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One-step degradation of cellulose to 5-hydroxymethylfurfural in ionic liquid under mild conditions

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ABSTRACT

One-step conversion of cellulose to HMF (5-hydroxymethylfurfural) has been achieved by using metal chlorides ($CrCl_3$, $CuCl_2$, $SnCl_4$, WCl_6) in [BMIM]Cl. The effects of temperature, reaction time, amount of catalysts, and the purity of [BMIM]Cl on the performance have been studied and discussed in detail. More than 63% yield of HMF and 80% yield of TRS (total reducing sugar) were obtained in [BMIM]Cl with $CrCl_3$ at 120 °C under atmospheric pressure. Filter paper and cotton were also used as a source for cellulose degradation to HMF, but only a moderate yield of HMF was obtained (40% for filter paper and 12% for cotton). The reutilization of this system was examined and the reaction mechanism was also discussed.

1. Introduction

Cellulose, the most abundant biomass in the world, has attracted a lot of attention in recent years and is an important renewable resource (Ragauskas et al., 2006). It will play an important role in the chemical industries of the future. However, its high degree of crystalline maintained partly by hydrogen bonds between different cellulose molecules make it insoluble in water or traditional organic solvents (Henriksson, Berglund, Isaksson, Lindstroem, & Nishino, 2008). As known, heterogeneous degradation of cellulose is an inefficient and energy-consuming process. If the degradation of cellulose can be processed under homogeneous condition, the reaction efficiency could be improved considerably. Compared to other solvents, ionic liquids have many advantages, including negligible vapor pressure, good solubility, a wide electrochemical window, flame retardant properties, and have been applied in many fields (Olivier-Bourbigou, Magna, & Morvan, 2010). Swatloski, Spear, Holbrey, and Rogers (2002) found that cellulose could be dissolved in ionic liquids, such as $[C_4mim]Cl$, $[C_4mim]Br$, $[C_4mim]SCN$. This research laid a foundation for the homogeneous degradation of cellulose.

It becomes more and more important to prepare chemical building blocks from renewable resources which allow fossil fuel-based platform chemicals to be replaced since the price of oil has risen significantly. HMF (5-hydroxymethylfurfural) is an attractive chemical among these new chemical building blocks (Roman-Leshkov, Chheda, & Dumesic, 2006; Zhao, Holladay, Brown, & Zhang, 2007), since it contains several functional groups which can be used for synthesis of drug, functional polymers, biomass fuel (like 2,5-dimethylfuran), and other useful chemicals (Rosatella, Simeonov, Fradea, & Afonso, 2011).

Much research has been done to produce HMF from fructose (Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2011). However, fructose is not available in sufficient quantity to satisfy the demands of the chemical industry. Another monosaccharide, glucose, is abundant in nature and is also the monomer of some plentiful nature polymers such as cellulose. But its molecule structure makes it hard to be converted to HMF in high yields. A breakthrough has been made by Zhao et al. (2007) who showed that glucose could be converted to HMF by chromium chlorides to give yields of about 70% in ionic liquid. Two years later, Hu, Zhang, Song, Zhou, and Han (2009) reported the degradation of glucose to HMF by $SnCl_4$ with yield of 60%. However, $SnCl_4$ can be easily hydrolyzed to $Sn(OH)_4$ and HCl. These studies suggest it is possible to produce of HMF from cellulose.

Zhang and Zhao (2010) converted cellulose with different polymerization degrees and different kinds of lignocellulose (corn stalk, straw and pine wood) to HMF in yield of 45–60% with $CrCl_3$

Abbreviations: HMF, 5-hydroxymethylfurfural; TRS, total reducing sugar.

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under microwave heating in [BMIM]Cl. However, industrialization of microwave heating still has a long way to go. Moreover, they got a high yield of furfural while the HMF yield decreased quickly under microwave heating. Su et al. used a pair of metal chlorides, $CuCl_2$ and $CrCl_2$, as the catalyst to convert cellulose to HMF at yield of 55% in [EMIM]Cl (Su et al., 2011). Though $CuCl_2$ is effective at degrading cellulose, it also has high catalytic activity for poly-reaction of the products and thereby reduces the yield of target products. In Zhang, Du, Qian, and Chen's work (2010), cellulose was firstly hydrolyzed cellulose by HCl and H_2SO_4 in [Emim]Cl followed by the addition of $CrCl_2$, the yield of HMF was improved and reached a high level 89% at last. However, mineral acids are corrosive to the equipment and the conversion of cellulose to HMF in two steps is inconvenient. Zhao, Cheng, Li, Tian, and Wang (2011) synthesized a dual functional catalyst, $Cr[(DS)H_2PW_{12}O_{40}]_3$, which has both Brønsted and Lewis acidity for conversion of cellulose to HMF in the yield of 52.7% in water at 150 °C for 2 h. However, this requires a high pressure and relatively high temperature, and a complicated synthesis process of the catalyst.

