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Fast Transformation of Glucose and Di-/Polysaccharides into 5-Hydroxymethylfurfural by Microwave Heating in an Ionic Liquid/Catalyst System

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An efficient method for converting glucose into 5-hydroxymethylfurfural (5-HMF), in the presence of $CrCl_3$ catalyst, is developed by using the ionic liquid 1-butyl-3-methyl imidazolium chloride as solvent. A 5-HMF yield of 71% is achieved in 30 s for 96% glucose conversion with microwave heating at 140 °C. The activation energy of glucose conversion is determined to be 114.6 kJ mol^{-1}, with a pre-exponential factor of 3.5×10^{14} min^{-1}. Fructose, sucrose, cellobiose, and cellulose are studied and 5-HMF yields of 54% are obtained for cellulose conversion at 150 °C during 10 min of reaction time. Recycling of the ionic liquid and $CrCl_3$ is demonstrated with six cycles of use.

Introduction

With growing concerns about global warming, the search for sustainable alternative energy sources is critically important. Biomass resources can possibly supplement our fuel supply and meet our demands for chemicals, provided that efficient transformation routes can be developed. 5-Hydroxymethylfurfural (5-HMF), for example, is an important intermediate for the production of fine chemicals, pharmaceuticals, and biofuels,[1] and its preparation through the dehydration of biomass-derived sugars has received much attention.[2–9] Many researchers have selected fructose as substrate for the acid-catalyzed production of 5-HMF, and high yields of 5-HMF, up to 96%, have been achieved.[3,4,7,10–13] On the other hand, glucose (an isomer of fructose) is a better candidate as a resource for 5-HMF because it is the monomeric unit in cellulose and because it is the most abundant monosaccharide in nature. Thus, finding efficient routes for converting glucose into 5-HMF constitutes an important research topic.

A reaction scheme describing the transformation of glucose, fructose, and other di-/polysaccharides is shown in Scheme 1. Glucose can be used as-is, or it can be isomerized to fructose. However, it has been shown that it is difficult to convert glucose into 5-HMF (yields <30%) in water,[13] organic,[14] and organic/water mixed solvents.[6] The apparent reason is that glucose tends to form a stable six-membered pyranoside structure that has a low enolization rate.[15]

Zhao et al. proposed an effective conversion technique for transforming glucose into 5-HMF by using an ionic liquid solvent (1-ethyl-3-methylimidazolium chloride) and $CrCl_2$ as catalyst.[5] A 5-HMF yield of 68% was obtained at a temperature of 100 °C in a reaction time of 3 h. Several other papers have reported the conversion of glucose into 5-HMF by using ionic liquids as solvents and chromium(II) chloride as catalyst.[2,16,17] Yong et al. studied the production of 5-HMF from glucose in 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) using NHC/$CrCl_2$ (NHC: N-heterocyclic carbene) as catalyst, and a 5-HMF yield of 81% was achieved at 100 °C in a 6 h reaction time.[2] Binder et al. developed a process that converted glucose to 5-HMF in *N*,*N*-dimethylacetamide in the presence of NaBr and $CrCl_2$, and achieved a 5-HMF yield of 81% at 100 °C with a reaction time of 5 h.[17] Hu et al. were able to convert glucose into 5-HMF in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) by using $SnCl_4$ as catalyst, and obtained a 5-HMF yield of ca. 60% at 100 °C in 3 h.[16] Although high 5-HMF yields (68–81%) from glucose were obtained at moderate reaction temperatures of ca. 100 °C, all of the proposed methods have required relatively long reaction times, from 3 to 6 h, and up to this point kinetic parameters are lacking. Li et al. presented a process for the production of 5-HMF with high yields from glucose and cellulose in an ionic liquid under microwave irradiation, but the experimental conditions such as reaction temperature and the detailed analyses were not well defined.[18]

Herein, we investigate the catalytic conversion of glucose into 5-HMF in the ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) by using $CrCl_3$ as catalyst and applying microwave heating. Compared to the strongly reductive Cr^{II}, the trivalent form Cr^{III} possesses a higher environmental stability. In addition, although Cr^{III} and Cr^{VI} are both chromium species that are stable in the environment, their biological activity and chemical reactivity are very different.[19] Cr^{VI} is a toxic com-

