One-pot conversion of disaccharide into 5-hydroxymethylfurfural catalyzed by imidazole ionic liquid

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Conversion of carbohydrate into 5-hydroxymethylfurfural (5-HMF), a versatile, key renewable platform compound is regarded as an important transformation in biomass-derived carbohydrate chemistry. A variety of ILs, not only acidic but also alkaline ILs, were synthesized and used as catalyst in the production of 5-HMF from disaccharide. Several factors including reaction temperature, IL dosage, solvent and reaction time, were found to influence the yield of 5-HMF from cellobiose. Of the ILs tested, hydroxy-functionalized ionic liquid ([AEMIM]BF4) showed the highest catalytic activity and selectivity. 5-HMF yield of 68.71% from sucrose was obtained after 6 hrs at 160 °C. At the same condition with cellobiose as substrate, 5-HMF yield was 24.73%. In addition, 5-HMF also exhibited good stability in this reaction system. Moreover, a kinetic analysis was carried out in both acidic and alkaline IL-catalyzed system, suggesting main side reaction in the conversion of fructose catalyzed by acidic and alkaline IL was polymerization of fructose and 5-HMF degradation, respectively.

The massive consumption of fossil resources has made it an essential task to find new feedstocks. Biomass has a remarkable potential to serve as an alternative of fossil resources for the production of energy and organic compounds1–3. 5-hydroxymethylfurfural (5-HMF) has been reported to be one of the top building block chemicals obtained from biomass4–5. A broad range of value added compounds can be synthesized from it, such as 1,6-hexanediol6, 5-hydroxymethyl-2-furancarboxylic acid (HMFCA)7, 5-ethoxymethylfurfural (EMF)8, 2,5-dihydroxymethylfurfural (DHMF) and 5-hydroxymethyl furanoic acid (HMFA)9, 2,5-furandicarboxylic acid10, 2,5-diformylfuran (2,5-DFF)11, 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA)12.

Since the emergence of room temperature ionic liquids (ILs), it has been playing an important role in various aspects of chemical researches. The distinctive properties give ILs a chance to be used extensively in catalysis13,14 and subsequently in biomass processing15,16. In marked contrast to many studies with the application of ILs as solvent or co-solvent on 5-HMF production17, very few have been focused on ILs’ catalytic activity. Although there is a growing literature on dehydration of C-6 carbohydrates, mainly fructose and glucose18,19, for the production of 5-HMF, little is available on conversion of disaccharide. When 1-methyl-3-octylimidazolium chloride was used as solvent and CrCl2/HCl as catalyst, 5-HMF yield could reach 82 ± 3.7% from sucrose, higher than that with ZnCl2/HCl as catalyst which was 58 ± 2.7%20. Ilgen21 demonstrated the production of 5-HMF in ILs with the presence of CrCl3 and a maximum 5-HMF yield of 42% was obtained from the dehydration of sucrose under 100 °C for 1 h. Lima et al.22 reported a 5-HMF yield of 58% achieved using [BMIM]Cl as reaction medium with a mass ratio of IL to sucrose as catalyst which was 58 ± 2.7%. Ilgen21 demonstrated the production of 5-HMF in ILs with the presence of CrCl2 and a maximum 5-HMF yield of 42% was obtained from the dehydration of sucrose under 100 °C for 1 h. Lima et al.22 reported a 5-HMF yield of 58% achieved using [BMIM]Cl as reaction medium with a mass ratio of IL to sucrose as catalyst which was 58 ± 2.7%. Ilgen21 demonstrated the production of 5-HMF in ILs with the presence of CrCl3 and a maximum 5-HMF yield of 42% was obtained from the dehydration of sucrose under 100 °C for 1 h. Lima et al.22 reported a 5-HMF yield of 58% achieved using [BMIM]Cl as reaction medium with a mass ratio of IL to sucrose as catalyst which was 58 ± 2.7%.

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bubbling CO₂ and NO₂ through the solution alternately 26–29, to our knowledge there have been little reports of the use of alkaline ILs as a catalyst for the conversion of carbohydrates to 5-HMF.

