

## Electronic Supplementary Information for

# Conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by $\text{ZnCl}_2$ in water

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## 1 Experimental Section

### 1.1 Material

Zinc chloride and ethanol were purchased from Tianjin Hengxing chemical preparation co., Ltd. 5-hydroxymethylfurfural (> 96 %) was from Tengzhou Fitian Aroma Chemical Co., Ltd.  $\text{ZnBr}_2$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were from Tianji Guangfu fine chemical institute, Tianji Hongyan chemical reagent factory and Beijing Kangpuhuiwei Technology Co., Ltd. Acetonitrile was from Tianjin Beichen Fangzheng chemical reagent factory, respectively. Glucose and crystalline cellulose were from Shijiazang glucose factory and Tianjin Aokai Industry Co., Ltd respectively. Sucrose, maltose, starch and fructose were from Beijing Greatlinks Co., Ltd. D-(+)-cellobiose (BR grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. All these carbohydrate materials

were dried at 80 °C for 12 h before use. Methylisobutyketone (MIBK) was from Tianjin Guangfu chemical reagent factory.  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was from Tianjin No.3 Chemical Reagent Factory. Hydrochloride acid was from Beijing Chemical Works. The rest of reagents used in this work were of analytical grade without further purification and the water was deionized.

## 1.2 Analytic methods

The samples of product mixture were cooled down to room temperature and 0.5 ml of the sample was diluted with ethanol (95 %) to the scale in a 25 ml volumetric flask, then filtered, analyzed with HPLC and quantified with the calibration curves generated.

Chromatographic analysis was performed on a Venusil ODS column (5.0  $\mu\text{m}$ , 250 mm  $\times$  4.6 mm) with an UV detector. The mobile phase consisted of acetonitrile and water (10:90, v/v) and its flow rate was 1.0 ml/min. The column temperature was maintained at 30 °C and the detection wavelength was set at 280 nm.

The quantitative analysis of carbohydrates such as fructose, glucose and cellobiose was carried out on an Agilent 126 HPLC with a RID detector and a Shodex packed column (Shodex sugar SC1011). The mobile phase was deionized water and its flow rate was 1.0 ml/min. The temperatures of the column and the detector were 80 °C and 40 °C, respectively.

The HPLC-MS analysis was performed on a Waters Alliance 2695/ZQ 4000 instrument. Waters Alliance 2695 HPLC is equipped with a Waters 996 PDA detector and a Venusil ODS column set at 30 °C, and its mobile phase consisted of acetonitrile and water (10:90, v/v) flowing at 0.8 ml/min. ZQ-4000 MS is equipped with a ESI+ ionization source. To avoid the influence of the  $\text{Zn}^{2+}$  and  $\text{Cl}^-$  on the MS signal, each sample was prepared by the following procedure: 1ml of each reaction sample was mixed with 3 ml of ethyl acetate and then washed by 6 ml of saturated  $\text{Na}_2\text{CO}_3$  solution, after that, the organic phase was collected and the water in it was removed by anhydrous  $\text{Na}_2\text{CO}_3$ ; afterwards, the organic phase was filtered and evaporated to remove the ethyl acetate, the remains were dissolved in the 1.5 ml of deionized water for HPLC-MS analysis.

### 1.3 IR Characterization

IR spectra were collected with a resolution of  $4\text{ cm}^{-1}$  on a Perkin Elmer SP-IR sp100 spectrometer equipped with a detector and a ZnSe window.

### 1.4 Reaction system

In a typical experiment for the conversion of carbohydrates in single phase, a 100 ml glass flask was charged with 100 g aqueous  $\text{ZnX}_2$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ ) solution alone or with a co-catalyst including  $\text{HCl}$  or metal salt, and a certain amount of carbohydrates. The reaction system was heated to the desired temperature in an oil bath under continuous stirring and  $\text{N}_2$  atmosphere. The experiment for the transformation of glucose in biphasic

system was performed in a batch reactor with a 250 ml Teflon vessel. 10 ml of the water phase was composed of a 63 wt % aqueous  $ZnCl_2$  solution mixed with HCl and a certain amount of glucose, while the organic phase was 150 ml methylisobutylketone.