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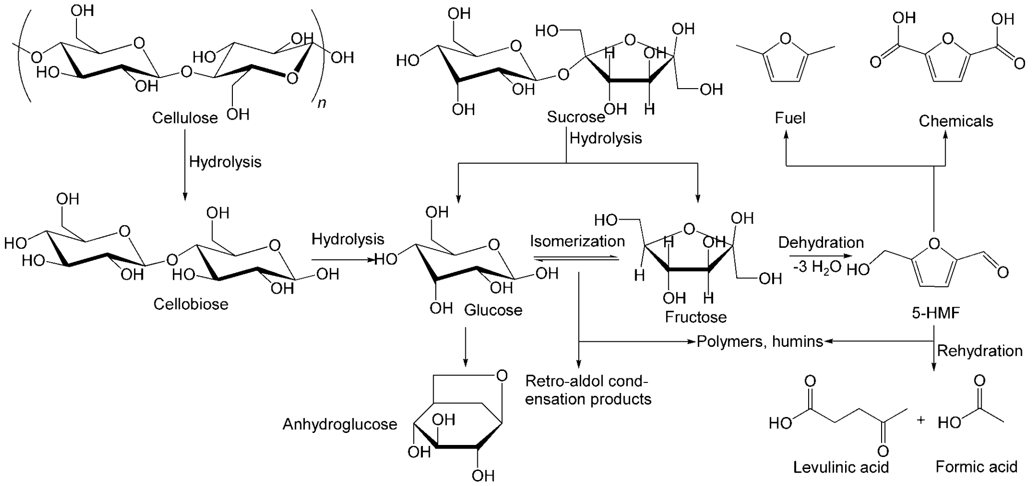

Scheme 1. Reaction scheme for the transformation of glucose, fructose, and other di-/polysaccharides.

pound with teratogenic and carcinogenic effects on humans, while Cr^{III} is essential to mammals for removing glucose from the bloodstream.[20] In this work, the [BMIM][Cl]/$CrCl_3$ system was found to be suitable for the conversion of biomass substrates such as glucose, fructose, sucrose, cellobiose, and cellulose into 5-HMF.

Results and Discussion

Effect of the reaction temperature and kinetics analysis

In our previous work, the ionic liquid [BMIM][Cl] was found to be a suitable solvent for the acid-catalyzed dehydration of fructose into 5-HMF.[10] In this work, we examined the conversion of glucose to 5-HMF in [BMIM][Cl] in the presence of a chromium(III) chloride catalyst.

Figure 1 a and b show the glucose conversion and 5-HMF yield versus reaction time, respectively, for the range of temperatures studied in this work. It is apparent that the reaction temperature has a large effect on the glucose conversion and 5-HMF yield. When the reaction temperature was 90 °C and the reaction time was 60 min, the conversion of glucose approached 53 % and the yield of 5-HMF was about 40 %. In a reaction time of 10 min, the 5-HMF yield increased to about 69 % when the temperature was increased to 120 °C. At a reaction temperature of 140 °C, a 5-HMF yield of 71 % was obtained in 0.5 min. Yong et al., in their study on the conversion of glucose into 5-HMF in [BMIM][Cl] with NHC/$CrCl_2$, reported that the 5-HMF yield from glucose increased with temperature below 100 °C, but then decreased with increasing temperature from 100 °C to 140 °C.[2] However, such a decrease of the 5-HMF yield with increasing temperature (for conditions below 140 °C) was not observed in our experiments.

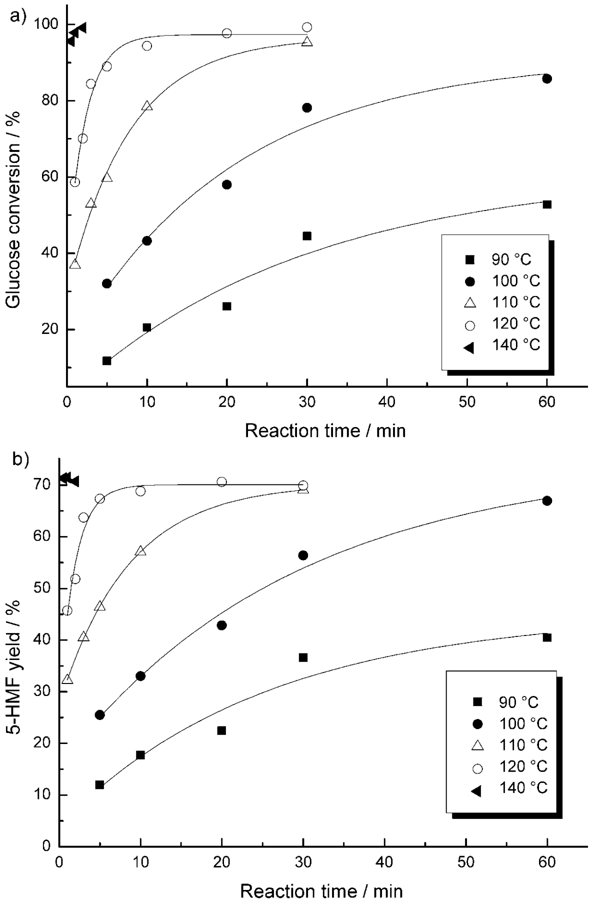

Figure 1. Effect of reaction temperature on a) glucose conversion and b) 5-HMF yield in a system using [BMIM][Cl] as solvent and $CrCl_3$ as catalyst. Conditions: 0.05 g glucose and 0.015 g $CrCl_3 \cdot 6H_2O$ were dissolved in 1 g [BMIM][Cl] at 70 °C for 10 min (water bath heating).