In this work, cellulose was directly converted to HMF in a high yield (more than 60%) with $CrCl_3$ in [BMIM]Cl without a cosolvent at relatively low temperature under atmospheric pressure. The effects including reaction temperature, time, catalyst amount, the purity of ionic liquid, and polymerization degree of cellulose, were studied and discussed. The reaction mechanism was also suggested.

2. Experimental

2.1. Material and methods

Microcrystalline cellulose (MCC, DP: 215–245), *N*-methylimidazole (AR), 1-chlorobutane (CP) and $CrCl_3{\cdot}6H_2O$ (≥99%) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Microcrystalline cellulose was dried in blast oven at 100 °C for 1 h before use. $CuCl_2{\cdot}2H_2O$ (≥99%) was obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Ionic Liquid [BMIM]Cl was prepared according to the reported procedures (Tao, Song, & Chou, 2011). All other chemicals were purchased from local suppliers and used without further purification.

2.2. Preparation of [BMIM]Cl

N-methylimidazole was added into a three-necked round bottom flask, and heated to 80 °C under stirring. 1-chlorobutane was added into the flask drop wise by using a tap funnel at the molar ratio of 1:1.1 and condensed reflux at the same time. After all of the 1-chlorobutane was added into the flask. Then the mixture was kept heating and stirring for 48 h. When the reaction was finished, it was cooled to room temperature and washed by double mixture volume of ethyl acetate for three times. Then double mixture volume of ethyl acetate, half mixture volume of acetonitrile and a little crystal of [BMIM]Cl were added to get pure [BMIM]Cl crystal. ^{1}HNMR spectra of [BMIM]Cl was recorded on Brucker Advance 400 MHz spectrometer which was purchased from Brucker Co. Ltd (Switzerland).

[BMIM]Cl: ^{1}H NMR (400 MHz, D_2O): δ0.95–1.00(t, 3*H*), 1.34–1.46(m, 2*H*), 1.87–1.97(m, 2*H*), 4.15(s, 3*H*), 7.51 (s, 1*H*), 7.61(s, 1*H*), 10.83(s, 1*H*).

2.3. Typical procedure for microcrystalline cellulose hydrolysis in [BMIM]Cl

0.1 g MCC was added into 2.0 g [BMIM]Cl in a round-bottom flask and the mixture was heated to 100 °C. After the mixture became clear which means all of MCC was dissolved into [BMIM]Cl, the temperature was increased to the target temperature and the catalyst was added into the solution for a certain time. At different time intervals, two samples were withdrawn, weighed and quenched immediately with cold water each time, one for HMF detection (recorded as M_1) and the other for TRS (recorded as M_2). Every reaction was repeated 3 times.

2.4. Analysis of HMF and TRS

The analysis of HMF and TRS was performed by the method as reported (Zhou, Liang, Ma, Wu, & Wu, 2013). Samples were dissolved in 1500 times samples volume of deionized water, and they were centrifuged at 4000 r/min for 5 min. The color intensity of supernatant fluid was measured in a TU-1810 Model spectrophotometer which was obtained by Purkinje General Co. Ltd (Beijing, China) at 284 nm with a slit width of 0.06 mm (De, Dutta, & Saha, 2011; Hu, Sun, & Lin, 2012; Li, Zhao, Wang, Zheng, & Zhang, 2010). The concentration of HMF was calculated based on a standard curve obtained with HMF. The yield of HMF was calculated as follows:

$$Y_{\mathrm{HMF}} = \frac{(C_{\mathrm{HMF}} \times M_1 \times 1500)}{\left(M_{\mathrm{cellulose}} \times 0.778 \times \left(M_1/M_0\right)\right)}$$

where C_{HMF} is the concentration of HMF, M_0 is the mass of the reaction solution, $M_{\mathrm{cellulose}}$ is the mass of cellulose in the reaction, and M_1 is the mass of sample withdrawn from the reaction mixture. 0.778 is a color intensity correction factor for different volumes of sample.

HMF was also confirmed by high-performance liquid chromatography (HPLC) (It was purchased from Waters (China) Co. Ltd (Shanghai). Waters 2487 dual λ absorbance detector, Waters Binary HPLC pump) with a C18AQ column which was purchased from Guangzhou Research & Creativity Biotechnology Ltd (Guangzhou, China) and used a 8:2 v/v methanol: water gradient at a flow rate of 1 ml/min and a column temperature of 293 K using a UV detector.

Total reducing sugar was detected by DNS method. The samples were taken periodically, and diluted with 150 times samples volume of deionized water. 1 ml DNS regent was added, then heated for 20 min in boiling water, and cooled with cold water. The color intensity of the mixture was measured in a TU-1810 Model spectrophotometer at 498 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose. The yield of TRS was calculated as follows:

$$Y_{\mathrm{TRS}} = \frac{(C_{\mathrm{TRS}} \times M_2 \times 1500)}{\left(M_{\mathrm{cellulose}} \times 1.11 \times \left(M_2/M_0\right)\right)}$$

2.5. FT-IR analysis

The residue was separated and dried for FT-IR analysis. All the FT-IR spectra were collected on an FT-IR spectrometer (Nicolet NEXUS670) with a resolution of 4 cm^{-1} and 32 scans in the region of 4000–400 cm^{-1}.

