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Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical

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ABSTRACT

The ability to use cellulosic biomass as feedstock for the large-scale production of liquid fuels and chemicals depends critically on the development of effective low temperature processes. One promising biomass-derived platform chemical is 5-hydroxymethylfurfural (HMF), which is suitable for alternative polymers or for liquid biofuels. While HMF can currently be made from fructose and glucose, the ability to synthesize HMF directly from raw natural cellulose would remove a major barrier to the development of a sustainable HMF platform. Here we report a single-step catalytic process where cellulose as the feed is rapidly depolymerized and the resulting glucose is converted to HMF under mild conditions. A pair of metal chlorides ($CuCl_2$ and $CrCl_2$) dissolved in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) at temperatures of 80–120 °C collectively catalyze the single-step process of converting cellulose to HMF with an unrefined 96% purity among recoverable products (at $55.4 \pm 4.0\%$ HMF yield). After extractive separation of HMF from the solvent, the catalytic performance of recovered [EMIM]Cl and the catalysts was maintained in repeated uses. Cellulose depolymerization occurs at a rate that is about one order of magnitude faster than conventional acid-catalyzed hydrolysis. In contrast, single metal chlorides at the same total loading showed considerably less activity under similar conditions.

1. Introduction

5-Hydroxymethylfurfural (HMF) is a versatile biomass-derived platform compound that can be used to synthesize a broad range of chemicals currently derived from petroleum [1,2]. In addition, liquid fuels derived from HMF using chemical processes are potential alternatives to ethanol obtained by fermentation processes [3]. Although fructose has been the preferred feed for optimal HMF yield [2], it is clear that large scale, sustainable use of HMF will require cellulosic biomass as feed. Such use necessarily involves depolymerization of cellulose to form glucose, the building unit of cellulose, followed by conversion of the glucose to HMF. Although we recently reported a catalytic system to efficiently convert glucose to HMF [4], it is the depolymerization process, which involves decrystallization followed by hydrolytic cleavage that has been the primary bottleneck limiting energy-efficient and economical utilization of cellulosic biomass. In this paper, we report a new pathway that enables cellulose depolymerization and glucose conversion to HMF in a single process under mild conditions.

Cellulose has a supramolecular structure of various chain-size, crystallinity, and complexity, depending on the type of biomass. While considerable research effort has been focused on improving the rate of the two most prevailing cellulose depolymerization processes in aqueous systems, one involving multiple enzymes as catalysts [5] and another involving strong mineral acids as catalysts [6], progress has been limited in part by the lack of solubility of cellulose in water. Enzymatic hydrolysis of cellulose is effective but characteristically slow near ambient temperature; it is also sensitive to contaminants originating from other biomass components. Pretreatment of cellulose, for example by ammonia or steam in a high-pressure process or by mechanical milling, is typically required to increase the accessible area of cellulose for a reasonable rate of enzymatic hydrolysis [7]. Mineral acids have been extensively investigated to catalyze hydrolysis at a variety of acid concentrations and temperatures. A rather high temperature (180–230 °C) has been used to obtain an acceptable rate of cellulose hydrolysis using only a dilute acid [8]. Degradation of the resulting glucose becomes an issue at this temperature.

Due to their characteristic properties such as low vapor pressure, good thermal stability and a range of tunable

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hydrophobicity/hydrophilicity, ionic liquids have recently used as solvent for Brønsted acids catalyzed biomass conversions [9,10]. In this paper, we report a new catalytic system using an ionic liquid that can convert cellulose to HMF in one step under mild conditions.

2. Experimental

D-(+)-Cellobiose (minimum 98%) and cellulose (fibrous, long, Catalog No. C6663-1 KG) in this work were purchased from Sigma–Aldrich. 1-Ethyl-3-methylimidazolium chloride ([EMIM]Cl, 99%) was supplied by Solvent-Innovation (Lot No. 99/972). $CuCl_2$ (99.9%) was obtained from Sigma–Aldrich, and $CrCl_2$ (99.9%) and $CrCl_3$ (99.9%) from Strem Chemicals.

