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### Direct catalytic conversion of glucose and cellulose

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#### Abstract

Biomass product 5-hydroxymethylfurfural (5-HMF) can be used to synthesize a broad range of value added compounds currently derived from petroleum. Thus, the effective conversion of glucose or cellulose (the major components of biomass) into fuels and chemical commodities has been capturing increasing attentions. Previous studies have been extensively focused on a two-step process for producing 5-HMF from glucose or cellulose, i.e., the isomerization of glucose into fructose and then the dehydration of fructose. We herein discovered that heterogeneous sulfonated poly(phenylene sulfide) (SPPS) containing strong Brønsted acid sites is able to convert glucose and cellulose into 5-HMF with a high yield in ionic liquids (ILs). The optimal activity of glucose conversion to 5-HMF achieves a yield of 87.2% after 4 h reaction at 140 °C. For direct cellulose conversion, a 5-HMF yield of 68.2% can be achieved. The reaction mechanism over SPPS catalyst in ILs was studied by DFT calculations, and results indicated that the SO<sub>3</sub>H group of SPPS plays a crucial role on glucose conversion into 5-HMF, and it acts as a proton donor as a Brønsted acid and functions as a proton acceptor as the conjugate base. Furthermore, the anions and cations of ILs together with SO<sub>3</sub>H-SPPS help to stabilize the reaction intermediates and transition states, which also resulted in glucose facile conversion into 5-HMF. The new catalyst system highlights new opportunities offered by optimizing the production of 5-HMF directly from glucose and cellulose.

#### Introduction

Concerns about global warming and energy security have led to the exploration of alternatives to fossil hydrocarbon resources to supply chemicals and energy<sup>1</sup>. For example, efficient routes are being explored for the conversion of carbohydrates, the main constituents of renewable biomass, into fuels and chemicals<sup>2-3</sup>. 5hydroxymethylfurfural (5-HMF) is considered to be a key biorenewable platform molecule and is one of the ten most important platform chemicals listed by U.S. Department of Energy, since 5-HMF and its derivatives are potential substitutes for petroleum-based chemicals that are consumed in high volume<sup>3-10</sup>. Although 5-HMF is already produced at an industrial level by AVA chemical from fructose in high yield by using Brønsted and Lewis acid catalysts<sup>3,8</sup>, the selective transformation of glucose into 5-HMF, the dominant sugar in cellulosic biomass, remains a great challenge since the stable pyran-type six membered ring structure makes it hard to dehydrate in the presence of acid catalysts<sup>11</sup>. At present, the conversion of glucose into 5-HMF is achieved in two steps. Glucose is first isomerized to fructose using catalysts such as an enzyme, a Lewis acid or a base, and then the fructose is dehydrated to yield 5-HMF under acidic conditions<sup>6-10</sup>. Recently, unprecedented 5-HMF yields were reported for glucose dehydration by chromium (II) chloride (CrCl<sub>2</sub>) in the ionic liquid (IL) 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). The yield of 5-HMF was in the range of 60-70%<sup>8</sup>. The CrCl<sub>3</sub><sup>-</sup> anion coordinates with an

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enediolate intermediate to promote hydrogen transfer and thus accelerates the isomerisation of glucose to fructose<sup>8-9</sup>. The ionic-liquid medium was thought to provide a non-coordinating polar environment to stabilize catalytically active low-coordinate metal species<sup>12</sup>. However, it is hard to further enhance the 5-HMF yield due to the inevitable isomerisation process, and it is impossible to achieve the scale of production (100-200 kTon per year) at low cost (~\$1.00/kg) required for commercial impact<sup>11</sup>. In addition, the homogeneous chromium based catalysts have serious environmental and operational problems for the large-scale production of 5-HMF from glucose. The high toxicity of Cr catalysts is incompatible with a green and environmentally benign biomass conversion process, and the high cost and inefficiency of separating homogeneous chromium catalysts from the products make their recovery impractical.