The HMF yield (mol %) and the content of catalysts was defined as below:

HMF yield (mol %):

$$y = \frac{\text{moles of HMF}}{\text{moles of glucose unit}} \times 100\%$$

Content of catalyst ( $\text{mol}_{(\text{catalyst})}/\text{mol}_{(\text{unit of substrate})}$ ):

$$x = \frac{\text{moles of catalyst}}{\text{moles of glucose unit}}$$

### 1.5 The kinetics of the conversion of glucose into HMF

On the assumption that the decomposition of glucose, formation of HMF and HMF decomposition are all first-order reactions, the reaction rates of the above three reactions can be expressed as following:

$$\gamma_{\text{glucose decomposition}} = k_g \times c_g; \quad (1)$$

$$\gamma_{\text{HMF formation}} = k \times c_g; \quad (2)$$

$$\gamma_{\text{HMF decomposition}} = k' \times c_{\text{HMF}} \quad (3)$$

where  $k_g$ ,  $k$  and  $k'$  represent rate constant of glucose conversion, rate constant of HMF formation and rate constant of HMF degradation; while  $c_g$  and  $c_{\text{HMF}}$  represent the concentrations of glucose and HMF, respectively.

Then, the reaction rates of glucose decomposition and HMF formation can be further expressed as follows:

$$dc_g/dt = -k_g c_g; \quad (4)$$

$$dc_{HMF}/dt = kc_g - k'c_{HMF} \quad (5)$$

Based on the equation (4) and equation (5), the concentration of HMF,  $c_{HMF}$ , can be expressed as following:

$$c_{HMF} = Ce^{-k't} - Ce^{(-2k-k')t} \quad (6)$$

On the condition of  $k' = 0$  and  $t \rightarrow \infty$ ,

$$c_{HMF} = k/k_g = s \quad (7)$$

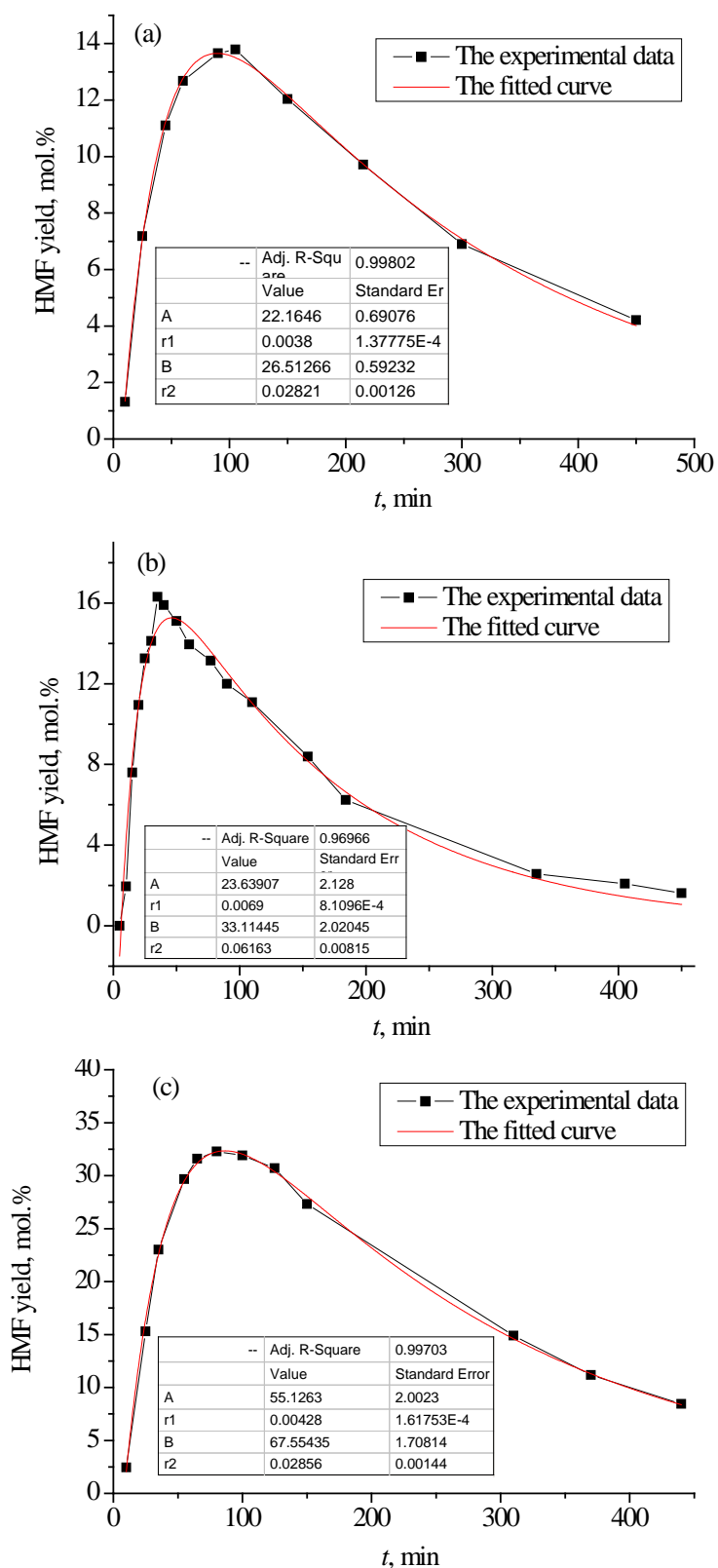
where  $s$  stands for the selectivity of HMF.

