Supplementary Material (ESI) for Green Chemistry

Supporting Information

Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid $SnCl_4$ in ionic liquid

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1. Experimetal

Materials: D-Glucose anhydrous, sucrose and Cellobiose were supplied by Sinopharm Chemical Reagent Co., Ltd.. D-Fructose (99%), Inulin was purchased from Alfa Aesar. Starch was purchased from Beijing Yili Fine Chemicals Co., Ltd.. $SnCl_4{\cdot}5H_2O$ was provided by Beijing ShuangHuan WeiYe Reagent Co., Ltd.. 5-Hydroxymethylfurfural (99%) was purchased from Aldrich, and the other starting materials (A. R. grade) were purchased from Beijing Chemical Reagents Company and used without further purification. The ionic liquids: [BMim]Cl, [BMim]PF_6, [BMim]Tf_2N, [BMim]TFA, [BMim]Trif, [BMim]Sacc. [BMim]BF_4, [Bpyr]BF_4 and [EMim]BF_4 were synthesized by the procedures reported.[S1, S2]

Instruments and analysis methods: ^{1}H NMR spectra at 80 ^{o}C and 100 ^{o}C were collected on a Brucker spectrometer at 300 MHz, and ^{1}H NMR spectra at room temperature were collected on a Brucker spectrometer at 400 MHz. The amount of HMF was analyzed by HPLC with Supelcosil LC-18 5μm column at 25 ^{o}C, Shimadzu LC-20AT pump, Sama UV-Vis LC-830 detector at 282.0 nm, methanol/water solution (50/50 V/V) was used as flowing phase at 0.8 mL/min. The amounts of sugars were also analyzed by HPLC with Hypersil NH2 5μm column at 25 ^{o}C, Shimadzu LC-20AT pump, Shimadzu RID-10A detectors at 40 ^{o}C, acetonitrile/water solution (75/25 V/V) was used as flowing phase at 0.8 mL/min. All of them were calculated by

using an external standard. HMF was characterized by ^{1}H NMR spectra and GC/MS (GC: Agilent technologies 6890N; MS: Agilent technologies 5973 inert MS Detector)

5-Hydroxymethylfurfural (HMF): M.S.: m/z (% of max intensity) 50 (8), 69 (32), 81 (7), 97 (100), 109 (11), 126 (75); ^{1}H NMR (400M, $CDCl_3$) δ (ppm): 4.75 (s, 2 H), 6.54 (d, *J*=3.4 Hz, 1 H), 7.24 (d, *J*=3.4 Hz, 1 H), 9.62 (s, 1 H).

Procedures of conversion of glucose into HMF in dimethylsulfoxide (DMSO): Glucose (100.0 mg, 0.56 mmol) and known amount of metal chloride (10 mol % based on glucose) were dissolved in DMSO (1 g). The mixture was stirred at 80 ^{o}C for 3 h. Then the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields and conversions. Each reaction was repeated at least two times.

Procedures of conversion of glucose into HMF in Ionic Liquids (ILs): In a typical experiment, known amounts of glucose and $SnCl_4{\cdot}5H_2O$ were dissolved in IL. The mixture was stirred at a fixed temperature for desired time. Then the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields and conversions. Each reaction was repeated at least two times.

Procedures of conversion of fructose, Sucrose, and cellobiose into HMF in [EMim]BF$_4$ In a experiment, suitable amounts of reactant and $SnCl_4{\cdot}5H_2O$ were dissolved in IL (1 g). The mixture was stirred at 100 ^{o}C for 3 h. Then the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields and conversions. Each reaction was repeated at least two times.

Procedures of conversion of inulin and starch into HMF in [EMim]BF$_4$ Desired amounts of reactant and $SnCl_4{\cdot}5H_2O$ were added into IL (1 g). The reaction mixture was stirred at 100 ^{o}C for a suitable time. Then the mixture was cooled to room temperature immediately. Ethanol (5 ml) was added into the mixture. Some solid was precipitated from the solution. The mixture was filtered and the filtrate and solid were collected separately. The filtrate was analyzed by HPLC to obtain the HMF

yield. The solid was weighted to calculate the conversion of the reactant. Each reaction was repeated at least two times.

Reuse of $SnCl_4$ and [EMim]BF_4: Glucose (200.0 mg, 1.12 mmol) and $SnCl_4{\cdot}5H_2O$ (39.0 mg, 0.112 mmol) were dissolved in IL (1 g). The mixture was stirred at 100 ^oC for 3 h. Then the mixture was cooled to room temperature immediately. Ethyl acetate (2 mL×4) was used to extract HMF. The combined ethyl acetate phase was analyzed by HPLC. Then the IL phase with $SnCl_4$ was used directly for the next run, and the reaction procedures were the same as that described above.