3. Results and discussion

3.1. Selection of catalysts

3.1.1. Degradation of cellulose in [BMIM]Cl by different chlorides

In this study, $CrCl_3$, $SnCl_4$, $CuCl_2$, and WCl_6, which have been reported as good catalysts for dehydration of glucose to HMF, were used for the degradation of cellulose (Guan, Cao, Guo, & Mu, 2011; Hu et al., 2009; Su et al., 2011; Zhao et al., 2007). As seen in Fig. 1, $CrCl_3$ exhibited good catalytic performance for degradation of cellulose to HMF. Furthermore, HMF was stable in [BMIM]Cl with $CrCl_3$, which may relate with the ability of $CrCl_3$ to recover HMF (Zhao et al., 2007). Cellulose was degraded fast in [BMIM]Cl

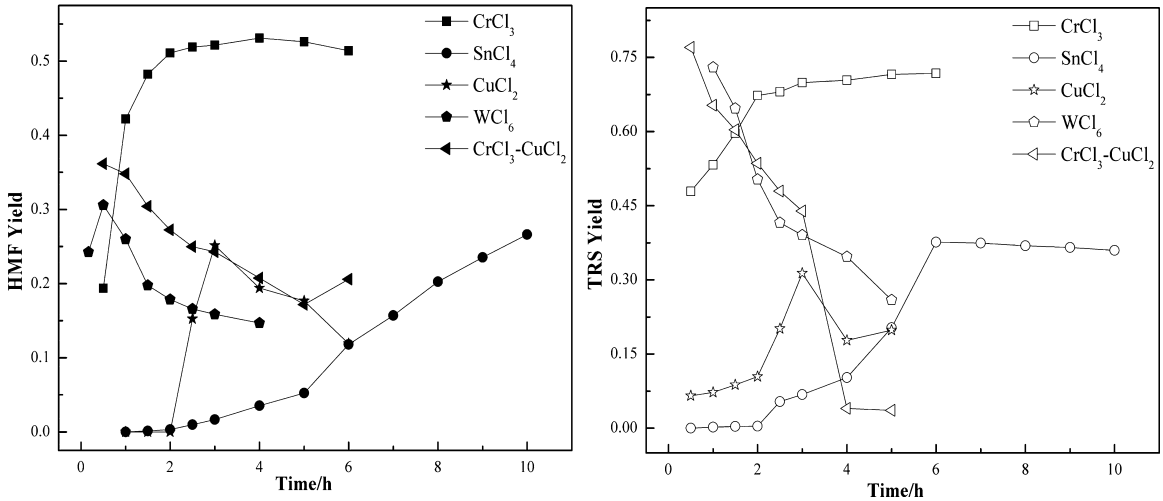

Fig. 1. Degradation of cellulose to HMF with different metal chlorides. (Cellulose 0.1 g, [BMIM]Cl 2.0 g, metal chlorides 0.05 g, reacted at 120 °C)

with WCl_6 or $CrCl_2$–$CuCl_2$. However, compared to $CrCl_3$ both TRS and HMF yields declined quickly. HMF displays its stability in [BMIM]Cl with $CrCl_3$. Meanwhile, there were a lot of black precipitates formed. The FT-IR spectra (Fig. 2) show that the black precipitates were different from those obtained with $CrCl_3$. The residue from cellulose catalyzed by $CuCl_2$ and WCl_6 shows different IR absorption peaks from cellulose, indicating it is obviously not cellulose. The absorption peaks at 1571 and 1458 cm^{-1}, 979 and 815 cm^{-1} can be ascribed to the vibration of carboxylic group and C=C which are not present in cellulose. Other absorption peaks which belong to cellulose are weakened or disappear. The leftovers of cellulose catalyzed by $CuCl_2$ and WCl_6 have almost the same absorption peaks as the residue formed by cellobiose which is commonly called as humin, probably polymerized from the cellulose hydrolysis products (Zhang et al., 2010). The results show that both $CuCl_2$ and WCl_6 have good ability to degrade cellulose, but degradation products are unstable with these two catalysts. While the leftover is mainly cellulose from the degradation by $CrCl_3$. Additionally, WCl_6 is more expensive than $CrCl_3$ and is prone to be hydrolyzed in air. $SnCl_4$ showed a poor performance for the degradation of cellulose, which is probably because $SnCl_4$ is easily hydrolyzed into $Sn(OH)_4$ in the reaction.

