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# Efficient production of 5-hydroxymethylfurfural through the dehydration of sugars with caprolactam hydrogen sulfate ([CPL]$HSO_4$) ionic liquid catalyst in a water/proprylene glycol monomethyl ether mixed solvent

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**Abstract** Efficient production of 5-hydroxymethylfurfural (HMF) through the dehydration of sugars was achieved by developing a new catalyst caprolactam hydrogen sulfate ([CPL]$HSO_4$) ionic liquid or using metal halide as the co-catalyst in a new water/proprylene glycol monomethyl ether solvent system. With an optimum synthesis condition, the yield of HMF derived from fructose dehydration at 105 °C for 90 min is as high as 80.5 % in the presence of [CPL]$HSO_4$. The nature behind the attractive results was revealed by proposing the catalysis mechanism of the fructose dehydration. The yield of HMF is about 70 % using [CPL]$HSO_4$ as the catalyst for fructose dehydration after being reused five times. The catalyst system [CPL]$HSO_4$/metal halide was used for the dehydration of sucrose, and the optimum yield is as high as 64–68 %.

**Keywords** 5-Hydroxymethylfurfural · Dehydration · Sugar · Catalyst · Caprolactam–sulfuric acid ionic liquid · Solvent

## Introduction

Owing to its furan structure and double functional groups (hydroxyl and aldehyde groups), 5-hydroxymethylfurfural (HMF) has been an important raw chemical and/or intermediate for producing many materials [1, 2]. For example, through an

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oxidation reaction, HMF can be transformed to 2,5-furandicarboxylic acid, which has similar structure to terephthalic acid and thus can replace terephthalic acid to produce polyester, used for bottles, cans, and foils, etc. [3]. In addition, HMF can produce dimethylfuran through hydrogenation, while dimethylfuran is a good biobased liquid fuel [4]. In addition, HMF in aqueous solution can be hydrolyzed into levulinic acid (LA) which is an important chemical for producing fuel additives, and polymer and resin precursors [5]. This importance and the great potential in applications make the green synthesis of HMF a very interesting topic.

About 100 years ago, HMF was synthesized from the conversion of $C_6$ sugars through a catalyzed hydrolysis, while the catalyst and solvent are two crucial aspects for the dehydration reactions of $C_6$ sugars [6, 7]. In recent years, imidazolium-based ionic liquids (ILs), such as 1-butyl-3-methylimidazole chloride ([Bmim]Cl) and 1-ethyl-3-methylimidazolium chloride (EmimCl), were used as catalysts and/or solvents for synthesizing HMF, and a high HMF yield from sugar or cellulose dehydration was obtained [8–13]; however, these ILs are too expensive and toxic to be accepted by industry. Compared with imidazole, caprolactam is relatively cheaper and less toxic; moreover, it is also a kind of amine derivative that could be quaternized to form new ionic compound cations [14] due to the presence of a carbonyl group on the caprolactam. On the other hand, the synthesis of caprolactam-cation-based ILs is easily carried out through the acid–base neutralization reaction. Recently, a series of caprolactam-cation-based Brønsted acid ILs were synthesized to be used as a catalyst and reaction media [15, 16]. However, unfortunately, no literature has reported the synthesis of HMF through the dehydration of sugars by using caprolactam hydrogen sulfate ([CPL]$HSO_4$) IL as the catalyst. With regard to the solvents for the dehydration of sugars, to get a high yield of HMF, the organic solvent with high-boiling point, such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl-formamide (DMF), or dimethylacetamide, is often used. However, it is difficult to separate the product from the solvent due to the high boiling point [13].

Here, we developed a new method based on a new catalyst and a new mixed solvent system with low boiling point, with the former being [CPL]$HSO_4$ or adding metal chloride as co-catalyst, and the latter makes up of proprylene glycol monomethyl ether and water (PGME/$H_2O$). Based on these, the influences of the key parameters including the catalyst, the ratio of water to PGME in the mixed solvent and the reusability of [CPL]$HSO_4$ on the conversion of sugar and the yield of HMF were systemically discussed. A similar investigation was also done for the catalytic conversion of sucrose to HMF. Some attractive results were obtained, and the nature behind them was revealed from discussing the catalysis mechanism of the dehydration.

