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Catalytic conversion of cellulose into 5-hydroxymethylfurfural over chromium trichloride in ionic liquid

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Abstract−An efficient method for converting cellulose into 5-hydroxymethylfurfural (5-HMF) using an inexpensive ionic liquid tetrabutylammonium chloride (TBAC) and relatively low-toxicity catalyst of chromium (III) trichloride ($CrCl_3 \cdot 6H_2O$) was developed. The effects of hydrochloric acid loading, catalyst dosage, reaction temperature and time on the yield of 5-HMF were surveyed to achieve optimal reaction conditions. A 5-HMF yield of 43.7% was obtained within 90 min at 140 °C using oil-bath heating. Glucose and starch were also investigated as feedstock to produce 5-HMF in TBAC/$CrCl_3 \cdot 6H_2O$ system, in which the 5-HMF yield was considerable. After 5-HMF was extracted, TBAC/$CrCl_3 \cdot 6H_2O$ could be used for several runs.

Keywords: Cellulose, 5-Hydroxymethylfurfural, $CrCl_3 \cdot 6H_2O$, TBAC, Ionic Liquid

INTRODUCTION

With the dwindling of fossil resources and the ecological environment deteriorating, developing a green and renewable resource has become a major topic. Biomass, the most abundant renewable resource in the world, has been widely used to produce fuels and useful chemicals [1-4]. Among those biomass chemicals, 5-hydroxymethylfurfural (5-HMF) is an important platform compound, which can be used to produce a series of chemicals (Fig. 1), such as levulinic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid [5,6]. Currently, catalytic hydrolysis of sugars is the main way to prepare 5-hydroxymethylfur-

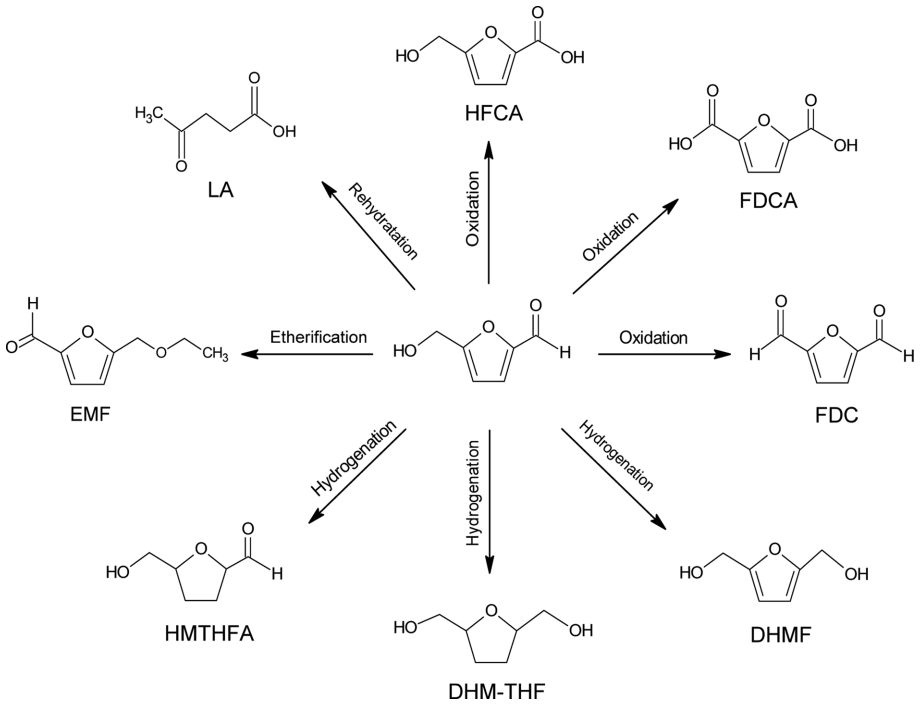

Fig. 1. Chemistry and applications of 5-HMF.