Then, the equation (6) can be expressed as following:

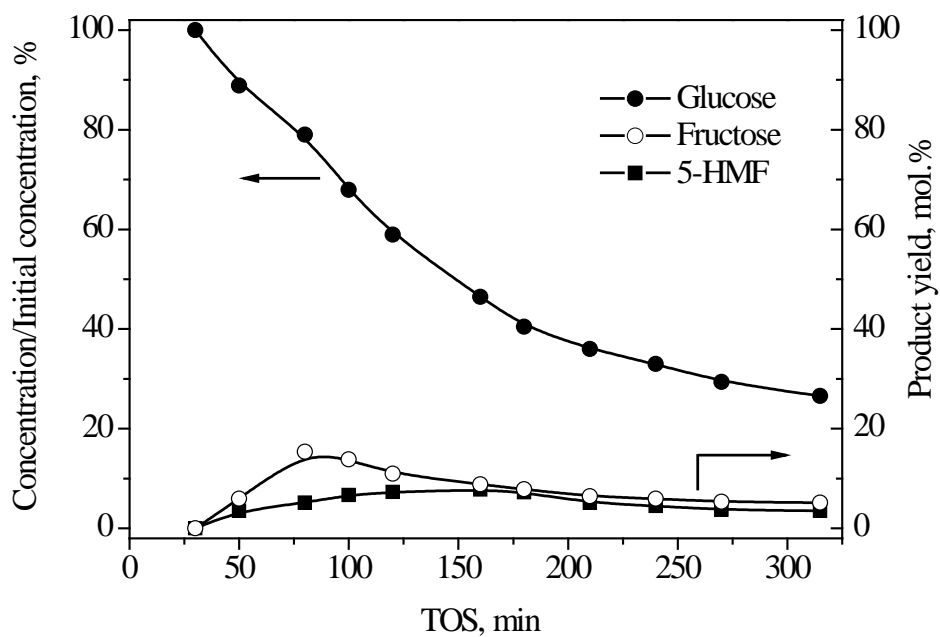
$$c_{HMF} = se^{-k't} - se^{(-2k-k')t} \quad (8)$$

The values of  $k_g$ ,  $k$  and  $k'$  can be calculated by fitting the experimental data with the equation (8).