## Experimental

### Materials

Sucrose was purchased from Chinasun Specialty Products. Fructose, caprolactam, sulfuric acid, benzene, PGME, ethyl acetate, $Na_2SO_4$, $FeCl_3$, $AlCl_3$, LiCl, and LiBr were supplied from China National Medicines. Chromic chloride ($CrCl_3 \cdot 6H_2O$) was purchased from Shanghai Yingrui Biotechnological, $ZnCl_2$ was obtained from Tianjin Damao Chemical Reagent Factory. The above reagents were of analytical grade. HMF (99.0 %) used as the control was purchased from Aladdin Chemical Reagent Factory in Shanghai.

Caprolactam (11.32 g, 0.1 mol) and $H_2O$ (10 mL) were added into a three-necked flask with a thermometer and a condenser, which was stirred until a clear solution was obtained, and then concentrated sulfuric acid (10 g, 0.1 mol) was added dropwise into the flask in an ice bath, followed by reacting at room temperature for 24 h. After that, $H_2O$ was removed by vacuum distillation, and the mixture was washed with benzene for three times, followed by drying at 70 °C in a vacuum oven to get the [CPL]$HSO_4$.

## Dehydration of sugars

A specific amount of sugar (fructose or sucrose), catalysts ([CPL]$HSO_4$ IL and metal halide), and solvents (PGME and $H_2O$) were added to the flask with magnetic stirring and a condenser. The mixture was stirred and preheated to a certain temperature in an oil bath, and then maintained at the temperature for a certain time. After that, the sample was decanted to a volumetric flask, and $H_2O$ was used as the diluent, then the obtained diluent sample was analyzed by a high performance liquid chromatography (HPLC).

## Separation for HMF

Firstly, the reaction mixture was fast cooled to 50 °C in an ice bath, and then was distilled under reduced pressure to remove the reacted solvent in the dark. Secondly, 10 mL ethyl acetate was added to extract the product three times, and then ethyl acetate was collected into a round-bottom flask, into which 5 mL $H_2O$ was added. Thirdly, the organic phase was collected and dried with sodium sulfate, followed by evaporation under reduced pressure to obtain a thick yellow liquid, which is HMF with a purity of 97 % (HPLC). $^1$H NMR: δ3.33 (d,1H), δ4.50 (s, 2H), δ6.61 (d, 1H), δ7.49 (d, 1H), δ9.54 (s, 1H).

## Analytic methods

FTIR spectra were recorded using a Nicolet (USA) FTIR spectrometer. The specimen was prepared by coating the sample on a potassium bromide disk, and then heating in an oven. NMR spectra were analyzed on a Unity Inova 400 NMR spectrometery system (USA). The melting point of [CPL]$HSO_4$ IL was determined by a microscopic melting point instrument made in Shanghai physical optics instrument factory, China. Mass spectra were recorded on a TSQ Quantun Ultra AM mass spectrometer (USA).

The quantitative analyses of the products were performed on a 1200 Agilent HPLC equipped with both UV and refractive index detectors (RID). HMF was quantified by HPLC on a silica gel column (C-18, 250 mm × 4.6 mm, 5-μm particle size; Agilent), using water/methanol (80 v/20 v) solution as the mobile phase at a flow rate of 1 mL/min, and the column temperature was maintained at 35 °C. The absorbance value for HMF was at 284 nm. The sugar concentration was quantified on a HPX-87C (460 × 7.5 mm) column using HPLC with RID. The mobile phase was $H_2O$/acetonitrile (25 v/75 v) solution with a flow rate of 0.8 mL/min at 35 °C. LA and formic acid (FA) were determined on a HPX-87H column by HPLC with RID using 2.5 mmol/L $H_2SO_4$ solution with a flow rate of 0.5 mL/min.

