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Electronic Supplementary Information for

Effect of cations and anions of ionic liquids on the production of 5-hydroxymethylfurfural from fructose

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1 Experimental Section

1.1 Material

Fructose was purchased from Beijing Solarbio Science & Technology Co., Ltd (≥99% purity). HMF was purchased from J & K Scientific Ltd (≥98% purity). trifluoromethanesulfonic acid (TfOH) (99% purity) was purchased from Research Institute of China Shipbuilding Industry Corporation. $CuCl_2 \cdot 2H_2O$ (98% purity) was purchased from Xilong Chemical Co., and H_2SO_4 (98% purity) and $FeCl_3$ (99% purity) were purchased from China National Medicines Co., Ltd.

All ionic liquids (ILs) were commercially available (purity>99%) and water was removed before using (water content≤5000 ppm), in which [Mim]Cl, [Emim]Cl,

[Hmim]Cl, [Omim]Cl, [Dmim]Cl were purchased from Lanzhou Institute of Chemical Physics, CAS. [Emim]HSO_4, [Hmim]HSO_4 and [Omim]HSO_4 were purchased from Shanghai Chengjie Chemical Co., Ltd. [Bmim]Cl, [Bmim]BF_4, [Bmim]PF_6 were purchase from Henan Lihua Pharmaceutical Co., Ltd. [Bmim]HSO_4, [Bmim]OTf, [Bmim]SCN were purchase from Beijing Zhongke Anyin Technology Co., Ltd. [Bdmim]Cl was supplied by Prof. Brennecke, University of Notre Dame. The structures of various imidazolium ionic liquids were shown in Fig. S2. Waters of all ionic liquids were removed by vacuum drying.

1.2 Reaction

Dehydration of fructose to produce HMF was conducted in a 100 mL glass reactor equipped with a magnetic stirrer and automatic temperature controller. Each kind of ionic liquid was added to the reactor with or without TfOH catalyst, and then fructose was fully dissolved in all ionic liquids by visual observation when stirring and mixing.

Reactions were performed at 80-120 ^{o}C in an oil batch. Concentration of catalyst，fructose and ionic liquids were pre-determined. The reactions were implemented at different reaction times in response to demand (times ranging from 5 min to 240 min). When reaction was over, the reactor was cooled to room temperature immediately and sample was taken for further analysis. To ensure the reliability and repeatability of experiment, each reaction was repeated at least three times and the average value was reported. HMF was completely extracted by continuous operation with ethyl acetate. The extraction conditions are 50 ml ethyl acetate, 0.1 g of HMF with 5 g of ILs for 5h. When the HMF was separated from the reaction system, remained ILs and TfOH were used again in next reaction entry. After 5 cycles, a decrease in HMF

yields was observed.

1.3 Analysis

The water contents in ionic liquids were tested by Intelligent Karl Fischer Coulometric Titrator C20X. HMF yields were tested by a Waters ACQUITY UPLC (column: BEH C-18, 2.1×100μm, 1.7μm at 40 ^{o}C, Waters L10UPB pump, Waters A11TUV UV-vis detector at 284 nm, acetonitrile/water (7/93 V/V) as flowing phase at 0.2 ml/min).

Fructose conversions were tested by an Agilent HPLC equipment with a Hypersil NH_2 5μm column at 40 ^{o}C, Agilent G1311A Quatpump, Schambeck SFD GmbH RI 2000 refractive index detector at 40 ^{o}C, and acetonitrile/water (50/50 V/V) as flowing phase at 1.0 ml/min. Each sample was diluted with ultra pure water and filtrated before analysis.

1.4 Simulation method

All molecular dynamics simulations were carried out using the parallel MDynaMix 5.2 package. The simulated system includes 128 ion pairs of IL ([Emim]Cl, [Bmim]Cl, [Hmim]Cl, [Omim]Cl and [Bmim]OTf) and 5 fructose molecules. The mole fraction of fructose is 0.75%. The initial configuration was prepared at a very low density in a cubic box, followed by a conjugate gradient energy minimization within 1000 steps. Due to the slow dynamics of the mixture system, the system was heated to 227 ^{o}C in NpT ensemble for about 500000 steps to overcome the possible energetic trapping. Then, the system was cooled to the target temperature at 120 ^{o}C, and followed by 2 ns equilibrium NpT simulation. Another 2 ns NpT run was performed to obtain the trajectories files.

