(+)-Glucose	2.0	50.61
4[b]	[BMIM]Cl	D-(+)-Glucose	2.0	59.15
5	[BMIM]Cl	Sucrose	0.5	85.10
6	[BMIM]Cl	Sucrose	1.0	88.21
7	[BMIM]Cl	Maltose	0.5	76.67
8	[BMIM]Cl	Maltose	1.0	70.51
9	[BMIM]Cl	α-Lactose	1/6	27.16
10	[BMIM]Cl	α-Lactose	0.5	39.19
11	[BMIM]Cl	α-Lactose	1.0	27.41
12	[BMIM]Br	α-Lactose	0.5	37.95
13	[EMIM]Br	α-Lactose	0.5	24.87
14	[BMIM]Cl	D-(+)-Galactose	1/6	3.43
15	[BMIM]Cl	D-(+)-Galactose	0.5	10.32
16	[BMIM]Cl	D-(+)-Galactose	1.0	16.15
17	[BMIM]Br	D-(+)-Galactose	1.0	10.67
18	[EMIM]Br	D-(+)-Galactose	1.0	6.39

[a] Reaction conditions: $MnCl_2$ (3 mol% to substrate), IL-1 (9 mol% to substrate), substrate (0.925 mmol), solvent (3 mL), H_2O (0.1 g), T = 120 °C. [b] Reaction without H_2O.

However, glucose and lactose had a lower HMF yield when the reaction time was 1 h. Glucose could not be effectively converted to HMF compared to the previous disaccharides, such as sucrose and maltose, which contain a glucose unit. We hypothesized that this may due to the presence of a large amount of α-glucose in the starting materials, and so a longer reaction time was needed to transform it into β-glucose in contrast to cellulose. Moreover, the present catalytic system seemed unsuitable for monosaccharide conversion, because when a small amount of water (0.1 ml) was added to the system, this prejudiced the degradation of glucose to a certain extent. Then we examined another two methods, prolonging the reaction time and not adding water. The result was remarkable, and the yield of HMF reached 59.15% after 2 h. Additional experiments substantiated our hypothesis about poor galactose reactivity. In [BMIM]Cl solvent with catalyst, the yields of HMF from galactose were typically 16.15% and a mass of humins were formed. On the other hand, both lactose and galactose delivered significantly lower HMF yields in either [BMIM]Br (37.95% and 10.67%) or [EMIM]Br (24.87% and 6.39%). Apparently, the different anion and cation content of the solvent can modulate the relative reactivity of lactose and galactose, perhaps by altering their tautomeric equilibria according to Binder *et al.*[27]

In our further study of the lignocellulosic biomass materials in Table 2, filter paper gave the highest yield (40.28%) of HMF, the yield from reed was lower, 32.62%, and lowest yield came from straw (without being activated), 28.54%. Nevertheless, the surprise was that the straw which was activated by 18 wt% NaOH solution was difficult to dissolve and was poorly converted in [BMIM]Cl; amounts of intractable gel formed when the catalyst and water were added into the reactor. We speculated that although the active surface area of straw (or cellulose) increased when activated by NaOH, it would promote permeation, diffusion and swelling of the reaction reagent. However, these approaches may need more solvent, otherwise the solution will become exceedingly sticky and difficult to deal with. Obviously, the present system was not suitable.

Experimental

Materials

Microcrystalline cellulose (AR, average particle size 90 μm) was a commercial product from J&K Chemical Company. *N*-Methylimidazole was obtained from the Changzhou Chemical Factory (Jiangsu, China) and further purified by distillation. 1,3-Propane sultone and imidazole were obtained from the Shanghai Chemical Factory (Shanghai, China). Butyl chloride and ethyl acetate were distilled and then stored over molecular sieves in tightly sealed glass bottles. Methane sulfonic acid (99%) and other chemicals (AR) are commercially available and were used without further purification unless otherwise stated.