## 2. Supporting Figures and Tables

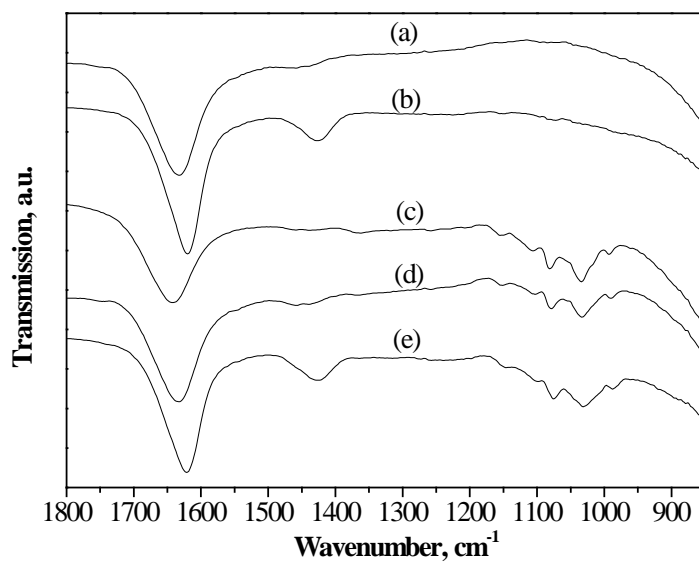


**Figure S1** The experimental and fitted curves of glucose conversion to HMF in the aqueous ZnCl<sub>2</sub> solution in the : (a) 55 wt.% ZnCl<sub>2</sub> solution, (b) 63 wt.% ZnCl<sub>2</sub> solution and (c) 63 wt.% ZnCl<sub>2</sub> solution + HCl (1:1).



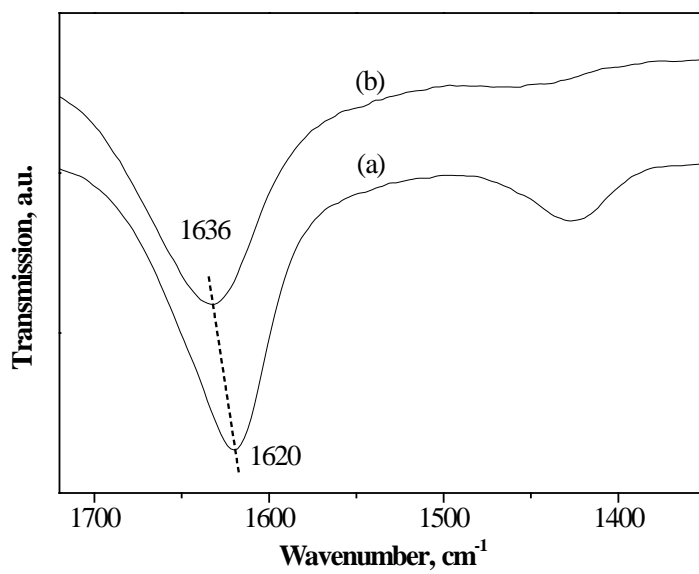
**Figure S2** Conversion of glucose to HMF in the 63 wt.% ZnCl<sub>2</sub> solution.

\* The reaction condition: 50 g of 63 wt.% ZnCl<sub>2</sub> solution, 20 g of glucose,  
120 °C, 1 atm.