The atom coordinates were stored every 20 fs for postanalysis. The double

time-step algorithm was adopted, and all simulations were performed in a time step of 2 fs. Periodic boundary conditions were employed in three dimensions. The temperature and pressure were controlled by a Nose Hoover thermostat and barostat, with update frequencies of 0.03 and 0.7 ps, respectively. Ewald summation method 37 was used to treat the long-range electrostatic interaction, in which the long-range parts were cut off at 13 Å. The neighbor lists were updated every 10 steps.

2. Supporting Figures

Table S1 The molecular interaction energy between ILs and fructose [a]

ILs	E_{inter} [b](kJ/g)
[Bmim]Cl	-2.2
[Bmim]OTf	-1.1

[a] *Simulation system*: 128 ion pairs of ionic liquid, 5 fructose moleculars, the mole fraction of fructose is 0.75%. [b] E_{inter}: the interaction energy of ILs with fructose.

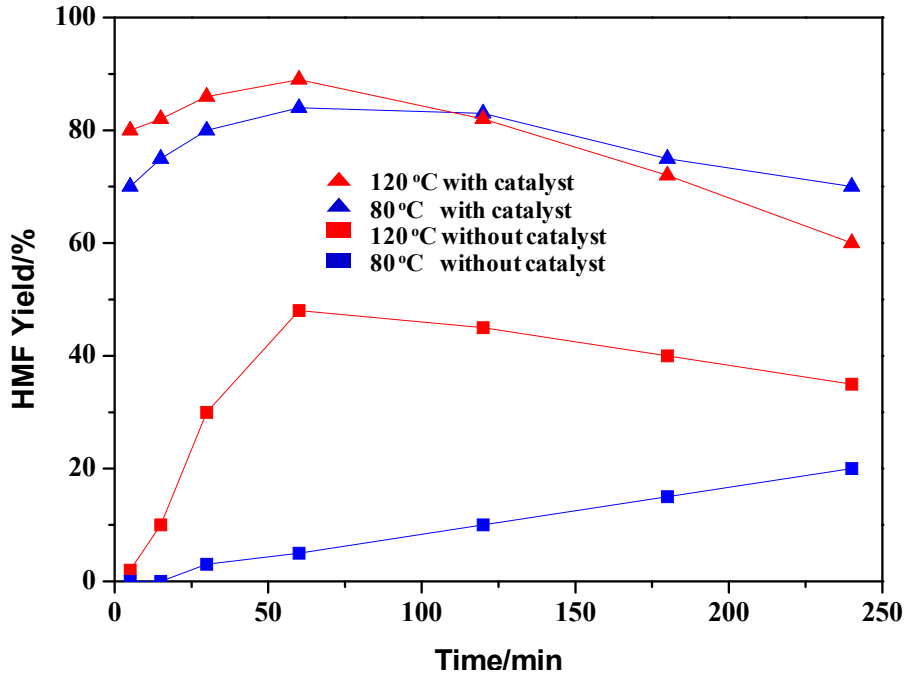

Fig. S1 Effects of reaction time and temperature on fructose conversion and HMF yield. *Reaction condition*: 0.15 g fructose, 0.1 g TfOH catalyst, 5 g [Bmim]Cl and 120 °C for 60 min.

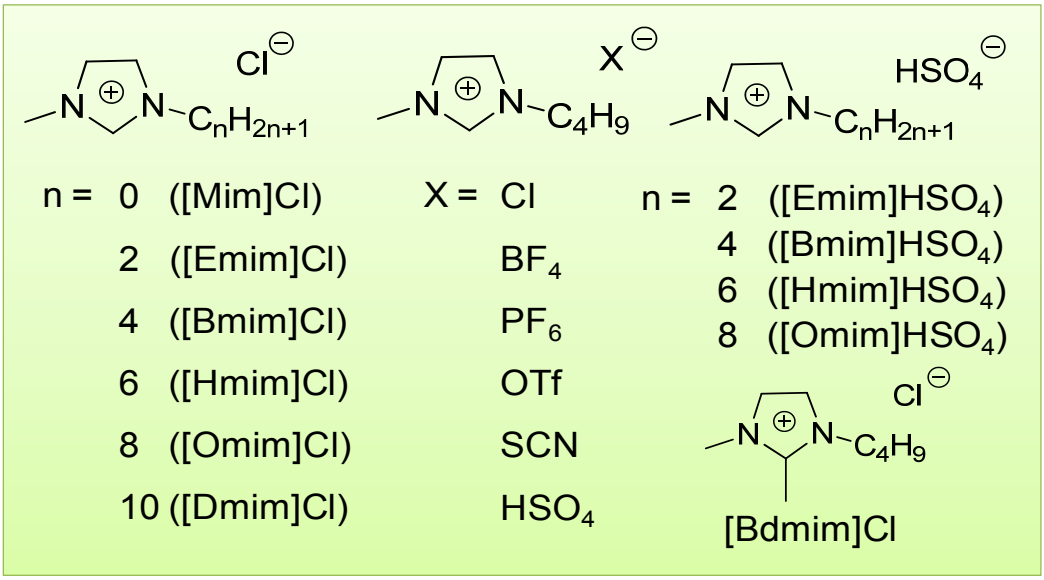

Fig. S2 The structures of ionic liquids used in this study for fructose conversion.