The reaction kinetics for the conversion of glucose into 5-HMF were fitted with first- and second-order reaction rate equations. First-order kinetics were found to be more applicable, and the rate constants at different temperatures (*T*) were used to make an Arrhenius plot (Figure 2). The activation energy and pre-exponential factor were determined to be 114.6 kJ mol^{-1} and 3.5×10^{14} min^{-1}, respectively. The value of the activation energy of this work is comparable with the value given by Antal and Mok, who reported an activation

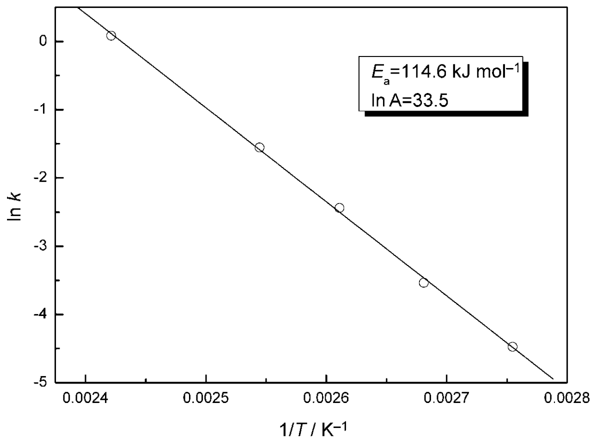

Figure 2. Arrhenius plot for glucose conversion into 5-HMF in ionic liquid [BMIM][Cl] solvent. First-order reaction kinetics constants at different temperatures were obtained for glucose conversion (X) at a certain reaction time (t) via $\ln(1-X)$ vs. t plots.

energy of 100 kJ mol^{-1} for the dehydration of glucose at sulfuric acid concentrations of 5 mmol L^{-1} in water.[21] Because no previous kinetic analyses on the dehydration of glucose into 5-HMF were found in the literature, we chose pre-exponential factors for the conversion of fructose into 5-HMF for comparison. The pre-exponential factors that have been reported show a wide variation, from 4.8×10^{6} to 8.7×10^{11} min^{-1}, depending on the solvents, catalysts, and even heating methods used.[3] The pre-exponential factor determined in this work is 3.5×10^{14} min^{-1}, which is 3–8 orders of magnitude larger than the values of previous works. Under microwave irradiation, the effective collision among reactant molecules in the homogeneous phase is probably enhanced, and as a result the pre-exponential factor in the Arrhenius law increases.[22]

Table 1. Comparison of 5-HMF yields for ionic liquid-catalyst systems.

Solvent	Catalyst, amount[a]	T [°C]	t	5-HMF Yield [%]	Heating method[b]	Ref.
[EMIM][Cl]	$CrCl_2$, 6 mol %	100	3 h	68	Oil bath	[5]
[BMIM][Cl]	NHC-$CrCl_2$, 9 mol %	100	6 h	81	Oil bath	[2]
([EMIM][BF_4]	$SnCl_4$, 10 mol %	100	3 h	60	Oil bath	[16]
[BMIM][Cl]	$CrCl_3$, 9 mol %	Unknown[c]	1 min	91	MW	[18]
		100	1 h	17	Oil bath	[18]
[BMIM][Cl]	$CrCl_3$, 10 mol %	100	1 h	67	MW	This work
		120	5 min	67	MW	
		120	5 min	45	Oil bath	
		140	0.5 min	71	MW	
		140	0.5 min	48	Oil bath	

[a] Based on glucose. [b] MW: Microwave heating. [c] The sample was treated under MW irradiation at 400 W for 1 min, and the reaction temperature was unknown.

The differences between the reaction in the IL system and in other solvents, such as water or organic solvents, should not solely attributed to the change of the pre-exponential factor in the Arrhenius law due to microwave heating effects, as the ionic liquid itself has a large effect on glucose or fructose dehydration. Binder et al. proposed that for ionic liquids that have a chloride anion, a hexacoordinated chromium complex catalyzes the isomerization of glucose into fructose through a enediolate intermediate, and fructose then transforms rapidly into 5-HMF through a nucleophilic pathway, where the fructofuranosyl oxocarbenium ion is readily attacked by the chloride ion of the ionic liquid to form a 2-deoxy-2-halo intermediate.[17] This intermediate would be prone to lose HCl to form the enol and finally yield 5-HMF. Thus, there are strong chemical effects that affect the kinetics.