In a standard experiment, 500 mg [EMIM]Cl with catalyst (i.e., $CuCl_2$, $CrCl_2$, or $CrCl_3$) corresponding to 6 mol% with respect to calculated glucose unit in the cellulose feed was loaded into vials of 15.5 mm × 50 mm. The vials were then sealed and inserted into a high-throughput batch reactor (Symyx Technologies, Inc., Sunnyvale, CA). The vials were heated to 150 °C and shaken at 600 rpm for 30 min. After the reactor was cooled to room temperature, 50 mg cellulose (or cellobiose, used as model compound) was added to each vial. The vials were sealed and reinserted into the high-throughput reactor. During the dissolution process, the vials were heated to 100 or 120 °C and shaken at 600 rpm for 1 h. Then the reactor was cooled to room temperature, and 50 μl H_2O was added to each vial. The vials were sealed and reinserted into the high-throughput reactor at 80, 100, or 120 °C for a time period as specified in the paper, and shaken at 600 rpm. 2.0 ml of water was consequently added to each vial after the reactor was cooled to room temperature. The vials were sealed and centrifuged at 2000 rpm for 30 min. A single liquid layer was formed and the liquid products were analyzed by HPLC. All results were replicated at least 5 times.

HPLC analysis was performed on an Agilent 1100 series system equipped with an Agilent 1100 Series Refractive Index Detector and a Bio-Rad Aminex HPX-87H Ion exclusion column (300 mm × 7.8 mm). During this process, the column temperature remained constant at 65 °C, while the mobile phase applied was 0.005 M H_2SO_4 at the flow rate of 0.55 ml/min and the volume for each injection was 10 μl. The retention time for the major compounds is listed as below (Table 1).

Differential Scanning Calorimeter (DSC) experiments were conducted on an instrument of Perkin Elmer Pyris-6. All the catalyst–ionic liquid mixtures investigated (i.e., $CuCl_2$, $CrCl_2$, and $CuCl_2$–$CrCl_2$) were prepared with constant catalyst loading by the same standard experimental procedure described above. Small amount of each sample (about 0.010 g) was then added into a 50 μl alumina pan (0.1 mm × 2.1 mm) and sealed it with a 30 μl alumina pan (0.1 mm × 2.1 mm) as the lid by a Universal Sealing Press (PerkinElmer). The sealed sample was then taken for DSC test, by using the same empty pans sealed identically as the blank. During each run, the sample was heated up to 180 °C with the heating rate of 5 °C/min. For samples with cellulose, 10% cellulose was added to each prepared catalyst–ionic liquid mixtures and consequently moved to the batch reactor. The reactor was heated to 150 °C for 20 min and cooled down to room temperature. The prepared samples were then weighed and sealed by the same process described above and were ready for DSC tests. All the sample weighing and consequent sealing process were conducted in the glove box to prevent its exposure to air and moisture. Each sample has been tested for several times and the results obtained are very consistent with each other.

Table 1
The retention time of major compounds analyzed by HPLC.

Compound	Retention time (min)
Ionic liquid (catalyst)	Not retained
Cellobiose	8.8
Glucose	10.3
Mannose	10.7
Fructose	11.2
Sorbitol	11.4
1,6-Anhydroglucose	13.3
Formic acid	16.6
Levulinic acid	17.4
HMF	31.2

DP (Degree of Polymerization) value of cellulose for the two catalytic systems, i.e., 0.5% H_2SO_4 in H_2O and $CuCl_2/CrCl_2$ in [EMIM]Cl, was determined by running each system in four vials in which only the reaction time was varied while all other parameters remained constant. To ensure uniform catalyst loading, each catalyst–[EMIM]Cl mixture was prepared in a single batch and then added to four vials (500 mg aliquots) containing cellulose (50 mg). The vials were divided between four high-throughput reactors. Each reactor was heated to 120 °C but allowed to react for a pre-determined period of time. After reaching the set reaction time, the corresponding vials were immediately quenched with 2.0 ml of water and DP measurement was conducted consequently by using the method as described elsewhere [11].