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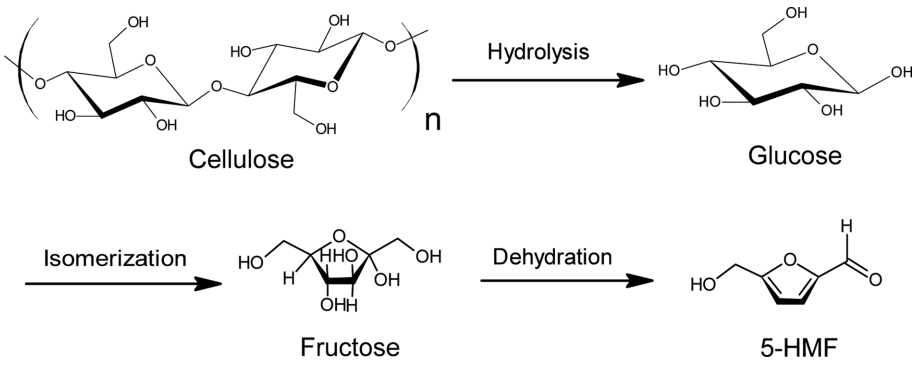

Fig. 2. The production of 5-HMF from cellulose.

fural. Cellulose is the oldest and the most abundant polysaccharide in nature, which is a major component of plant cell walls. Most biomass has luxuriant cellulose, like crop straw and wood scrap. If cellulose can be used as the raw material to produce 5-HMF, the production cost will drop considerably. Fortunately, cellulose can be hydrolyzed to glucose under acid condition, and glucose can be further isomerized to fructose, which dehydrates to 5-HMF (Fig. 2) more easily. Recently, 5-HMF has been obtained successfully from cellulose [7-10].

Cellulose is composed of D-glucose monomers by β-1,4-glycosidic bonds [8] and there are large numbers of hydrogen bonds in cellulose. Consequently, cellulose is hardly soluble in H_2O or common organic solvents such as ethanol, ethyl acetate, and acetonitrile. DMSO and other polar organic solvents that serve as the media of cellulose hydrolysis achieved good results [11,12], but 5-HMF is difficult to be separated, because of the higher boiling point. Some researchers have chosen subcritical or supercritical fluids as solvents to dissolve cellulose, but it needs high temperature and high pressure [13]. Therefore, finding a green and efficient solvent to dissolve cellulose is still a challenge.

Ionic liquid (IL) with many specific properties, including good chemical and thermal stability, non-ammability, immeasurable low vapor pressure, and recyclability, has attracted more attention as a new 'green' solvent in past few years [14-16]. Swatloski et al. [17] applied a series of imidazolium ionic liquid to dissolve cellulose and achieved good results. They also reported that especially ILs containing chloride had more solubility for cellulose. Su and his coworkers [7] studied the production of 5-HMF from cellulose in 1-ethyl-3-methylimidazolium chloride using $CuCl_2/CrCl_3 \cdot 6H_2O$ as a catalyst and achieved a 5-HMF yield of 55.4±4.0% by holding the system at 120 °C for a long time of 8 h. Liu et al. [18] reported that metal chlorides could effectively depolymerize cellulose in 1-butyl-3-methylimidazolium chloride. A high HMF yield up to 51.4% was obtained from cellulose in 3.5 min under microwave at 400 watts in this system. The solvents to prepare 5-HMF imidazolium-based ionic liquids have reached famous result, but the cost of imidazolium-based ionic liquids is too high, which is a main problem for its actual industrial application [19].

Compared to imidazolium-based ionic liquids tetrabutylammonium chloride (TBAC) is an inexpensive and environment friendly ionic liquid. Moreover, as far as we know there is no report on using TBAC as a solvent to produce 5-HMF from cellulose. In this work, a relatively inexpensive ionic liquid TBAC was used as solvent and harmful chromium trichloride ($CrCl_3 \cdot 6H_2O$) acting as catalyst were used for the preparation of 5-HMF from cellulose in acid condition. Other effects were also investigated to optimize the reaction condition.

EXPERIMENTAL SECTION

1. Materials and Experimental Procedures

Tetrabutylammonium chloride (≥97%) and $CrCl_3 \cdot 6H_2O$ (≥99%) were purchased form Tianjin Guangfu Chemical Fine Chemical Research Institute (Tianjin, China). Microcrystalline cellulose (degree of polymerization: 210-240, MCC) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). MCC was dried in a drying oven at 100 °C for 60 min before use. All the other reagents of this experiment were purchased from a local dealer and used without further treatment.

