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Catalytic hydrolysis of cellulose into furans in MnCl₂-ionic liquid system

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ABSTRACT

Production of 5-hydroxymethylfurfural (HMF) and furfural from microcrystalline cellulose (MCC) was studied in 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1) with catalytic amount of MnCl₂ under atmospheric pressure within 300 min at 150 °C, in which 88.62% of conversion was obtained. With the presence of a catalytic amount of MnCl₂, HMF and furfural yields were up to 37% and 18%, respectively, and generated small amount of levulinic acid (LA) and the total reducing sugars (TRS). Dimer of furans compounds as the important by-products were analyzed through HPLC–MS; some small molecular substances, methane, ethane, CO, CO₂ and H₂, as gas products were detected using mass spectrometry analysis. Comparing with the previous reports, our catalytic system is simple, and it provides an effective route for the conversion of microcrystalline cellulose into biofuels and important platform chemicals.

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1. Introduction

Biomass is the most abundant renewable resource that can be converted to energy, chemicals, foods and feedstocks (Chheda, Huber, & Dumesic, 2007; Dodds & Gross, 2007). An excellent strategy for providing a new energy source is the immediate use of the inedible biomass, such as cereal straws, bagasse and even used paper. Cellulose is the major component of such biomass, which occupies 60–80% of biomass (Ohno & Fukaya, 2009). Utilization of biomass, especially inedible cellulosic biomass, is highly desirable for the construction of sustainable society (Ragauskas et al., 2006).

Cellulose is stabilized by intra- and inter-molecular hydrogen bonds so as to form tough bundles, which make it almost impossible to solubilize with water and common organic solvents (Michael et al., 2007). Therefore, it is essential to design solvents for cellulose and to propose a system with minimum energy. Pioneer studies by Robin Rogers (Swatloski, Spear, Holbrey, & Rogers, 2002) demonstrated 1-butyl-3-methylimidazolium ([C₄mim]) salts as solvents for cellulose, they also investigated the solubilizing mechanism of cellulose in ionic liquids (ILs) using NMR spectroscopy (Remsing, Swatloski, Rogers & Moyna, 2006). From then on, it has attracted much attention (Zhu et al., 2006), subsequently, chemical hydrolysis (Li, Wang, & Zhao, 2008; Li & Zhao, 2007) and hydrogenolysis (Fukuoka & Dhepe, 2006; Luo, Wang, & Liu, 2007) of cellulose in ILs were reported.

Recently, studies on the direct conversion of cellulose into furans (Binder & Raines, 2009) or compounds with longer carbon chains (Wu, Guo, Wang, & Yang, 2009) have been one of the most intensive pursuits worldwide. Specifically, Seri and co-workers (Seri, Sakaki, Shibata, Inoue, & Ishida, 2002) reported that LaCl₃ could catalyze the degradation of cellulose to 5-hydroxymethylfurfural (HMF) in water at 250 °C with about 19% yield. In parallel, Mascal (Mascal & Nikitin, 2008) demonstrated concentrated hydrochloride promoted conversion of cellulose into 5-chloromethylfurfural with up to 84% yield. Later, Binder (Binder & Raines, 2009) showed transformation of Lignocellulosic Biomass into Furans in DMA-LiCl system at 140 °C with the yield of HMF up to 48%. Zhao (Zhang & Zhao, 2009) studied the conversion of lignocellulosic biomass into furans in ionic liquid in the presence of CrCl₃ under microwave irradiation, the yield of HMF and furfural could be up to 45-52% and 23-31%, respectively. Hu, Zhang, Song, Zhou, and Han (2009) demonstrated that the common Lewis acid SnCl₄ could efficiently convert glucose into 5-hydroxymethylfurfural in 1ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄). Zhao, Holladay, Brown, and Zhang (2007) first reported metal chlorides in ionic liquid solvents convert sugars to 5-HMF, the yield near 70% can be obtained.