Catalytic conversion of cellulose to HMF

The as-received cellulose was dried for 24 h at 80 °C prior to hydrolysis. The catalytic conversion of cellulose to HMF was carried out in a stainless steel autoclave with a glass liner tube that was heated in an oil bath. Typically, 0.15 g cellulose (0.925 mmol) was added into 3 mL preheated [BMIM]Cl solvent

Table 2 Results of the direct transformation of lignocellulosic biomass into HMF with IL-1 catalyst and co-catalyst $MnCl_2$ in [BMIM]Cl[a]

Entry	Substrate	Time (h)	Coversion (%)	Yield (%)		HMF selectivity (%)[d]
				HMF	TRS	
1	Straw[c]	1.0	78.65	30.54	8.33	38.83
2	Straw[b,c]	1.0	—	—	—	—
3	Reed[c]	1.0	79.70	32.62	7.56	40.93
4	Filter paper[c]	1.0	80.32	40.28	8.01	50.15
5	Cellulose	1.0	84.15	62.63	4.97	74.43

[a] Reaction conditions: $MnCl_2$ (3 mol% to substrate), IL-1 (9 mol% to substrate), substrate (150 mg), [BMIM]Cl (3 mL), H_2O (0.1 g), T = 120 °C. [b] Activated by 18 wt% NaOH. [c] Mol% and HMF yield (HPLC) are relative to glucose monomers within the substrate, which was assumed to be pure cellulose. [d] Partially depolymerized or deeply dehydrated cellulose (humins) account for the remaining percentages of HMF selectivity for the values in the table.

under vigorous stirring until a transparent solution was obtained (about 0.5 h), followed by the addition of the desired catalyst and H_2O at the reaction temperature. After the appointed reaction time, 0.2 mL samples were pipetted out, quenched immediately with NaOH solution and diluted with deionized water (× 50). The solution was centrifuged at 10 000 rpm for 10 min and the upper clear liquid was pipetted off and diluted with deionized water (× 6). Any humins were removed prior to HPLC analysis. Only low levels of colored products, other than HMF, were detected by HPLC.

HMF analysis

The catalytic conversion of cellulose to HMF by acidic ILs is an extremely complex process in which a variety of reactions can take place simultaneously and many products are formed. Based on our observation that the main product detected was HMF, the yield of byproducts such as sugars, furfural and levulinic acid were found to be low and were not considered. The HMF was analyzed by HPLC on a Waters Alliance 2695 series chromatograph equipped with a UV detector and a Hedera ODS-2 C18 reversed-phase column (250 mm × 4.6 mm, 5 μm). The mobile phase was water–methanol (70 : 30, v/v) at a flow rate of 0.6 mL min^{-1}. HMF was detected at 283 nm, and the volume for each injection was 10 μL. The concentration of HMF was calculated based on the standard curve obtained with known concentrations of the standard substance.

Definitions of yield and selectivity

The yield and selectivity were based on the conversion of the substrate and confirmed by calibration with standard solutions of the products and reactants involved. With a known molar amount of all components, the yield and selectivity were calculated by the equations below (for details, see the ESI†):

$$\text{HMF yield (\%)} = [M_{\text{HMF}}\ (\text{mg})/\text{MW}_{\text{HMF}}]/[M_{\text{CL}}\ (\text{mg})/[\text{MW}_{\text{GL}} - \text{MW}_{\text{WT}}]] \times 100\% \quad (1)$$

$$\text{Selectivity of HMF} = (\text{Yield of HMF/Substrate conversion}) \times 100\% \quad (2)$$

Conclusions

In conclusion, the effective catalytic conditions using ILs and $MnCl_2$ in [BMIM]Cl to transform cellulose into HMF were found to be efficient under mild conditions. [bi-C_3SO_3HMIM][CH_3SO_3] showed the highest catalytic activity among different ILs. Moreover, Mn^{2+} could play an important role in the conversion of cellulose to HMF as co-catalyst and a 66.5% yield of HMF (selectivity 74.43%) was obtained. The effective catalyst system may be proved valuable in facilitating the conversion of cellulose into HMF. Recycling of both the solvent and catalyst for reuse in several runs was successfully performed. Finally, both various sugars and lignocellulosic raw materials were investigated in this study, and could be directly converted into HMF in reasonable yields under these conditions.

Although the process developed was efficient for the conversion of cellulose to HMF, further work is still required to improve the HMF yields. Moreover, to better utilize the synthesized HMF product, we suggest that HMF could be converted to 5-(ethoxymethyl)furfural (EMF), which is one of the promising next generation biofuels, by adding EtOH and using one-pot synthesis methods, and these will be the subject of future studies.

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