The yield of HMF ($M$), the conversion of sugar ($C$), and the yield of glucose and fructose ($N$) from dehydration of sucrose were calculated by using Eqs. (1), (2), and (3), respectively:

$$M = \frac{(\text{Moles of 5}-\text{HMF formed})}{(\text{Moles of sugar in substrate})} \times 100\% \tag{1}$$

$$C = \left[1 - \frac{(\text{Moles of carbohydrates loaded in production})}{(\text{Moles of sugar in substrate})}\right] \times 100\% \tag{2}$$

$$N = \left[\frac{(\text{Moles of sugar loaded in production})}{(\text{Moles of sucrose in substrate})}\right] \times 100\% \tag{3}$$

## Results and discussion

### Characterization of [CPL]$HSO_4$

The structure of [CPL]$HSO_4$ was characterized using many techniques. The mass spectrometry shows that the molecular ion peak of the cationic appears at $m/z = 114.09$, which is identical to the calculated value of caprolactam cationic ($m/z = 114.1$). The melting point of [CPL]$HSO_4$ is 26 °C, which is lower than that of caprolactam (68–70 °C), suggesting that a new hydrogen bonding is formed between the hydrogen ions and the carbonyl of caprolactam, and thus reducing the electrostatic force of the anion and cationic of caprolactam.

Figure 1 gives the FTIR spectrum of [CPL]$HSO_4$, which shows the characteristics peaks of [CPL]$HSO_4$ including the stretching vibrations of O–H ($H_2O$, 3,410 $cm^{-1}$), N–$H_2^+$ (CPL, 3,237 $cm^{-1}$). N–C–H (CPL, 2,943 $cm^{-1}$), C=O (CPL, 1,690 $cm^{-1}$), and N–H (CPL, 1,445 $cm^{-1}$).

The structure of [CPL]$HSO_4$ was further confirmed by the NMR spectra as shown in Fig. 2. As shown in Fig. 2a, the $^1H$ NMR spectrum gives multiplet resonances in the range from 1.73 to 1.80 ppm, assigned to the protons in two –$CH_2$– and one –$CH_2$–, respectively. The protons in –$CH_2$– near carbonyl and –NH– group shift to 2.56 and δ3.34 ppm, respectively, showing triplet resonances. The single resonance at 7.41 or 8.77 ppm reflects the proton in –$NH_2^+$– or $HSO_4^-$. The chemical shift of each carbon in the structure of [CPL]$HSO_4$ can be observed in the $^{13}C$ NMR spectrum of [CPL]$HSO_4$ (Fig. 2b).

Based on the above data, it is concluded that caprolactam-sulfuric acid IL has been synthesized.

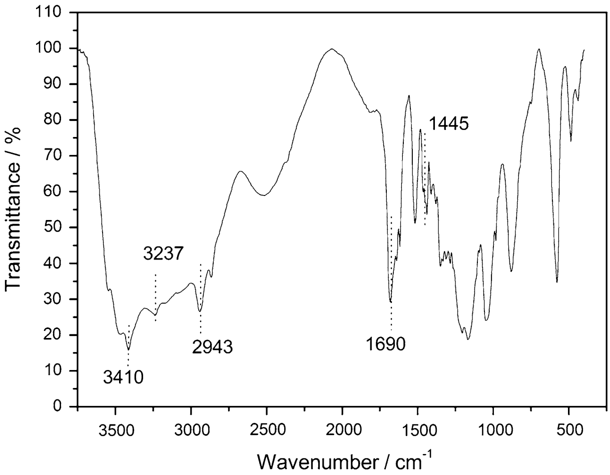


**Fig. 1** The FTIR spectrum of [CPL]$HSO_4$

## Dehydration of fructose

### *Effect of the catalyst*

Figure 3 shows the conversion of fructose and yield of HMF using different contents of [CPL]$HSO_4$ at 105 °C for 90 min. Without [CPL]$HSO_4$, both the yield of HMF and the conversion of fructose are near zero. This phenomenon is obviously changed with the use of [CPL]$HSO_4$. As the content of [CPL]$HSO_4$ increases, both the conversion of fructose and HMF yield remarkably increase, and then reach the highest HMF yield (80.5 %) and conversion of fructose (91.1 %) when the content of [CPL]$HSO_4$ is 8.6 mmol. Therefore, a higher content of [CPL]$HSO_4$ is beneficial to achieve a better catalytic effect on the dehydration of fructose, but the produced HMF tends to decompose into acids under acidic condition, so there is an optimum content of [CPL]$HSO_4$ to get the maximum yield of HMF.