Most of the chemical reactions of cellulose were performed at elevated temperature, high pressure, catalyzed either by enzymes or by inorganic proton-acid catalysts (Hu, Lin, Liu, & Liu, 2010; Rogalinski, Ingram, & Brunner, 2008; Xu, Wang, Jiang, Yang, & Ji, 2007). Until now, almost all the efforts toward furans production from cellulose have used metal chlorides, which have yielded promising results, but the reported processes of these reactions

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Scheme 1. Schematic illustration of the main products from microcrystalline cellulose.

were very complicated and these methods mostly depends on poisonous CrCl₃ as cocatalyst. Here, we first report our results on the hydrolysis of cellulose, which was catalyzed by 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1) by addition of a catalytic amount of MnCl₂ at 150 °C under atmospheric pressure. The schematic illustration of HMF and furfural production from microcrystalline cellulose (MCC) is shown in Scheme 1.

2. Methods

2.1. Materials

Microcrystalline cellulose (extra pure, average particle size is 90 μ m), a commercial product from J&K chemical company (Beijing, China) was dried for 24 h at 90 °C prior to cellulose hydrolysis; 4-methyl-2-pentanone (A.R., >90%), MnCl₂·4H₂O (A.R., >99%) and acetonitrile (HPLC) was purchased from Tianjin chemical reagent company (Tianjin, China); 1-methyl imidazole (CP, >99%), 1,4-butanesultone (>99%), 1-chlorobutane (CP, >99.5%), 1bromobutane (CP, >99.5%) were from Alfa Aesar; 5-HMF (>99%) was purchased from Aldrich; levulinic acid was from DaoCheng chemical company (Hong Kong, China); furfural (A.R., >99%) was from Sinopharm Chemical Reagent Co., Ltd.; all other reagents and solvents were reagent grade and were used as received.

2.2. Preparation of IL-1

16.4 g (0.2 mol) 1-methyl imidazole, 27.28 g (0.2 mol) 1,4butanesultone were mixed in a flask (250 mL) and stirred at 42–45 °C for 17 h to receive white solid, then the white solid was grinded, washed repeatedly with small portion of ether, filtrated, vacuumized for 4 h in the room temperature. Equimolar white solid was added to 98% H₂SO₄, and the mixture was stirred at 80 °C for 6 h, the obtained viscous liquid was washed with ether three times and dried in vacuum to form ionic liquid–1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1). ¹H NMR (400 MHz, D₂O): δ 1.53 (m, 2H), 1.80 (m, 2H), 2.72 (t, 2H), 3.67 (s, 3H), 4.02 (t, 2H), 7.24 (d, 2H), 8.47 (s, 1H); ESI-MS: *m/z* (+)218.6, *m/z* (–)96.3.

Other ILs, such as C_4 mimBF₄, C_4 mimPF₆, C_4 mimBr, C_4 mimCl, C_4 mimH₂PO₄, were synthesized according to the known procedures (Dupont, Consorti, Suarez, & Souza, 2004).

2.3. Typical procedure for conversion of cellulose into furanic compounds

Experiments were carried out in a stainless steel autoclave with glass liner tube (100 mL), the reactor was loaded with 0.5 g microcrystalline cellulose, 2.0 g catalysts, 1 mL H_2O (0.2 M $MnCl_2$ aq.) and 8 mL 4-methyl-2-pentanone (MIBK), MIBK was used as phase

modifier to extract continuously the products from aqueous phase (Leshkov, Chheda, & Dumesic, 2006). The reactor was then placed into an electrical heating jacket, it would take about 20 min to reach the specified temperature (150 °C), after the appointed reaction time, the reactor was removed from the electrical heating jacket and quickly quenched in a cool water bath at atmospheric temperature and pressure. Then MCC was fractionated into four portions: aqueous phase, organic phase, gaseous products and solid residue. The liquid and solid fractions were collected by repeatedly washing the inside of the reactor with 5 mL distilled water and 40 mL pure ethanol. The solid residues recovered were dried at 100 °C for 8 h, then weighed to calculate the yield of liquefaction. After filtration, extraction and separation, the phases of organic and water were collected to character the production. All results were replicated at least three times; the range of experimental errors for the HPLC analysis was $\pm 1\%$ and $\pm 2\%$ for the TRS analysis.

Meanwhile, cellulose conversion was determined by the change of cellulose weight before and after the reaction. The yield of products were calculated from the equation: yield (%)=(weight of products)/(weight of cellulose put into the reactor) \times 100.

