

Supplementary Materials

Direct Catalytic Conversion of Glucose and Cellulose

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Materials and Methods

Reagents and Materials

N-ethyl bromide and 1-methylimidazole (>99%), SnCl₄, TiCl₄, CrCl₂, CrCl₃, benzenesulfonic acid, leucine, tyrosine, tryptophan, proline, H₂SO₄, chlorosulfonic acid, cellulose, cellobiose, sucrose, lactose, maltose, glucose, fructose, galactose et al. were all obtained with AR degree from Sigma-Aldrich. The 5-HMF used as the standard sample was purchased from Sigma-Aldrich.

Anhydrous 1-methyl-3-ethyl imidazolium bromide ([EMIM]Br) was synthesized from n-ethyl bromide and 1-methylimidazole at 298 K for 24 h. The resulting solid was purified by acetonitrile and ethyl acetate to wipe off the residual n- ethyl chloride and 1-methylimidazole, and the purified [EMIM]Br was dried in vacuum drying oven at 343 K for 24 h. Other ILs was synthesized by similar methods.

Sulfonated poly(thiophenylene) preparation

PPS was synthesized in a stainless steel 5 L autoclave. The autoclave was equipped with a variable speed mechanical stirrer, external heating chamber, cooling coils, N₂ inlet and outlet. After 1, 4-dichlorobenzene, Na₂S, NMP and Na₃PO₄ were loaded into the reactor, the air in the autoclave was flushed out using N₂. The autoclave was heated to its target temperature and maintained at this value for the required time, and the stirring speed was maintained at 300 r/min. When the reaction was finished, the autoclave was cooled with tap water, and PPS was washed by NMP, water and ethanol respectively.

The PPS molecular weight was characterized using HTGPC (PL-GPC220) at Huatong Sichuan Research Center in China. Samples were injected in slurry form at ambient temperature and re-dissolved by an in-line pre-column heater at 523 K. A viscometer consisting of a capillary tube with inlet and outlet taps connected to a sensitive differential pressure transducer was used as the sole detector, with deflections converted to a concentration using the column calibration. The columns and viscometer were operated at 483 K, and 1-chloronaphthalene was used as mobile phase.

Sulfonation of PPS ($M_w 2.69 \times 10^4 \text{ g mol}^{-1}$) was performed by the following procedure. PPS was dissolved in 10 mL of 10% $\text{SO}_3\text{-H}_2\text{SO}_4$. The suspension was heated to 353 K, and stirred for 3 h under a dry nitrogen atmosphere. After the reaction, the mixture was poured into 300 mL of distilled water to precipitate a white powder. The powder was dried under reduced pressure.

Characterization of SPPS sulfonation degree

Titration Procedure: The IEC (Ion-Exchange Capacity) value for each SPPS was determined through the back-titration method. Sulfonated PPS in acid (H^+) form was dried overnight at 100 °C under vacuum, weighed, and then immersed in saturated NaCl for 24 h. The amount of H^+ ion released from the samples was determined by titration with 0.01 M NaOH using phenolphthalein as an indicator. The IEC value of the SPPS was calculated with the following equation.

$$IEC = \frac{CxV}{M}$$

Where C and V are the concentration and volume of NaOH, respectively, and M is the weight of SPPS.

XPS Procedure: XPS spectra were acquired using a Kratos Axis Ultra spectrometer, equipped with a monochromatic Al KR source ($h\nu = 1486.6$ eV), operated at 225 W (15 mA, 15 kV) and a base pressure of 1×10^9 Torr. Samples were degassed overnight at 1×10^8 Torr prior to analysis. Photoelectrons were counted with an 8-channel hemispherical detector. Photoelectron pass energies were set at 160 eV for survey spectra and 40 eV for high resolution spectra. Survey spectra are the average of two sweeps from 600 to 4 eV, with a 0.5 eV step size and a 100 ms dwell time at each step. High-resolution S 2p spectra are the average of five sweeps, with a 0.1 eV step size and an 800 ms dwell time. Spectra were processed and deconvoluted using Casa XPS version. A background subtraction was performed using the Shirley method. Binding energies were calibrated to extrinsic/adventitious carbon at 284.8 eV. The Marquardt root-mean-squares method was used to fit components in the high-resolution spectra.

FT-IR spectrum was obtained on a Nicolet Nexus 470 FT-IR analyzer using the KBr method. Reaction products were analyzed by LC-MS (ThermoFinnigan LCQ Advantage) and GC-MS (HP5972) (capillary column: 30m SE-30, 0.25mm ID, and 0.25 μ m film thickness) to identify products and polycarbonate precursors.