To explain the above statement, the catalysis effect of [CPL]$HSO_4$ in the dehydration of fructose needs to be revealed. The possible reaction mechanism is shown in Scheme 1. Initially, fructose loses one water molecule with the presence of [CPL]$HSO_4$ IL at the hemiketal carbon, leading to the formation of the intermediate II. As the oxygen atom in the carbonyl group has a nucleophilic effect and can form a hydrogen bond with fructose, so fructose is activated and the intermediate II is stabilized [17]. Secondly, the dehydration will produce the intermediate III, which can hence make a proton transfer from C1 to C2 [18], leading to the formation of intermediate V. Thirdly, as the proton transfers from O1 to the carbonyl group, the appearance and rearrangement of the enolic species produce the intermediate VI. Finally, intermediate VI loses two water molecules in the acid condition, and then HMF is produced.

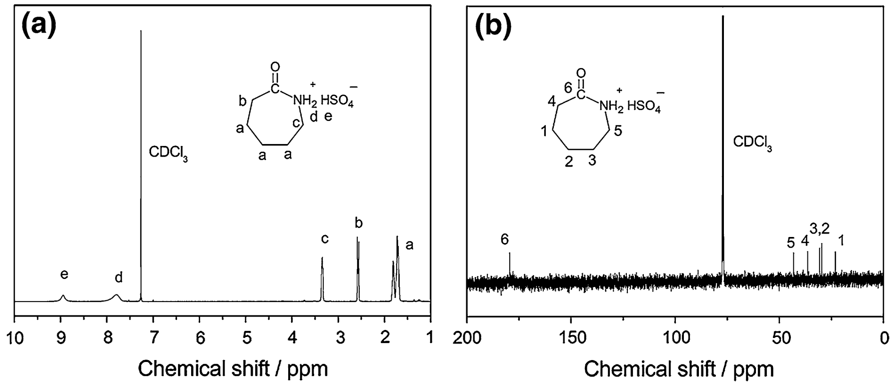


**Fig. 2** The $^1$H NMR (**a**) and $^{13}$C NMR (**b**) spectra of [CPL]HSO$_4$

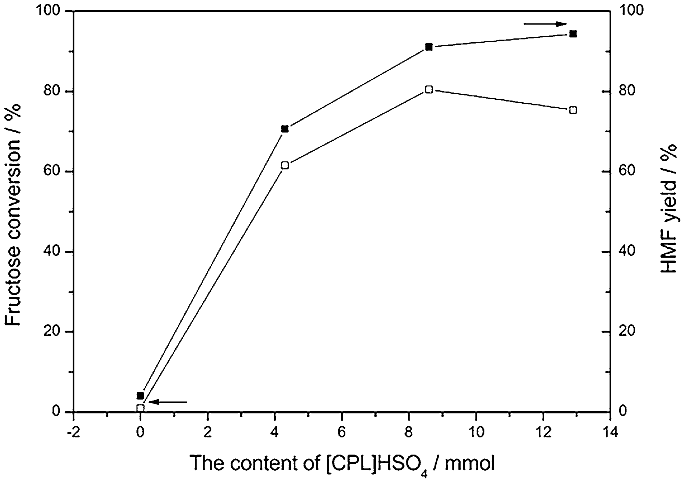
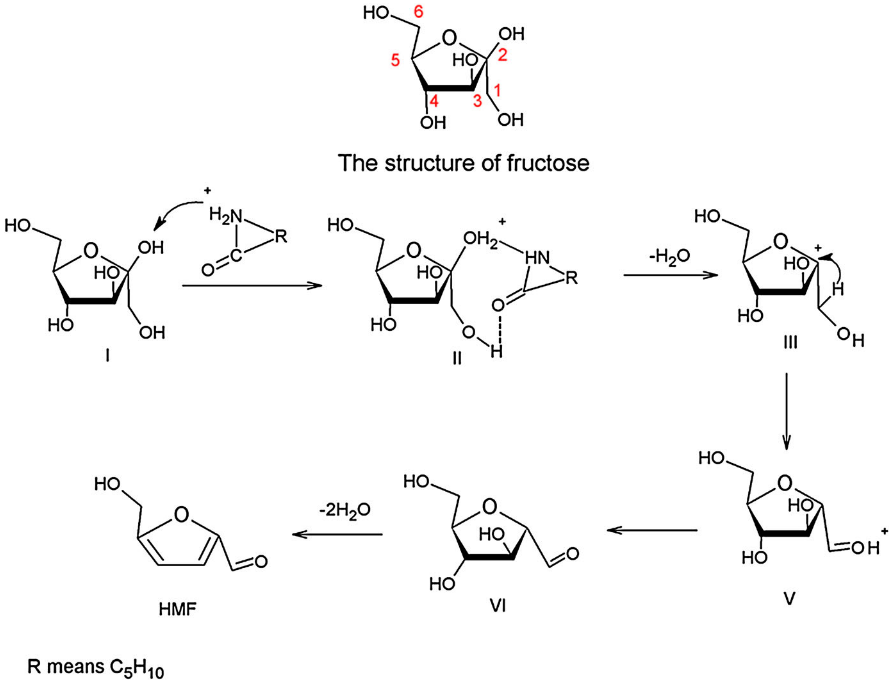