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If an efficient and environmentally friendly catalyst system can be invented for the effective dehydration of glucose into 5-HMF, 5-HMF synthesis from glucose or glucose-based carbohydrates can be an economic and sustainable strategy to replace fossil-based chemicals or energy. However, acid catalysts for fructose conversion into 5-HMF via fructose dehydration to the furanose form<sup>13</sup> usually exhibit very low activity in glucose conversion into 5-HMF<sup>6-10</sup>. Those acid catalysts include homogeneous mineral acids such as sulphuric acid<sup>14</sup> or hydrochloric acid and heterogeneous acids such as strong acid cation exchange resins<sup>5,15-16</sup>, H-form zeolites<sup>17-18</sup>, and supported heteropolyacids<sup>19</sup>. To achieve economically feasible production of 5-HMF from glucose, a new efficient catalyst system is highly desired.

Herein, we report that sulfonated poly(phenylene sulfide), abbreviated as SPPS, in ionic liquids can catalyse the effective conversion of glucose and cellulose to 5-HMF at a high yield (87.2% and 68.2%, respectively). SPPS is chemically and thermally stable and has been employed as the base polymer for proton-conducting electrolytes<sup>20-21</sup>. The SO<sub>3</sub>H group of SPPS acts as a proton donor as a Brønsted acid and functions as a proton acceptor as the conjugate base, and ILs help to stabilize the reaction intermediates or transition states and promote glucose facile conversion into 5-HMF<sup>22</sup>. Furthermore, SPPS catalyst is heterogeneous, much more easily separated from the product and recycled than homogeneous catalysts. This new catalyst system enables a novel process for large scale synthesis of 5-HMF directly from glucose and cellulose in the future.

#### Experimental

**Materials.** N-ethyl bromide and 1-methylimidazole (> 99%), SnCl<sub>4</sub>, TiCl<sub>4</sub>, CrCl<sub>2</sub>, CrCl<sub>3</sub>, benzenesulfonic acid, leucine, tyrosine, tryptophan, proline, H<sub>2</sub>SO<sub>4</sub>, chlorosulfonic acid, cellulose, cellobiose, sucrose, lactose, maltose, glucose, fructose, galactose et al. were all obtained with AR degree from Sigma-Aldrich. 5-HMF used as the standard sample was purchased from Sigma-Aldrich.

Anhydrous 1-methyl-3-ethyl imidazolium bromide ([EMIM]Br) was synthesized from ethyl bromide and 1-methylimidazole at 25 °C for 24 h. The resulting solid was purified by acetonitrile and ethyl acetate to wipe off the residual ethyl chloride and 1-

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methylimidazole, and the purified [EMIM]Br was dried in vacuum drying oven at 70 °C 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,  $N_2$  inlet and outlet. After 1, 4-dichlorobenzene,  $Na_2S$ , NMP and  $Na_3PO_4$  were loaded into the reactor, the air in the autoclave was flushed out using  $N_2$ . 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 water, and PPS was washed by NMP, ethanol and water 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 250 °C. 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 210 °C, and 1-chloronaphthalene was used as mobile phase.

Sulfonation of PPS (Mw  $2.69 \times 10^4$  g mol<sup>-1</sup>) was performed by the following procedure. PPS was dissolved in 10 mL of 10% SO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>. The suspension was heated to 80 °C, and stirred for 3 h under a dry nitrogen atmosphere. After the

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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<sup>+</sup>) form was dried overnight at 100 °C under vacuum, weighed, and then immersed in saturated NaCl for 24 h. The amount of H<sup>+</sup> ion released from the samples was determined by titration with 0.01 M NaOH using phenol phthalein 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 (hv = 1486.6 eV), operated at 225 W (15 mA, 15 kV) and a base pressure of 1 ×10<sup>9</sup> Torr. Samples were degassed overnight at 1× 10<sup>8</sup> 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 (ThermofinniganLCQ Advantage) and GC-MS (HP5972) (capillary column: 30 m SE-30, 0.25 mm ID, and 0.25 μm film thickness) to identify products and polycarbonate precursors.