3.1.2. Degradation of cellulose in [BMIM]Cl by different chromium salts

The effect of Cl^- in $CrCl_3$ was investigated by using different chromium salts with different anions as catalysts. The results (Fig. 3) show that only $CrCl_3$ has a good ability in degradation of cellulose to HMF. It indicates that the Cl^- in $CrCl_3$ plays an important role in this reaction. First, Cl^- takes part in coordination of Cr^{3+} with β-1,4-glycosidic bonds in depolymerization of cellulose to glucose. SO_4^{2-} and $NO_3{}^-$ also can coordinate with Cr^{3+} in the reaction (Tao et al., 2011). However, their larger radius than Cl^- makes them hard to coordinate with Cr^{3+} and attack β-1,4-glycosidic bonds between two glucopyranosyl units. Thus compared to $CrCl_3$, the TRS yields for $Cr(NO_3)_3$ and $Cr_2(SO_4)_3$ were lower. Also, since $NO_3{}^-$ is smaller than SO_4^{2-}, HMF and TRS yield catalyzed by $Cr(NO_3)_3$ are higher than those of $Cr_2(SO_4)_3$. As suggested by Zhao et al. (2007) Cl^- may also takes part in the coordination of Cr^{3+} with glucose to convert glucose to fructose which is the most important step in conversion of

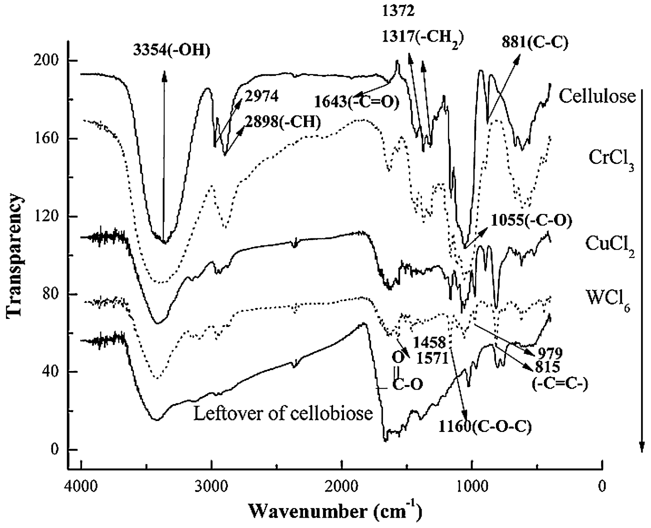

Fig. 2. The FT-IR spectra of hydrolysis leftover catalyzed with [BMIM]Cl and different chromium salts.

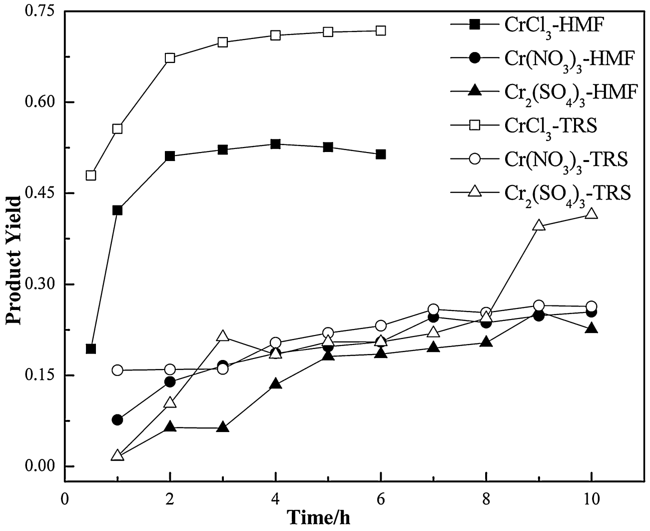

Fig. 3. Degradation of cellulose to HMF with $CrCl_3$ at different temperature. (Cellulose 0.1 g, [BMIM]Cl 2.0 g, $CrCl_3$ 0.05 g.)

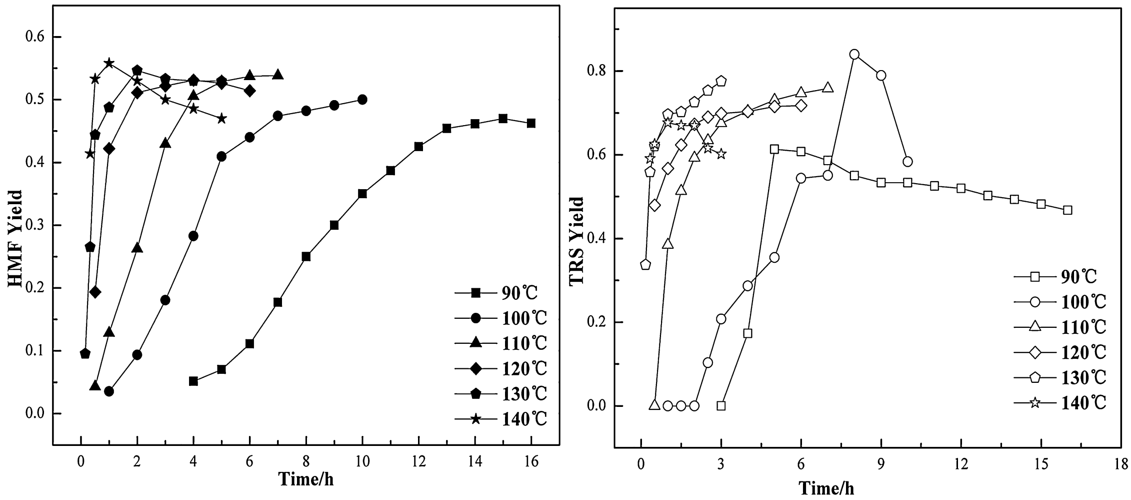

Fig. 4. Conversion of cellulose to HMF with different amount of $CrCl_3$. (Cellulose 0.1 g, [BMIM]Cl 2.0 g, reacted at 120 °C)