2.4. Analytical methods

The yield of the total reducing sugars (TRS) was analyzed by phenol–sulfuric acid method (Dong, Zheng, & Fang, 1996). A mixture containing 0.1 mL reaction sample (water-soluble portion), 0.9 mL deionized water, 1 mL 5% phenol (new distilled) and 5 mL 98% concentrated sulfuric acid was prepared, the analysis was performed on a HP8453 UV–vis spectrophotometer at about 490 nm. The concentration of TRS was calculated based on the standard curve obtained with glucose. The yield of TRS was calculated from the equation: yield (wt%) = (weight of TRS)/(weight of cellulose put into the reactor) × 100. The aqueous phase containing HMF and furfural was determined on a HP8453 UV–vis spectrophotometer at 282 nm (for HMF) and 277 nm (for furfural) with a slit width of 0.06 mm based on their corresponding standard curves (Lian & Peng, 2008).

The liquid products for HMF, furfural and levulinic acid were analyzed by high-performance liquid chromatography (HPLC) on an Waters Alliance 2695 series equipped with Waters 2996 PDA detector and a zorbax eclipse plus C18 reversed-phase column (150 mm \times 4.6 mm, 5 μ m). During this process, the column temperature remained constant at 30 °C, while the mobile phase applied was water–acetonitrile (15:85, v/v) at the flow rate of 0.5 mL/min, with UV detection at 280 nm for furfural and HMF, 250 nm for levulinic acid, and the volume for each injection was 10 μ L. The concentration of HMF, furfural and levulinic acid was calculated based on the standard curve obtained with the standard substances.

The liquid products for dimer of furan compounds were analyzed by high performance ion trap mass spectrometers detector (LC–MSD) on an Agilent 1100 series LC–MSD trap VL equipped with Agilent 1100 detector and a zorbax eclipse plus C18 reversed-phase column (150 mm × 4.6 mm, 5 μ m). During this process, the column temperature remained constant at 25 °C, while the mobile phase applied was water–acetonitrile (50:50, v/v) at the flow rate of 1.0 mL/min, with UV detection at 250 nm (Ferrer, Alegríaa, Farré, Abellán, & Romero, 2002; Nozal, Bernal, Toribio, Jiménez, & Martín, 2001), and the volume for each injection was 5 μ L. The dry gas was N₂ at the flow of 5 L/min and dry temperature was 350 °C. With the analysis of mass spectrum, the hit gas was He.

In addition, the gas fractions were analyzed by mass spectrometry (Inficon, Transpector 2). Molecular weight distributions of liquid phase products were measured through gel permeation chromatography (Waters 2695 GPC), which was performed on a Waters Alliance 2695 series equipped with Waters 2996 PDA detector. During this process, the column temperature remained constant at 25 °C, while the mobile phase applied was trichloromethane at the flow rate of 1.0 mL/min, with UV detection at 270 nm.

After the catalyzed hydrolysis reaction was completed, the organic phase was separated to carry out vacuum distillation, and the distilled components were collected ($25-27 \circ C$), submitted for Fourier transform infrared spectroscopy (FT-IR) analysis. All the FT-IR spectra were collected on an FT-IR spectrometer (Nicolet Nexus 870) with a resolution of $4 \, \text{cm}^{-1}$ and 64 scans in the region of $4000-400 \, \text{cm}^{-1}$, the test temperature was $25 \circ C$ and humidity was 50%.

3. Results and discussion

Fig. 1 shows the hydrolysis of MCC with various acidic catalysts. As indicated in Fig. 1, for various acids as catalysts, the present system was effective on the hydrolysis of MCC. When the reaction was carried out in the absence of catalyst, the conversion of MCC was only 3.90%. The presence of Al_2O_3 , having both acidic and basic characters, reduced the conversion to 6.48%. The conversion of MCC was up to 40–60% while the hydrolysis reaction was catalyzed by protonic acids. However, using ionic liquids IL-1 as catalyst, the conversion could reach 70%. Collectively, the results confirmed that strong acidity of solution was an important aspect to the hydrolysis of MCC.



Fig. 1. Hydrolysis of MCC with various acid catalysts: 0.5 g MCC; 2.0 g catalysts; 1 mLH₂O; 8 mLMIBK; $T = 150 \degree$ C; t = 300 min; P = 1 atm (the concentration of protonic acids was 0.1 M).