5-HMF yield characterization

All reaction products were analyzed using a high performance liquid chromatograph (Waters1525 equipped with UV and a 996 photodiode array detector) and quantified with 1-

chloronaphthalene as an interior standard (or calibration curves generated from commercially available standards). Following a typical reaction, the product mixture was diluted with a known mass of CH₃OH, centrifuged to sediment insoluble products, and 1-chloronaphthalene was added into the product solution. The concentrations of products were calculated from HPLC-peak integrations and used a 1-chloronaphthalene interior standard to calculate molar yields.

5-HMF and other products were analyzed by reversed-phase chromatography on a Varian Microsorb-MV 100-5 C18 column (250×4.6 mm, 93:7 water/acetonitrile, 1 mL/min, 308 K).

General procedure for the conversion of carbohydrates to 5-HMF

The catalytic experiments were performed in a 20 ml flask. In a typical experiment, 0.9 mg glucose and 10 mass% of various catalysts with respect to glucose were added into 5 ml solvent. After it had been purged with nitrogen, the reaction mixture was heated in an oil-bath at elevated temperature and stirred at 500 rad/min. After the desired reaction time elapsed, the reaction mixture was cooled to room temperature immediately.

Computational methods

All structures were optimized at the B3LYP/6-31+G(d,p) level of theory using the Gaussian 09 program (revision D.01).^[1] Dispersion-corrected B3LYP optimisations incorporating Grimme's D3 correction with Becke-Johnson damping (keyword empiricaldispersion=gd3bj) were carried out on the geometry optimizations. We decided to use water as our model solvent, which is easier to introduce in the form of discrete molecules,

moreover, because of its high polarity (dielectric constant, 78) will provide a stronger solvation effect than ionic liquid. Water solvation effects will give an upper limit to the effect of a conventional solvent the reaction rate. Water solvation effects are often introduced in a satisfactory and computationally economic way through continuum models like Polarized-Continuum Model (PCM).^[2,3] Herein, Continuum calculations in water were performed for the barrier of reaction using PCM method. We followed the usual approach of introducing solvation effects through single point calculations on the structures of the minima and transition states obtained in the gas phase. The structures of the reactants, intermediates, transition states, and products were fully optimized without any symmetry restriction. Only the favoured conformations are presented and these are in good agreement with previous computational studies.^[4,5,6] Transition states were identified by having one negative frequency.