glucose to HMF. SO_4^{2-} and $NO_3{}^-$ may play the same role as Cl^- (Tao et al., 2011), thus the selectivity of HMF on $Cr(NO_3)_3$ and $Cr_2(SO_4)_3$ catalysts is also high, more than 80%. The anions of chromium salts may mainly influence the depolymerization of cellulose to glucose by their size, but they have little effect on the dehydration of glucose to HMF.

3.2. Effects of reaction conditions

3.2.1. Reaction temperature

Temperature is an important factor in this reaction. As temperature increases, both the yield and reaction rate increases (Fig. 4). From 90 °C to 140 °C, HMF yield and TRS yield were increased about 10% and 15%, respectively. The reaction rate was also accelerated. It can be attributed to the reduced the viscosity of this reaction system which will accelerate the mass transfer rate and facilitated cellulose chain degradation. Although the reaction rate increased with temperature, the production of HMF was reduced (by about 10% within 4 h) if the temperature was too high (≥130 °C). The reason may be that HMF is unstable at high temperature and is much easier to be polymerized into by-products like furan dimer, humin than at low temperature (Tao et al., 2011). Therefore, 120 °C was chosen as the optimal reaction temperature.

3.2.2. Amount of catalyst

Increasing catalyst amount can accelerate the reaction rate (Fig. 5). However, it showed a different trend to the production yield. Increasing $CrCl_3{\cdot}6H_2O$ from 0.01 g to 0.03 g, all products yields were improved. When more than 0.03 g catalyst was loaded, the product yields decreased. The reason may be that too much catalyst leads to some side reactions. Considering the loss of the catalyst during the extraction step, 0.05 g catalyst was chosen for the reaction.

3.2.3. Reaction time

Figs. 1, 3–6 show the effect of reaction time on the yield of HMF and TRS yield. Prolonging the reaction time can improve products yield. However, after reaching the maximal yield, HMF yield declined slightly (10% at 140 °C and 3% at 130 °C in 4 h). It indicates that HMF is relatively stable in this reaction system (<130 °C). After a long period of reaction, HMF was converted to other chemicals such as furan dimers. Compared to the process using microwave heating (Zhang & Zhao, 2010), less furfural was generated (less than 5%) in this work. Oil bath is more favorable for producing HMF. There is no obviously decrease in HMF yield in 4 h at 120 °C. So it's convenient to use the traditional equipments with traditional heating to produce HMF in the future.

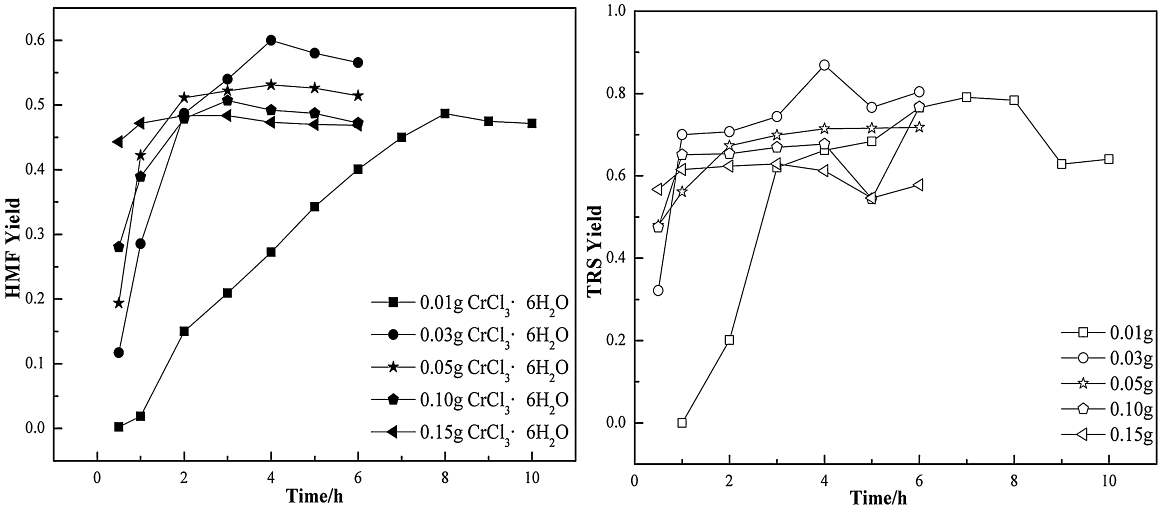

Fig. 5. Degradation of cellulose of different degrees with $CrCl_3$. (Cellulose 0.1 g, [BMIM]Cl 2.0 g, $CrCl_3$ 0.05 g, reacted at 120 °C)