In the present study, Brønsted acidic IL, 1-(3-sulfonic acid) propyl-3-methylimidazolium phosphotungstate ([MIMPS]₃PW₁₂O₄₀), and a variety of alkaline ILs, 1-butyl-3-methylimidazolium hydroxide ([BMIM]OH), 1-ethyl-3-methylimidazolium hydroxide ([EMIM]OH), 1-butyl-3-methylimidazolium carbonate ([BMIM]HCO₃) and hydroxy-functionalized IL, 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ([AEMIM]BF₄) were synthesized and used as catalyst in the conversion of disacharide (sucrose and cellobiose) to 5-HMF, which has not been reported. In addition, kinetic analysis on reaction catalyzed by different ILs was carried out to identify the catalytic effect of different ILs-catalyst on the conversion of disaccharide to 5-HMF.

**Results**

**Sucrose conversion with different IL catalysts.** The effect of ILs with different cations and anions, employed as catalysts for the transformation of sucrose was shown in Table 1 (P < 0.05). Among different kinds of solvents used for the conversion of sucrose with [MIMPS]₃PW₁₂O₄₀ as catalyst (P < 0.05) (Table 1, entry 1–4), a comparable high yield of 5-HMF was obtained using 2-Butanol as solvent (Table 1, entry 1), compared to DMAc, NMP and DMSO (Table 1, entry 2–4), consistent with the results in a previous study 30. The 5-HMF yield, catalyzed by alkaline ILs (Table 1, entry 5–8) was invariably higher than that obtained with the acidic catalyst (Table 1, entry 1–4). The highest yield was found to be 68.71% catalyzed by [AEMIM]BF₄ in DMSO (Table 1, entry 8), suggesting that weak alkaline condition favored the reaction. Moreover, the yield sustained growth during the reaction time (Table 1, entry 8–10) demonstrating that 5-HMF exhibited good stability in this reaction system (P < 0.05).

**Effect of composition of the reaction medium on cellobiose conversion.** As shown in Fig. 1, there was a huge difference in the conversion of cellobiose into 5-HMF with different solvents. The 5-HMF yield reached 34.25% in 6hrs. However, the yield was only 23.77% under the same condition with DMF as solvent.

| Entry | ILs             | Solvent | Time (min) | 5-HMF yield (%) |
|-------|-----------------|---------|------------|-----------------|
| 1     | [MIMPS]₃PW₁₂O₄₀ | 2-Butanol | 180        | 30.29 ± 1.14    |
| 2     | [MIMPS]₃PW₁₂O₄₀ | DMAc    | 300        | 25.92 ± 0.78    |
| 3     | [MIMPS]₃PW₁₂O₄₀ | NMP     | 150        | 15.81 ± 0.48    |
| 4     | [MIMPS]₃PW₁₂O₄₀ | DMSO    | 360        | 18.90 ± 0.78    |
| 5     | [BMIM]HCO₃     | DMSO    | 180        | 41.17 ± 1.44    |
| 6     | [EMIM]OH       | DMSO    | 30         | 46.29 ± 1.22    |
| 7     | [BMIM]OH       | DMSO    | 180        | 54.39 ± 1.19    |
| 8     | [AEMIM]BF₄     | DMSO    | 480        | 68.71 ± 0.90    |
| 9     | [AEMIM]BF₄     | DMSO    | 30         | 35.46 ± 1.38    |
| 10    | [AEMIM]BF₄     | DMSO    | 180        | 62.16 ± 1.41    |

Table 1. Dehydration of sucrose with different ILs. Conditions: 0.5 g substrate, 0.25 g ILs, 60 mL solvent, 160°C.
bility is dependent on reaction solvent, i.e., DMSO > DMF > DMAc > NMP > MIBK > 2-butanol > DMAc-LiCl. Moreover, the huge difference between DMAc-LiCl and DMAc indicates that the addition of metal chloride was not conducive to 5-HMF production, which was different from the reported system with ILs as solvent catalyzed by metal chloride\(^3\)\(^1\)\(^,\)\(^2\)\.

**Effect of temperature and reaction time on cellobiose conversion.** Figure 2 shows the effect of temperature and reaction time on the conversion of cellobiose catalyzed by [AEMIM]BF\(_4\), using DMSO as solvent (\(P < 0.05\)). At 120 °C and 140 °C, the yields of 5-HMF increased slowly to 9.44% and 14.86% respectively after 300 mins. It presented the similar trend at 160 °C. However, the 5-HMF formation was obviously enhanced. At 180 °C, although the 5-HMF yield increased rapidly at the initial stage and the maximum 5-HMF yield of 24.73% was obtained at 90 min, it then dropped dramatically. It could thus be concluded that higher temperature could accelerate the conversion of cellobiose into 5-HMF and in the mean time, it raised the risk of 5-HMF degradation.