Supplemental Figures

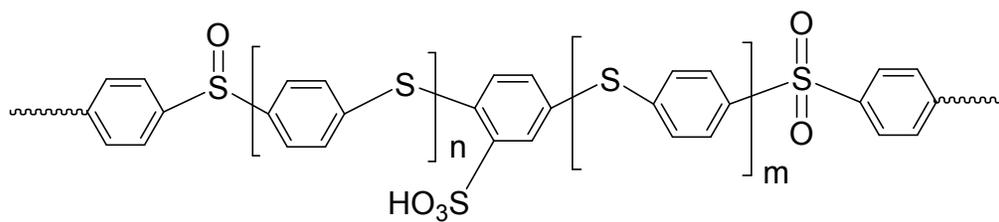


Figure S1. The small sketch on the polymeric structure of SPPS

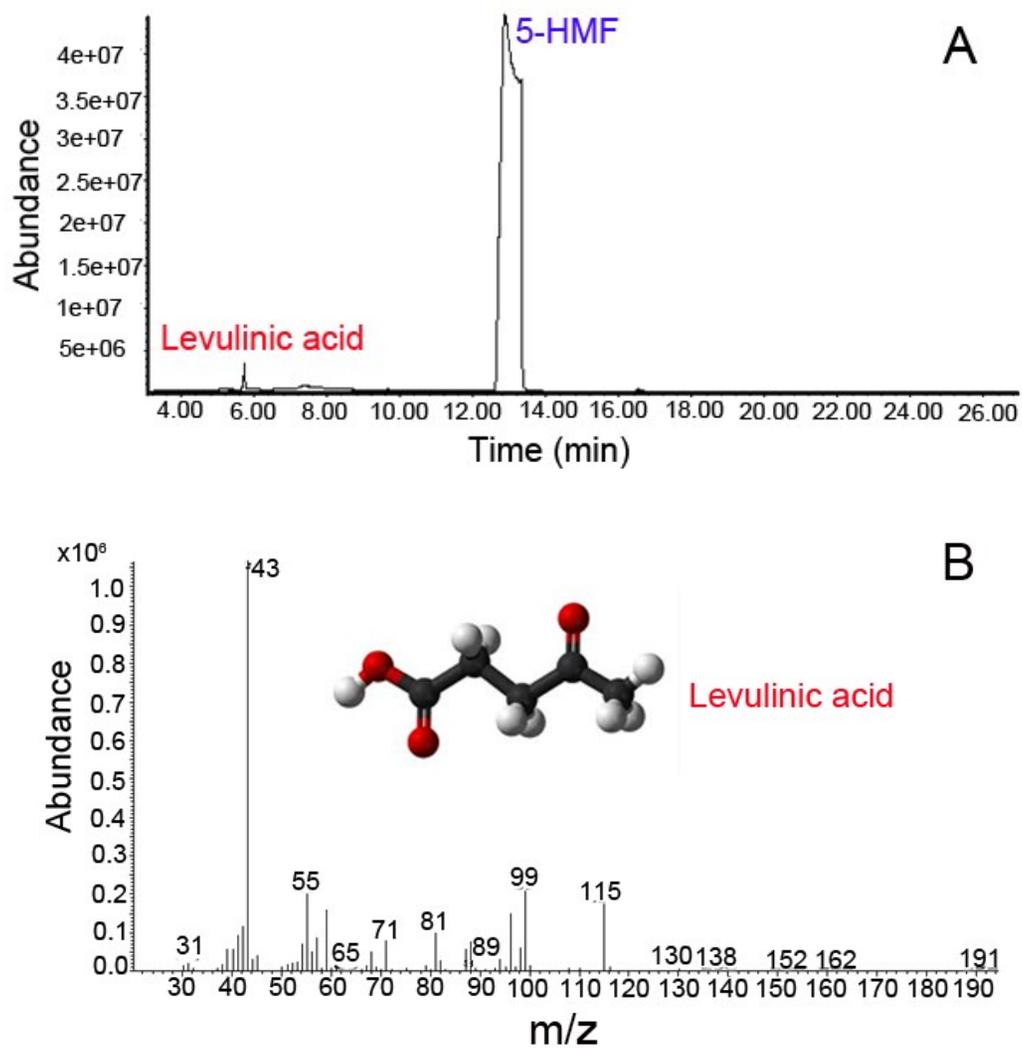


Figure S2. The by-products from glucose in [EMIM]Br were confirmed by GC-MS (Condition: 0.18 g of the SPPS catalyst with 10 mol% sulfonation degree, solvent 20 ml, 413 K for 12 h, glucose 1.8 g reaction mixture was diluted with CH₃OH), trace levulinic acid (LA) was detected, the most product was 5-HMF.

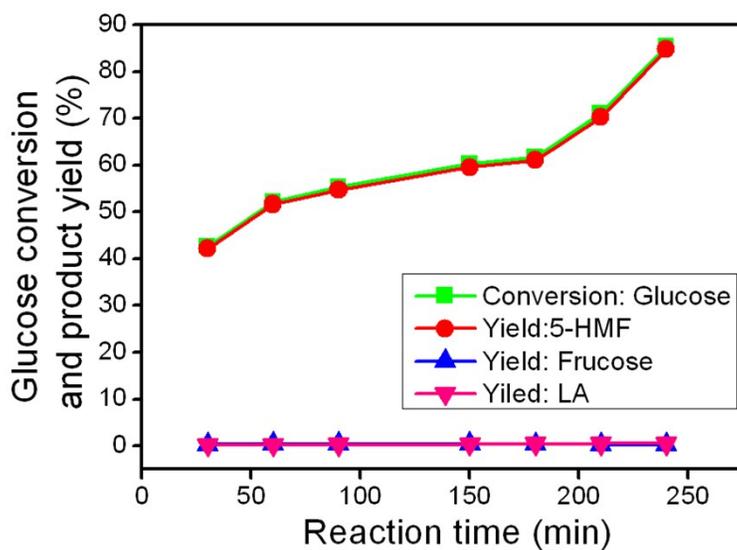


Figure S3. 5-HMF synthesis from glucose detected using high performance liquid chromatography–evaporative light scattering detector (HPLC-ELSD). Conditions: 0.9g glucose, 0.09g SPPS (26.2% sulfation degree), 5mL [EMIM] Br, 4 h, 140 °C). This differs from the results over CrCl_2 , in that there is much more formation of the isomerisation product fructose, and 5-HMF can hydrolyze to generate LA (see *J. Am. Chem. Soc.* **135**, 3997, 2013).