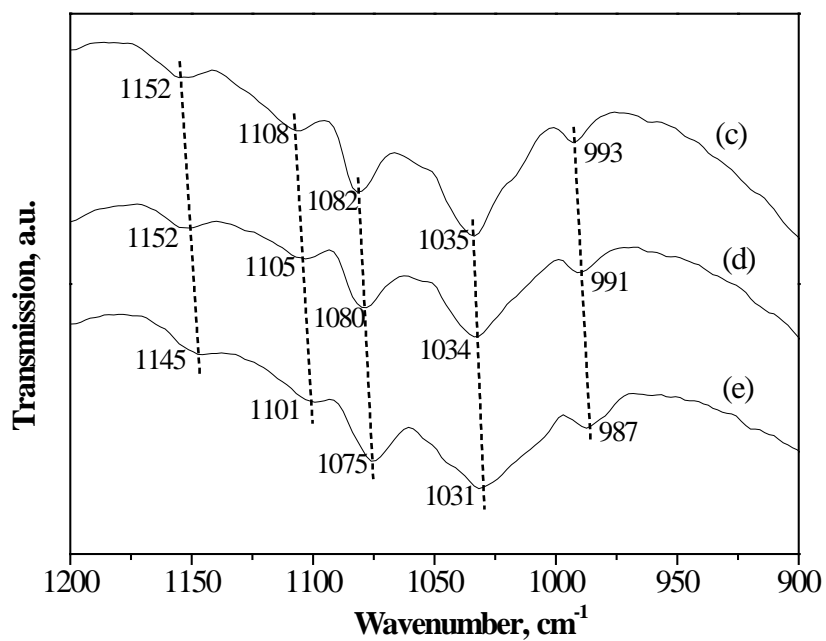


**Figure S3** IR spectra of (a) a 32 wt.% ZnCl<sub>2</sub> aqueous solution, (b) a 63 wt.% ZnCl<sub>2</sub> aqueous solution, (c) a 30 wt. % glucose aqueous solution, (d) a 32 wt. % ZnCl<sub>2</sub>-30 wt.% glucose aqueous solution, and (e) a 63 wt. % ZnCl<sub>2</sub>-30 wt.% glucose aqueous solution.