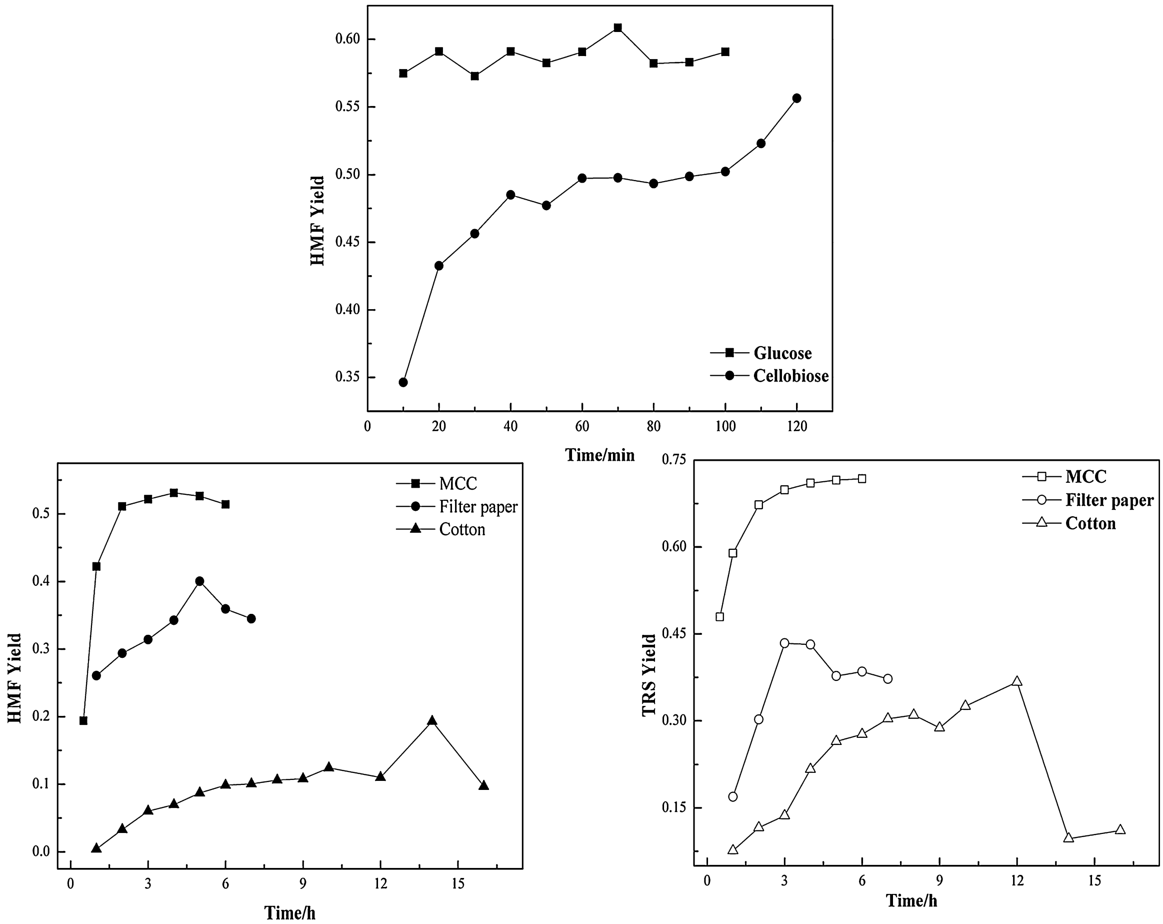

Fig. 6. Conversion of cellulose to HMF with different chromic salts (Cellulose 0.1 g, [BMIM]Cl 2.0 g, chromic salt 0.05 g, reacted at 120 °C).

3.2.4. *Influence of polymerization degree*

This catalysis system was explored to reduce the degrees polymerization of cellulose (Fig. 6). The results show that with the polymerization degree increasing, both reaction rate and HMF yield declined. In early studies (De et al., 2011; Hu et al., 2012; Su et al., 2011; Tao et al., 2011), cellulose was first depolymerized to glucose, then the glucose was dehydrated to HMF. There are at least two steps to convert cellulose to HMF. So a long time is needed to complete this process. Because of long cellulose chain and high crystallinity in cotton and filter paper, longer time should be needed for their depolymerization to glucose than MCC. The reason why HMF yield declined may be that cellulose needs to be depolymerized to glucose first before HMF is obtained. This whole reaction may reach equilibrium and HMF yield cannot be improved further. Another reason may be that as the polymerization degree of cellulose increases, it becomes much harder to dissolve cellulose in [BMIM]Cl. For instance, cotton cannot be dissolved in [BMIM]Cl, but only at swelling state. After addition of $CrCl_3$, cotton began to break up into pieces and dissolve into [BMIM]Cl. But only low yield of HMF was obtained for 16 h.

