Supporting Information

Green catalytic conversion of bio-based sugars to 5-(chloromethyl) furfural in deep eutectic solvent, catalyzed by metal chlorides

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Materials and method

Materials

Fructose (99%), glucose (99%)，inulin (99%)，sucrose (99%) Choline chloride (99%), metal chlorides were purchased from Aladdin Chemical Technology Co. Ltd. (Shanghai, China). Methyl isobutyl ketone (MIBK), Gamma-valerolactone (GVL)，Acetonitrile (MeCN), Dimethyl Formamide (DMF), Dimethylsulfoxide (DMSO) were purchased from sinopharm Chemical reagent Co. Ltd. (Shanghai, China), CMF (95%) was purchased from Toronto Research Chemicals Co. Ltd. (Beijing, China), HMF (99%) was purchased from Sigma-Aldrich Chemical Technology Co. Ltd. (Shanghai, China).

Typical procedure for the conversion of bio-based sugar into 5-CMF

In a typical procedure, the synthesis of substrate into 5-CMF reacted in glass flask (100ml) with reflux device, 900 mg bio-based sugar and 5mmol metal chloride catalyst and 25mmol ChCl were introduced into flask, and 30ml MIBK was added in the reactor as a extracting solvent, the solution was then stirred at 120 °C. At the desire time, separated the extracting solvent after the reactor was cooled down to room temperature, and extracted the reaction mixture with 30ml additional extracting solvent. The organic phase containing 5-CMF & 5-HMF was analyzed by GC-MS, the solid phase was also analyzed to determine the amount of unreacted bio-based sugar. To this end, the solid phase was dissolved with deionized water and analyzed by HPLC.

GC-MS analysis

5-CMF and 5-HMF in the extracting solvent was diluted with acetonitrile (MeCN) and quantitatively analyzed by a Thermo-fisher Trace 1300 & ISQ LT GC-MS instrument with an TR-5MS column (15.0 m × 250 μm × 0.25 μm). The following programmed temperature was used in the analysis: 323 K (1 min) - 8 K/min - 423 K (1 min). The carrier gas was He with a flow rate of 1.2 mL min^{-1} and the split ratio was 1:50. The mass spectra were obtained by electron impact ionization (EI), at an electron energy of 70 eV and with a 25 μA emission current. 5-CMF and 5-HMF yield and glucose conversion were calculated as follows:

$$5-CMF\ yield\ (\%) = \frac{mole\ of\ 5-CMF\ in\ products}{starting\ mole\ of\ fructose} \times 100\%$$

$$5-HMF\ yield\ (\%) = \frac{mole\ of\ 5-HMF\ in\ products}{starting\ mole\ of\ fructose} \times 100\%$$

HP-LC analysis

The fructose conversion was analyzed using HPLC method on an Waters 2695 Separation Module equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm). The column oven temperature was 60 °C and the mobile phase was 0.005 M H_2SO_4 at a flow rate of 0.6 mL min^{-1}. After the 5-CMF preparation reaction and the separation of organic phase, the reaction mixture was dissolved in 50ml deionized water. The fructose conversion was calculated as follows:

$$Frcutose\ conversion\ (\%) = \frac{mole\ of\ fructose\ in\ reaction\ mixture}{starting\ mole\ of\ fructose} \times 100\%$$

Effect of Lewis acid strength of metal chlorides on the reaction

The Lewis acid strength of various metal chlorides were calculated according to Equation 1[1]. Z is the charge number of the atomic core, r_k is the ionic radius and the metal electronegativity is marked as X_z, as shown in Table 1. It was noted that the Lewis acid strength have a great effect on the selectivity and conversion of fructose into 5-CMF and 5-HMF. Metal chlorides with low Lewis acid strengths provided much higher 5-HMF yields than 5-CMF, while A highest 5-CMF yield of 37% was obtained in the presence of $AlCl_3 \cdot 6H_2O$ without any optimizing conditions, which had much higher Lewis acid strength. $FeCl_3 \cdot 6H_2O$ with a rather high Lewis acid strength also provided higher 5-CMF yield (28%) than 5-HMF (15%). Thus, $AlCl_3 \cdot 6H_2O$ was chosen as catalyst for further investigation.

