= CHEMICAL KINETICS AND CATALYSIS =

Catalytic Hydrolysis of Cellulose into Furans¹

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Abstract—Chromium chloride in 4-(3-methylimidazolium-1-yl)butane-1-sulfonic acid hydrogen sulfate (IL-1) was found to effectively catalyze the hydrolysis of microcrystalline cellulose (MCC) at 150°C for 300 min to achieve 87.8% conversion to a slate of products. With a catalytic amount of $CrCl_3$, the yields of 5-hydroxymethyl furfural (HMF) and furfural were up to 32.4 and 15.2%, respectively, small molecules levulinic acid (LA, 10.8%) and the total reducing sugars (TRS, 10.7%) were also generated. Through LC-MSD analysis and mass spectra, dimer of furan compounds as the main by-products were speculated, and the components of gas products were methane, ethane, CO, CO_2 , and H_2 . We suggested that IL-1 and $CrCl_3$ exhibited a coordination interaction; the formation of the intermediate *via* the hydride shift played a key role in the formation of HMF. The catalyst was recycled and exhibited constant activity for five successive trials.

Keywords: microcrystalline cellulose, hydrolysis, HMF, ionic liquids, CrCl₃ **DOI:** 10.1134/S0036024416130045

1. INTRODUCTION

Biomass is an important resource that can be converted to energy [1], chemicals [2], foods and feedstocks [3]. As the global petroleum economy draws to a close, the portfolio of derived products from biomass will need to be diversified in order to satisfy feedstock requirements across a range of markets. Cellulose, which is the most abundant natural polymeric carbon source in the word, occupies 30-40% of biomass. However, cellulose is a high molecular polymer of Danhydroglucopyranose units joined together in long chains by β -1,4-glycosidic bonds. The tight hydrogen bonding network and van der Waals interactions greatly stabilize cellulose [4], making it notoriously resistant to hydrolysis. Thus, the development of a reliable non-fermentative process for the conversion of cellulose to bio-based products remains important.

Recently, extensive research and development programs have been initiated worldwide to convert lignocellulosic biomass into valuable products, such as monosaccharides, ethylene glycol, ethanol, 5-HMF [5–9]. Up to now, the processes of cellulose hydrolysis to chemicals including catalysis by mineral acids [10, 11], enzyme-driven reactions [12, 13], the use of subcritical and supercritical water [14, 15] and solid acid catalysts [16–18]. These processes generally require harsh conditions and cause several troubles, such as high temperature and pressure, so it is still a great challenge today either from an environmental or an efficiency point of view.

Due to the increased interest and demand for industrial application, more efficient catalytic systems were recently developed; the utilization of metal ions in ionic liquids (ILs) was demonstrated to be efficient for the conversion of cellulose into furans. Wu et al. [19] studied the hydrolysis of microcrystalline cellulose, using double-functionalized ionic liquids Cr([PSMIM]HSO₄)₃ as catalyst, BmimCl as solvent, the yields of TRS and HMF were up to 94 and 53%, respectively. Binder et al. [20] showed transformation of lignocellulosic biomass into furanes in DMA-LiCl system at 140°C with the yield of HMF up to 48%. In our previous work [21, 22], we also suggested that ionic liquids containing metal ions are the promising systems for cellulose hydrolysis. Based on an early report describing effective conversion of glucose into HMF over chromium catalysts [23], herein, we describe an efficient method for the direct conversion of microcrystalline cellulose (MCC) into 5hydroxymethylfurfural (HMF) and furfural in ionic liquid IL-1 in the presence of CrCl₃.

2. EXPERIMENTAL

2.1. Materials

Microcrystalline cellulose (extra pure, 90 μ m, J and K chemical company) was dried for 24 h at 90°C prior to cellulose hydrolysis; 4-methyl-2-pentanone (AR, >90%), furfural (CP, >90%) and acetonitrile

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Scheme 1. Synthesis of IL-1.

(HPLC) were purchased from Tianjin chemical reagent company (Tianjin, China); 1-methylimidazole (CP, >99%), 1,4-butanesultone (>99%), 1-chlorobutane (CP, >99.5%), 1-bromobutane (CP, >99.5%) were from Alfa Aesar and were used as received; 5-HMF (>99%) was from Aldrich; levulinic acid (>98%) was from DaoCheng chemical company (Hong Kong, China). All other reagents and solvents were reagent grade and were used as received.