For comparison, the reaction was carried out with oil-bath heating and microwave heating at identical conditions for two temperatures (Table 1). Microwave heating gave yields that were roughly 48 % higher than oil-bath heating. That higher yields can be obtained with microwave heating than with oil-bath heating for this reaction and catalyst system was also reported by Li et al., who obtained a 91 % 5-HMF yield with microwave irradiation at 400 W in a reaction time of 1 min and under catalytic conditions similar to this work.[18] An unknown reaction temperature was used by those researchers, and analyses were made by UV/Vis at 282 nm. The results of Li et al. could not be reproduced in this work. The Supporting Information provides other experimental runs and shows clearly separated ionic liquid, reactant, and product peaks (by HPLC, with refractive index detection). Data in the Supporting Information of this work shows that increasing the temperature or reaction time gave lower yields than our results in Table 1 at 140 °C. Results obtained on the conversion of glucose into 5-HMF with ionic liquids are summarized in Table 1. The results achieved in this work show that the conversion is more efficient than in previous works, with respect to the reaction times. The reaction time required for a 5-HMF yield of 71 % was 0.5 min at 140 °C, while 3-6 h were required to achieve 5-HMF yield of 60-81 % at 100 °C.

Effect of catalyst amount

Table 2 shows how varying the amount of catalyst affects the glucose conversion and 5-HMF yield. The molar ratios of catalyst to glucose (C/G) were 0, 0.1, 0.2, and 0.4. No glucose conversion occurred in the absence of catalyst, for a reaction time of 30 min and a temperature of 120 °C. At C/G = 0.1, a glucose conversion of 34 % with a 5-HMF yield of 27 % was obtained in a reaction time of 1 min reaction time. In the same reaction time, the glucose conversion increased to 59 % and 61 % when using C/G ratios of 0.2 and 0.4, respectively. The data show that the use of catalyst leads to a remarkable increase of the glucose conversion and 5-HMF yield at the beginning of the reaction (1 min), but that then the 5-HMF yield reaches a pla-

Table 2. Effect of the C/G ratio on glucose conversion and 5-HMF yield.[a]

Catalyst [g]	C/G ratio (mol/mol)	t [min]	Glucose conv. [%]	5-HMF yield [%]	5-HMF selec. [%]
0	0	30	0	0	0
0.0075	0.1	1	34	27	81
		3	64	48	75
		10	88	66	75
0.0150	0.2	1	59	46	78
		3	84	64	75
		10	94	69	73
0.0300	0.4	1	85	61	71
		3	94	68	72
		10	99	70	70

[a] Different amounts of $CrCl_3{\cdot}6H_2O$ and 0.05 g glucose were dissolved in 1 g [BMIM][Cl] at 70 °C for 10 min with a water bath. Reaction mixtures were placed in a microwave oven and heated to 120 °C for different reaction times. Glucose conversions and 5-HMF yields are based on HPLC analyses with RI detector.

teau value between 66 % to 70 % at 10 min reaction time, because most of the glucose has been converted.

Effect of initial glucose concentration

In practical applications it is desirable to use reactants at high concentrations, and so the initial concentrations of glucose were varied as shown in Figure 3. When the glucose/[BMIM][Cl] weight ratio was varied from 0.01 to 0.3, the 5-HMF yield gradually decreased from 74 % to 55 %. The byproducts were fructose (< 5 % yield), 1,6-anhydroglucose (< 1 % yield), formic acid (< 2 % yield), levulinic acid (< 1 %), and mainly soluble polymers. The soluble polymers were not characterized. The losses in 5-HMF yield with increasing glucose concentration are most likely due to cross-polymerization occurring between glucose and 5-HMF.[15] This is similar to effects observed with aqueous solutions in the conversion of fructose, where losses due to the formation of humins can amount to up to 35 % with a 1 M fructose solution while this value reduces to ca. 20 % with 0.25 M fructose solutions.[15] Polymerization losses cannot be avoided with the present techniques, and so achieving high yields of 5-HMF from highly concentrated glucose stocks remains a challenge.