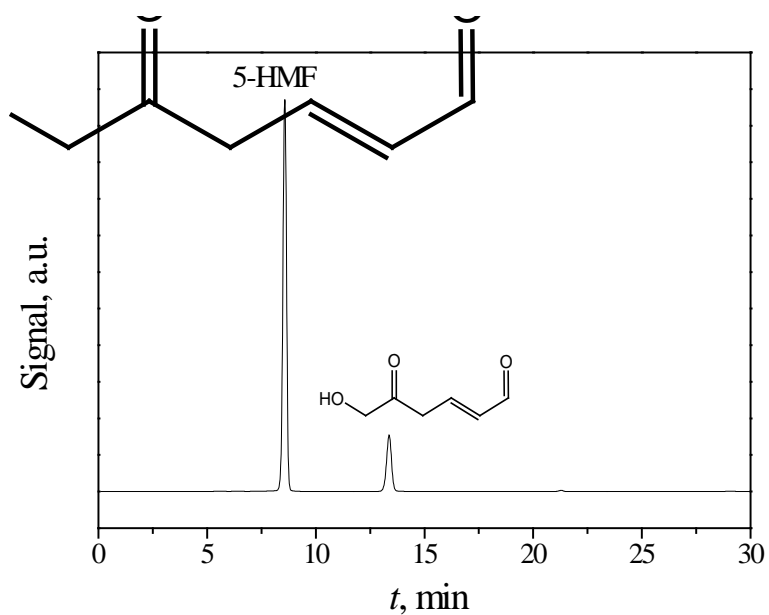




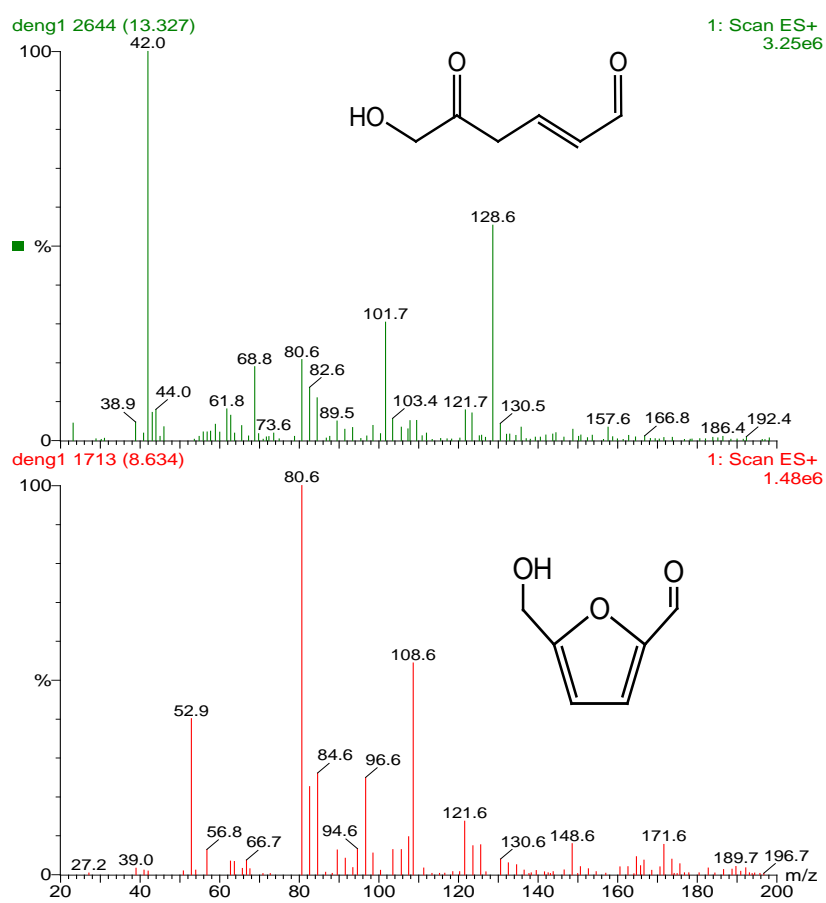
**Figure S4** IR spectra of the 1750-1350 cm<sup>-1</sup> region of (a) a 32 wt.% ZnCl<sub>2</sub> aqueous solution, and (b) a 63 wt.% ZnCl<sub>2</sub> aqueous solution.



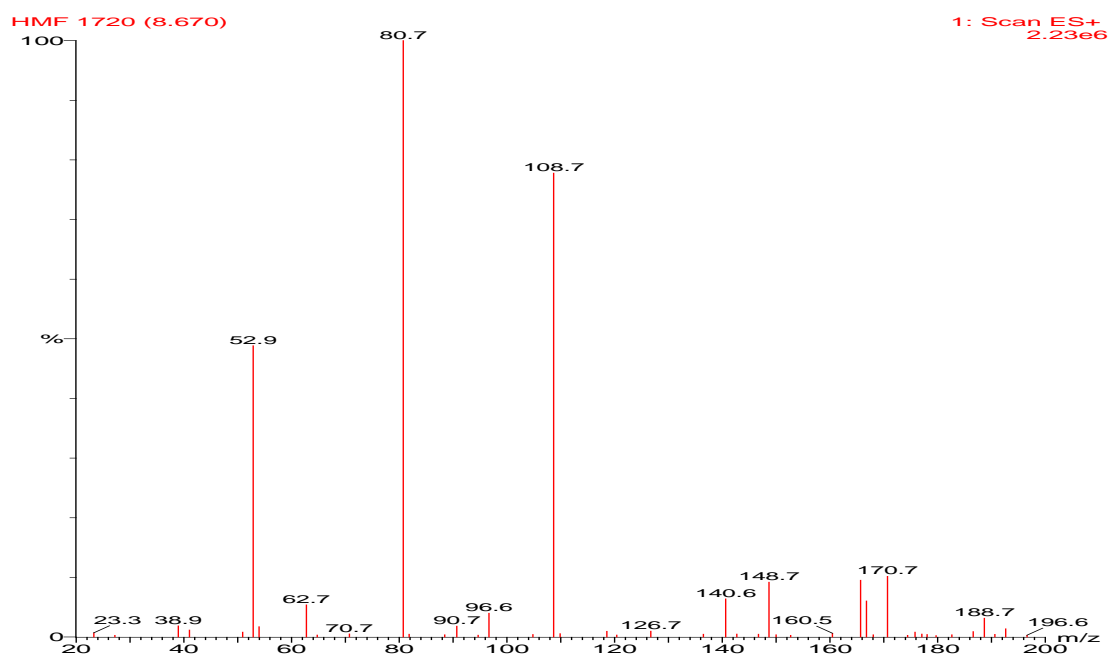
**Figure S5** IR spectra in the 1200-900 cm<sup>-1</sup> range of (c) a 30 wt. % glucose aqueous solution, (d) a 32 wt. % ZnCl<sub>2</sub>-30 wt. % glucose aqueous solution, and (e) a 63 wt.% ZnCl<sub>2</sub>-30 wt. % glucose aqueous solution.