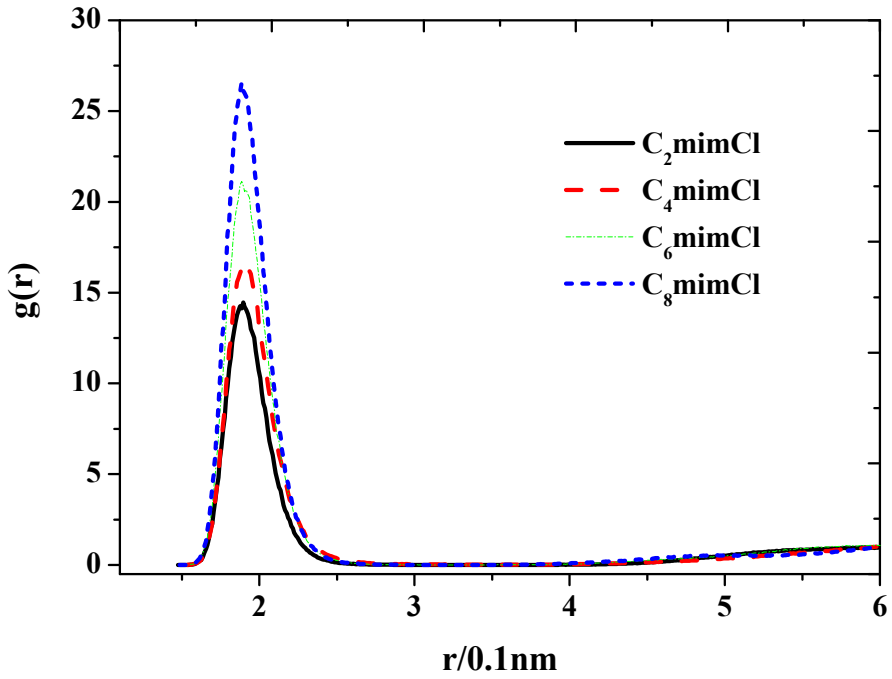

Fig. S3 The radial distributions of Cl- for IL with different alkyl chain around H of -OH on fructose.

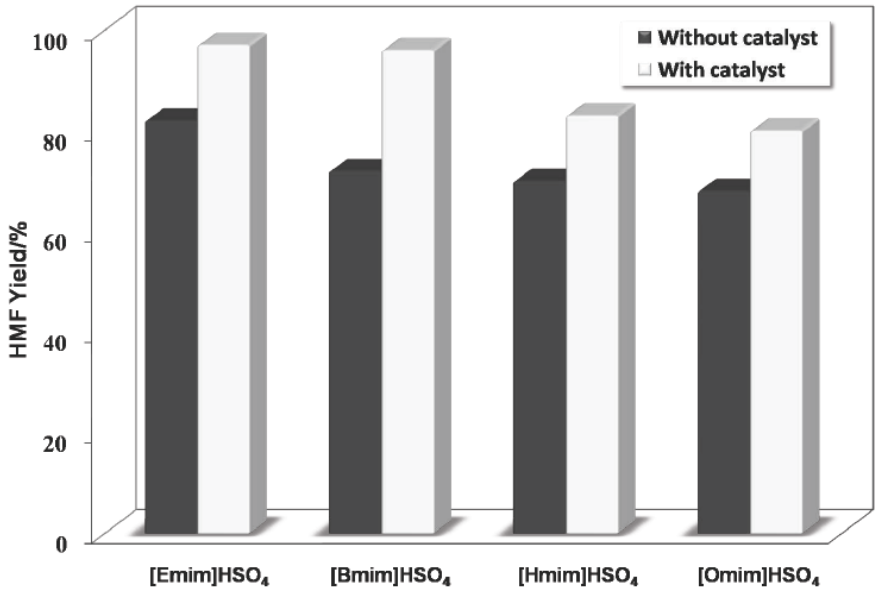

Fig. S4 Yields of HMF from fructose in HSO_4^- anions of ILs with different alkyl chains. *Reaction condition*: 0.15 g fructose, 0.1 g catalyst, 5g ionic liquids and 120 ^oC for 60 min.