3. Results and discussion

We evaluated a large number of metal chlorides, in catalytic amounts, dissolved in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, one member of the 1-alkyl-3-methylimidazolium chloride [AMIM]Cl, class of solvents capable of dissolving cellulose [12]. Among the metal chlorides including $CrCl_2$, $CrCl_3$, $CuCl_2$, CuCl, $FeCl_2$, $FeCl_3$, $PdCl_2$, $PtCl_2$, $PtCl_4$, $MnCl_2$, $LaCl_3$, $SnCl_2$, LiCl, $SnCl_4$, $NiCl_2$ and $AlCl_3$, $CrCl_2$ displayed the highest activity for cellulose hydrolysis at 120 °C, but the product yield was still less than 10%. It is particularly interesting to note that the Lewis acidic metal chlorides, such as $AlCl_3$ and $LaCl_3$ showed low activities (data not shown).

For this work, we report the most striking results obtained with $CuCl_2$, $CrCl_2$, and their mix as catalysts in the same solvent at a constant molar loading. The cellulose loading in the solvent was 10 wt%. Unless otherwise specified, the total metal chloride loading was maintained at 37 μmol/g of [EMIM]Cl solvent, corresponding to 6 mol% with respect to the calculated glucose monomer concentration based on the amount of the cellulose feed. At this total metal chloride loading, the molar ratio of metal chloride to [EMIM]Cl solvent is 0.005. Each metal chloride catalyst was first dissolved in the solvent to obtain a homogeneous solution. Cellulose was then added to this solution and fully dissolved at 100 or 120 °C. Lastly, we initiated depolymerization and the subsequent conversion of glucose by adding 10 wt% water at a specified temperature (100 or120 °C) for a specified period. The upper limit of 120 °C was selected to minimize degradation of glucose and particularly its derivatives.

A series of depolymerization experiments were conducted with two metal chlorides, $CuCl_2$ and $CrCl_2$. The total metal chloride loading was maintained constant at 37 μmol/g of [EMIM]Cl, while the relative proportions of the two metals varied from a $CuCl_2$ mole fraction (χ_{CuCl_2}) of 0–1. For these experiments, the cellulose was dissolved in [EMIM]Cl at 100 °C for 1 h before adding water and raising the reaction temperature to 120 °C. After 1 h of reaction, very low activity (total product yield <10%) for cellulose hydrolysis was seen for the solutions containing a single metal chloride (i.e., $\chi_{CuCl_2} = 0$ or 1, Fig. 1). In strong contrast, mixtures of the two metal chlorides resulted in total product yields as high as 65% ($\chi_{CuCl_2} = 0.95$) with the most active range being χ_{CuCl_2} of 0.83–

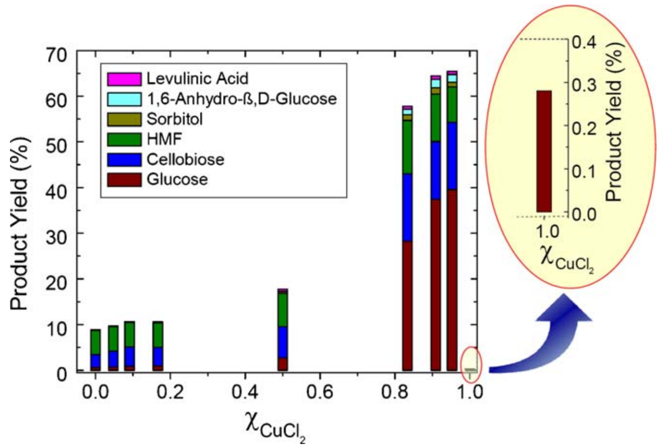

Fig. 1. Hydrolysis product yield from cellulose using single and paired $CuCl_2/CrCl_2$ catalysts having χ_{CuCl_2} ranging from 0 to 1 at 120 °C for 1 h. The cellulose was dissolved in [EMIM]Cl at 100 °C for 1 h before initiating the reaction by adding water. Total metal chloride loading is 37 μmol/g [EMIM]Cl (6 mol% with respect to the glucose monomer concentration present in the cellulose feed).