Fig. 2. Effect of V (MIBK):V (MnCl₂) on the hydrolysis of MCC: 0.5 g MCC; 2.0 g IL-1; 8 mL MIBK; $T = 150 \degree$ C; $t = 300 \min; P = 1 \text{ atm.}$



Fig. 3. Temperature course of the products during the hydrolysis of MCC: 0.5 g MCC; 2.0 g IL-1; 1 mL 0.2 M MnCl₂; 8 mL MIBK; *t* = 300 min; *P* = 1 atm.



Fig. 4. Time course of the products during the hydrolysis of MCC: 0.5 g MCC; 2.0 g IL-1; 1 mL 0.2 M MnCl₂; 8 mL MIBK; $T = 150 \degree$ C; P = 1 atm.



Fig. 5. Putative mechanism of MnCl₂ promoted conversion of glucose into the main products.

The hydrolysis results for MCC in different ionic liquids with catalytic amount of $MnCl_2$ were also investigated. It could be seen from Table 1, the conversion of MCC in C₄mimBF₄, C₄mimPF₆ and C₄mimBr was lower than the one without ionic liquids; these are

Table 1

The results of MCC hydrolysis reactions promoted by different ILs: 0.5 g MCC; 2.	.0 g
ILs; 1 mL 0.2 M MnCl _{2;} 8 mL MIBK; <i>T</i> = 150 °C; <i>t</i> = 300 min; <i>P</i> = 1 atm.	

Entry	Catalysts	Yield (v	Conv. (%)			
		HMF	Furfural	Levulinic acid	TRS	
1	None	0	0	0	2.97	5.43
2	C ₄ mimBF ₄	0.93	0	0	2.08	4.77
3	C ₄ mimPF ₆	1.12	0	0	2.46	5.18
4	C4mimBr	0.62	0	0	1.69	3.76
5	C ₄ mimCl	1.94	0.99	0.72	5.18	10.98
6	C_4 mim H_2PO_4	7.91	2.05	2.53	3.15	22.83
7	IL-1	37.48	18.42	6.73	7.95	88.62
8 ^a	IL-1	15.43	7.45	2.56	10.24	70.00

^a The reaction was performed with 1 mL H₂O.

in accordance with the research results of Swatloski et al. (2002). It was also shown that the conversion of MCC in IL-1 (88.62%) was much higher than in C₄mimCl (10.98%) and C₄mimH₂PO₄ (22.83%), which further illuminated the importance of solution acidity. As MCC was catalyzed by IL-1, the PH of solution was about 1-2, which facilitated MCC's hydrolysis greatly. By addition of catalytic amount of MnCl₂, the MCC conversion ranging from 70.00% to 88.62% for hydrolysis was achieved when the reaction was catalyzed with IL-1 (Table 1, entries 7–8), the yield of HMF and furfural was up to 37.48% and 18.42%, respectively, also small amount of levulinic acid and the total reducing sugars (6.73% and 7.95%). In addition, the promoting catalysis of MnCl₂ was not obvious when the reaction was catalyzed in the absence of ILs (Table 1, entry 1); we suggested that there was a synergistic coordination interaction between IL-1 and MnCl₂ for MCC catalytic hydrolysis in Mn-ILs system. Based on the results above, we considered that IL-1 in the reactions had double functions, not only could it dissolve the MCC like other ionic liquids, but also its acidity could weaken the glycosidic bonds through binding with a glycosidic oxygen atom, then promote the hydrolysis of

Table 2

Hydrolysis of MCC with various manganese salts: 0.5 g MCC; 2.0 g IL-1; 1 mL 0.2 M manganese salts; 8 mL MIBK; $T = 150 \degree$ C; t = 300 min; P = 1 atm.

Manganese salt	nganese salt Yield (wt%)					
	HMF	Furfural	Levulinic acid	TRS		
None	15.43	7.45	2.56	10.24	70.0	
$Mn(NO_3)_2$	26.73	9.28	3.46	8.48	67.60	
MnSO ₄	35.21	14.38	4.07	6.98	83.10	
MnCl ₂	37.48	18.42	6.73	7.95	88.62	
$Mn(CH_3COO)_2$	32.47	11.85	3.99	8.22	83.84	
$Mn(H_2PO_4)_2$	30.87	16.33	4.16	7.93	79.40	

MCC effectively.