**Fig. 3** The yields of HMF and conversions of fructose to HMF with different contents of [CPL]HSO$_4$. Reaction conditions: fructose = 1.5 g; water: PGME = 2.5:12.5 (W/W); $T$ = 105 °C, and $t$ = 90 min

### *Effect of the solvent*

Table 1 shows the fructose conversion and the product yield using different ratios of $H_2O$ to PGME. Apparently, the ratio of $H_2O$ to PGME has a large influence on the dehydration of fructose. When only water or PGME is used as the solvent, the HMF yield is 40.0 or 54.2 %. However, interestingly, with a small addition of $H_2O$ into PGME, the HMF yield significantly increases, to as high as 80.5 % when the ratio is 1:5. When the content of $H_2O$ is the domain in the mixed solvent, for example, 1:0.5, the HMF yield is only 68.3 % obtained from the HPLC result.

The above results are attributed to the nature of PGME and $H_2O$. Specifically, the hydroxyl group of PGME and the aldehyde group of HMF tend to form hydrogen



**Scheme 1** The possible reaction mechanism of fructose dehydration with the aid of [CPL]$HSO_4$

**Table 1** Yields of HMF and conversions of fructose using the mixed solvent with different compositions

| Water:PGME (W:W) | Yield of HMF (%) | Conversion of fructose (%) |
|---|---|---|
| 0:15 | 54.2 | 63.5 |
| 1:4 | 73.7 | 82.4 |
| 1:5 | 80.5 | 91.1 |
| 1:2 | 76.9 | 87.8 |
| 1:0.5 | 68.3 | 80.7 |
| 15:0 | 40.0 | 65.9 |

Reaction conditions: fructose = 1.5 g; [CPL]$HSO_4$ = 8.6 mmol; $T$ = 105 °C; $t$ = 90 min

bonds, so the polymerization and decomposition of HMF will be reduced. When pure PGME is used as the solvent, fructose cannot be dissolved completely, and thus the dehydration of fructose is relatively difficult to take place. When a small content of $H_2O$ is added into PGME, the resultant mixed solvent becomes a good solvent for fructose, so the reaction system becomes clear and homogeneous, leading to high HMF yield and conversion of fructose. However, note that HMF easily undergoes cross-polymerization and decomposition with the presence of water [19], so a large content of $H_2O$ is not beneficial to get a high yield of HMF. Previous researches show that, when aqueous systems were used as the reaction solvent, HMF was easy to decompose into LA and FAs [20, 21]; consequently, the purity of HMF synthesized using the mixed solvent (2.5:12.5, W/W) as the reaction solvent should be tested. The HPLC result shows that the purity of HMF synthesized here is as high as 97 %, that is, the yields of the two by-products are very low. Therefore, there is an optimum composition of the mixed solvent, and 2.5:12.5 (W/W) is found to be good for getting a high yield of HMF and fructose conversion. Besides the high yield of HMF, another advantage of the water/PGME mixed solvent is that HMF is easily separated from the reaction liquid through distilling.

Biphasic water–organic systems have been reported to be used as the reaction media for fructose dehydration [22–25]; these results are listed in Table 2. Due to the low boiling points of these water–organic systems, these reaction systems usually need high temperature under high pressure and a long reaction time. For example, it needs a 170 °C reaction temperature and a 70-min reaction time in the water/butanol system to get a 69.2 % yield of HMF [23]. For a comparison, the advantage in this work is using a relatively mild reaction condition to obtain a relatively high yield of HMF.