0.95. A separate experiment determined that as little as 3 mol% of $CrCl_2$ in the paired metal chlorides (i.e., $\chi_{CuCl_2} = 0.97$) was sufficient to activate the $CuCl_2$-dominant catalyst in the [EMIM]Cl solvent (data not shown). In these experiments, glucose was the major product, along with lower yields of cellobiose and HMF. The presence of cellobiose suggests that higher saccharide oligomers, such as cellotriose and cellotetrose, also may be present, although not analytically quantified. Humin oligomers account for the balance of the uncharacterized products.

To establish the hydrolytic bond-cleaving activity of the paired metal chloride catalyst in the absence of mass diffusion limitations associated with polymeric cellulose, we conducted experiments with cellobiose and maltose, which are both readily soluble in [EMIM]Cl. These two model compounds serve as the basic structural units for cellulose (cellobiose) and starch (maltose) and consist of glucose dimers joined by either a β-1,4-glucosidic bond (cellobiose) or an α-1,4-glucosidic bond (maltose). Three-hour experiments at 100 °C with a $CuCl_2$ catalyst, and for a paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.91$), show that the paired metal chlorides yield more than three times the amount of product than the $CuCl_2$ catalyst (Fig. 2). The results clearly verify the activation effect of $CrCl_2$ on the $CuCl_2$-rich catalyst for catalytic hydrolysis of both α- and β-1,4-glucosidic bonds, both at comparable rates. Although the enhanced hydrolysis of starch in this catalytic system can be expected by the paired metal chloride catalysts versus the single metal chlorides based on these results, it falls outside of the scope of this report.

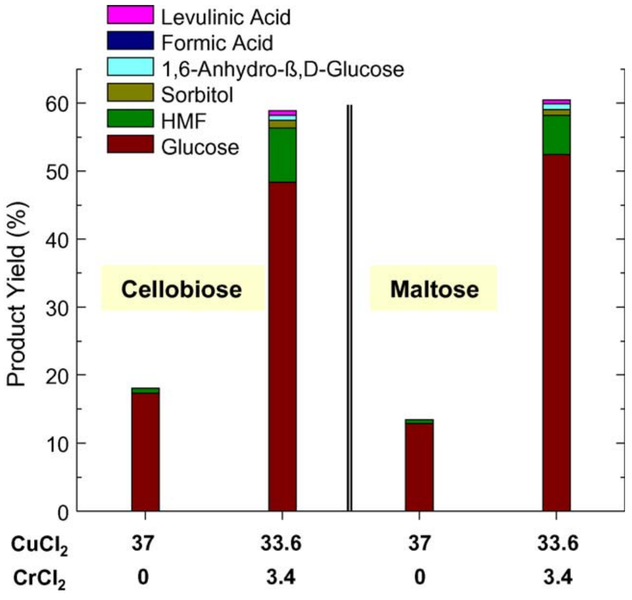

Fig. 2. Hydrolytic product yield from cellobiose and maltose using $CuCl_2$ or paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.91$) at 100 °C for 3 h.

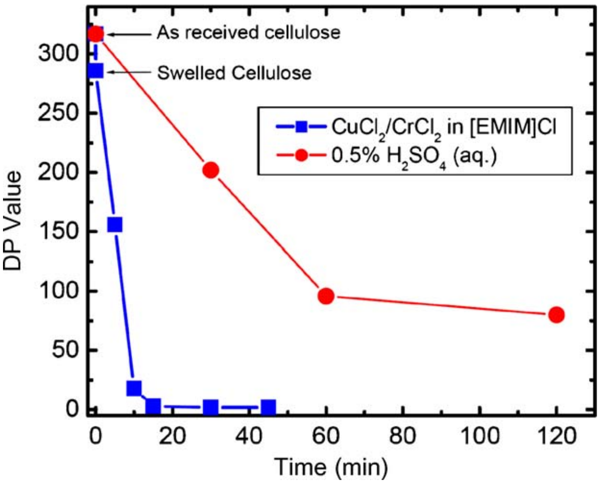

Fig. 3. Changes in the degree of polymerization (DP) values of cellulose/hydrolyzed cellulose in aqueous 6 mol% H_2SO_4 (●) and in [EMIM]Cl containing 6 mol% (i.e., 37 μmol/g [EMIM]Cl) total $CuCl_2$ and $CrCl_2$ ($\chi_{CuCl_2} = 0.91$) (■) at 120 °C.

