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Hydrolysis of Cellulose by Using Catalytic Amounts of FeCl₂ in Ionic Liquids

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Microcrystalline cellulose (MCC) is hydrolyzed to an appreciable extent (70%) by using 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1) as effective catalyst. Valuable chemicals, such as 5-hydroxymethyl furfural (HMF) and furfural, are obtained in relatively high yields (15% and 7%, respectively). Interestingly, the introduction of FeCl₂ as catalyst into IL-1 further enhances the app:ds:catalytic activity, as proved by the higher conversion of MCC (84%) and higher yields of HMF and furfural (34% and 19%, respectively) under the same experimental conditions, although small amounts of levulinic acid (LA) and total reducing sugars (TRS) were also found. The hydrolysis of MCC scarcely proceeded, or showed a lower efficiency, in the absence of catalyst (4%) or with Al₂O₃ (7%), inorganic acids (\leq 65%), or several other ionic liquids (\leq 24%) as catalyst. Dimers of furan compounds were detected as the main byproducts, as analyzed by HPLC–MS; from the mass spectrometry analysis, the components of the gas-phase products were determined to be methane, ethane, CO, CO₂, and H₂. A mechanism to explain the high activity of FeCl₂ in the IL-1 system is proposed. Recycling of the IL-1 catalyst showed an almost constant activity during five successive trials. The simple and effective catalyst system may prove valuable in facilitating the energy-efficient and cost-effective conversion of biomass into biofuels and platform chemicals.

Introduction

The diminishing fossil fuel reserves and global warming effects have become major concerns, and the search for sustainable and alternative energy is of critical importance.^[1] Recently, various biomass resources which can be transformed into fuels, chemicals, and energy products have been furiously discussed.^[2–8] The focus is on the catalytic conversion of biomass from cellulose, which is the most abundant natural polymeric carbon source in the world. Unfortunately, it is almost impossible to solubilize cellulose with water and common organic solvents^[9] because of its special complex structure.

In recent years, extensive research and development programs have been initiated worldwide to convert lignocellulosic biomass into valuable products, such as monosaccharides, ethylene glycol, ethanol, and 5-HMF.^[10–14] However, the hydrolysis of cellulose is usually catalyzed either by enzymes or by inorganic proton-acid catalysts, and none of the known methods are yet cost-effective for large-scale applications.^[15–19] Accordingly, it is essential to design solvents for cellulose and to propose a system which requires minimal energy.

Pioneer studies indicated that the ionic liquid (IL) 1-butyl-3methylimidazolium chloride (C₄mimCl) was a powerful solvent for cellulose,^[20] and soon later, the solubilizing mechanism of cellulose in ILs using NMR spectroscopy was also investigated by Robin Rogers et al.^[21] Since then, it has attracted much attention and subsequent chemical hydrolysis and hydrogenolysis of cellulose in ILs were reported.^[22] In particular, the metal ions in ionic liquid was demonstrated to be an efficient catalyst system for the conversion of cellulose into furans.^[13,23–25]

Therefore, we imagined that metal ions in acidic ILs might act as an eco-friendly polar catalyst system for the hydrolysis of cellulose. Earlier researchers mostly used CrCl₂ or CrCl₃ as co-

catalyst, however, considering their toxicity and environmental pollution, in the present paper, we first report our results on the hydrolysis of microcrystalline cellulose (MCC), which was catalyzed with 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1) by addition of a catalytic amount of FeCl₂ under mild conditions. The conversion of MCC is shown in Scheme 1.

Results and Discussion

Hydrolysis of MCC with various catalysts

Table 1 summarizes the different catalytic performances using various acidic catalysts on the reaction system. For various acids as catalysts, the present system was effective on the hydrolysis of MCC. The conversion of MCC was only 3.90% when the reaction was carried out in the absence of the catalyst (Table 1, entry 1). As the reaction was performed with a catalytic amount of FeCl₂, using IL-1 as catalyst (Table 1, entry 9), the conversion could be up to 84.42%. The presence of Al₂O₃

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Scheme 1. Schematic illustration of products from microcrystalline cellulose.