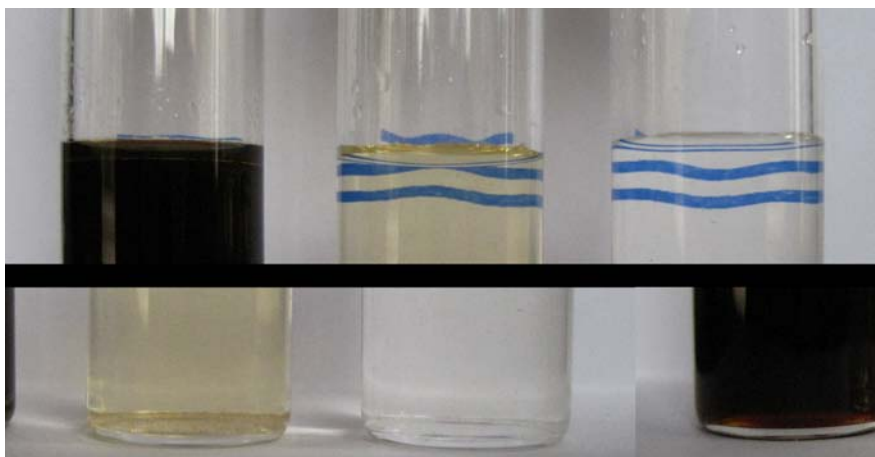
**Figure S6a** HPLC of the products in the reaction mixture.



**Figure S6b** Mass spectra of the products in the reaction mixture.

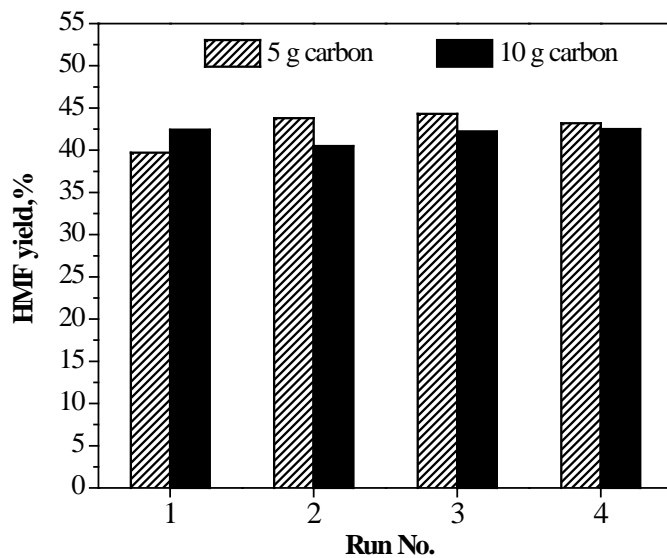


**Figure S6c** The typical Mass spectroscopy of 5-HMF.



**Figure S7** Recycling of the aqueous  $\text{ZnCl}_2$  reaction medium: left: non-recycled solution; middle: reaction solution recycled with 5 g active carbon; right: reaction solution recycled with 10 g active carbon

\* Recycling conditions: aqueous  $\text{ZnCl}_2$  solution (63 wt %): 100 g,  $T = 60$  °C.