Confirming the promoting catalysis of $MnCl_2$, the effect of other manganese salts on the reaction was studied. As can be seen from Table 2, the existence of manganese salts could improve the conversion of MCC, compared with others, the promoting catalysis of $MnSO_4$ and $MnCl_2$ was remarkable, which demonstrated the coordination of IL-1 we proposed latter. Although the conversion of MCC reduced little when $Mn(NO_3)_2$ was used as the cocatalyst, the selectivity of HMF and furfural was also improved correspondingly. We considered the reason for the decreasing conversion was that nitrate anion should be unfavorable to the reaction. Usually, NO_3^- cannot directly act as single-ligand to form stable coordination compounds, so we suggested that the formation of metal nitrate complex was difficult with relative to others.

Figs. 2–4 show the influence of hydrolysis conditions on the reaction. The results confirmed that water had a negative effect on the dehydration of sugar to HMF, which was consistent with the previous reports by Hu et al. (2008). As shown in Fig. 2, when the ratio of MIBK to MnCl₂ was 8:1, the conversion of MCC reached 89%, much higher than the results of the reaction in which the ratio was 8:4 (38%) and 8:3 (45%). Also, the selectivity of HMF and furfural was higher too as V(MIBK): $V(MnCl_2)$ was 8:1. The time and temperature courses of products for the MnCl₂-catalyzed hydrolysis of MCC in IL-1 are shown in Figs. 3 and 4, respectively. As shown in the figures, when the reaction time was 300 min and the reaction temperature was 150°C, the optimal results were obtained, the yield of HMF and furfural reached 37% and 18%, respectively. From Fig. 4, after 600 min reaction, the yield of sugars decreased from 12% to 4%, however, the yield of levulinic acid increased from 0.3% to 13%. And Fig. 3 shows similar pattern to the products, which illustrated that with the increasing of reaction temperature and prolonging of reaction time, the hydrolysis of monosaccharide performed more thoroughly. In our work, the yield of furfural was high, next to HMF, we thought that the formation of furfural was attributed to the loss of formaldehyde in HMF. To verify our points, the reaction of HMF was studied in the same condition, after 300 min reaction at 150 °C, the yields of furfural and levulinic acid were up to 24.91% and 10.33%, respectively. Therefore, we considered that there were two pathways for the decomposition of HMF in hydrolysis of MCC which was catalyzed by IL-1, as depicted in Scheme 1. One is the rehydration of HMF into levulinic acid and formic acid; the other is the loss of formaldehyde in HMF to furfural.

Although many previous works used CrCl₃ as cocatalyst in the hydrolysis of cellulose, considering the toxicity of CrCl₃, we first chose MnCl₂ in our present system. The comparison of the promoting catalytic activity of CrCl₃ and MnCl₂ in the hydrolysis system indicated that the conversion of MCC was little higher when MnCl₂ was used as cocatalyst, and the yields of HMF and furfural were also higher (37% and 18%, respectively) than the one catalyzed by CrCl₃ (32% and 15%, respectively). In contrary, the yields of levulinic acid and reducing sugars in MnCl₂–ILs system were lower than CrCl₃ system. We already noted that the yield of HMF dropped to 15% in the absence of MnCl₂, which also suggested that MnCl₂ played



Fig. 6. Recycling of IL-1 for the hydrolysis of MCC to the main products: 0.5 g MCC; 2.0 g IL-1; 1 mL 0.2 M MnCl₂; 8 mL MIBK; $T = 150 \degree$ C; $t = 300 \min; P = 1 \text{ atm.}$

an important role in the isomerization of glucose and fructose, and the promoting catalysis of CrCl₃ and MnCl₂ maybe attributed to the coordination between IL-1 and metal ions.