Table 1. Hydrolysis of MCC with various acidic catalysts: 0.5 g MCC, 1.0 g							
catalysts, 0.2 μ FeCl ₂ (1 mL), MIBK (8 mL), T=150 °C, t=300 min, P=							
101 325 Pa.							

Entry	Catalysts		Conv. [%]					
		HMF	Furfural	Levulinic acid	TRS			
1 ^[a]	None	0	0	0	2.42	3.90		
2	None	0	0	0	2.47	4.32		
3	AI_2O_3	2.58	0	0	1.97	7.05		
4 ^[b]	HCI	14.41	2.97	8.03	26.25	62.34		
5 ^[b]	HNO ₃	11.75	5.91	4.21	21.37	51.28		
6 ^[b]	H₃PO₄	9.51	5.62	3.02	17.98	49.65		
7 ^[b]	H_2SO_4	16.37	6.14	7.76	25.36	65.24		
8	C₄mimH₂PO₄	10.89	3.75	2.46	1.58	23.68		
9	IL-1	33.81	18.61	5.93	8.35	84.42		
10 ^[c]	H_2SO_4	9.08	4.81	5.39	17.62	53.17		
11 ^[c]	IL-1	15.43	7.45	2.56	10.24	70.00		
[a] The reaction was performed in the absence of catalyst. [b] The reaction was performed with $0.2 $ m inorganic acids. [c] The reaction was per-								

formed with 1 mL H_2O (not FeCl₂).



Figure 1. The hydrolysis results for MCC in different ionic liquids: MCC (0.5 g), ionic liquids (1.0 g), 0.2 μ FeCl₂ (1 mL), MIBK (8 mL), $T = 150 \degree$ C, t = 300 min, P = 101 325 Pa.

(Table 1, entry 3), having both acidic and basic character, resulted in a conversion of 7.05%. The reactions which were catalyzed by a protonic acid (Table 1, entries 4-7) were also effective with the conversions ranging from 49-65%, and the main products were the total reducing sugars (TRS). Collectively, the results above suggested that the strong acidity of a solution was an important aspect in promoting the hydrolysis of MCC. Different ionic liquids as catalysts were also investigated, which are shown in Figure 1. The conversions of MCC in C₄mimBF₄, C₄mimPF₆, and C₄mimBr were slightly lower than the one without ionic liquids; these results are in agreement with the research results of Rogers et al.^[20] It was also shown that the conversion of MCC in IL-1 (84%) was much higher than in C₄mimCl (8%) and C₄mimH₂PO₄ (24%), which further illuminated the importance of the solution acidity. The functions of IL-1 in the reaction were considered to be two-fold. It can dissolve MCC comparable to other ionic liquids, but also its acidity can promote the hydrolysis of MCC effectively. Comparing with the results in the absence of FeCl₂ (Table 1, entry 11), the conversion of MCC increased by 14% in the presence of FeCl₂, and correspondingly, the yields of HMF and furfural went up to 33.8% and 18.6%, respectively. When the reaction was performed with FeCl₂ in the absence of IL-1 (Table 1, entry 2), the conversion was only 4.32%, thus, we suggested that ILs-1 and FeCl₂ have synergistic and coordination interactions, which can facilitate the hydrolysis of MCC.

Effect of iron salts on the hydrolysis of MCC

Knowing the promoting effect of FeCl₂, other iron salts were investigated. As shown in Table 2, the existence of iron salts can improve the hydrolysis of MCC. Compared with other iron salts, the promoting effects of FeSO₄ and FeCl₂ were remarkable. In the presence of Fe³⁺ or Fe²⁺, the yields of HMF and furfural were also improved. The reason for the promotional effects of the iron salts may be due to the Fe³⁺ or Fe²⁺ coordi-

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Table 2. Hydrolysis of MCC with various iron salts: MCC (0.5 g), IL-1 (1.0 g), 0.2 μ iron salts (1 mL), MIBK (8 mL), $T = 150 \degree$ C, t = 300 min, P = 101325 Pa.