Tetrabutylammonium chloride was dried with a rotary evaporator at 90 °C for 4 h to remove water. MCC (100 mg), TBAC (1.0 g) and catalyst were added into a round-bottom flask (50 ml) at 100 °C. The mixture was stirred magnetically to be homogeneous. Hydrochloric acid was added to accelerate the hydrolysis of cellulose, then adjusted to the appropriate temperature reaction needed 30 min later. After desired reaction time arrived, the reaction system was cooled to room temperature immediately. 10 ml distilled water was added to the reactor and then the aqueous solution was centrifuged at 10,000 rpm for 5 min. The 5-HMF concentration of supernatant fluid was measured by HPLC.

2. Analytical Methods

The HMF was quantied using HPLC (Shimadzu LC-20AT) with an ultraviolet detector at 284 nm and an Inertsil ODS-SP column (4.6×150 mm) at 35 °C. The mobile phase was methanol/water (20/80 v/v) at a ow rate of 0.7 ml/min. The amount of total reducing sugars (TRS) was measured using a SGD-IV reducing sugars analyzer (Shandong Academy of Sciences, Jinan, China).

The yield of 5-HMF and TRS was calculated by Eqs. (1) and (2).

$$\text{5-HMF yield } (\%) = \frac{\text{moles of 5-HMF}}{\text{moles of glucose unit of cellulose}} \times 100\% \quad (1)$$

$$\text{TRS yield } (\%) = \frac{\text{moles of TRS}}{\text{moles of glucose unit of cellulose}} \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

1. The Effect of Catalysts

We explored the effects of a series of catalysts including mineral

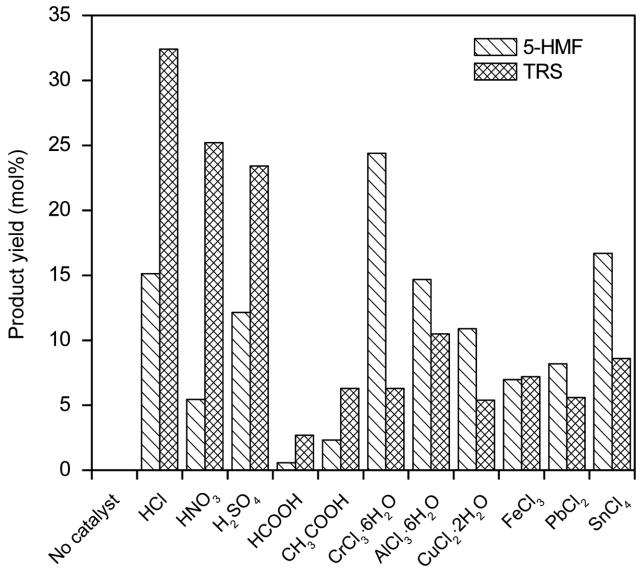

Fig. 3. Effect of different catalysts on 5-HMF yield (Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, 130 °C, 120 min).

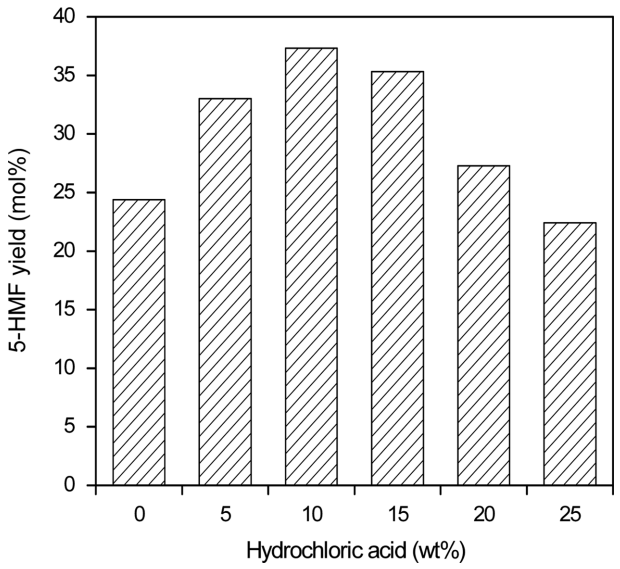

Fig. 4. Effect of hydrochloric acid loading on 5-HMF yield (Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, $CrCl_3{\cdot}6H_2O$ 0.09 mol, 130 °C, 120 min).