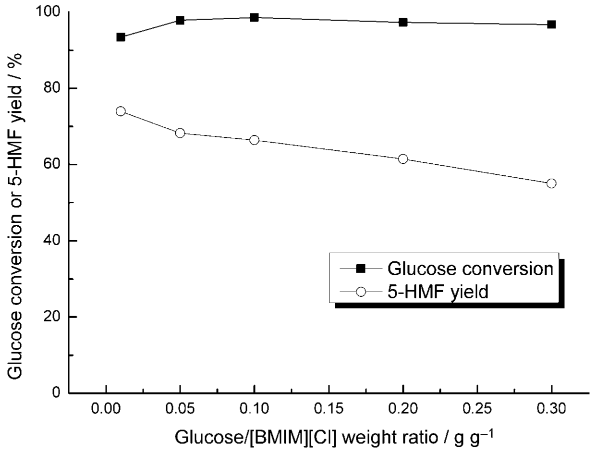

Figure 3. Effect of glucose loading on 5-HMF yield from glucose. Different amounts of glucose and corresponding amounts of $CrCl_3{\cdot}6H_2O$ (catalyst/glucose molar ratio = 0.2) were dissolved in 1 g [BMIM][Cl] at 70 °C for 10 min (water bath heating). The mixtures were reacted in a microwave oven at 120 °C for 10 min. Glucose conversions and 5-HMF yields are based on HPLC analysis.

We examined the stability of 5-HMF in the system at 120 °C by adding 0.05 g of 5-HMF and 0.015 g $CrCl_3{\cdot}6H_2O$ into 1 g of [BMIM][Cl] in the absence of glucose. After a reaction time of 10 min, 96 % of the 5-HMF could be recovered, indicating that it is stable under these experimental conditions in the absence of glucose. This is a further indication that the lower yields of 5-HMF can be attributed to the formation of soluble polymers that result from self-polymerization of glucose and cross-polymerization between glucose and 5-HMF.

Recycling of the ionic liquid and catalyst

The ability to recycle both the solvent and the catalyst is an important consideration for practical biomass transformations. The activity of the ionic liquid/catalyst system was studied by recycling both ionic liquid and catalyst six times with different glucose loadings. Experiments were conducted at 120 °C for a reaction time of 10 min. Ethyl acetate was used to extract the 5-HMF product from the reaction mixture after each reaction cycle, since 5-HMF can be extracted into ethyl acetate while [BMIM][Cl] and glucose have practically no solubility in the ethyl acetate phase.[2,4,10] After extraction of 5-HMF from the ionic liquid phase, the reaction mixture was heated at 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate, and an equal amount of glucose was added and used for the next reaction cycle. As shown in Figure 4, when successive reactions were performed with recycled solvent and catalyst comparable 5-HMF yields of 62–70 % were obtained, showing that the catalyst retained most of its activity. When the glucose loading was increased to 0.2 g, the yield of 5-HMF decreased somewhat compared to the yield obtained for a lower glucose loading, giving 5-HMF yields ranging from 52 % to 59 %. The oligomeric humin byproducts that remained in the solvent did not seem to affect the subsequent dissolution and conversion of glucose, but there did seem to be a systematic decrease in the obtained yields as the number of recycling iterations increased. The humins were not quantified, but their presence could be ascertained from the color of reaction mixtures (changing into a deep-brown color).[11,15] In some cases the 5-HMF yield increased compared to previous cases, which can be attributed to the retention of some 5-HMF and unreacted glucose from the previous cycle. It is clear that separation of the product and solvent requires energy. In the case of ethyl acetate as extraction solvent, the energy costs of the separation may be low due to the use of a low-boiling-point solvent.

Conversion in various ionic liquids

As shown by the results described herein, $CrCl_3$ is an effective catalyst for the conversion of glucose into 5-HMF in [BMIM]

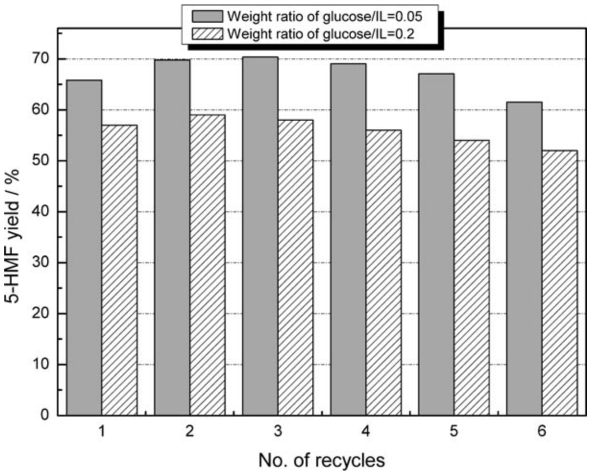

Figure 4. Successive use of [BMIM][Cl] and catalyst with different glucose loadings. Conditions: 0.05 or 0.2 g glucose with corresponding amount of $CrCl_3 \cdot 6H_2O$ (catalyst/glucose molar ratio = 0.2) was dissolved in 1 g [BMIM][Cl] at 70 °C for 10 min (water bath heating). The mixture was reacted in a microwave oven at 120 °C for 10 min. 5-HMF was separated from the mixture by extraction with 6 mL of ethyl acetate, 5 times, after 0.5 g of water was added. After extraction, the ionic liquid solvent was heated to 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate, and the solvent was used directly in subsequent runs by adding glucose.