3.2.5. *Effect of water*

Water content influences this reaction significantly (Table 1). [BMIM]Cl was heated to remove water in vacuum oven at 100 °C for 12 h. Different amount of water was added to [BMIM]Cl to examine the effect of water. The results show that with water content increasing, the product yield decreased. It may be attributed to two reasons. One is that HMF is hydrolyzed to levulinate acid and formic acid. However, in these experiments, the conversion of cellulose declined a lot with high water content (lower than 55%). The other reason is that water can reduce the solubility of cellulose in [BMIM]Cl. When water content is more than 1 wt%, the solubility of cellulose in [BMIM]Cl drops clearly (Nishiyama, Sugiyama, Chanzy, & Langan, 2003; Swatloski et al., 2002). Hydrogen bonds formed by [BMIM]Cl with hydroxyl groups on the cellulose is positive to the breakage of β-1,4-glycosidic bonds (Heinze, Schwikal, & Barthel, 2005). But water can form hydrogen bonds with hydroxyl groups on the cellulose more easily than [BMIM]Cl, which could reduce the solubility of cellulose [BMIM]Cl (Pinkert, Marsh, Pang, & Staiger, 2009). To confirm this, $CrCl_3$ was added before cellulose was dissolved into [BMIM]Cl. Then the reaction rate slowed down and the products yield reduced a little.

The experimental results show that the purity of [BMIM]Cl is important. When $CrCl_3$ was added to pure [BMIM]Cl, the colorless transparent solution became purple red. This phenomenon shows

Table 1
Degradation of cellulose to HMF by $CrCl_3$ and [BMIM]Cl with different impurity.

Entry	*Impurity*	*Reaction time*	*HMF yield (%)*	*TRS yield (%)*
1	–	20	8	75
2	0.05 g $CrCl_3$	3	53	70
3	0.02 g imidazole	3	11	17
4	0.03 gH_2O	3	48	70
5	0.13 gH_2O	3	15	28

There was 0.1 g cellulose in 2.0 g [BMIM]Cl reacted at 130 °C. 2~4 were carried out with 0.1 g cellulose in 2.0 g [BMIM]Cl by 0.05 g $CrCl_3$ at 120 °C.

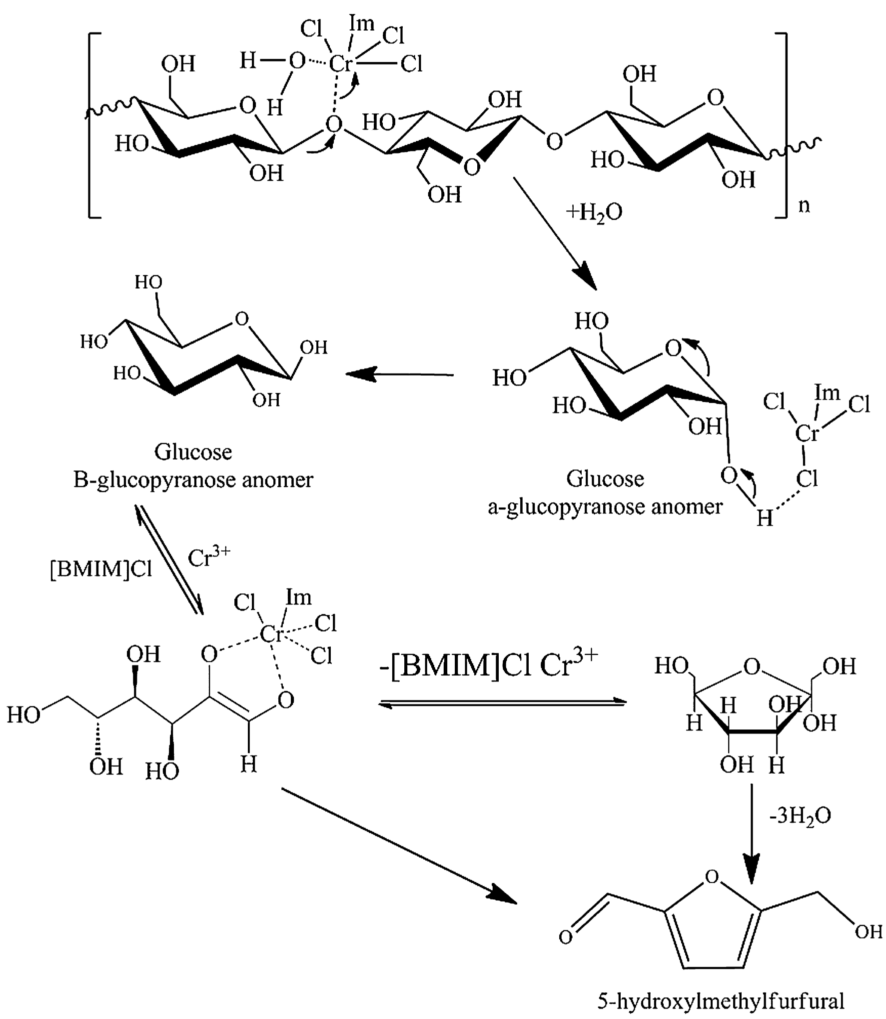

Fig. 7. The mechanism of conversion of cellulose to HMF in [BMIM]Cl with $CrCl_3$.