acid, organic acid and metal chlorides on the conversion of cellulose into 5-HMF, and the results are shown in Fig. 3. In the absence of catalyst, the yield of HMF and total reducing sugars (TRS) was nearly 0%, respectively. When HCOOH, CH_3COOH, HCl, H_2SO_4, NHO_3 were added, the yield of 5-HMF and TRS was up to 15.12% and 32.41%, respectively. This shows that acid can promote the hydrolysis of cellulose into glucose, but it cannot effectively promote the transformation of glucose into 5-HMF [20]. According to the previous report [11,21-23], metal chlorides can effectively convert glucose and fructose into 5-HMF with catalysts. In this work, we investigated several kinds of commonly used metal chloride as catalysts to produce HMF from cellulose. When $PdCl_2$, $CuCl_2$, $FeCl_3$, $AlCl_3$, $CrCl_3{\cdot}6H_2O$, $SnCl_4$ were used, the yield of HMF was greatly increased and the range was from 6.98% to 24.38%. Compared with the other catalysts, $CrCl_3{\cdot}6H_2O$ displayed higher activity for the conversion of cellulose into 5-HMF. This phenomenon might be due to the stronger Lewis acidity of Cr^{3+}, which helps isomerize glucose to fructose [24,25]. Thus, $CrCl_3{\cdot}6H_2O$ was chosen as catalyst for the conversion of cellulose into 5-HMF.

2. The Effect of Hydrochloric Acid Loading

Although hydrochloric acid is corrosive, an appropriate addition of hydrochloric acid can effectively promote the hydrolysis of cellulose, improve the 5-HMF yield and reduce the cost for industry application [25]. In our experiments, the effect of the concentration of hydrochloric acid on the yield of HMF was studied. As shown in Fig. 4, in the absence of hydrochloric acid, the yield of 5-HMF is only 24.38%. When 5 wt%-10 wt% (relative to cellulose) hydrochloric acid was added, the yield of HMF was increased with the increasing of hydrochloric acid loading, and when 10wt% hydrochloric acid was applied, the yield of 5-HMF achieved a maximum of 37.31%. This result might be because the Lewis acidity of Cr^{3+} cannot fully hydrolyze cellulose, while hydrochloric acid has strong acidity to promote the hydrolysis of cellulose into glucose [26] and high activity to improve fructose dehydrate to 5-HMF [27]. Therefore, the catalysis reaction can be improved with both HCl and Lewis acids. However, when hydrochloric acid was added to 25 wt%, the yield of HMF decreased to 22.40%. This phenomenon might be attributed to the decomposition of 5-HMF to levulinic acid, which can be accelerated at high dosage of hydrochloric acid [28, 29]. Hence, 10 wt% hydrochloric acid was chosen as an appropriate concentration in the following experiments.

3. The Effect of Water Dosage

Cellulose into glucose is a hydrolysis process, which requires the participation of water. Although hydrochloric acid contains a certain amount of water, it is not enough for the hydrolysis of cellulose in theory. Therefore, different amounts of water were added into the system to investigate the effect of water addition on the yield

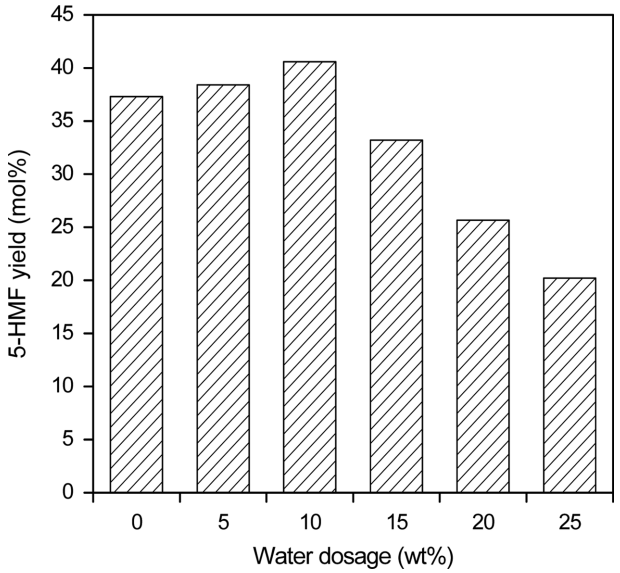

Fig. 5. Effect of water dose on 5-HMF yield (Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, hydrochloric acid 10 wt%, $CrCl_3{\cdot}6H_2O$ 0.09 mol, 130 °C, 120 min).