Iron salts		Conv. [%]			
	HMF	Furfural	Levulinic acid	TRS	
none	15.43	7.45	2.56	10.24	70.00
FeCl ₂	33.81	18.61	5.93	8.35	84.42
FeCl₃	30.15	16.48	5.47	7.14	84.18
FeSO ₄	31.73	17.09	6.02	7.83	84.14
$Fe_2(SO_4)_3$	28.45	17.75	4.88	7.74	80.28
Fe(NO ₃) ₃	21.96	7.38	3.26	5.36	57.60

nation interaction; in addition, Fe^{3+} or Fe^{2+} could play an important role in the selective dehydration of glucose, which improved the yields of HMF and furfural. Based on the decreasing conversion of MCC in the presence of $Fe(NO_3)_3$, the nitrate anion is most likely unfavorable to the reaction. Typically, NO_3^- cannot directly be used as a single ligand to form stable coordination compounds, therefore we concluded that the formation of metal nitrate complex was difficult relative to the others. However, the selectivity of HMF and furfural was also improved in the presence of $Fe(NO_3)_3$, which confirmed the promoting effect of Fe^{3+} .

Influence of reaction conditions on the hydrolysis of MCC

Figures 2 and 3 show the effects of reaction temperature and time on MCC hydrolysis. As the figures show, the reaction temperature and time had large effects on both the MCC conversion and product selectivity. The MCC conversion was 84.48%, the HMF and furfural yields were 33.87% and 18.61%, respectively, at 150 °C for 300 min reaction time. The HMF yield increased from 6.58% to 33.87% when conditions changed from 60 min to 300 min for 150 °C reaction temperature, and the time curve shows a similar pattern. As the reaction temperature was increased and the reaction time was prolonged, the yield of levulinic acid increased, but in contrast, the TRS yields









Figure 3. Effect of the reaction time: MCC (0.5 g), IL-1 (1.0 g), $0.2 \text{ M} \text{ FeCl}_2$ (1 mL), MIBK (8 mL), T = 150 °C, P = 101 325 Pa.

decreased. These results were in accordance with the hydrolysis path of MCC; the hydrolysis of glucose was more complete. We considered that there were two pathways for the decomposition of HMF in the 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 and the other is the loss of formaldehyde in HMF to furfural.

We also investigated the influence of water content on the reaction. As shown in Figure 4, when V_{MIBK} : V_{FeCl2} was 8:1, we obtained the optimum results; the yields of HMF and furfural reached 33.87% and 18.61%, respectively. As the water content increased, the selectivity of the products decreased, in accordance with the previous reports,^[26–27] which indicated that water has a negative effect on the dehydration of sugars to HMF. The effect of the IL-1 dosage on MCC hydrolysis is shown in Figure S1 (see the Supporting Information); the amounts of IL-1 used were 0.5 g, 1.0 g, 2.0 g, 3.0 g. In the absence of the catalyst, at a reaction temperature of 150 °C, the MCC conversion was only 4.32% for a reaction time of 300 min (Table 1,



Figure 4. Influence of water content on the hydrolysis of MCC: MCC (0.5 g), IL-1 (1.0 g), MIBK (8 mL), $T = 150 \degree \text{C}$, t = 300 min, P = 101325 Pa.

entry 2). In the presence of IL-1 (0.5 g), the yield of HMF was up to 20%. When the IL-1 dosage increased from 0.5 g to 1.0 g, the HMF and furfural yields remarkably increased from 20% and 14% to 34% and 19%, respectively. However, when the amount of IL-1 was increased from 1.0 g to 3.0 g, there was little change in the HMF and furfural yields, which implied that there were sufficient catalytic active sites available for the substrate MCC in the system under the experimental conditions.