$$Z = {}^{z}\!/_{{r_k}^2} - 2.99 \times X_z + 0.67$$

Table S1. Effect of Lewis acid strength of metal chlorides on the reaction

Catalysts	Lewis acid strength Z	Y_{CMF} (%)	Y_{HMF} (%)
$AlCl_3 \cdot 6H_2O$	2.4401	37	17
NaCl	-1.3697	0.5	48
$CrCl_3 \cdot 6H_2O$	0.9696	5	39
$FeCl_3 \cdot 6H_2O$	1.4993	28	15
$LiCl \cdot H_2O$	-1.0262	0.6	57
$ZnCl_2$	-0.6115	0	1
$MgCl_2 \cdot 6H_2O$	-0.5429	1	47
$CaCl_2 \cdot 2H_2O$	-1.3849	0.6	46
$SnCl_4 \cdot 5H_2O$	0.6156	0.9	54
$CuCl_2 \cdot 2H_2O$	-2.369	16	4.5
$MnCl_2 \cdot 4H_2O$	-0.9165	0.5	49
$NiCl_2 \cdot 6H_2O$	-2.1678	0.5	47
$CoCl_2 \cdot 6H_2O$	-1.7462	0	9

Reaction conditions: 5 mmol fructose, 5 mmol catalysts, 25 mmol ChCl, 30 ml MIBK, 110 ^{o}C, 2 h