2. Results

Table S1. The results of conversion of glucose to HMF in DMSO: DMSO (1 g), glucose (100.0 mg, 0.56 mmol), catalyst (10 mol % based on glucose), 80 ^{o}C, 3 h.

Entry	Catalyst	Yield (%)	Conversion (%)	Selectivity (%)
1	NaCl	0	9.4	0
2	KCl	0	13.8	0
3	$MgCl_2 \cdot 6H_2O$	0	11.2	0
4	$CaCl_2$	0	7.1	0
5	$SrCl_2 \cdot 6H_2O$	0	1.0	0
6	$BaCl_2 \cdot 2H_2O$	0	15.5	0
7	$CrCl_3 \cdot 6H_2O$	1.5	25.0	6.2
8	$MnCl_4 \cdot 4H_2O$	0	5.2	0
9	$FeCl_3 \cdot 6H_2O$	0	45.0	0
10	$FeCl_2 \cdot 4H_2O$	0	29.0	0
11	$CoCl_2 \cdot 6H_2O$	0	8.5	0
12	$NiCl_2 \cdot 6H_2O$	0	7.8	0
13	$CuCl_2$	0	13.8	0
14	$ZnCl_2$	0	2.1	0
15	$RuCl_3 \cdot 3H_2O$	0	44.2	0
16	$RhCl_3 \cdot 3H_2O$	0	27.6	0
17	$PdCl_2$	0	28.3	0
18	$CdCl_2 \cdot 2.5H_2O$	0	7.1	0
19	$AlCl_3 \cdot 6H_2O$	3.9	27.1	14.5
20	$InCl_3 \cdot 4H_2O$	0	2.1	0
21	$LaCl_3 \cdot nH_2O$	0	35.8	0
22	$SnCl_4 \cdot 5H_2O$	10.8	33.0	32.7

Table S2. The results of conversion of glucose into HMF in [EMim]BF_4 (1 g).

Entry	Glucose (mg)	Catalyst (mol %)	Temperature (^oC)	Time (h)	Yield (%)	Conversion (%)	Selectivity (%)
1	100	10	80	3	18.4	50.6	36.4
2	100	10	90	3	41.5	80.7	51.4
3	100	10	100	3	53.0	96.5	54.9
4	100	10	110	3	51.7	96.7	53.5
5	100	10	100	2	42.3	98.5	42.9
6	100	10	100	4	51.6	98.5	52.4
7	100	10	100	5	52.4	100	52.4
8	100	0	100	3	0	18.9	0
9	100	5	100	3	43.8	95.1	46.1
10	100	15	100	3	60.0	99.8	60.2
11	100	20	100	3	59.9	100	59.9
12	100	25	100	3	60.8	100	60.8
13	50	10	100	3	46.7	92.5	50.5
14	150	10	100	3	62.3	99.5	62.6
15	200	10	100	3	62.1	98.1	63.3
16	250	10	100	3	60.5	99.0	61.1
17	300	10	100	3	61.3	99.1	61.9
18	350	10	100	3	56.6	99.0	57.1

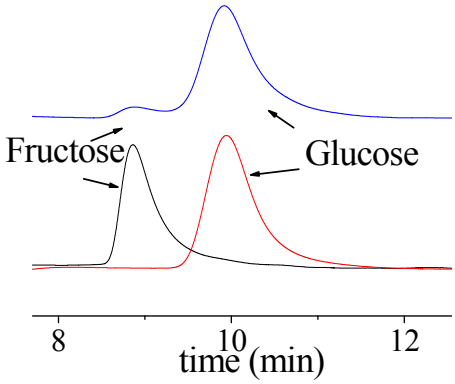

Fig. S1. HPLC chromatograms of fructose(black), glucose(red), and the reaction mixture (blue) in [EMim]BF_4 catalyzed by $SnCl_4$ at 80 ^oC (other conditions were the same as that in Fig. 1a).

References

(S1). Li, W. J., Zhang, Z. F., Han, B. X., Hu, S. Q. & Yang, G. Y. *J. Phys. Chem. B* **111**, 6452-6456 (2007).

(S2). Tao, G. H., Zou, M.; Wang, X. H., Chen, Z. Y., Evans, D. G. & Kou, Y. *Aust. J. Chem.* **58,** 327-331 (2005).