The relative rates of cellulose hydrolysis catalyzed by (1) mineral acid in an aqueous solvent (i.e., a conventional hydrolysis medium), and (2) the paired metal chlorides in [EMIM]Cl solvent were determined using measured values [11], of the degree of polymerization (DP, a measure of the average number of glucose units in the polymer chains) during hydrolysis (Fig. 3). The as-received cellulose has a DP value of 317 [13]. Dissolution of the crystalline cellulose in [EMIM]Cl solvent containing a $CuCl_2/CrCl_2$ ($\chi_{CuCl_2} = 0.91$) catalyst at 120 °C did not appreciably change the DP value (DP = 286). However, upon addition of water, hydrolysis occurred rapidly in this paired metal chloride/[EMIM]Cl system. The DP value dropped to 18 after 10 min and to 1.9 after 30 min. The initial rate of depolymerization, defined as the rate of decrease of the DP value, is about 30 min^{-1}. In the dilute aqueous H_2SO_4 system, the depolymerization of cellulose was much slower, requiring 60 min to reach a DP value of 96. The initial rate of depolymerization of cellulose in the dilute aqueous H_2SO_4 was only 3.7 min^{-1}, and about an order of magnitude slower after 60 min. Moreover, the hydrolysis products in the H_2SO_4 aqueous system consisted only of fragmented cellulose polymers. Little glucose was detected after mineral acid hydrolysis for 2 h.

The total product yield of the most active $CuCl_2$-rich catalyst decreased with reaction time due to product degradation. For example, a paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.90$) gave a high total product yield (63%) from cellulose in 1 h at 120 °C, but this catalyst also continuously degraded the products during prolonged reaction time (Fig. 4), decreasing the total yield to 23% after 8 h. On the other hand, a less-active paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.17$) showed continued increase in total product yield for the first 6 h and then seemed to stabilize at a maximum value of about 60% (Fig. 4).

The ability to hydrolyze crystalline cellulose at low temperature, together with the synergism and ability to tune the $CuCl_2$/$CrCl_2$ catalyst system opens the possibility of directly converting crystalline cellulose to HMF in a single step. We therefore conducted a series of experiments using the less-active paired

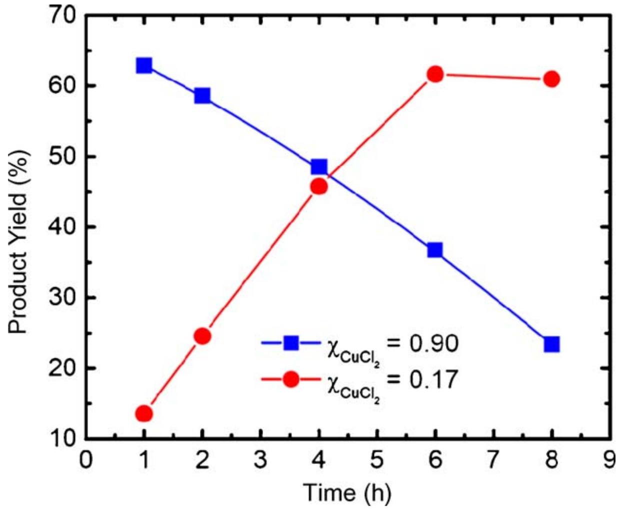

Fig. 4. Hydrolysis product yield from cellulose using paired $CuCl_2$ and $CrCl_2$ catalysts at 120 °C having $\chi_{CuCl_2} = 0.90$ (■) or 0.17 (●). Total metal chloride loading is 37 μmol/g [EMIM]Cl (6 mol% with respect to the glucose units present in the cellulose feed). The cellulose was swelled in [EMIM]Cl at 100 °C for 1 h before initiating the reaction.