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**5-HMF yield characterization.** All reaction products were analyzed using a high performance liquid chromate graph (Waters 1525 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 CH<sub>3</sub>OH, 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-MV100-5 C18 column (250×4.6 mm, 93:7water/acetonitrile, 1 mL/min, 308 K). The reaction product was also analyzed by gas chromatography-

mass spectrometry (GC-MS) and high performance liquid chromatography using an evaporative light scattering detector (HPLC-ELSD).

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.

**DFT calculations.** All the geometries of the  $\beta$ -glucose and the corresponding intermediates were optimized in vacuo using hybrid density functional methods with B3LYP/6-311+G(d,p) level of theory implemented in Gaussian 09<sup>23</sup>. The same level of theory and basis sets were used for the computations of vibrational frequencies, in order to verify the optimized structures (zero imaginary frequencies) as minima or first-order saddle points (one imaginary frequency for transition states structures). Then, the intrinsic reacton coordinate (IRC)<sup>24, 25</sup> pathways of transition states have been traced to confirm that each of them actually connects the desired reactant and product. Dispersion-corrected B3LYP optimisations incorporating Grimme's D3 correction with Becke-Johnson damping (keyword empiricaldispersion=gd3bj) were carried out on the geometry optimizations. To consider the effects of water and ionic liquid at the same time, 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).<sup>26,-28</sup> (Computational details can be found in *Supplementary Materials*).

#### **Results and discussion**

# Sulfonated poly(thiophenylene) preparation and its usage in biomass conversion into 5-HMF

Poly(phenylene sulfide) (PPS), which was synthesized from Na<sub>2</sub>S and 1,4dichlorobenzene in N-methylpyrrole, was the starting point for the synthesis of SPPS by a simple sulfonation process in oleum under a dry nitrogen atmosphere. The molar ratio of basic divalent sulfide (S) to strong Brønsted acid (SO<sub>3</sub>H) in SPPS can be wellcontrolled by the sulfonation temperature and time. SPPS catalyst has a hydrophobic PPS backbone matrix and hydrophilic SO<sub>3</sub>H ionic sites. We can characterize the degree of sulfonation of SPPS by titration, XPS and FT-IR (Figure 1). In the XPS spectra of SPPS, four major signals with different intensities are observed in the sulfur 2p region, at approximately 170, 168, 166 and 164 eV. On the basis of their binding energies, we assign them to the sulfone (-SO<sub>2</sub>-), sulfate (-SO<sub>3</sub>H), sulfoxide (or sulfite -SO-) and sulfide groups (-S-), respectively (Figure S1). Two minor components at 170 and 166 eV are formed by partial oxidation of the thioether during the sulfonation of PPS. The SO<sub>3</sub>H groups were also detected in the IR spectrum, where strong

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characteristic peaks at 1201 and 1055 cm<sup>-1</sup>, assigned to the S=O stretching vibration, were observed. These peaks were not observed in the IR spectrum of the pristine PPS<sup>29</sup>. In general, the hydrophobic PPS matrix and hydrophilic SO<sub>3</sub>H group are sarepartially or completely phase-separated in SPPS<sup>24</sup>.

#### (Figure 1)

In the present study, we use SPPS as an environmentally friendly heterogeneous catalyst for 5-HMF synthesis directly from fructose, glucose and cellulose in an IL solvent. 5-HMF yields from fructose, glucose and cellulose, catalysed by a SPPS catalyst with 26.2% sulfation in an anhydrous [EMIM]Br solvent, are shown in Figure 2.