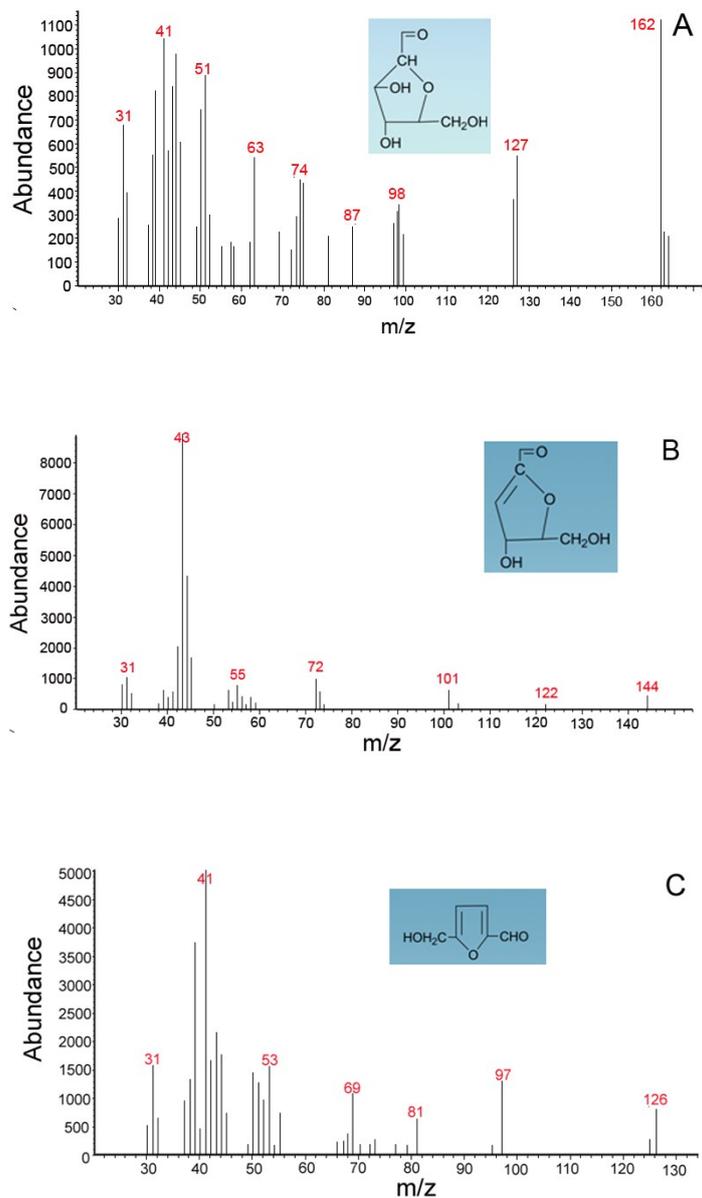


Figure S4. The intermediates (A and B) and 5-HMF (C) detected by HPLC-MS. (Condition: 0.18g SPPS with 26.2 mol% sulfonation degree, solvent 20 ml, 140 °C for 1h, glucose 1.8 g reaction mixture was diluted with acetone)

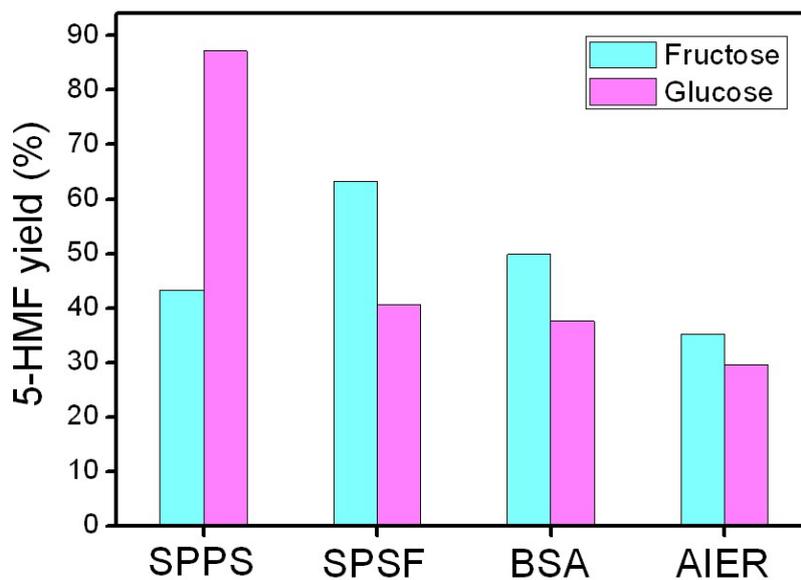


Figure S5. Glucose and fructose conversion to 5-HMF over SPPS, SPSF (sulfonated polysulfone), benzenesulfonic acid (BSA) and acidic ion-exchange resin (AIER). Conditions: 0.9 g glucose or fructose, 0.09 g catalyst, SPPS with 26.2% sulfonation degree, SPSF and acidic ion-exchange resin with 25.6 to 27.5% sulfonation degree, 5mL [EMIM] Br, 140 °C, 4 h.