### *Reusability of [CPL]HSO$_4$ in the fructose conversion to HMF*

The reusability experiments of [CPL]HSO$_4$ were conducted in the water/PGME solvent. Firstly, separation for HMF was carried out after the first run, then the catalyst system was used directly in the next run, that is to say, new fructose and water/PGME solvent were added into the flask with the catalyst system; finally, the reaction was carried out under the same conditions. The results for five runs are shown in Fig. 4. The yield of HMF was slightly reduced after each run, the yield reached approximately 70 % after the catalyst was reused for five times, indicating that the catalyst [CPL]HSO$_4$ could be effectively reused in the fructose conversion reaction.

**Table 2** Comparison of water/PGME solvent with water–organic systems in the literature for the dehydration of fructose to HMF

| Refs. | Solvent | Catalyst | Temp (°C) | Time (min) | Yield (%) |
|---|---|---|---|---|---|
| [22] | Water+4-methyl-2-pentanone (MIBK) | 1-(4-Sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate (IL-1) | 120 | 180 | 94.6 |
| [23] | Water+butanol | 2.5 mol/L formic acid | 170 | 70 | 69.2 |
| [24] | Water+actonitrile | 1-Methyl-3-(butyl-4-chlorosulfonyl) imidazolium chlorosulfate | 80 | 320 | 87.0 |
| [25] | Water+nitromethane | SBA-15-PrSO$_3$H | 140 | 30 | 69.7 |
| This work | Water+PGME | [CPL]HSO$_4$ | 105 | 90 | 80.5 |

Reaction conditions: fructose = 1.5 g; water: PGME = 2.5:12.5 (W/W)

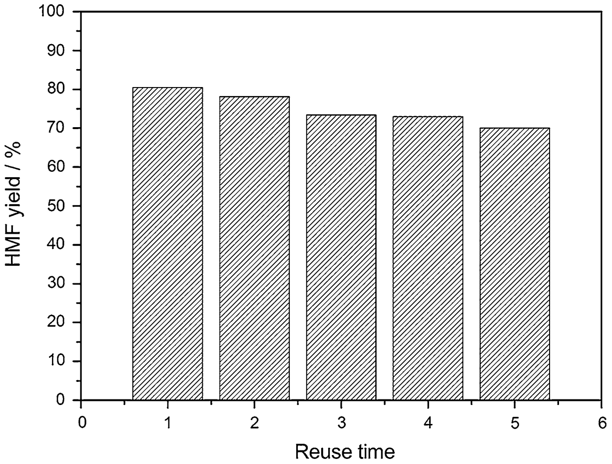


**Fig. 4** The yield of HMF in the reusability of the [CPL]$HSO_4$/$CrCl_3$ catalyst system. Reaction conditions: water: PGME = 2.5:12.5 (W/W); [CPL]$HSO_4$ = 8.6 mmol; $T$ = 105 °C; $t$ = 90 min

## Dehydration of sucrose

It is known that sucrose can release single units of fructose and glucose after hydrolysis, and the acid catalyst with stronger Brønsted acidity is good for increasing the hydrolysis rate [26], so HMF can be synthesized through the isomerization of glucose into fructose and the dehydration of fructose.

To evaluate the effect of [CPL]$HSO_4$ on synthesizing HMF through the transformation of sucrose, [CPL]$HSO_4$/$FeCl_3$ systems with different loadings of [CPL]$HSO_4$ were used, and the yields of HMF in sucrose dehydration are depicted in Fig. 5. It can be seen that the yield of HMF is nearly zero without the acid IL, which increases to 40.4 % when 4.3 mmol [CPL]$HSO_4$ is used; further increasing the loading of [CPL]$HSO_4$, the yield of HMF continuously increases to about 66.0 % and then almost levels off when the loading of [CPL]$HSO_4$ is 17.2 mmol. On the other hand, if only $FeCl_3$ is used, even its content is as high as 10 mol %, the yield of HMF is nearly zero, so [CPL]$HSO_4$ is the decisive catalyst, and can effectively catalyze the formation of HMF derived from the hydrolysis of sucrose and the dehydration of the monosaccharide. To the best of our knowledge, no literature has reported the synthesis of HMF from sucrose by using IL as the catalyst except for Tong's group [18], who used $[NMM]^+[CH_3SO_3]^-$as the catalyst, and the mixed DMF/LiBr as the solvent; however, the yield of HMF was 47.5 %. Obviously, the new catalyst and the solvent used in this paper have advantages in synthesizing HMF.