#### (Figure 2)

It can be seen that the yield of 5-HMF from glucose in anhydrous [EMIM]Br solvent at moderate temperatures (80-110 °C) ranges from 5 to 40% in 4 h (Figure 2A). At the temperatures between 100 and 140 °C, the yield of 5-HMF from the direct conversion of cellulose is in a range of 10-20%. These yields are lower than that of conversion from fructose (30-45%). Nonetheless, when the reaction temperature was raised to between 140 °C and 180 °C, excellent 5-HMF yields from glucose and cellulose of 87.2% and 64.3% respectively, were achieved. Only trace unwanted levulinic acid (LA) (<0.5 mol%) was detected according to the GC-MS and HPLC-ELSD data (Figure S2 and Figure S3). A very high selectivity (>99%) was achieved in the SPPS catalyzed system. The glucose turnover number (TON) and turnover

frequency (TOF) over SPPS reach  $1.95 \times 10^3$  and 0.14/s, respectively. These yields are much higher than the highest 5-HMF yield (45.2%) from the fructose dehydration catalyzed by SPPS at the optimal conditions. To the best of our knowledge, this is the highest yield from non-toxic heterogeneous catalysts for 5-HMF production from glucose and cellulose.

A high yield of 5-HMF was achieved on the SPPS catalyst when macromolecular cellulose was used as feed stock. This is surprising because there is a steric hindrance between the SPPS polymer and cellulose macromolecules, which should impede their reaction. This steric hindrance is possibly weakened by proton exchange between the IL and the SPPS<sup>30</sup>. We also investigated the performance of SPPS in other ILs such as 1-butyl-3-methylimidazolium bromide ([BMIM]Br), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-allyl-3-methylimidazolium chloride ([AMIM]Cl, 1-butyl-3-methylimidazolium hydrate ([BMIM]OH) and N-ethyl-pyridinium bromide ([EPy]Br). As presented in Figure 2C, the catalytic reaction over SPPS in other neutral ionic liquids shows similar catalytic results, namely that the 5-HMF yields from glucose are much higher than those from fructose. An exception appeared in the basic [BMIM]OH, where the 5-HMF yield from fructose was little higher than that from glucose or cellulose, since the Brønsted acidic centre of SPPS could be neutralized by the basic [BMIM]OH.

The formation of 5-HMF from fructose, glucose and cellulose catalyzed by SPPS in [EMIM]Br mixtures at 100, 140, and 180 °C, respectively, was investigated (see

Figure 2B). The 5-HMF yield from the fructose conversion is a maximum at 100 °C; further increase in temperature does not improve the yield. The highest 5-HMF yields from glucose and cellulose were achieved at 140 and 180 °C, respectively. The activation energies of fructose and glucose conversion into 5-HMF were estimated from the kinetic data at different temperatures to be 25.5 kcal/mol and 34.6 kcal/mol, respectively. It is also noted that the highest yield of the fructose and cellulose conversions was achieved within the first 2 h of the reaction, but within 4 h for glucose conversion. The further prolonged reaction resulted in a declining yield of 5-HMF, due to the formation of by-products similar to the results of conventional catalytic processes<sup>31-33</sup>.

#### The effects of SPPS sulfonation degree on biomass conversion into 5-HMF

The sulfonation degree of SPPS catalyst is found to influence its catalytic activity. For example, 65-88% 5-HMF yields from glucose were obtained in [EMIM]Br solvent when the sulfonation degree was between 10.0 and 35.0 mol% (Figure 3). At a sulfonation degree of 26.2 mol%, the SPPS catalyst displays the best activity for 5-HMF yield of 87.2%. When cellulose was the reactant and the reaction was conducted at 180 °C, using the SPPS catalyst with a sulfonation degree of 21.8 mol% led to a high 5-HMF yield of 68.2%.

(Figure 3)

#### Biomass conversion into 5-HMF over different catalysts

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The performance of various other common acidic catalysts such as metal chlorides,