2.2. Preparation of the Ionic Liquids

1-Methylimidazole (16.4 g, 0.2 mol) and 27.28 g (0.2 mol) of 1,4-butanesultone were mixed in a flask (250 mL) and stirred at 42-45°C for 17 h. The obtained white solid was ground, washed repeatedly with small amount ether, filtered and vacuum dried for 4 h in the room temperature. Equimolar quantity of the obtained product was added to 98% H₂SO₄, and the mixture was stirred at 80°C for 6 h. The obtained viscous liquid was washed with ether for three times and dried in vacuum to form ionic liquid-4-(3-methylimidazolium-1-yl)butane-1-sulfonic acid hydrogen sulfate (IL-1). The synthesis of IL-1 was indicated in Scheme 1. ¹H-NMR (400 MHz, D_2O): 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 ionic liquids, such as $C_4 \text{mimBF}_4$, $C_4 \text{mimPF}_6$, $C_4 \text{mimBr}$, $C_4 \text{mimCl}$, $C_4 \text{mimH}_2 PO_4$, were synthesized according to the method reported by Dupont et al. [24].

2.3. Typical Procedures for MCC Hydrolysis in IL-1

Experiments were carried out in a glass-lined stainless steel autoclave (100 mL). The reactor was loaded with 0.5 g of microcrystalline cellulose, 2.0 g of the catalyst, 1 mL of H₂O (0.2 M CrCl₃ aq.), and 8 mL of 4-methyl-2-pentanone (MIBK). MIBK was used as phase modifier to extract continuously the products from aqueous phase [21]. An electrical heating jacket was employed to heat the reactor to the desired temperature. After the appointed reaction time reached, 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 reactor with distilled water and pure ethanol; the aqueous phase and organic phase were recovered by extraction and separation using separating funnel; the gaseous products were recovered by filling N₂ after reaction; the solid residue recovered by filtration was dried at 100°C for 8 h, then weighed to calculate the yield of liquefaction. After filtration, extraction and separation, organic and water phases were collected to characterize the products. All results were replicated at least three times. The range of experimental errors for the HPLC analysis and TRS analysis were ± 1 and $\pm 2\%$, respectively.

The weight yields of the products were calculated based on weight of cellulose. We considered that the recovered solid residues were all cellulose. Cellulose conversion was determined by the change of cellulose weight before and after the reaction. The yield of products was calculated from the equation: yield (wt %) = (weight of products)/(initial weight of cellulose) \times 100%.

2.4. Sugars Analysis

The yield of the total reducing sugars (TRS) was analyzed by phenol-sulfuric acid method [25]. A mixture containing 0.1 mL reaction sample (water-soluble portion), 0.9 mL deionized water, 1 mL 5% phenol (freshly distilled), and 5 mL 98% concentrated sulfuric acid was prepared. The analysis was performed on a HP8453 UV–Vis spectrophotometer at about 490 nm with a slit width of 0.06 mm. 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 %) = (initial weight of TRS)/(initial weight of cellulose) × 100%.

2.5 HMF, Furfural and Levulinic Acid Analysis

The liquid products (HMF, furfural, and levulinic acid) were analyzed by high-performance liquid chromatography (HPLC) on a Waters Alliance 2695 chromatograph equipped with Waters 2996 PDA detector and an Intersil ODS-EP C18 reversed-phase column ($250 \times 4.6 \text{ mm}$, 5 µm) thermostatted at 30°C. The mobile phase (water-acetonitrile 15 : 85, vol/vol) flow rate was 0.5 mL/min. UV detection was performed at 280 nm for HMF and furfural, and 250 nm for levulinic acid. The sample volume was 10 μ L. The concentration of HMF, furfural and levulinic acid were calculated based on the standard curves obtained with standard substances.

