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Conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by $ZnCl_2$ in water[†]

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The incompletely coordinated zinc ions in the concentrated aqueous ZnCl₂ solution catalyze the direct conversion of carbohydrates into 5-hydroxymethylfurfural, and a moderate HMF yield up to 50% can be achieved.

Biomass shows potential as an alternative feedstock to fossil resources for a variety of chemicals and fuels.¹ Carbohydrates including cellulose and semicellulose are the main components of biomass. However, they cannot be applied directly as fuels due to their high oxygen contents. Many research efforts are aimed at exploring routes to simply and efficiently lower their oxygen contents.² One of the attractive routes is dehydration of carbohydrates to produce platform chemical 5-hydroxymethyl-furfural (HMF).³

Presently, production of HMF is primarily started from carbohydrates such as fructose, glucose and cellulose. HMF production from fructose is effortless and high HMF yields can be obtained,⁴ whereas effective production of HMF from glucose is challenging because the isomerization of glucose into fructose is usually achieved in the reaction systems with powerful basicity⁵ while the dehydration of fructose into HMF demands an acidic environment.⁶ Two strategies for this problem include: (1) the application of acid–base solid catalysts⁷ and (2) the introduction of metal salt catalysts including lanthanide ions,8 chromium ions,9 germanium ions,10 stannum ions11 and aluminium ions.¹² It is more challenging to convert cellulose into HMF since dissolution is required beforehand. Ionic liquids and N,N-dimethylacetamide containing lithium chloride (DMA-LiCl) are capable of dissolving cellulose well⁹ and hence applied as the reaction media to convert cellulose into HMF. Despite their effectiveness toward HMF production, they are expensive.¹³ Therefore, it is still indispensable to develop a more economical reaction system for the large-scale production of HMF.



Scheme 1 Transformation of cellulose into 5-hydroxymethylfurfural (HMF).

It is reported that the catalytic effects of metal ions stem from the fact that they could coordinate with the hydroxyl groups of glucose to form an enediol structure, which is considered as the key intermediate in the isomerization of glucose to fructose.8-12,14 This suggested to us that Zn^{2+} ions could play the same role in catalyzing the conversion of glucose to HMF, since the Zn²⁺ ions in the concentrated aqueous ZnCl₂ solutions could coordinate with two neighboring hydroxyl groups of carbohydrates.^{15,16} We also noticed that the aqueous ZnCl2 solution with a concentration ≥ 60 wt% can dissolve cellulose well by forming a Zn-cellulose complex.¹⁷ Besides, it exhibits strong acidity which would enable the hydrolysis of cellulose and the dehydration of fructose to HMF. In addition, it is much less expensive than ionic liquids and organic reaction media, and it is far less toxic. Hence, it shows potential as a green and economical reaction medium in the industrial production of HMF from bio-based carbohydrates (Scheme 1). Herein, we report using concentrated aqueous ZnCl₂ solution as the reaction medium to produce HMF in a single step from carbohydrates including cellulose, glucose, sucrose, maltose, starch and fructose.

In 55–65 wt% aqueous ZnCl₂ solutions, the conversion of glucose was high whereas the HMF yield was relatively low (Table 1). Humins that are produced from glucose and their dehydration products were also observed (Table S1, ESI†),⁴ whereas levulinic acid was not detected. The reactivity of glucose towards HMF was also explored in a 1.6 wt% HCl aqueous solution whose acidity is identical to that of 63 wt% ZnCl₂. However, a negligible HMF yield was obtained. This indicates that the conversion of glucose to HMF is catalyzed by the Zn²⁺ ions. Previous studies indicated that the Zn²⁺ ions in aqueous ZnCl₂ solutions could coordinate with oxygen atoms of carbohydrates to