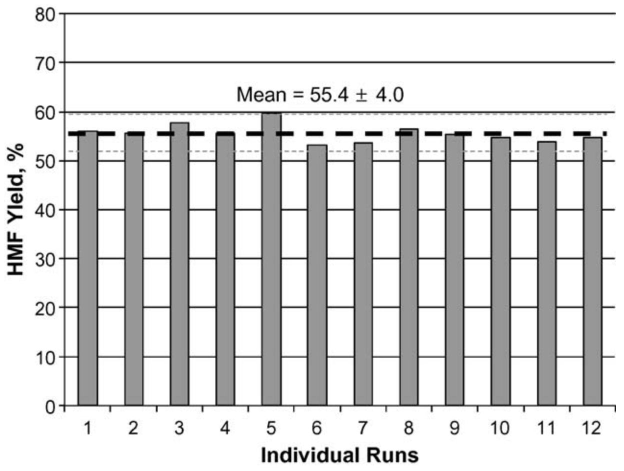

Fig. 5. Twelve reproducibility tests for single-step cellulose conversion to HMF by a paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.17$) at 120 °C for 8 h. The cellulose was dissolved in [EMIM]Cl at 100 °C for 1 h before initiating the reaction. Total metal chloride loading is 37 μmol/g [EMIM]Cl (6 mol% with respect to the glucose units present in the cellulose feed). Confidence interval (95%) is shown as dashed lines.

$CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.17$) that were allowed to continue for 4 or 8 h. In addition to its minimal impact on product degradation while achieving high total product yield (Fig. 4), this catalyst pair resulted in a high HMF yield, consistent with our recent work showing that $CrCl_2$ is a highly selective catalyst for the conversion of glucose to HMF [4]. Our first experiment at 100 °C for 4 h produced a total monomer product yield of 67% with an HMF selectivity of 25% among the products recovered from the [EMIM]Cl solvent (Table 2, column 1). In an identical experiment conducted at 120 °C, the HMF selectivity improved to 64% while total monomer yield remained constant (Table 2, column 2). HMF in even higher purity (96%) was obtained by extending the reaction period at 120 °C to 8 h, with only a slight decrease in total yield of recovered products to 60% (Table 2, column 3). The high HMF yield was confirmed by the results of 12 independent experiments (Fig. 5).

The ability to recover the HMF product from the [EMIM]Cl solvent with minimal impact on the catalyst activity is an important practical consideration. We used methylisobutylketone (MIBK) [2] to extract the HMF product at 100 °C after cellulose conversion for 8 h at 120 °C in the [EMIM]Cl solvent containing the paired $CuCl_2/CrCl_2$ catalyst ($\chi_{CuCl_2} = 0.17$). Three successive 8-h runs were conducted. After each run, three successive MIBK extractions recovered more than 90% of the HMF (Table 3A). The [EMIM]Cl solvent and catalyst were then dried to remove any residual moisture before adding fresh cellulose and repeating the same cellulose swelling and reaction conditions as used in the first run. The total product and HMF yields showed little change from the first run (Table 3A) suggesting that little catalyst deactivation occurred. It is interesting to note that, in the two reuses of the solvent and the catalyst, the oligomeric humin by-products remaining in the solvent did not affect the subsequent dissolution and conversion of cellulose. However, some loss of catalyst activity did occur if moisture was not removed between runs (stoichiometrically, three water molecules are released during the conversion of one molecule of glucose to HMF). We also found that we could regenerate the [EMIM]Cl solvent and catalyst by removing solid residues from the hot solvent by filtration. After

Table 2

Product yields from different temperatures and reaction times. The total loading of $CuCl_2/CrCl_2$ was 37 μmol/g [EMIM]Cl and $\chi_{CuCl_2} = 0.17$.