that $CrCl_3$ has coordinated with [BMIM]Cl and high yield of HMF and TRS were gained. However, if imidazole existed in [BMIM]Cl, green solution was formed with $CrCl_3$ and low yield of HMF and thus TRS were obtained (Table 1). Because imidazole is a weak base and $CrCl_3$ is a Lewis acid, imidazole can coordinate with $CrCl_3$ to hinder $CrCl_3$ from attacking β-1,4-glycosidic bonds and converting glucose to HMF.

3.3. Degradation mechanism

According to the above results and related literatures, the mechanism of cellulose degradation to HMF by $CrCl_3$ was proposed (Fig. 7). $CrCl_3$ first attacks β-1,4-glycosidic bonds. [BMIM]Cl forms hydrogen bond with hydroxyl groups of cellulose to help the breaking of β-1,4-glycosidic bands. Then $CrCl_3$ coordinates with the generated glucose, α-glucose is isomerized to β-glucose which is more easily to be dehydrolyzed. Cr^{3+} interacts with the hemiacetal portion of glucopyranose and aldehyde group becomes enol (Zhao et al., 2007). [BMIM]Cl acts as both proton donor (C2—H) and acceptor (Cl^-) in H-bonding interactions with glucose to improve dehydration efficiency at the same time (Guo, Fang, & Zhou, 2012). Then aldehyde group is converted to a ketone group and glucose is isomerized to fructose. Three molecules of water is removed from fructose to form HMF. The degradation of cellulose to HMF catalyzed by other salts should follow the similar mechanism. This mechanism still needs further work to confirm it.

3.4. Recycling of catalysis system

The reusability of the catalysis system was tested. After the reaction, some de-ionized water was added into the reaction mixture. Then the solid and liquid were separated by centrifugation.

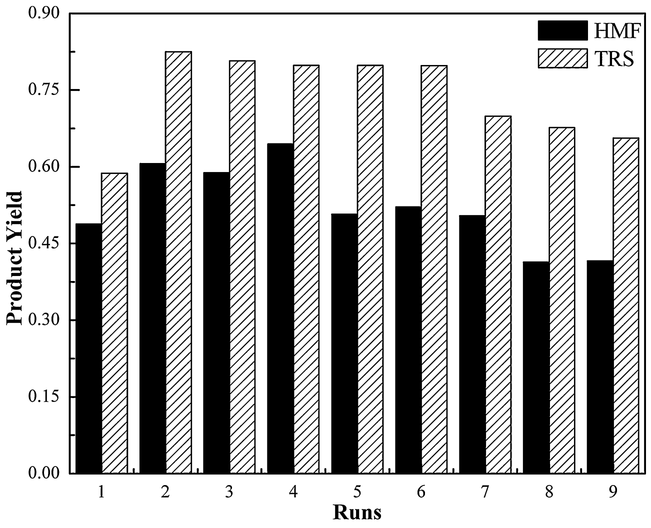

Fig. 8. Recycle of catalysis system for the hydrolysis of microcrystalline cellulose to the main products.

HMF was extracted by ethyl acetate for 3 times and the remaining aqueous phase was heated to remove water at 100 °C for the next reaction cycle. As seen in Fig. 8, both HMF and TRS yield increased in the first four runs, and then decreased for further runs. The reason why products yield increased is that sugars including glucose and cellobiose which come from the depolymerization of cellulose cannot be dissolved in ethyl acetate. They continue be dehydrated to HMF in the next run, resulting in the improved product yield. HMF and TRS contents were analyzed in the mixture after extraction. About 2% HMF and 24% TRS were left in mixture. After this part was deducted from the results, the catalyst was found to keep same activity at first four runs. There are many shortcomings in this reuse process, such as water is not easy to remove and low extraction efficiency. The recycle of the catalysis system still needs further improvement.

4. Conclusions

Four different metal chlorides ($CrCl_3$, $CuCl_2$, $SnCl_4$, WCl_6) catalysts were used to convert cellulose to HMF in one step. $CrCl_3$ exhibited the best performance. More than 63% yield of HMF and 80% yield of TRS were obtained at 120 °C in 4 h containing 0.1 g microcrystalline cellulose and 0.05 g $CrCl_3$ in 2.0 g [BMIM]Cl at atmospheric pressure. However, when filter paper or cotton was used as the raw material instead of MCC, a low yield of HMF (40% for filter paper and 12% for cotton) was obtained. Low content of water in reaction mixture is beneficial for the production of HMF. In addition, this system can be reused for many times.

Acknowledgements

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