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Substrate	Solvent, wt%	Cocatalyst ^b , mol/mol	$T/^{\circ}\mathrm{C}$	Conv. (%)	HMF yield, mol%
Glucose	ZnCl ₂ , 32		98	Trace	Trace
	$ZnCl_2, 63$		98	81.7	13.0
	ZnCl ₂ , 55		110	94.3	13.8
	$ZnCl_2, 60$		110	95.7	14.9
	$ZnCl_2, 63$		120	99.7	16.1
	$ZnCl_2, 65$		120	98.3	15.7
	HCl, 1.6		98	Trace	Trace
	ZnBr ₂ , 76		120	82.3	29.1
	$ZnBr_2, 44$		98	Trace	Trace
	$ZnCl_2, 63$	$FeCl_2, 1:1$	120	96.4	15.8
	ZnCl ₂ , 63	MnCl ₂ , 1 : 1	120	95.6	14.1
	$ZnCl_2, 63$	LiCl, 1 : 1	120	96.5	14.2
	$ZnCl_2, 63$	LiBr, 1 : 1	120	93.3	15.3
	ZnCl ₂ , 63	HCl, 0.8 : 1	120	94.3	25.5
	$ZnCl_2, 63$	HCl, 1 : 1	120	80.5	32.3
	$ZnCl_2, 63$	HCl, 1 : 1	120	60.5	12.3 ^c
	$ZnCl_2, 63$	HCl, 1.1 : 1	120	88.5	25.6
	$ZnCl_2$, 63	$CuCl_2, 1:1$	120	97.6	17.7
	$ZnCl_2$, 63	$CrCl_3, 0.5:1$	120	96.7	25.4
	$ZnCl_2, 63$	$CrCl_3, 0.3 : 1$	120	96.1	24.9
Cellulose	$ZnCl_2, 63$		120		11.5
	$ZnCl_2, 63$	$CrCl_3, 0.6:1$	120		15.0
	$ZnCl_2, 63$	HCl, 1 : 1	120		22.1
	$ZnCl_2, 63$	HCl, 1 : 1	120		30.4^{d}
	$ZnCl_2, 63$	HCl, 0.8 : 1	120		20.8
	$ZnCl_2$, 63	HCl, 1.2 : 1	120		15.3
Fructose	$ZnCl_2$, 63	HCl, 1 : 1	120	97.3	53.3
Sucrose	$ZnCl_2$, 63	HCl, 1 : 1	120	96.5	38.8
Maltose	$ZnCl_2$, 63	HCl, 1 : 1	120	95.2	32.8
Starch	$ZnCl_2^2$, 63	HCl, 1 : 1	120		29.3

^{*a*} Reaction system: 100 g ZnCl₂ aqueous solution, 2 g carbohydrate. ^{*b*} Cocatalyst loading is relative to moles of monosaccharide in carbohydrates. ^{*c*} The glucose concentration is 15 wt%. ^{*d*} The reaction system was treated at 70 °C for 12 h before reaction.

form different complexes, and their coordination state was dependent on the concentration of ZnCl₂. At high concentrations, a complex with a Zn²⁺ ion coordinating with two neighboring hydroxyl groups of a carbohydrate was reported.^{15,16} Noticeably, the concentration of ZnCl₂ solution in the previous work is 67 wt%,16 which is at the same level as our work. Therefore, it is reasonable to deduce that such a complex could also form in our concentrated aqueous ZnCl₂ solutions, which facilitates the isomerization of glucose into fructose and consequently the synthesis of HMF. This assumption was proved by the increase and decrease of fructose as a function of reaction time in the 63 wt% ZnCl₂ solution during the conversion of glucose (Fig. S2, ESI[†]). To further verify this hypothesis, the conversion of glucose to HMF was tested in a 32 wt% aqueous ZnCl2 solution. This was based on acknowledgement that the above-mentioned complex is unable to form in low-concentrated ZnCl₂ solutions. As expected, the conversion of glucose and the HMF yield in the 32 wt% ZnCl₂ solution are negligible (Table 1), and no fructose was detected during the reaction. This assumption was further proved by a negligible HMF yield in the 44 wt% ZnBr2 solution whose H₂O : Zn molar ratio is identical to that of the 32 wt% ZnCl₂ solution (16:1). Noticeably, a higher HMF yield was obtained in the 76 wt% ZnBr₂ solution whose H₂O : Zn molar ratio (4 : 1) is similar to that of the 65 wt% ZnCl₂ one. This result indicates that although the halogen ions alone show no catalytic activity, they could affect the catalytic performances of the active Zn²⁺ ions.