[Cl]. Because some ionic liquids readily dissolve carbohydrates such as fructose, glucose and cellulose, the $CrCl_3$-catalyzed conversion of glucose into 5-HMF was studied in a series of ionic liquids, namely [BMIM][Cl], 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]), 1-hexyl-3-methyl imidazolium chloride ([HexylMIM][Cl]), 1-methyl imidazolium hydrogen sulfate ([HMIM][HSO_4]) and 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]). The results, shown in Figure 5, demonstrate that ionic liquids with Cl^- as anion in the presence of $CrCl_3$ are the most effective for converting glucose into 5-HMF. Even though glucose conversions were high for Brønsted-acidic ionic liquids with HSO_4^- as anion, the 5-HMF yields were below 10%, which is most likely due to the formation of soluble polymers and insoluble humins.

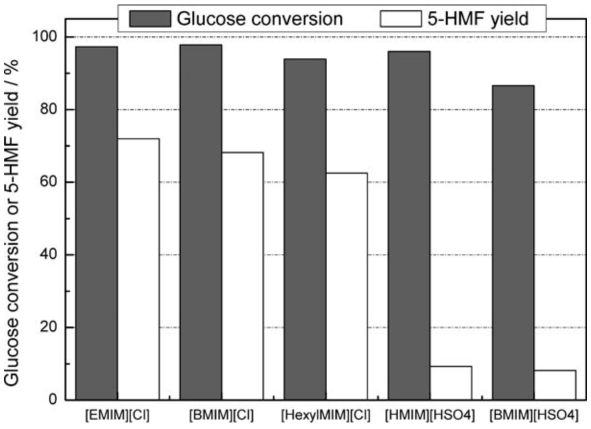

Figure 5. Catalyzed conversion of glucose into 5-hydroxymethylfurfural (5-HMF) in various ionic liquids by $CrCl_3$. Conditions: 0.05 g glucose with 0.015 g $CrCl_3 \cdot 6H_2O$ was dissolved in 1 g ionic liquid at 70 °C for 10 min (water bath heating). The mixture was reacted with microwave heating at 120 °C for 10 min. Glucose conversions and 5-HMF yields are based on HPLC analysis.

Zhao et al. postulated a mechanism for the chromium-catalyzed transformation of glucose into 5-HMF in [EMIM][Cl] in the presence of $CrCl_2$.[5] They proposed that a hexacoordinate chromium(II) complex catalyzes the isomerization of glucose into fructose, probably via an enediolate intermediate, and fructose is then rapidly converted into 5-HMF. Hu et al. proposed a mechanism for the conversion of glucose to 5-HMF in [EMIM][BF_4] catalyzed by $SnCl_4$, where the formation of a five-membered-ring chelate complex of the Sn atom with the two neighboring hydroxyl groups in glucose is thought to play a key role in the catalytic reaction, and the Sn in $SnCl_4$ interacts with O atoms and promotes the formation of straight-chain glucose and the enediol intermediate.[16] The latter intermediate is further transformed into fructose, which can be dehydrated to form 5-HMF rapidly.

In our previous work, base catalyst was shown to favor the isomerization of glucose to fructose while acid catalyst was shown to favor the conversion of fructose into 5-HMF.[13] However, the transformation of glucose becomes nonselective under acidic reaction environments because many other reaction pathways, such as retro-aldol condensation and polymerizations, become promoted. It has been reported that the acidity or basicity of alkylimidazolium chloro-metal ionic liquids can be controlled by changing the amount of metal chloride added to the ionic liquids. When the molar fraction of metal chloride (x) was below 0.5, the ionic liquids became basic, whereas for the cases of $x = 0.5$ and $x > 0.5$, the ionic liquids exhibited neutral and acidic reaction environments, respectively.[23] In this work, the catalytic amount of $CrCl_3$ dissolved into [BMIM][Cl] ($x \ll 0.5$), and the formed [BMIM][$CrCl_4$] ionic liquid exhibited basicity that probably accelerated the isomerization of glucose to fructose and the dehydration of fructose into 5-HMF via the mechanism depicted above. On the other hand, [HMIM][HSO_4] and [BMIM][HSO_4] are Brønsted-acidic ionic liquids so that even after a small amount of $CrCl_3$ is added, reactions such as polymerization other than isomerization and dehydration are promoted. This probably leads to low 5-HMF yields and large amounts of soluble polymers and insoluble humins.