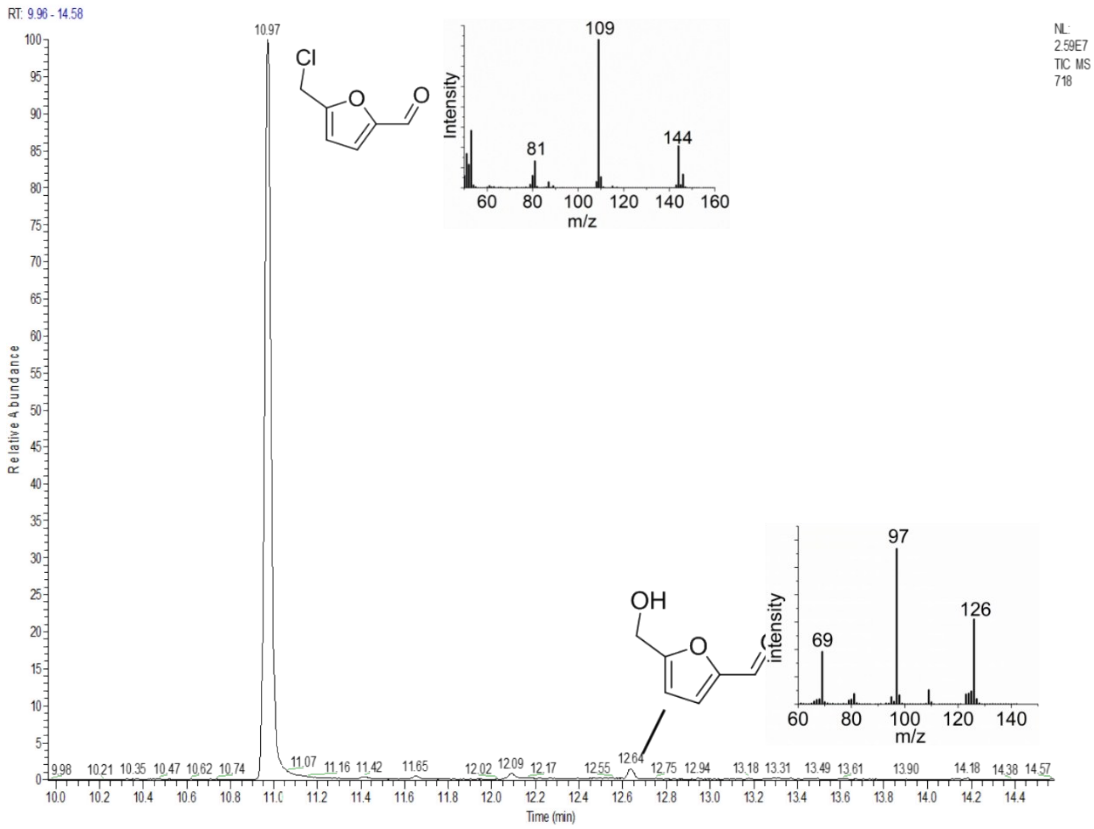

Figure S1. GC-MS graphic of the product

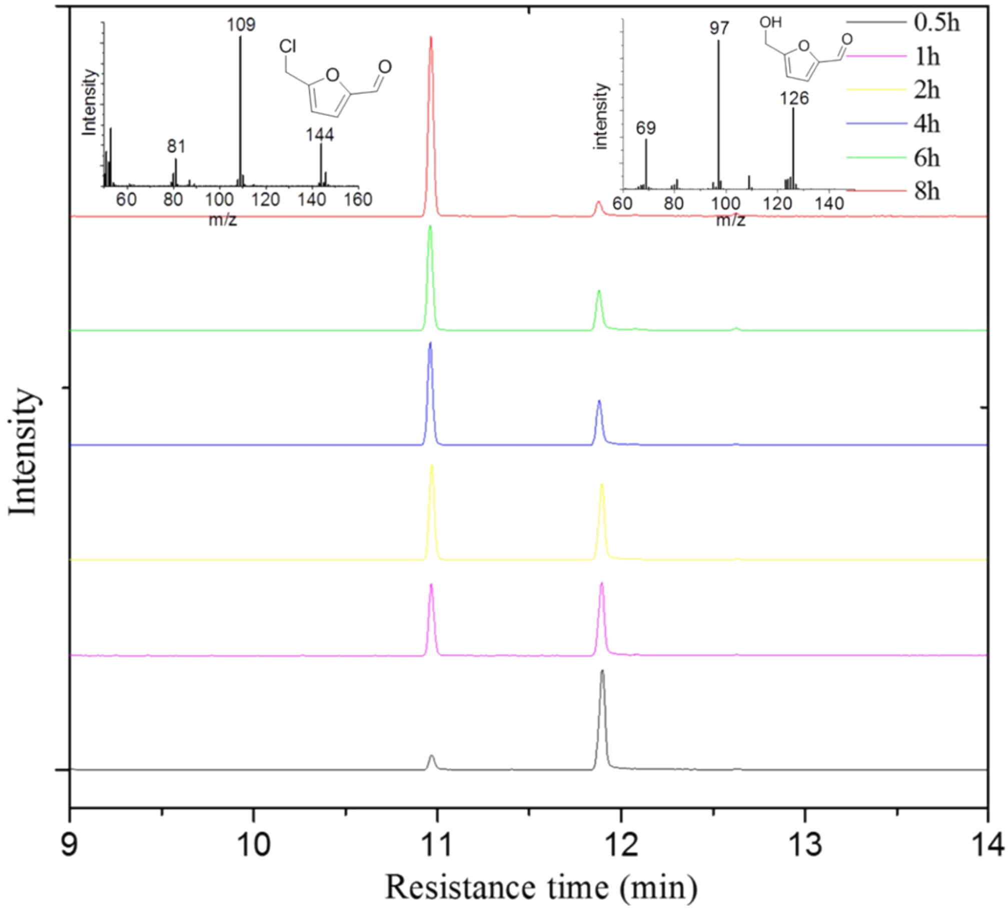

Figure S2. GC-MS spectra of the reaction time affected product distribution. Reaction condition: 5 mmol fructose, 5 mmol $AlCl_3·6H_2O$, 25 mmol ChCl, 30 ml MIBK, 90 °C.

Table S2. The effect of IL and DES in the conversion of fructose to 5-CMF and 5-HMF

Ligand part of IL & DES	Y_{CMF} (%)	Y_{HMF} (%)
[BMIM]Cl	6	4
$[BMIM]BF_4$	0	0
ChCl	50	8

Reaction conditions: 0.5 mmol fructose, 0.5 mmol $AlCl_3·6H_2O$, 3.6 g IL or ChCl, 30 ml MIBK, 120 °C, 5 h

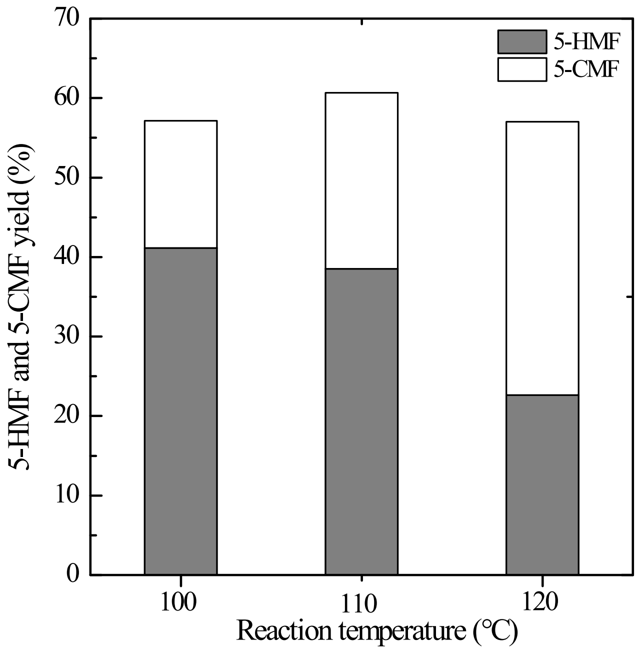

Figure S3. Conversion of frutose into 5-CMF & 5-HMF with continuous solvent extraction. Reaction conditions: 5 mmol fructose,5 mmol $AlCl_3{\cdot}6H_2O$, 25 mmol ChCl, 5h, 30 ml * 3 times MIBK extraction in 1.5 h, 3 h, 5 h.