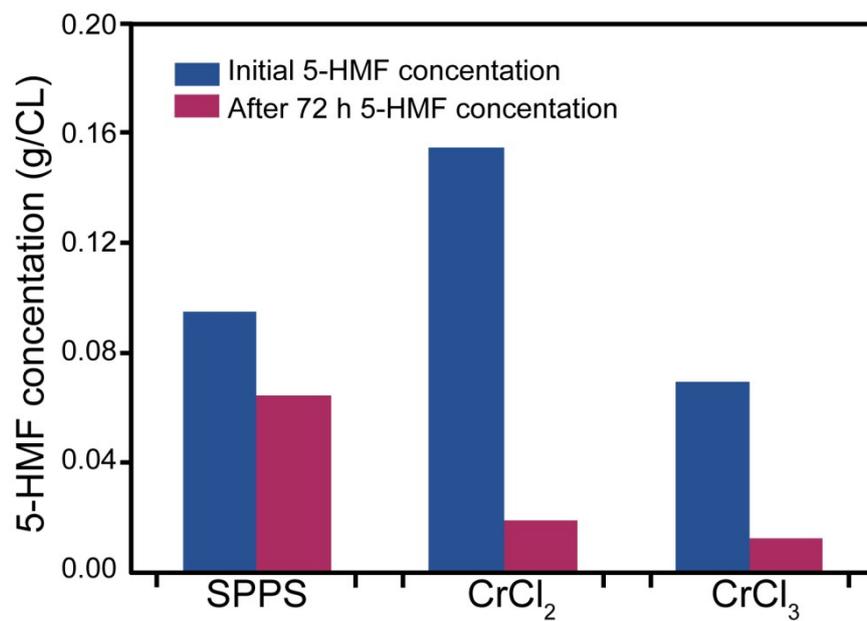


Figure S6. The stability of 5-HMF in presence of SPPS, CrCl₂ and CrCl₃ at 80 °C, respectively. The solvent is the mixture of 5ml [EMIM] Br and 0.27 g H₂O.



Figure S7. Glucose conversion to 5-HMF over SPPS (left) and CrCl_2 (right) in ionic liquid solvent (Reaction condition: 0.18 g catalyst, solvent 20 ml, 140 °C for 1 h, glucose 1.8 g)

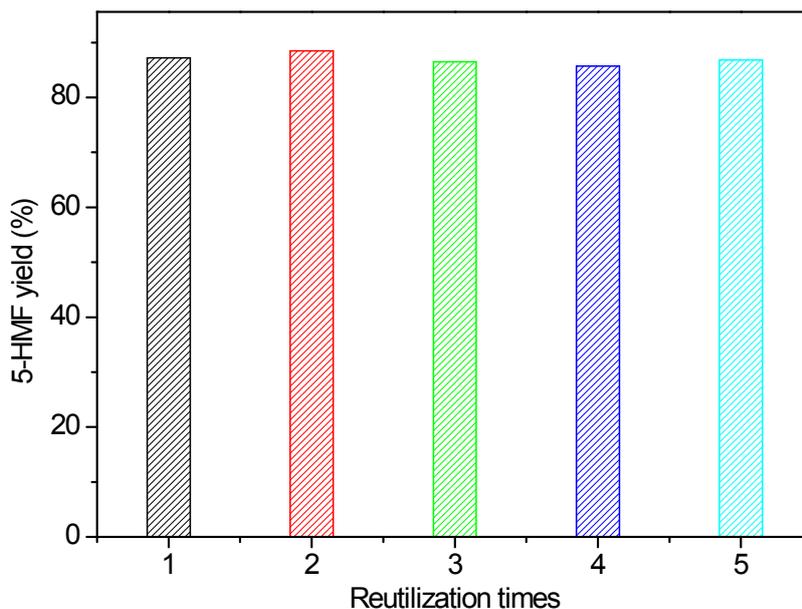


Figure S8. The study on stability of SPPS catalyst

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