The formation of the above-mentioned complex in high concentrated ZnCl₂ solutions should have resulted from the coordination state of Zn^{2+} ions. The Zn^{2+} ions could coordinate with groups/ligands containing electron pairs. In a low concentrated ZnCl₂ solution, H₂O molecules are abundant, like in the case of the 32 wt% one which has a H₂O : ZnCl₂ molar ratio of 16:1. A Zn^{2+} ion can readily combine with 6 H₂O molecules to reach a complete coordination sphere, $[Zn(H_2O)_6]^{2+}$. These coordinated H₂O are unlikely to be replaced by carbohydrates, since the coordination between the hydroxyl group(s) of carbohydrates and zinc is weaker than that between H₂O and zinc. This implies that $[Zn(H_2O)_6]^{2+}$ is "inert" toward carbohydrates. While in concentrated ZnCl₂ solutions, there are not enough H_2O molecules for all of the Zn^{2+} ions to reach the complete coordination. For example, the H₂O : Zn molar ratio of the 63 wt% ZnCl₂ solution is 4.5, indicating the incomplete coordination of the Zn^{2+} ions in this solution. The incompletely coordinated Zn^{2+} ions are able to coordinate with one or more hydroxyl groups of carbohydrate. The interaction of incompletely coordinated Zn2+ ions with H2O and glucose molecules was supported by IR characterization (Fig. S3-S5, ESI⁺). It is also reasonable to deduce that the possibilities for a Zn^{2+} ion to coordinate with two hydroxyl groups of a carbohydrate would be largely enhanced with the increase of the ZnCl₂ concentration. This is likely to be the reason for the observation of such coordination between Zn²⁺ and carbohydrate in a 67 wt% ZnCl₂ solution whose H₂O : ZnCl₂ molar ratio is approximately 3.7.¹⁶

Furthermore, the effects of HCl and several metal ions on HMF yield were investigated (Table 1). The addition of HCl promoted the HMF yield. The added chromium also improved the HMF yield, but its promotional effect is less pronounced. The introduction of Fe²⁺, Mn²⁺ and Li⁺ decreased the HMF yield. To understand the promotional effect of HCl on the HMF yield, the kinetics of glucose conversion in the 63 wt% aqueous ZnCl₂ solution was studied, both alone and with HCl (for details see ESI†). The added HCl increased drastically the value of k/k_{gr} indicating that HCl promotes glucose selectively converting into HMF (Table 2). However, an expected large improvement in the HMF yield was not observed. This is because the degradation of HMF was not slowed down by HCl, as indicated by the slight change in the k'. From this point of view, a satisfactory HMF yield could be obtained by suppressing the degradation of HMF.

To achieve this goal, a two-phase method was carried out in this work aiming at transferring the formed HMF away from the reaction medium as soon as possible (details in ESI[†]). The ZnCl₂ reaction system that showed the maximal HMF yield was first chosen as the aqueous phase. It is surprising to find that the introduction of organic phase drastically decreased the HMF yield from 32.3% to 5.2% (Fig. 1a). After the reaction, Zn²⁺ ions were detected in the organic phase, indicating the

 Table 2
 Effect of HCl on the reaction rate constants^a

HCl/glucose mol/mol	$k_g^{\ b}/min^{-1}$	k^c/\min^{-1}	k'^d/\min^{-1}	$k/k_{\rm g}$
0	0.0904	0.0397	0.0051	0.44
1:1	0.0146	0.0134	0.0044	0.92

^{*a*} Reaction temperature: 120 °C. ^{*b*} k_g : rate constant of glucose conversion. ^{*c*} k: rate constant of HMF formation. ^{*d*} k': rate constant of HMF degradation.