2.6. Dimeric Furan Compounds Analysis

Dimeric furan compounds were analyzed using high performance ion trap mass spectrometeric 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 ($150 \times 4.6 \text{ mm}, 5 \mu\text{m}$). During this process, the column temperature remained constant at 25°C, while the mobile phase applied was water-acetonitrile (50 : 50, vol/vol) at the flow rate of 1.0 mL/min, with UV detection at 250 nm [26], 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 characterization of ionic liquids, NMR spectra were recorded on an INOVA-400 spectrometer; ESI-MS analyses were performed using a Waters micromass ZQ Alliance spectrometer. The gas fractions were analyzed by mass spectrometry (Inficon, Transpector 2). The mass spectrum analysis of liquid phase was performed on micrOTOF-Q II electrospray ionization mass spectrometer. Molecular weight distributions of liquid phase products was measured through gel permeation chromatography (GPC), which was performed on a Waters Alliance 2695 chromatograph equipped with Waters 2996 PDA Detector. During this process, the column temperature remained constant at 25°C. The mobile phase was trichloromethane at the flow rate of 1.0 mL/min, with UV detection at 270 nm.

2.7. FT-IR Analysis

After the catalyzed hydrolysis reaction was completed, the organic phase was separated and distilled in vacuum. The low-boiling fraction $(25-27^{\circ}C)$ was studied by Fourier transform infrared spectroscopy (FT-IR). All the FT-IR spectra were collected on an FT-IR spectrometer (Nicolet Nexus 870) with a resolution of 4 cm⁻¹ and 64 scans in the region of 4000– 400 cm⁻¹, the test temperature was 25°C and humidity was 50%.

3. RESULTS AND DISCUSSION

3.1. Hydrolysis of MCC with Various Catalysts

The effects of different catalysts on the reactions are summarized in Table 1. The conversion of MCC was only 3.9% in the absence of catalysts (entry 1); the presence of Al_2O_3 (entry 2), having both acidic and basic active sites, increased the conversion to 6.48%. Also, the reactions catalyzed by protic mineral acid

Table 1. Hydrolysis of MCC with various catalysts: 0.5 g MCC, 2.0 g catalysts, 1 mL H₂O (0.2 M CrCl₃ aq.), 8 mL MIBK, $T = 150^{\circ}$ C, t = 300 min, P = 2.5 atm

Entry	Catalysts	Yield (wt %)				
		HMF	fur- fural	levu- linic acid	TRS	Conv. (%)
1	None	0	0	0	1.42	3.90
2	Al_2O_3	1.98	0	0	2.63	6.48
3 ^a	HCl	10.71	4.53	4.08	25.62	57.43
4 ^a	HNO ₃	7.45	4.01	3.54	19.83	44.37
5 ^a	H ₃ PO ₄	6.93	3.46	2.19	21.37	47.56
6 ^a	H_2SO_4	12.96	5.02	3.96	24.18	52.18
7	$C_4 mim H_2 PO_4$	5.89	1.46	2.04	1.58	14.46
8	IL-1	15.43	7.45	2.56	10.24	70.00
9 ^b	None	0	0	0	3.07	5.72
10 ^b	$C_4 mim BF_4$	0.92	0	0	1.75	4.13
11 ^b	C ₄ mimPF ₆	0.73	0	0	1.18	3.16
12 ^b	C ₄ mimBr	0.19	0	0	1.76	2.37
13 ^b	C ₄ mimCl	1.72	1.35	0.92	2.37	8.72
14 ^b	$C_4 mim H_2 PO_4$	6.09	4.37	2.96	1.93	19.46
15 ^b	IL-1	32.41	15.18	10.83	10.73	87.80

^a With 2.0 g 0.1 M inorganic acid: HCl, HNO₃, H₃PO₄, H₂SO₄. ^b With 1 mL 0.2 M CrCl₃ aq.

(entries 3-6) were also non-ideal, the conversion of MCC was only 44-58%, and the main products were the reducing sugars. When ionic liquids (ILs) were used as catalysts (entries 7-8), the activity of IL-1 (70%) was much better than C₄mimH₂PO₄ (14.46\%). Collectively, the results above confirmed that strong acidity of solution promoted the hydrolysis of MCC effectively. In addition, the hydrolysis results for MCC in different ILs with catalytic amount of CrCl₃ (entries 9-15) were also investigated. As shown in the table, the conversion of MCC in C₄mimBF₄, C₄mimPF₆, C₄mimBr was lower than in the absence of ionic liquids (entry 9), this is in accordance with the results of Rogers et al. [27]. Meanwhile, we referred to 4-(3-methylimidazolium-1-yl)butane-1sulfonic acid hydrogen sulfate as IL-1, and other ionic liquids, which were referred using their chemical formula, are ionic liquids themselves. Also, we suggested that acidity of solution was very important for MCC hydrolysis, the main reason for lower activity of C₄mimBF₄, C₄mimPF₆, C₄mimBr was that