For the conversion of MCC, the FTIR spectra of the solid residues and hydrolysis products catalyzed by IL-1 are shown in Figure 5 a and b, respectively. It is obviously different from (a)



Figure 5. The FTIR spectra of a) solid residues catalyzed with IL-1; b) hydrolysis products catalyzed with IL-1: MCC (0.5 g), IL-1 (1.0 g), 0.2 mmm FeCl₂ (1 mL), MIBK (8 mL), T=150 °C, t=300 min, P=101325 Pa.

and (b) in some spectral bands. The absorbances at around 3346 cm⁻¹ and 3122 cm⁻¹ are associated with the hydroxyl group stretching vibrational bands. Around 2901 cm⁻¹ and 1368 cm⁻¹ are methyl, methylene, and methyne stretching vibrational bands. The absorbance at 1370 cm⁻¹, 1282 cm⁻¹, and 1165 cm⁻¹ are the characteristic bands of C–O–C stretching vibrational bands. Collectively, these data suggested that both spectra shared the framework of sugars. However, spectrum (b) shows additional bands. The band at 1714 cm⁻¹ was assigned to C=O stretching vibrational bands; the absorbance at 1641 cm⁻¹ was assigned to C=C stretching vibrational bands; and the absorbance bands at 973 cm⁻¹, 1165 cm⁻¹, and 1208 cm⁻¹ proved the existence of a furan ring.^[28] Based on the results of the FTIR spectra, with our present hydrolysis system, it was confirmed the existence of furan compounds and the complicated distribution of hydrolysis products, which were catalyzed by IL-1.

Mechanism of cellulose and glucose transformation to HMF and furfural

To explain the results of the reactions in the presence of FeCl₂, we proposed a mechanism (Scheme 2) in which FeCl₂ in IL-1 forms $[FeCl_2(SO_4)_n]^{2n-}$ complexes in a similar manner to $LnCl_3$

as reported by Rogers et al.^[29] We suggested that [FeCl₂-(SO₄)_n]²ⁿ⁻ anion played a role in proton transfer, facilitating mutarotation of glucose in IL-1. 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 SO₄²⁻ and the hydroxyl groups.

The ring aldoses could then reverse to a straight-chain form, combining with the iron 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 help of an acidic solution, the HMF was combined with water to generate levulinic acid or lost formaldehyde to produce furfural. To confirm the coordination of SO_4^{2-} in the hydrolysis of glucose in 0.2 M H_2SO_4 was carried out. The results showed that in the H₂SO₄ catalyst system, by adding a catalytic amount of FeCl₂, the yields of HMF and furfural increased by 7% and 2% (Table 1, entry 7 and entry 10), which confirmed that the coordination effect of SO_4^{2-} and FeCl₂ promoted the hydrolysis of glucose.

Moreover, because all the ionic species may be detected by electron spray ionization mass spectrometry (ESI-MS) analysis, the interaction between IL-1 and FeCl₂ was also studied by ESI-MS. As shown in Figure S2 (see the Supporting Information), the ESI-MS gave rise to complicated spectra both in positive and negative ion modes. Under the ESI negative ion mode, a proton-removing guasi-molecular ion $[M'-H]^-$ from IL-1 was formed, an adduct ion from the complex (M=IL-1+FeCl₂) was [M+Cl]-(m/z 478.7), and there were several other ESI–MS [HSO₄]-(*m*/*z* 97.1), peaks in the spectrum: $[M+CI+H_2SO_4]-(m/z 576.7), [M+CI+2H_2SO_4]-(m/z 674.7), and$ $[M+CI+Na-H+2H_2SO_4]-(m/z 794.6)$. The ion peak (m/z 280.0)was the background and the existence of $\mathsf{H}_2\mathsf{SO}_4$ was due to the inadequate purification of IL-1. The results above confirmed the rationality of the mechanism.

In addition, small amounts of important byproducts were obtained. Through gel-permeation chromatography (GPC) analysis, the molecular weight distributions of the hydrolysis products for MCC were found to be below 2000 Da. Dimers of furan compounds were detected by LC–MSD and second order mass spectra analysis. The gas products were also analyzed using mass spectrometry; methane, ethane, CO, CO₂, and H₂ were detected for the hydrolysis of MCC at 150 °C for 300 min reaction.