Fig. 1 Effect of glucose concentration in the aqueous solution on the HMF yield in two-phase reaction system: (a) 2 wt%; (b) 10 wt%; (c) 12.5 wt%; (d) 15 wt%. *Reaction conditions*: 150 ml MIBK, 20 g 63 wt% ZnCl₂ aqueous solution, HCl/glucose = 1 : 1 (mol : mol), T = 120 °C.

transfer of Zn^{2+} ions from aqueous phase to organic phase. However, this transfer of Zn²⁺ ions was not observed in the 32 wt% ZnCl₂ aqueous phase-organic phase system. This phenomenon implies that only the Zn^{2+} ions with a certain coordination state, namely, the incompletely coordinated Zn^{2+} ions, are able to coordinate with the oxygen atoms in methylisobutylketone (MIBK) and hence "dissolve" in the organic phase. They could catalyze the degradation of HMF in MIBK, and consequently lead to a lower HMF vield. Hence, it is of vital importance to "lock" the Zn^{2+} ions in the aqueous phase to improve the HMF yield. To solve this problem, we increase the glucose content in the aqueous phase, and reason that the Zn²⁺ ions with incomplete coordination could be saturated by glucose molecules and thus be locked in the aqueous phase, as the coordination between glucose and Zn^{2+} ions is stronger than that between MIBK and Zn^{2+} ions. This assumption was confirmed by the substantial improvement in HMF yield with the gradual increase in the glucose content in the aqueous phase (see Fig. 1b-1d). A HMF yield of 40% can be reached with a glucose concentration of 15 wt%, and maintained at this level (Fig. 1d).

Next, the conversion of cellulose to HMF was investigated in the 63 wt% ZnCl₂ solution, and a 22.1% HMF yield was obtained with the added HCl (Table 1). Cao *et al.* reported that cellulose can hydrolyze into small carbohydrates in concentrated ZnCl₂ solutions at 70 °C for 12 h.¹⁷ Considering the synthesis of HMF from small carbohydrates is easier than that of cellulose, the pretreatment of cellulose in the 63 wt% ZnCl₂ was also used in this work. This pretreatment improved HMF yield to 30.4%. The incompletely coordinated Zn ions in the 63 wt% ZnCl₂ solution could also catalyze the conversion of carbohydrates with different structures such as sucrose, fructose, maltose and starch (Table 1).

Finally, the recycling of aqueous ZnCl₂ solution was investigated. Active carbon is used as an adsorbent to remove the undesired humins in the sugar refining industry. This suggested to us that the humins in our reaction system might be removed by active carbon. As expected, active carbon effectively removed the byproducts from the reaction medium (Fig. S7 and S8, ESI†). Another four runs of glucose conversion were carried out in the recycled ZnCl₂ solution, and no obvious decrease in the HMF yield was observed. In summary, the Zn^{2+} ions with incomplete coordination can be created by simply modifying the concentration of $ZnCl_2$ in water. These Zn^{2+} ions could coordinate with the carbohydrates and catalyze their transformation into fructose and further into HMF. The HMF yield for bio-based carbohydrates ranges from 30% to 50% under a mild reaction condition. Especially, using the two-phase method a HMF yield of 40% is obtained when the carbohydrate content in the aqueous phase is high (15 wt%). Furthermore, active carbon is applied to efficiently remove the byproducts and recycle the concentrated aqueous $ZnCl_2$ solution. All these results indicate the potential of the concentrated aqueous $ZnCl_2$ solution as a green and economical reaction solution to produce HMF from bio-based carbohydrates on a large scale.

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