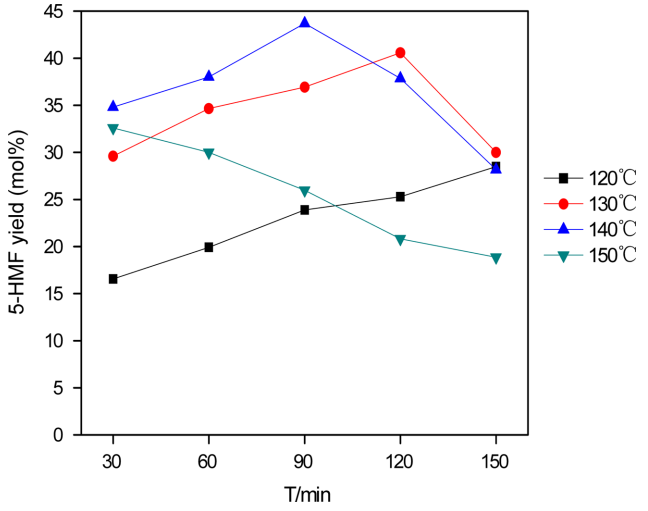

Fig. 6. Effect of reaction temperature and time on 5-HMF yield (Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, hydrochloric acid 10 wt%, $CrCl_3 \cdot 6H_2O$ 0.09 mol, water 10 wt%).

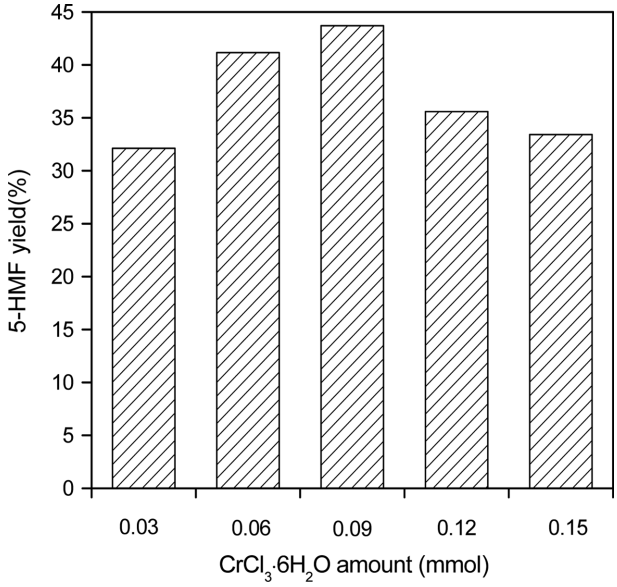

Fig. 7. Effect of catalyst amount on 5-HMF yield (Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, Hydrochloric acid 10 wt%, water 10 wt%, 140 °C, 90 min).

of 5-HMF. Fig. 5 shows 5-HMF yield increased with the increase of water content. When the amount of water reached 10 wt% (related to the mass of cellulose), the yield of 5-HMF with 40.59% was obtained. As the proportion of water in the system was increased, 5-HMF yield began to decrease. When the initial water content was increased to 25 wt%, the yield of 5-HMF was only 20.2%. It might be that a small of water is helpful for the hydrolysis of cellulose, but a large amount of water can promote the rehydration of 5-HMF [24,30]. From the above investigation, it can be concluded that water content had a significant effect on cellulose conversion to 5-HMF.

4. The Effect of Temperature and Time

The reaction temperature and time are important influence factors for the preparation of 5-HMF. From Fig. 6, only 16.57% of 5-HMF was observed at 120 °C for 30 min. When the reaction time reached 150 min, the yield of 5-HMF increased to 28.49%. But there is an opposite trend at 150 °C, due to the decomposition of TBAC at the high temperature for a long time. From this we also can confirm that the coordination compound of TBAC with $CrCl_3 \cdot 6H_2O$ plays a key role in the catalytic reaction. In addition, higher temperature gives rise to the formation of byproducts [31]. When the temperature was increased to 130 °C and 140 °C for 30 min, the yield of HMF achieved 29.60% and 34.82%, respectively. What's more, at both temperatures, the yield of 5-HMF increased with the adding of time at first. But when the yield got maximum value, further increase of time resulted in reducing of 5-HMF yield. It can be put down to the extension of time being advantageous to the decomposing of 5-hydroxymethylfurfural [32]. Clearly, the maximum value 43.70% of HMF yield was obtained at 140 °C for 90 min.