Catalyzed conversion of various substrates in [BMIM][Cl]/$CrCl_3$

The [BMIM][Cl]/$CrCl_3$ system was tested for catalyzing other substrates, including fructose, sucrose, cellobiose, and cellulose. This catalytic system was also effective for fructose conversion and a 5-HMF yield of 78% was obtained at 100 °C in 1 min. Sucrose is a disaccharide consisting of glucose and fructose. Normally, the 5-HMF yield from sucrose is mainly obtained from the fructose moiety and the glucose moiety is for the most part wasted.[6,8] Here, both the glucose and fructose moiety could be converted into 5-HMF and a 5-HMF yield of 76% could be achieved. As a disaccharide consisting of two molecules of glucose, when cellobiose was used as a substrate,

Table 3. Formation of 5-HMF from various substrates in the [BMIM][Cl] ionic liquid/$CrCl_3$ catalytic system.[a]

Substrate	T [°C]	t [min]	5-HMF yield [%]
Fructose	100	1	78
Sucrose	100	5	76
Cellobiose	120	10	49
	140	2	52
	140	5	55
Cellulose	120	10	9
	150	5	49
	150	10	54

[a] 0.05 g sugar and 0.015 g $CrCl_3{\cdot}6H_2O$ were dissolved in 1 g [BMIM][Cl] at 70 °C for 10 min (water bath heating). Reaction mixtures were transferred to a microwave oven and heated for different reaction times. 5-HMF yields are based on HPLC analyses.

55 % of cellobiose was converted to 5-HMF at 140 °C for 5 min. When cellulose was used as the feedstock, 54 % could be converted into 5-HMF at 150 °C in 10 min (Table 3).

Conclusions

The ionic liquid [BMIM][Cl] and $CrCl_3$ is an excellent and environmentally safe reaction solvent system for converting glucose into 5-HMF. Both microwave heating and convective heating can be used. The conditions in this work were carefully controlled to ensure that the kinetics based on microwave heating are both reliable and reproducible. A high 5-HMF yield of 69 % was obtained from glucose at 120 °C in 10 min, and the 5-HMF yield increased to 71 % in a reaction time of 30 s when the reaction temperature was increased to 140 °C. Good results were achieved when fructose, sucrose, cellobiose, and cellulose were used as feedstocks. The 5-HMF yields decreased with increasing initial glucose concentration due to soluble polymer formation. The ionic liquid [BMIM][Cl] and $CrCl_3$ could be recycled without loss of activity after the product 5-HMF was separated. The combination of neutral ionic liquids with Cl^- as anion, such as [BMIM][Cl], [EMIM][Cl], and [HexylMIM][Cl], with $CrCl_3$ was effective for converting glucose into 5-HMF, but the acidic ionic liquids with HSO_4^- as anion had a negative influence on 5-HMF formation.

Experimental Section

Materials and methods: Glucose (99 %) and fructose (99 %) were purchased from Wako Pure Chemical Company; sucrose, cellobiose, cellulose, 5-hydroxymethylfurfural, $CrCl_3{\cdot}6H_2O$, [BMIM][Cl], [HMIM][Cl], [EMIM][Cl], [HexylMIM][Cl], [HMIM][HSO_4], and [BMIM][HSO_4] were purchased from Sigma–Aldrich Company. The water content of the ionic liquids was lower than 1 %, although it should be noted that the reaction under investigation generates water through dehydration. All chemicals were used without further purification.

In a typical run, 0.100 g of glucose (0.556 mmol) and 0.015 g $CrCl_3{\cdot}6H_2O$ (0.056 mmol) were dissolved in 1 g of [BMIM][Cl] at 70 °C using a water bath. The conversion with this procedure was not more than 3 %. Initially, the glucose, $CrCl_3$, and ionic liquid mixture was green, and dissolution caused the mixture to change into a clear homogeneous rose-colored solution. The reaction mixture was placed into a microwave oven (Shikoku Keisoku µReactor, SMW-087, 2.45 GHz, maximum power 700 W) with magnetic stirring and could be heated to the desired temperature within about 15 s. The reaction mixture was held at the reaction temperature for a given period of time. At a given elapsed time, power was cut and the reaction mixture was cooled quickly by the addition of 10 g of pure water that was followed by solution analyses. For recycling of the ionic liquid and catalyst, 5-HMF was extracted from the mixture by contact with 6 mL of ethyl acetate 5 times after 0.5 g of water was added. The addition of water to the ionic liquid greatly promoted the transport of 5-HMF from the IL phase to the ethyl acetate phase, and a separation efficiency of about 97 % for 5-HMF removal from IL to ethyl acetate could be achieved. After extraction, the ionic liquid was heated to 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate. It was then used directly in subsequent runs by adding glucose.