Recycling of IL-1 for the hydrolysis of MCC

Catalyst recycling is always important in metal-catalyzed liquidphase reactions. In our hydrolysis system, the FeCl₂ and IL-1 catalysts can be reused directly after extraction of products with diethyl ether and water, then pouring out the solvent MIBK and water. Figure 6 shows the recycling of FeCl₂ and IL-1 over five runs. It can be seen from Figure 6 that although a decrease of the conversion from 84% to 77% was observed in the second run, no further obvious decrease in activity was observed in the subsequent runs, that is to say, a stable MCC conversion of about 74% could be obtained. In addition, the yields of HMF, furfural, and levulinic acid had only slight loss

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Scheme 2. Putative mechanism of FeCl₂ promoted conversion of glucose into HMF and furfural.



Figure 6. Recycling of IL-1 for the hydrolysis of MCC to the main products: MCC (0.5 g), IL-1 (1.0 g), 0.2 μ FeCl₂ (1 mL), MIBK (8 mL), T = 150 °C, t = 300 min, P = 101325 Pa.

over five repeated runs, about 26%, 14%, and 4% could be obtained, respectively. The decrease of activity in the second run could be attributed to incomplete extraction of byproduct from the liquid phase, which may limit the conversion of MCC and the further hydrolysis of glucose. How to improve the reusability of the catalysts remains a problem for a future study.

Conclusions

FeCl₂ in IL-1 was demonstrated to function as a highly active catalyst system for the direct hydrolysis of microcrystalline cellulose. By comparing different acidic catalysts, we indicated that acidic ionic liquids have higher activity than protonic acid. High conversion, usually 84-85%, was realized under mild condition with a catalytic amount of FeCl₂ in the reaction catalyzed by IL-1. We considered that there was not only a synergistic interaction but also a coordination interaction between IL-1 and FeCl₂. Our methods provided a simple and effective catalyst system to facilitate energyefficient and cost-effective conversion of biomass into important platform chemicals. However, a detailed mechanism in-

volved in the coordination of IL-1 and FeCl₂ and the separation and purification of the main products are remaining subjects of future studies.

Experimental Section

Preparation of IL-1 (Scheme S1, see the Supporting Information): *N*-Methyl imidazole (16.4 g, 0.2 mol) and 1,4-butanesultone (27.28 g, 0.2 mol) were mixed in a flask (250 mL) and stirred at 42–45 °C for 17 h to give a white solid, which was grinded, washed repeatedly with a small portion of ether, filtrated, and vacuum dried for 4 h at room temperature. Equimolar white solid was added to 98% H₂SO₄, and the mixture was stirred at 80 °C for 6 h, then we obtained the sticky ionic liquid of 1-(4-sulfonic acid) butyl-3-methyl-imidazolium 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 ppm. Other ILs, such as C₄mimBF₄, C₄mimPF₆, C₄mimBr, C₄mimCl, and C₄mimH₂PO₄, were synthesized according to the method reported by Jairton Dupont.^[30]

Typical procedures for microcrystalline cellulose hydrolysis in IL-1: Experiments were carried out in a stainless steel autoclave with a glass liner tube (100 mL); the reactor was loaded with MCC (0.5 g), catalysts (1.0 g), H₂O (1 mL, 0.2 \times FeCl₂), and 4-methyl-2-Pentanone (8 mL).^[31] The reactor was then placed into an electrical heating jacket to heat the system 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. The liquid and solid fractions were collected by repeatedly washing the inside of the reactor with distilled water and pure ethanol. The recovered solid residue was dried at 100 °C for 8 h, then weighed to calculate the yield of liquefaction. After filtration, extraction, and separation, the organic and water phases were collected to characterize the products. All results were replicated at least three times.

After the reaction, the amount of total reducing sugars was determined by a phenol–sulfuric acid method;^[32] other liquid-phase products were analyzed by HPLC (Waters 2695) and LC–MSD (Agilent 1100).^[33,34] The gas products were detected by mass spectrometry (Inficon, Transpector 2); FTIR analysis were carried out on Nicolet Nexus 870 and the ESI–MS analysis were performed on an Agilent 1100 series LC–MSD Trap VL equipped with an Agilent 1100 detector (see the Supporting Information). Cellulose conversion was determined by the change of cellulose weight before and after the reaction. The yields of the products were calculated from the equation: Yield (%) = (weight of products)/(weight of cellulose put into the reactor) × 100%.

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