**Figure S8** Reuse of the  $\text{ZnCl}_2$  reaction medium. Recycling conditions: aqueous  $\text{ZnCl}_2$  solution(63 wt %): 100 g, Active carbon: 5 g or 10 g,  $T = 60^\circ\text{C}$ ; reaction conditions: Glucose (15 g),  $\text{HCl}/\text{Glucose} = 1:1$  (mol:mol),  $T = 120^\circ\text{C}$ ,  $t = 2$  h.

**Table S1** The humin formation in the aqueous ZnCl<sub>2</sub> solution

Entry	Reaction condition	Humins
1	32 wt.% ZnCl <sub>2</sub> solution (100 g), glucose (1 g), 100°C	No
2	32 wt.% ZnCl <sub>2</sub> solution (100 g), HMF (1 g), 100°C	No
3	63 wt.% ZnCl <sub>2</sub> solution (100 g), glucose (1 g), 120°C	Yes
4	63 wt.% ZnCl <sub>2</sub> solution (100 g), Fructose (1 g), 120°C	Yes
5	63 wt.% ZnCl <sub>2</sub> solution (100 g), HMF (1 g), 120°C	Yes
6	63 wt.% ZnCl <sub>2</sub> solution (100 g), glucose (1 g), 80°C	Yes
7	64 wt.% ZnCl <sub>2</sub> solution (100 g), fructose (1 g), 80°C	Yes

**Table S2** The reaction time needed for the maximum HMF yield <sup>a</sup>

Substrate	Solvent wt %	Cocatalyst <sup>b</sup> mol/mol	T °C	Conv. %	HMF yield mol %	Time min
Glucose	ZnCl <sub>2</sub> , 32		98	Trace	Trace	275
	ZnCl <sub>2</sub> , 63		98	81.7	13.0	108
	ZnCl <sub>2</sub> , 55		110	94.3	13.8	105
	ZnCl <sub>2</sub> , 60		110	95.7	14.9	95
	ZnCl <sub>2</sub> , 63		120	99.7	16.1	35
	ZnCl <sub>2</sub> , 65		120	98.3	15.7	45
	ZnCl <sub>2</sub> , 63	HCl, 0.8:1	120	94.3	25.5	80
	ZnCl <sub>2</sub> , 63	HCl, 1:1	120	80.5	32.3	80
	ZnCl <sub>2</sub> , 63	HCl, 1:1	120	60.5	12.3 <sup>c</sup>	120
	ZnCl <sub>2</sub> , 63	HCl, 1.1:1	120	88.5	25.6	100
Cellulose	ZnCl <sub>2</sub> , 63		120		11.5	90
	ZnCl <sub>2</sub> , 63	HCl, 1:1	120		22.1	160
	ZnCl <sub>2</sub> , 63	HCl, 1:1	120		30.4 <sup>d</sup>	125
	ZnCl <sub>2</sub> , 63	HCl, 0.8:1	120		20.8	80
	ZnCl <sub>2</sub> , 63	HCl, 1.2:1	120		15.3	60
Fructose	ZnCl <sub>2</sub> , 63	HCl, 1:1	120	97.3	53.3	40

<sup>a</sup> Reaction system: 100 g ZnCl<sub>2</sub> aqueous solution, 2g carbohydrate;

<sup>b</sup> Cocatalyst loading is relative to moles of monosaccharide in carbohydrates; <sup>c</sup> the glucose concentration is 15 wt %; <sup>d</sup> the reaction system was treated at 70 °C for 12 h before reaction



**Table S3** The change in the volumes of ZnCl<sub>2</sub> solution

Entry	Concentration of ZnCl <sub>2</sub> solution	Temp. °C	MIBK ml	Glucose g	V <sub>water phase</sub> ml
1	32 wt.%	25	-	-	6
2		25	50	-	6
3	54 wt.%	25	-	-	8
4		25	50	-	6
5	65 wt.%	25	-	-	11.5
6		25	50	-	3.5
7		100	-	-	12
8		100	50	-	6.5
9		100	50	1	7.8
10		100	50	2	9.5
11		100	50	3	10.5