Entry no.	1	2	3
Feed	Cellulose	Cellulose	Cellulose
Reaction temp. (°C)	100	120	120
Reaction time (h)	4	4	8
Product yield (%)			
Cellobiose	15	12.9	0
Glucose	23	8.5	0.96
Mannose	7.5	0	0
Sorbitol	0	0	1.27
1,6-Anhydro-β, D-glucose	3.6	1.8	0.26
Formic acid	0	0	0
Levulinic acid	1.2	1.4	0
HMF	17	43	57.5
Total yield	67	67	60
HMF concentration in product	25	65	96

Table 3A

Recovery of HMF from [EMIM]Cl solvent and catalyst ($CuCl_2/CrCl_2$, $\chi_{CuCl_2} = 0.17$) after cellulose conversion in a 10-g batch using methylisobutylketone (MIBK) as an extractant at 100 °C, followed by successive reuse of the solvent and the catalyst. The total catalyst loading is 37 μmol/g [EMIM]Cl and the reaction occurred at 120 °C for 8 h. The total product and HMF yields given in the table correspond to the results of the three successive runs. The amount of HMF extracted corresponds to the total of three MIBK extractions after each run.

	Total product yield (%)	HMF yield (%)	% HMF extracted[a]
1st run	62	57 ± 2%	>90
2nd run	61	55 ± 2%	>90
3rd run	61	57 ± 2%	>90

[a] Additional HMF was formed during extraction at 100 °C.

Table 3B

Activity of solvent and catalyst before and after removal of solid residues by filtration. Before regeneration, yield had decreased as a result of multiple runs without drying between runs.

	Total yield (%)	HMF yield (%)	HMF selectivity
Before regeneration	49	46	92
After regeneration, without additional catalyst	58	52	90
After regeneration, with additional catalyst	61.5	59	96

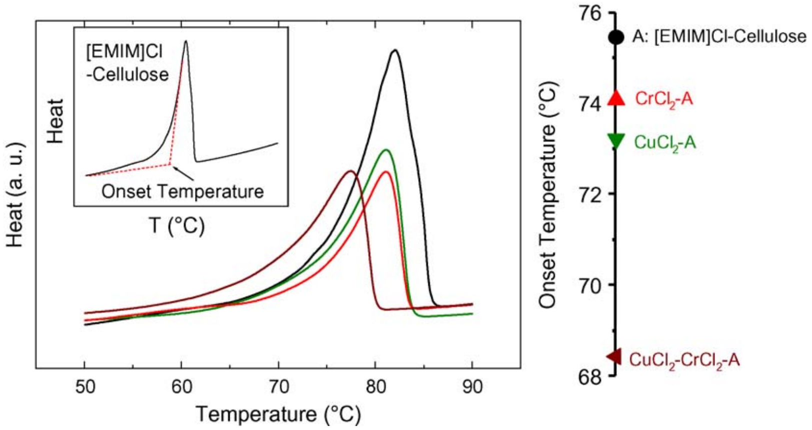

Fig. 6. Endotherms measured by differential scanning calorimetry (left) and their corresponding onset temperatures (right) for [EMIM]Cl containing 10 wt% cellulose (A), and for this mixture to which $CuCl_2$, $CrCl_2$, or $CuCl_2 + CrCl_2$ ($\chi_{CuCl_2} = 0.91$), was added at a total metal chloride loading of 37 μmol/g of [EMIM]Cl (6 mol% with respect to the glucose units present in the cellulose feed). Color of symbols on right panel indicates endotherm curves in left panel. The insert in the left panel defines the method for obtaining the onset temperature.

Table 4
DSC endothermic results (corresponding to Fig. 6).

	Peak max (°C)	Heat endo (J/g)	Onset of heat endo (°C)
[EMIM]Cl	86.7	94	82.2
[EMIM]Cl–cellulose	82.0	57	75.5
$CuCl_2$–[EMIM]Cl–cellulose	81.1	46	73.2
$CrCl_2$–[EMIM]Cl–cellulose	81.0	46	74.1
$CuCl_2/CrCl_2$–[EMIM]Cl–cellulose	77.4	42	68.4

removing the solid residues, one part of the regenerated liquid was reused without additional catalyst, and another part was reused by adding a fresh catalyst in the same original composition and concentration. Remarkably, the homogeneous catalyst was well retained in the solvent during the filtration and total yield increased from 49% before regeneration to 58% afterwards (Table 3B). Adding fresh catalyst to the regenerated liquid yielded a slightly higher total product yield (61%) and HMF purity (96%) in the recovered product that were comparable to the original yield and selectivity. Based on these results we conclude that if long-term degeneration of product yield and purity occurs, regeneration by filtration and minor make-up of the catalyst can be used to restore performance to the original level.