Fig. 1. The FT-IR spectra of sample catalyzed with HCl (a) and IL-1 (b): 0.5 g MCC, 2.0 g catalysts, 1 mL 0.2 M CrCl₃ aq., 8 mL MIBK, $T = 150^{\circ}$ C, t = 300 min, P = 2.5 atm.

maybe they could not provide enough acidic sites the hydrolysis reaction needed. It was obviously that MCC conversion (hydrolysis) ranging from 70.0 to 87.8% was achieved when the reaction was catalyzed by IL-1 in the same conditions. Based on the fact that CrCl₃ has almost no catalytic effect in MCC hydrolysis in the absence of other catalysts, we suggested that IL-1 and CrCl₃ had a synergistic interaction, which could promote the hydrolysis of MCC efficiently. We considered that IL-1 in the reaction had double function, not only it could dissolve the MCC like other ionic liquids, its acidity could weaken the glycosidic bonds through binding with a glycosidic oxygen atom, then promote the hydrolysis of MCC effectively.

Table 2. The influence of $CrCl_3$ concentration on the hydrolysis of MCC: 0.5 g MCC, 2.0 g IL-1, 1 mL CrCl₃ aq., 8 mL MIBK, $T = 150^{\circ}C$, t = 300 min, P = 2.5 atm

C		Conv			
(mol/L)	TRS	HMF	furfural	levulinic acid	(%)
None	10.24	15.43	7.45	2.56	70.00
0.05	11.89	27.38	13.05	5.09	83.76
0.1	11.06	29.45	14.72	5.73	85.47
0.2	10.73	32.41	15.18	10.83	87.80
0.3	9.75	25.51	15.97	7.06	83.45
0.5	9.03	24.03	13.88	5.98	79.91

3.2. The FT-IR Spectra of Hydrolysis Products Catalyzed with HCl and IL-1

Figure 1 shows the FT-IR spectra of the products of MCC hydrolysis catalyzed by HCl (a) and IL-1 (b), respectively. There are some obviously different vibrational bands in the two spectra. The absorbance at around 3346 and 3122 cm^{-1} is associated with the hydroxyl group stretching vibrations; around 2968 and 1368 cm^{-1} are methyl, methylene and methyne stretching vibrational bands; the absorbance at 1370, 1282, and 1165 cm⁻¹ correspond to the characteristic C-O-C stretching vibrational bands; collectively, these data suggest clearly that sample (a) shows the basic framework of sugars. In addition, it is also clear that spectrum (b) shows lots of different bands. The band at 1715 cm⁻¹ is assigned to C=O stretching vibrations; the absorbance at 1641 cm^{-1} is C=C stretching vibrational bands; and 973, 1165, 1208 cm⁻¹ bands correspond to furane ring [28]. Based on results of FT-IR spectra, with our present hydrolysis method, the products of MCC hydrolysis catalyzed by HCl are mainly the reducing sugars, but the spectra also showed the presence of furanes in hydrolysis products when the reaction was catalyzed by IL-1.

3.3. Influence of Different CrCl₃ Concentration on the Hydrolysis of MCC

To confirm the promoting action of $CrCl_3$, we studied the effect of chromium chloride's concentration on the reaction. As shown in Table 2, comparing with the reaction in the absence of $CrCl_3$ (70.0%), the addition of $CrCl_3$ could promote the reaction effectively, the conversion of MCC increased by 10–18%. However, the concentration of $CrCl_3$ was higher, the



Fig. 2. The effect of hydrolysis conditions on the reaction: 0.5 g MCC, 2.0 g IL-1, $1 \text{ mL} 0.2 \text{ M CrCl}_3 \text{ aq.}$, 8 mL MIBK, $T = 150^{\circ}\text{C}$, t = 300 min, P = 2.5 atm. (a) Reaction temperature; (b) reaction time; (c) content of water; (d) dosage of IL-1.

results were not corresponding better. When the CrCl₃ concentration was 0.2 M aq., we get the optimum results, the yields of HMF and furfural reached 32.4 and 15.2%, respectively, and small amounts of levulinic acid (10.8%) and TRS (10.7%) were also generated. We considered that maybe the coordination of IL-1 and CrCl₃ played an important role on MCC hydrolysis. To support the connection between IL-1 and CrCl₃, we performed the dehydration of glucose in 0.2 M H₂SO₄. The results showed that in this case after the addition of catalytic amount of CrCl₃, the yields of HMF and furfural increased by 8.3 and 4.5%, respectively, which confirmed that the CrCl₃ promoted the dehydration of glucose effectively.