Table S3. Effects of DES composition on the conversion of 5-HMF to 5-CMF

Entry	Raw material	$AlCl_3{\cdot}6H_2O$	ChCl	water	HCl	$C_{5\text{-HMF}}$ [a] (%)	Y_{CMF} (%)
1	5-HMF	√		√		34	5
2	5-HMF	√				19	2
3	5-HMF		√			15	0
4	5-HMF		√	√		16	0
5	5-HMF	√	√			100	82
6	5-HMF	√	√	√		100	86
7	5-HMF				√	100	85

Reaction conditions: mole ratio of 5-HMF, $AlCl_3{\cdot}6H_2O$, ChCl, water=1:1:5:3. 120 °C, 5h, MIBK 30 ml, HCl 0.5 ml (37 wt%).

Table S4. The verification tests of the conversion from 5-HMF to 5-CMF with two steps

entry	Step 1						Step 2		
	Raw material	$AlCl_3 \cdot 6H_2O$	ChCl	Water	$C_{5\text{-HMF}}$ (%)	Y_{CMF} (%)	Addition	$C_{5\text{-HMF}}$ (%)	Y_{CMF} (%)
1	HMF		√	√	7	0	$AlCl_3 \cdot 6H_2O$	76	68
2	HMF	√		√	14	5	ChCl	86	79

Reaction conditions: mole ratio of substrate, $AlCl_3 \cdot 6H_2O$, ChCl, water=1:1:5:3. 120 °C, Step 1: reaction time 2.5 h, Step 2: reaction time 2.5 h, MIBK 30 ml.

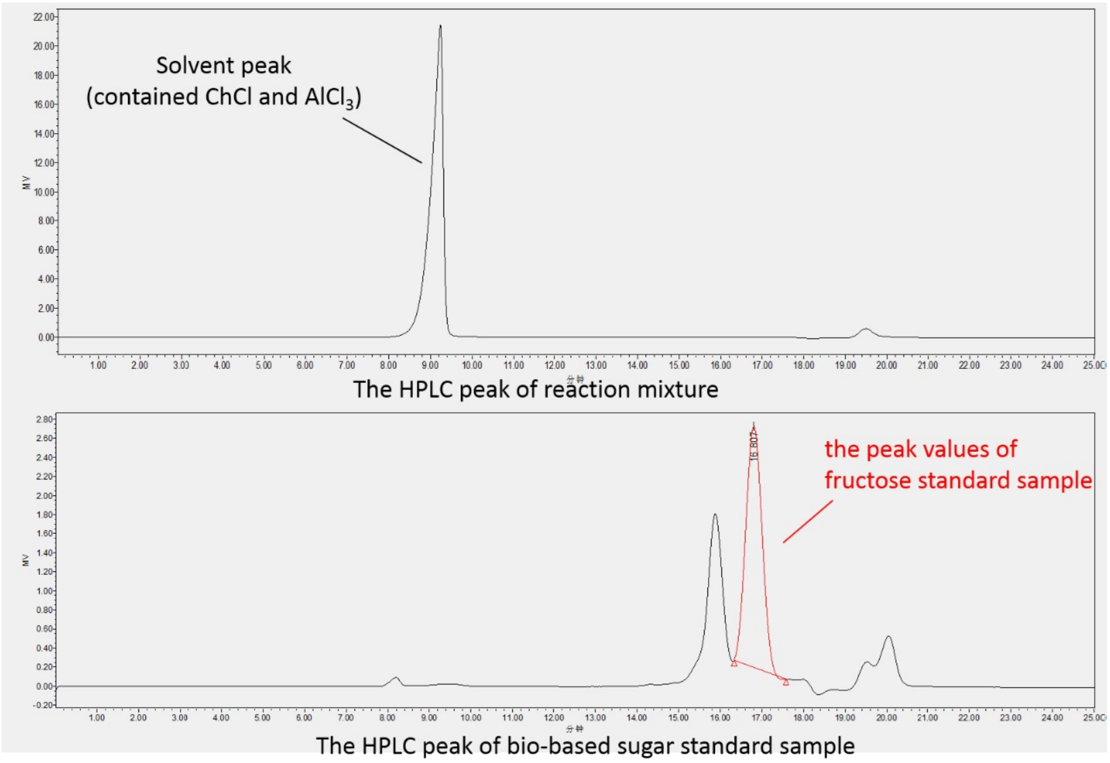

Figure S4. HPLC analysis graphic of the reaction mixture

Notes and references

1. P. Panagiotopoulou, N. Martin and D. G. Vlachos, *ChemSusChem*, 2015, 8(12), 2046–2054.