Differential scanning calorimetry (DSC) analyses of the metal chlorides in [EMIM]Cl containing dissolved cellulose (Fig. 6, Table 4) yielded endothermic onset temperatures that mark the beginning of the phase conversion from solid to liquid. The DSC peak maxima, which provide a more intuitive, but less accurate, description of phase-transition behavior, and the magnitudes of the DSC heat endotherms, follow the same trend. For neat [EMIM]Cl, the onset temperature was 82.2 °C. After dissolving 10 wt% cellulose in the [EMIM]Cl, the onset temperature dropped to 75.5 °C. Single metal chlorides, $CrCl_2$, and $CuCl_2$ in 37 μmol/g of [EMIM]Cl (i.e., in metal chloride/[EMIM]Cl ratio of 5×10^{-3}) further lowered the onset temperature by 1.4–2.2 °C, as compared to [EMIM]Cl containing dissolved cellulose. While the total metal chloride loading was unchanged, replacing only 10% of the $CuCl_2$ (i.e., in 5×10^{-4} mole per mole of [EMIM]Cl) with an equal amount of $CrCl_2$ to form a paired $CuCl_2/CrCl_2$ catalyst led to a substantial drop in the endothermic onset temperature, i.e., by 7.1 °C. These results suggest that the paired metal chlorides are more effective than individual metal chloride additives in disrupting the long-range bonding network between the solvent ions. Although impurities are known to lower the melting point of ionic solvents, the presence of a low concentration of single metal chlorides (in 5×10^{-3} mole per mole of [EMIM]Cl, far below the stoichiometric amount that is typical of [EMIM]Cl·$MeCl_x$ or [EMIM]$MeCl_{x+1}$ based ionic liquids), induced only a moderate 1.4–2.2 °C decrease in the onset temperature. It is therefore most unusual that only 5×10^{-4} mole per mole of [EMIM]Cl of $CrCl_2$ replacing an equal amount of $CuCl_2$ from a total of 5×10^{-3} mole of paired metal chloride per mole of [EMIM]Cl caused a dramatic 7.1 °C drop in endothermic onset temperature.

In conclusion, we stress that the paired metal chloride catalyst system described here is quite different from the chlorometallate complexes typically described in the ionic-liquid literature. While a number of metal chlorides ($MeCl_x$) are known to form ionic liquids with [AMIM]Cl, typically in 1:1 stoichoimetry resulting in [AMIM] $MeCl_{x+1}$ (mononuclear), but also with excess $MeCl_x$ in multiples ($n > 1$) of the amount of [AMIM]Cl resulting in [AMIM]Me_nCl_{nx+1} (polynuclear) [14], ionic liquids involving $CuCl_2$ and [EMIM]Cl have rarely been studied [15]. The very small amount of $CuCl_2$ used in our work paired with an even smaller amount of $CrCl_2$ ($n = 0.005$ in total) in [EMIM]Cl is a unique composition that functions as an effective catalyst for the hydrolysis of cellulose at low temperatures. We restate that the most active paired metal chloride catalysts also cause product degradation even at 120 °C. A balanced metal chloride composition, such as $CuCl_2$ and $CrCl_2$ at $\chi_{CuCl_2} = 0.17$ ($n_{total} = 0.005$), offers the highest HMF yield that is not appreciably degraded at the reaction temperature of 120 °C. While this remarkable effect of paired metal chlorides that enabled low temperature cellulose depolymerization and further conversion to HMF in the alkylmethylimidazolium chloride solvent, a detailed mechanism involved in the cooperation of the paired metal chlorides and this type of unique solvents, is a subject of future study.

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