Analysis: HPLC equipped with a refractive index detector (HPLC-RI, SH 1011 column) was employed for the analysis of the liquid samples. The column oven temperature was 60 °C, and the mobile phase was a 0.5 mM sulfuric acid aqueous solution at a flow rate of 1 $mL\,min^{-1}$.

Additional experiments: We investigated if water might be removed from the liquid phase due to microwave heating, so that the dehydration reaction might be promoted. Microwave heating of solution in open vessels did not affect the general reaction trends reported in Figure 1.

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Keywords: biofuels · biomass · carbohydrates · cellulose · sustainable chemistry

[1] J. Lewkowski, *Arkivoc* **2001**, *2*, 17 – 54; Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen, A. Riisager, *ChemSusChem* **2009**, *2*, 672 – 675.

[2] G. Yong, Y. G. Zhang, J. Y. Ying, *Angew. Chem.* **2008**, *120*, 9485 – 9488; *Angew. Chem. Int. Ed.* **2008**, *47*, 9345 – 9348.

[3] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Green Chem.* **2008**, *10*, 799 – 805; X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Ind. Eng. Chem. Res.* **2008**, *47*, 9234 – 9239; M. Bicker, D. Kaiser, L. Ott, H. Vogel, *J. Supercrit. Fluids* **2005**, *36*, 118 – 126; M. Bicker, J. Hirth, H. Vogel, *Green Chem.* **2003**, *5*, 280 – 284.

[4] S. Q. Hu, Z. F. Zhang, Y. X. Zhou, B. X. Han, H. L. Fan, W. J. Li, J. L. Song, Y. Xie, *Green Chem.* **2008**, *10*, 1280 – 1283.

[5] H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597 – 1600.

[6] J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, *Green Chem.* **2007**, *9*, 342 – 350.

[7] Y. Roman-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933 – 1937.

[8] C. Moreau, A. Finiels, L. Vanoye, *J. Mol. Catal. A: Chem.* **2006**, *253*, 165 – 169.

[9] F. Salak Asghari, H. Yoshida, *Ind. Eng. Chem. Res.* **2006**, *45*, 2163 – 2173; C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, *Appl. Catal. A: Gen.* **2004**, *275*, 111 – 118; A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, *Chem. Commun.* **2009**, 6276 – 6278; F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger, B. Konig, *Green Chem.* **2009**, *11*, 1948 – 1954; X. L. Tong, Y. D. Li, *ChemSusChem* **2010**, *3*, 350 – 355.

[10] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Green Chem.* **2009**, *11*, 1327 – 1331.
[11] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *ChemSusChem* **2009**, *2*, 944 – 946.
[12] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Catal. Commun.* **2009**, *10*, 1771 – 1775; Q. X. Bao, K. Qiao, D. Tomida, C. Yokoyama, *Catal. Commun.* **2008**, *9*, 1383 – 1388; T. S. Hansen, J. M. Woodley, A. Riisager, *Carbohydr. Res.* **2009**, *344*, 2568 – 2572.
[13] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Catal. Commun.* **2008**, *9*, 2244 – 2249.
[14] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982 – 985.
[15] B. F. M. Kuster, *Starch/Staerke* **1990**, *42*, 314 – 321.
[16] S. Q. Hu, Z. F. Zhang, J. L. Song, Y. X. Zhou, B. X. Han, *Green Chem.* **2009**, *11*, 1746 – 1749.
[17] J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979 – 1985.
[18] C. Z. Li, Z. H. Zhang, Z. B. K. Zhao, *Tetrahedron Lett.* **2009**, *50*, 5403 – 5405.
[19] A. Beni, R. Karosi, J. Posta, *Microchem. J.* **2007**, *85*, 103 – 108.
[20] T. M. Florence, *Talanta* **1982**, *29*, 345 – 364.
[21] M. J. Antal, W. S. L. Mok, G. N. Richards, *Carbohydr. Res.* **1990**, *199*, 91 – 109.
[22] M. Hosseini, N. Stiasni, V. Barbieri, C. O. Kappe, *J. Org. Chem.* **2007**, *72*, 1417 – 1424.
[23] J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263 – 1264; M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton, *Inorg. Chem.* **1999**, *38*, 5637 – 5641.

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