**Effect of the dosage of IL catalyst on the yield of 5-HMF.** Figure 3 shows the effect of the amounts of [AEMIM]BF\(_4\) on 5-HMF yield in the cellobiose transformation reaction (\(P < 0.05\)). An evident conclusion could be drawn from Fig. 3 that increasing the ratio of catalyst to cellobiose (R) from 0.2 to 0.5 will promote significantly the conversion of cellobiose to 5-HMF from 31.87% to 40.19% after 5 h, respectively. Further increasing the dosage of catalysts to 1.0, although the time to obtain the maximum 5-HMF yield was reduced to within 2 hrs, it was only 21.1%, much lower than that from R at 0.2 and 0.5. Moreover, the 5-HMF yield showed a sharp decrease after 2 hrs for R at 1.0. The reactivity difference might be ascribed to be the fact that IL catalyst typically exhibit high activity not only in conversion of cellobiose, but also in the polymerization of cellobiose, glucose, 5-HMF, and other small molecule compounds during degradation process.

**Kinetic analysis of the dehydration of fructose.** During conversion of disaccharide into 5-HMF, three reactions are involved, namely the hydrolysis of the disaccharide into its components (fructose and glucose), isomerization of glucose into fructose, and dehydration of fructose. In order to study the process of 5-HMF formation, the kinetic analysis of the dehydration of fructose catalyzed by ILs in DMSO was performed based on two
Kinetic model for dehydration of fructose catalyzed by ILs.

\[ \frac{dC_{\text{Fructose}}}{dt} = -kC_{\text{Fructose}} = -k_1C_{\text{Fructose}} - k_3C_{\text{Fructose}} \]  \hspace{1cm} (1)

\[ \frac{dC_{5-HMF}}{dt} = k_1C_{\text{Fructose}} - k_2C_{5-HMF} \]  \hspace{1cm} (2)

Eq. (3) and (4) can be achieved by integrating Eq. (1) and (2), \( k_1 \) and \( k_2 \) are step rate constants, which are constant at a definite temperature:

\[ C_{\text{Fructose}} = C_{\text{Fructose}}e^{-kt} \]  \hspace{1cm} (3)

\[ C_{5-HMF} = \frac{k_1C_{\text{Fructose}}}{k_2-k_1}(e^{-k_1t} - e^{-k_2t}) \]  \hspace{1cm} (4)

Substituting \( C_{\text{Fructose}} \) from Eq. (3) into Eq. (4) gives Eq. (5):

\[ Y_{5-HMF} = \frac{k_1}{k_2-k_1}(e^{-k_1t} - e^{-k_2t}) \times 100\% \]  \hspace{1cm} (5)

By integrating the above equation leads to the following:

\[ \frac{C_{\text{Fructose}}}{C_{\text{Fructose}0}} = 1 - X_{\text{Fructose}} \]  \hspace{1cm} (6)

\[ -\ln(1 - X_{\text{Fructose}}) = kt \]  \hspace{1cm} (7)

Values of \( \ln(1 - X_{\text{Fructose}}) \) (where \( X \) is conversion of fructose) are plotted against reaction time \( (t) \) at different temperatures in order to obtain rate constants \( (k) \). Table 1 shows the relationship between the rate constant and reaction temperature. The results show that \( k \) value increases as temperature increases, meaning that the higher temperature accelerates the fructose dehydration reaction rate.

Compared to alkaline system (Table 2, entry 5–8), \( k_3 \) in acidic system (Table 2, entry 1–4) grows faster when temperature is increased from 100 °C to 160 °C. It is why the rate of humin, coming from polymerization of fructose and 5-HMF, lactic acid, etc., rises faster at a higher temperature.
The Arrhenius Equation is given by:
$$ k = A \exp\left(\frac{-E_a}{RT}\right) $$
(8)

The deformation is described by:
$$ \ln k = -\frac{E_a}{RT} + \ln A $$
(9)

Figure 5A,B show the relationship of $\ln k$ and $-10^{-4}/RT$, using the rate constants, an Arrhenius plot is generated based on Eq. (8) & (9). The kinetic parameters for ILs catalyzed dehydration of fructose to 5-HMF, $E_a$ (slope) and $A$ (intercept is $\ln A$) are summarized in Table 3.