5. The Effect of Catalyst Amount

The dependence of cellulose conversion on the amount of $CrCl_3 \cdot 6H_2O$ employed is shown in Fig. 7. The amount of $CrCl_3 \cdot 6H_2O$ was varied from 0.03 mmol to 0.15 mmol. When the 0.03 mmol (5 mol% relative to glucose) $CrCl_3 \cdot 6H_2O$ was added into the reaction system, the yield of 5-HMF reached 15.12% at 140 °C for 90 min. For instance, the 5-HMF yield could reach 43.70%, when the dosage of $CrCl_3 \cdot 6H_2O$ increased to 0.09 mmol. As the usage of catalyst increased, the yield of 5-HMF decreased due to the decomposition being accelerated at high usage of catalyst. When the amount of $CrCl_3 \cdot 6H_2O$ increased to 0.15 mmol, the yield of 5-HMF decreased to 33.42%. This decrease attributed to the excessive catalyst not only accelerated the cellulose conversion into fructose and then dehydrated to 5-HMF, but also favored the rehydration of HMF to levulinic acid [33]. Therefore, we selected 0.09 mmol of $CrCl_3 \cdot 6H_2O$ as the optimal catalyst loading in subsequent experiments.

Table 1. Comparison of 5-HMF yield from different feedstock

Entry	Feedstock	5-HMF yield (%)
1	Glucose[a]	50.27
2	Cellulose[b]	43.70
3	Starch[b]	40.55

[a]Reaction conditions: Glucose 100 mg, TBAC 1.0 g, $CrCl_3 \cdot 6H_2O$ 0.09 mol, water 10 wt%, 140 °C, 90 min

[b]Reaction conditions: Cellulose or Starch 100 mg, TBAC 1.0 g, hydrochloric acid 10 wt%, $CrCl_3 \cdot 6H_2O$ 0.09 mol, water 10 wt%, 140 °C, 90 min

6. The Yield of 5-HMF from Different Feedstock

TBAC/$CrCl_3 \cdot 6H_2O$ was also used for catalyzing other substrates to produce 5-HMF. From Table 1, we can see that the yield of 5-HMF was obtained in 50.27% when glucose was used. When starch was used, the yield of 5-HMF was also received by 40.55% at 140 °C for 90 min. The results show that TBAC/$CrCl_3 \cdot 6H_2O$ can also be used for the conversion of glucose and starch.

7. The Reuse of TBAC/$CrCl_3 \cdot 6H_2O$

After the first reaction finished, 5-HMF was separated from the mixture by ethyl acetate according to the reported method [34] and the amount of 5-HMF in ethyl acetate was detected by HPLC. Then TBAC/$CrCl_3 \cdot 6H_2O$ was heated at 75 °C in a rotary evaporator for 24 h to remove the residual ethyl acetate and water. The dried TBAC and $CrCl_3 \cdot 6H_2O$ were directly reused for the next experiment. As

Table 2. Recycle of TBAC/$CrCl_3 \cdot 6H_2O$ system for produce 5-HMF from cellulose

Cycle	5-HMF yield (%)
1	43.70
2	42.05
3	45.33
4	41.84
5	41.26

Reaction conditions: Cellulose 100 mg, TBAC 1.0 g, hydrochloric acid 10 wt%, water 10 wt%, 140 °C, 90 min

shown in Table 2, the system could be reused more than five times, which means that the system was stable in this reaction. The yield of number 3 is higher than number 1, which may be due to the residual glucose and 5-HMF from the previous cycle [35].

8. Discussion

The effects on the conversion of cellulose into 5-HMF in TBAC for 90 min at 140 °C were investigated. A relatively inexpensive ionic liquid, TBAC, just like previous reported ionic liquids [19,22] not only acted as a basic mediator, but also served as a ligand for chromium, promoting the isomerization and dehydration of glucose into 5-HMF. Brønsted acid hydrochloric acid was used for the hydrolysis of cellulose into glucose and then glucose converted to 5-HMF with satisfying yield. Using Brønsted acid to make up with the defect of Lewis acid may be a promising aspect to realize the large-scale production of 5-HMF in ionic liquid. The process of the reaction is shown in Fig. 8. When the 1,4-glycosidic bond of cellulose was broken with H^+, it formed β-glucose, and then β-glucose transformed to an enol intermediate in the presence of a complex compound of $CrCl_3 \cdot 6H_2O$ and TBAC. Subsequently, D-fructose was generated though the enol intermediate discharged the complex compound and finally D-fructose converted into 5-HMF by losing three water molecules.