As we know, in most cases, the glycosidic bonds in cellulose were weakened by Bronsted acid attack. A Lewis acid would also weaken the glycosidic bonds through binding with a glycosidic oxygen atom in a similar manner to protonic acid, leading to the hydrolysis of polysaccharide to produce monosaccharide. We proposed a mechanism (Fig. 5) in which MnCl₂ in IL-1 formed $[MnCl_2(SO_4)_n]^{2n-1}$ complexes in a similar manner to LnCl₃ as reported by Rogers et al. (Hines et al., 2008). These complexes would promote rapid conversion of the α -anomers of glucose to the β -anomers through hydrogen bonding between the chloride anions or oxygen atom in SO_4^{2-} and the hydroxyl groups. Then the ring aldoses would reverse to straight chain form, combining with the manganese complex to form an enolate structure. Enolate formation would enable conversion of the aldoses into ketoses, followed by dehydration to produce HMF. Then with the effect of acidic ionic liquids, the HMF was combined with water to generate levulinic acid or lost formaldehyde to produced furfural. To confirm the coordination of SO₄²⁻ in the reaction system, we contrast the hydrolysis of glucose in 0.5 M H₂SO₄. The results showed that in the H₂SO₄ catalyst system, by addition of catalytic amount of MnCl₂, the yields of HMF, furfural and levulinic acid increased by 17%, 12% and 4%, respectively, which confirmed that the coordination effect of SO₄^{2–} and MnCl₂ promoted the hydrolysis of glucose effectively.

In addition, small amount of important side-products was obtained. Through gel permeation chromatography (GPC) analysis, the molecular weight distributions of the hydrolysis products for MCC were below 2000. Besides the main products HMF and furfural, dimer of furan compounds was detected through LC–MSD and the second order mass spectra analysis was conducted to determine their structures. The gas products were also analyzed using mass spectrometry; methane, ethane, CO, CO_2 and H_2 as the components of gas product were detected for the hydrolysis of MCC at 150 °C for 300 min reaction.

In the principles of green engineering, catalyst recycling is always important in metal-catalyzed liquid-phase reactions. Therefore, the reusability for $MnCl_2$ and IL-1 catalysts was tested. After the reaction, IL-1 was separated by extraction of products with diethyl ether and water, and then solvent MIBK and water were removed, the catalyst was recycled. It can be seen in Fig. 6, although a decrease of the conversion from 88% to 79% was observed in the second run, and slight decrease in activity was observed in the subsequent four recycles, a stable MCC conversion of about 72% could be obtained. Also, the yield of HMF and furfural has only slight loss over five repeated runs, about 33% and 14% could be obtained, respectively. It was considered that the decrease of activity in the second run should be attributed to non-complete extraction of little by-product from the liquid-phase, which restrained the conversion of MCC. How to further improve the reusability of ionic liquids remained a problem for future study.

4. Conclusions

Preparation of HMF and furfural through the hydrolysis reaction of cellulose is one of the most important approaches to utilize biomass as promising substitutes for petroleum-based chemicals. It was demonstrated herein that our reaction could be smoothly carried out in the mild condition. By comparing different acid catalysts, we indicated that acidic ionic liquids have higher activity than protonic acid, and IL-1 showed higher catalytic activity among different ILs. High conversion, usually 88-89%, was realized under mild condition with catalytic amount of MnCl₂ in the reaction catalyzed by IL-1, HMF and furfural yields reached 37% and 18%, respectively, and generated small amount of levulinic acid and the total reducing sugars. The existence of other manganese salts could improve the conversion of MCC too; maybe the reason was manganous coordination interaction. With the increasing of reaction temperature and prolonging of reaction time, the hydrolysis of monosaccharide performed more thoroughly, the yield of sugars reduced and the yield of levulinic acid increased. The results also confirmed that water had a negative effect on the dehydration of sugars to aldehyde. Contrasting the promoting catalysis of CrCl₃ and MnCl₂ in our reaction system, MnCl₂ had little advantage than CrCl₃ in the selectivity of HMF and furfural. Dimer of furans compounds as the main by-products was detected through HPLC-MS characterization methods; mass spectrometry analysis indicated that the components of gas products at 150 °C for 300 min reaction were methane, ethane, CO, CO₂ and H₂. Although the process developed was efficient for the conversion of cellulose to HMF and furfural, further work will be required to improve the HMF yields, and a detailed mechanism involved in the coordination of IL-1 and MnCl₂, well, the separation and purification of the products remain a subject of future study.

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