### Table 3. Pre-exponential factor and activation energy of fructose conversion.

|                | Pre-exponential factor, $A$ (min$^{-1}$) | Activation energy, $E_a$ (kJ·mol$^{-1}$) |
|----------------|-----------------------------------------|-----------------------------------------|
|                | $A_1$ | $A_2$ | $A_3$ | $E_{a1}$ | $E_{a2}$ | $E_{a3}$ |
| Acidic ILs     | 5.06 $\times 10^{10}$ | 4.95 $\times 10^{11}$ | 1.32 $\times 10^7$ | 99.78 | 136.48 | 58.84 |
| Alkaline ILs   | 5.44 $\times 10^9$ | 1.47 $\times 10^7$ | 9.17 $\times 10^{14}$ | 110.81 | 96.48 | 153.47 |

Discussion

An efficient synthesis of 5-HMF by conversion of disaccharide has been achieved using ILs as catalysts. Several factors were found to influence the yield of 5-HMF from cellobiose, such as reaction temperature, the dosage of IL, solvent and reaction time. Of the ILs tested, [AEMIM]BF$_4$ showed the highest catalytic activity and selectivity, and a 68.21% yield of 5-HMF from sucrose was obtained after 6 h when it was employed at 160 °C. At the same reaction, 5-HMF yield was 24.73% in the conversion of cellobiose. In addition, a kinetic analysis was carried out on both acidic and alkaline IL-catalyzed system, suggesting main side reaction in the conversion of fructose catalyzed by acidic and alkaline IL was polymerization of fructose and 5-HMF degradation, respectively. Although the catalyzed mechanism needs to be further studied, the results obtained from the present investigation might encourage researchers to consider ILs as potential catalysts for organic reactions rather than simply as solvents.

Methods

Materials and experimental methods. N-methylimidazole was purchased from Aladdin Chemical Co., Ltd. 2-Chloroethylaminehydrochloride, dichloroethanol, and acetone from Shanghai Jingchun Chemical Reagent Company. Dimethylsulfoxide (DMSO), dimethyl acetamide (DMAC), N,N-dimethylformamide (DMF), n-butanol, 2-butanol, methylisobutylketone (MIBK), sodium tetrafluoroborate, ether, ethanol, sodium borate (NaBF$_4$), sucrose, cellobiose, glucose and fructose were purchased from Beijing Chemical Reagent Company. All reagents were used as supplied without further purification.

The hydroxy-functionalized ILs, [AEMIM]BF$_4$ was synthesized as follows: 0.10 mol N-methylimidazole (8.20 g) and 0.10 mol 2-bromoethylamine hydrobromide (20.50 g) were dissolved into 60 ml ethanol, and stirred at 80 °C under nitrogen atmosphere. After 24 hrs, the mixture was filtered, and washed with ethanol for three times. The residue was dissolved into 40 ml of CH$_3$CN/H$_2$O (1:1, v/v) with the addition of 0.10 mol NaBF$_4$ (10.98 g). It was stirred at 30 °C for another 24 hrs and then, evaporated in vacuum. The obtained yellow liquid was washed...
BF₄ was obtained with the yield of 74.4%.

[MIMP₅]₃PW₁₂O₄₀, [BMIM]OH₃7, [EMIM]OH₂₄ and [BMIM]HCO₃₃⁹ were prepared.

**General procedure for the conversion of carbohydrates to 5-HMF.** In the dehydration reaction, 0.5 g of carbohydrate, 0.25 g of catalyst and 60 mL of solvent were mixed in a 100-mL flask equipped with a condenser and heated to certain reaction temperature. After dehydration, the mixture was analyzed by HPLC. During the dehydration reaction, disaccharide was hydrolyzed into glucose and fructose, glucose can be isomerized into fructose and the later loses three water molecules to produce HMF in the presence of catalyst (Fig. 6).

After reaction, the mixture was filtered through 0.45μm pore size membrane and the filtrate was transferred into a volumetric flask and diluted with water. 5-HMF and furfural were analyzed by HPLC (Agilent LC1260 system, 865 nm) for the detection. The P value was calculated, which less than 0.05 was considered as statistically significant.

**Statistical Analysis.** Based on data distribution, one-way and two-way analyses of variance (ANOVA) was used to compare different groups. The P value was calculated, which less than 0.05 was considered as statistically significant with P < 0.05.

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Author Contributions

Y.Q, C.H. and J.X. conceived and designed experiments. Y.Q., L.L., Q.W. and P.O.P. carried out experiments. Y.Q., L.L., Q.W., P.O.P. and J.X. analyzed data and prepared figures. Y.Q., Q.W., P.O.P. and J.X. wrote the manuscript. All authors reviewed the manuscript.

Additional Information

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