CONCLUSION

A relatively inexpensive ionic liquid tetrabutylammonium chloride and low-toxicity catalyst $CrCl_3 \cdot 6H_2O$ reaction system was developed for the preparation of 5-HMF from cellulose in acid condition. After all conditions were investigated, 5-HMF yield from cellulose was obtained as high as 43.7% at 140 °C for 90 min and the system can be easily regenerated without loss of both activity and selectivity, and reused at least five times. What's more, when glucose and starch were also used as feedstock to produce 5-HMF in TBAC/$CrCl_3 \cdot 6H_2O$, the results were comparable to that from cellulose. Most importantly, our work provides a cheaper and environment friendly reaction system for transformation of biomass into 5-HMF.

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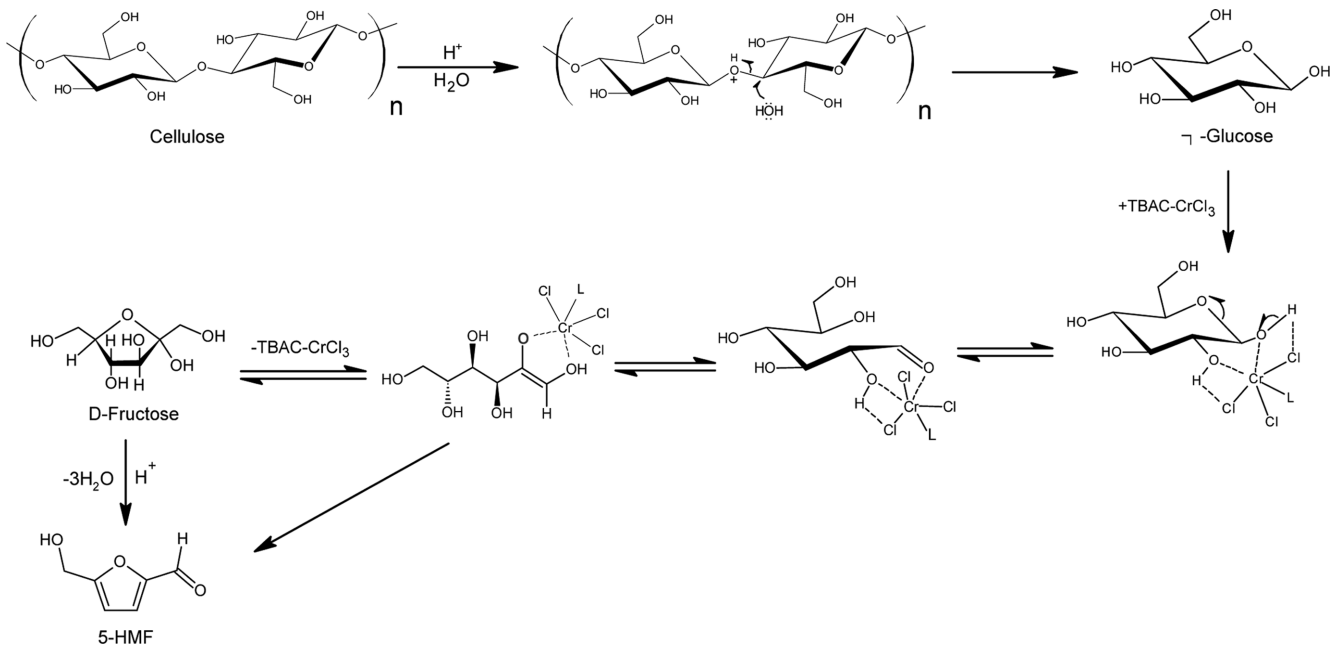

Fig. 8. The proposed mechanism of cellulose conversion to produce 5-HMF catalyzed by $CrCl_3$ in TBAC. L stand for TBAC.

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