3.4. The Effects of Hydrolysis Conditions on the Reaction

Figure 2 summarizes the influences of hydrolysis conditions on the reaction yields. The temperature and time dependences of the yields of products for the $CrCl_3$ -catalyzed hydrolysis of MCC in IL-1 were shown in Figs. 2a, 2b, respectively. As shown in the figures, when the reaction time was 300 min and the reaction temperature was 150°C, we get the optimal

results; the yield of HMF and furfural reached 32.4 and 15.2%, respectively. From Fig. 2b, after a 600 min reaction, the yield of TRS decreased obviously, but oppositely, the yield of levulinic acid increased from 1.2 to 15.38%. Figure 2a shows similar pattern to the products, which indicated that with the increasing of reaction temperature and prolonging of reaction time, the dehydration of glucose was favored. These are consistent with the hydrolysis path of MCC in this system, which is shown in Scheme 2. Glucose was dehydrated with formation of HMF, which subsequently is fragmented into levulinic and formic acids. When the further decomposition reaction goes on, these compounds are eventually converted to gaseous products. Also, our results proved that the formation of furfural was from the loss of formaldehyde in HMF. Meanwhile, Fig. 2a also shows that the hydrolysis results were slightly better at 180°C compared to 150°C, however, when the reaction system was carried out above 150°C, an odoriferous compound was generated, it was black, viscous, fluffy, and did not dissolve in water. We did not consider that it was the degradation



Scheme 2. Schematic illustration of HMF and furfural production from MCC.

products of cellulose or IL-1. At present, we were not sure what it was about the substance, but maybe it is one subject of future study, so we chose 150°C as an optimum treatment temperature.

According to the previous reports [29], water is generally thought to have a negative effect on the dehydration of glucose to HMF. Our work also confirmed this point, as shown in Fig. 2c, when the ratio of MIBK to $CrCl_3$ was 8 : 1, the conversion of MCC reached 87.8%, much higher than the results of the reaction in which the ratio was 8:4(37.7%) and 8:3(49.1%), and the selectivity of HMF and furfural were higher too when V(MIBK) : $V(CrCl_3)$ was 8 : 1, probably, the reason was that the increasing ratio of MIBK to the aqueous layer decreases side reactions of the HMF product. The dosage of IL-1 was also studied which was shown in Fig. 2d. When the dosage of IL-1 was 3.0 g, we get the optimal results, the yields of HMF and furfural could reach 36.5 and 17.4%, respectively. However, considering the cost of reaction and green engineering, we chose the dosage of IL-1 was 2.0 g.

3.5. The Analysis of By-products

Except for the main products, small amount of important by-products were detected. Through gelpermeation chromatography (GPC), it was found that molecular weights of the hydrolysis products were distributed below 2000. Using LC-MSD analysis, the main protonated molecules with m/z 410.4 and m/z 354.4, were detected. Then the second order mass spectra analysis was performed to determine their structure clearly. For m/z 354.4, the main fragment peaks were m/z 103.9, 110.8, 125.0, 192.9, 229.1, 254.0, 278.5, 322.2, 337.1 and for m/z 410.4, the main fragment peaks were m/z 134.9, 213.9, 258.9, 284.9, 311.9, 351.9, 366.9. Analyzing these two groups fragment peaks, we can not get the

exactly structure of the main by-products, however, we inferred that the products were furans, and according to the molecular weight, the by-products should have two furan rings at least, so we speculated them to be dimer of furans compounds.

Trace of the gas products were also analyzed using mass spectrometry and the compounds detected were methane, ethane, CO, CO_2 , and H_2 for hydrolysis of MCC at 150°C for 300 min reaction. This meant that the long chain hydrocarbons gaseous products were not generated, and we suggested MCC did not gasify directly under this condition in the reaction system. So we speculated that the generation of gas products may be due to the further decomposition of the primary reaction products.