On the other hand, we evaluated [CPL]$HSO_4$ with other common metal halides as the catalyst system in the dehydration of sucrose into HMF, and the results are listed in Table 3. We found that the 44.0 % yield of HMF is obtained at 105 °C for 120 min when [CPL]$HSO_4$ is used as the catalyst. For a comparison, it can be seen that the presence of 10 mol % metal halide will lead to a higher yield of HMF. It may be that cations have high affinity for oxygen atoms, and thus can coordinate

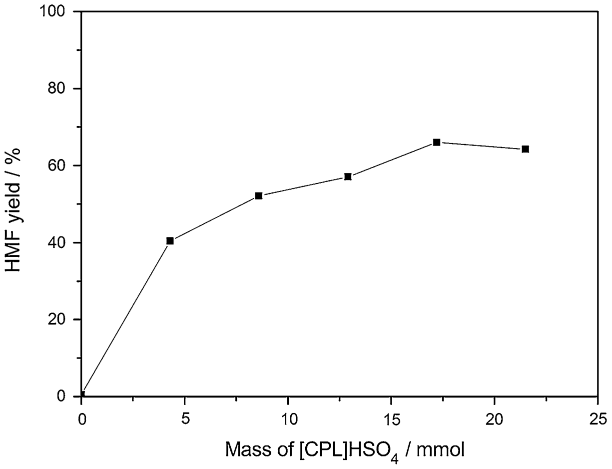


**Fig. 5** The yields of HMF in the dehydration of sucrose using the [CPL]$HSO_4$/$FeCl_3$ catalyst system with different loadings of [CPL]$HSO_4$. Reaction conditions: sucrose = 5 g; $FeCl_3$ = 0.23 g (10 mol %); water: PGME = 10:20 (W/W); $T$ = 105 °C; $t$ = 120 min

**Table 3** The effect of catalyst for the dehydration of sucrose to HMF

| Catalyst | Temp. (°C) | Time (min) | Yield (%) |
|---|---|---|---|
| [CPL]$HSO_4$ | 105 | 120 | 44.0 |
| [CPL]$HSO_4$/$CrCl_3 \cdot 6H_2O$ | 105 | 120 | 68.2 |
| [CPL]$HSO_4$/$ZnCl_2$ | 105 | 120 | 56.3 |
| [CPL]$HSO_4$/$AlCl_3$ | 105 | 120 | 64.3 |
| [CPL]$HSO_4$/LiCl | 105 | 120 | 45.6 |
| [CPL]$HSO_4$/LiBr | 105 | 120 | 47.3 |

Reaction conditions: sucrose = 5 g; water: PGME = 10:20 (W/W); [CPL]$HSO_4$ = 17.2 mmol; Mole percent of metal halides is 10 mol % based on sucrose

with the monosaccharide (glucose and fructose) in the reaction mixture [27]; at the same time, $Cl^-$ shows a positive effect in the conversion as a base and a nucleophile [28, 29] in the isomerization of glucose into fructose and the dehydration of fructose. Note that $CrCl_3$ and $AlCl_3$ have a similar but larger effect.

Compared with the dehydration of fructose, the synthesis of HMF from sucrose dehydration is relatively difficult. However, the price of sucrose is much lower than that of fructose, so the synthesis of HMF based on sucrose is still a promising strategy.

## Conclusions

By developing [CPL]$HSO_4$ IL or [CPL]$HSO_4$ IL/metal halide as the catalyst and water/PGME as the mixed solvent, an efficient production of HMF through the dehydration of fructose or sucrose is achieved. With the suitable parameters at 105 °C for only 90 or 120 min, the yield of HMF is as high as 80.5 or 64–68 %, respectively. When metal halide is used as a co-catalyst, a high HMF yield from the dehydration of sucrose can be obtained. In addition, the separation of HMF is easy to carry out owing to the relatively low boiling point of the water/PGME solvent.

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