3.6. Mechanism of MCC Hydrolyze to HMF in Cr-IL-1 System

In most cases, the glycosidic bonds in cellulose were weakened by Brønsted 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 propose a mechanism (Fig. 3) in which CrCl₃ in IL-1 forms $[CrCl_3(SO_4)_n]^{2n-}$ complexes in a similar manner to LnCl₃ as reported by Rogers et al. [30]. 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 chromium to form an intermediate on the way to HMF via the hydride shift [31, 32]. The hydride shift would enable conversion of the aldoses into ketoses, followed by dehydration to produce HMF.

Then with the help of acidic solution, the HMF was



Fig. 3. Putative mechanism of CrCl₃ promoted conversion of glucose into the main products.

combined with water to generate levulinic acid or loss of formaldehyde to produce furfural. In addition, we conducted the ESI-MS analysis using solution after the reaction, let $M = IL-1 + CrCl_3$, the m/z (–) 529.13 in the negative ion mode indicated the existence of $[M + Cl + H_2O]^-$, which supported the mechanism we put forward above on the other hand.

3.7. Recycling of IL-1 Catalysts

In the principles of green engineering, catalyst recycling is always important in metal-catalyzed liquid-phase reactions. Therefore, the reusability of $CrCl_3$ and IL-1 catalysts was tested over five runs. After the first reaction run for MCC, the catalyst IL-1 and $CrCl_3$ were only existed in aqueous phase, so the



Fig. 4. Recycling of IL-1 and CrCl₃ for the hydrolysis of MCC: 0.5 g MCC, 2.0 g IL-1, 1 mL 0.2 M CrCl₃ aq., 8 mL MIBK, $T = 150^{\circ}$ C, t = 300 min, P = 2.5 atm.

organic phase was separated. Then 1.5 g of distilled water was added into the reaction mixture to decrease the viscosity of ionic liquid and facilitate the extraction of main products. The HMF and furfural were then separated from aqueous phase by extracting 8 times with 5 mL of ethyl acetate. After extraction, $CrCl_3$ was still in the aqueous phase, then the solution was heated at 60°C in a vacuum drier until the water and residual ethyl acetate were removed absolutely. The dried IL-1 catalyst with CrCl₂ was used directly in the next run by adding fresh feedstock under the same reaction conditions. It can be seen from Fig. 4, although a decrease of the conversion from 88.2 to 74.6% was observed in the second run, no further decrease in activity was observed in the subsequent runs, that is to say, an average MCC conversion of about 72.5% could be obtained. Also, the yields of HMF, furfural and levulinic acid decrease only slightly over five repeated runs. The decrease of activity in the second run may be attributed to non-completely extraction of little by-products from the liquid-phase, which may be restrained the conversion of MCC and the further dehydration of glucose. How to improve the reusability of ionic liquids remained a problem for future study.

4. CONCLUSION

In summary, we demonstrated that CrCl₃ and IL-1 system was an excellent combination for the conversion of MCC into small molecular weight compounds (HMF, furfural, LA). By comparing different acidic catalysts, we indicated that acidic ionic liquids had higher activity than protonic acid, and IL-1 showed higher catalytic activity among different ILs. High conversion, usually 87–88%, was realized under spon-

87-88%, was realized under spon- Today **234**, 24 (2014).

taneous pressure with a catalytic amount of 0.2 M CrCl₃ aq. in the reaction catalyzed by IL-1. HMF, furfural and LA yields were up to 32.4, 15.2, and 10.8%, respectively, small amount of TRS (10.7%) were also generated. With the increasing of reaction temperature and prolonging of reaction time, the dehydration of glucose proceed more thoroughly, the yield of TRS decreased but levulinic acid yield increased. Our results also confirmed that water had a negative effect on the dehydration of TRS to HMF. Using FT-IR analysis, the formation of furans compounds were confirmed in our reaction system. Collectively, our method provided a new opportunity for transformation of cellulose through a non-fermentative process into bio-based products. However, a detail mechanism involved in the cooperation of IL-1 and CrCl₃ and the separation, purification of the products are remaining subjects of future study.

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