amino acids and supported acids, were also investigated for the production of 5-HMF from fructose, glucose and cellulose in [EMIM]Br. As shown in Figure 4, the SPPS catalysts display much higher activity for the conversions of glucose and cellulose to 5-HMF although they have much smaller BET specific surface areas than those of the heterogeneous solid supported acid catalysts, such as SO<sub>4</sub><sup>2-</sup>/Al<sub>2</sub>O<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>/Al<sub>2</sub>O<sub>3</sub> and  $SO_4^2$ /SBA-15. For instance, the specific surface areas are 0.23, 1.56, and 3.23 m<sup>2</sup>/g for the catalyst with 40.5, 26.2, and 21.8 mol% sulfation degree, respectively. Apparently, the porosity degree of SPPS decreases with the increase of sulfonation. This is due to the fact that the hydrogen bonds resulting from the introduced -SO<sub>3</sub>H groups leads to a stronger interaction among SPPS macromolecules, which makes the SPPS volume shrink. The yields of 5-HMF from glucose conversion catalyzed by homogeneous catalysts of CrCl<sub>2</sub>, CrCl<sub>3</sub> and SnCl<sub>4</sub> are merely 19.5, 26.0 and 18.9%, respectively, at 140 °C for 4 h. These yields can be improved to 50.1, 48.5 and 44.9% when the reaction was conducted at 100 °C for 4 h (Figure 4B, the bars indicated with a prefixed number of 100). But such yields are still substantially lower than those achieved by the SPPS catalysts. The only exception is the yield of 5-HMF from fructose catalyzed by CrCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, which is 58.3 and 55.1%, respectively, which is higher than that catalyzed by SPPS (45.2%). Moreover, in our experiment the process using homogeneous CrCl<sub>2</sub>, CrCl<sub>3</sub> and SnCl<sub>4</sub> catalysts produced many more by-products than that using the SPPS catalysts. For instance, the most important side reactions are the rehydration of 5-HMF into levulinic and formic acids, and either

polymerization of 5-HMF or cross polymerization of 5-HMF and carbohydrate<sup>34</sup>. These polymeric humins consume initial carbohydrate, leading to an increase in viscosity and thus limiting mass transfer.

(Figure 4)

# Biomass conversion mechanism into 5-HMF catalyzed by SPPS in presence of ILs

The prevailing view in the literature is that converting glucose and cellulose directly into 5-HMF is much more difficult than converting fructose to 5-HMF. Hence, the isomerization of glucose or cellulose into fructose is an essential step for producing 5-HMF from glucose or cellulose and has been extensively studied. However, the present study demonstrates that in the SPPS catalysed systems using ILs as solvent, the conversion of glucose and cellulose into 5-HMF is much easier and more efficient than the conversion of fructose.

In order to explore the glucose conversion mechanism over SPPS at high temperature (at which excellent yields were achieved), high performance liquid chromatography mass spectrometry (HPLC-MS) was used to characterize the product distribution of the reaction at 140 °C. Three products were detected and their base peaks in the mass spectrum corresponding to molecular ions ( $M^+$ ) at m/z=126, 144 and 162, respectively (see Figure S4). No fructose was detected. However, fructose was detected in the systems catalyzed by the SPPS catalyst at low temperature (<100 °C) or catalyzed by conventional acid catalysts<sup>31</sup>. These systems exhibit relatively low

5-HMF yields. In addition to the target 5-HMF (m/z = 126), the by-products were identified as 3,4-dihydroxy-5-(hydroxymethyl)-tetrahydrofuran-2-carbaldehyde (intermediate A, m/z = 162), and 4-hydroxy-5-(hydroxymethyl)-4,5-dihydrofuran-2carbaldehyde (intermediate B, m/z = 144), respectively.

Similar to the spherulite compounds of pristine PPS<sup>20-21, 29, 35</sup>, SPPS displays a spherical particle structure in ILs, and the hydrophilic sulfonic groups mainly distribute on the outer surface of SPPS spheres because the sulfonation took place on the PPS surface in oleum. The ion-exchange of [BMIM]Br with the Brønsted acid sites of SPPS promote the release of H<sup>+</sup> ions<sup>36</sup>, and the surface of the catalyst is partly modified by [EMIM]<sup>+</sup> cations. The sugar-solubilizing [EMIM]<sup>+</sup> cations improve the affinity of glucose for SPPS heterogeneous catalysts<sup>8</sup>, making the catalytically active centres readily accessible to glucose molecules. To verify our assumptions, DFT calculations (Supplementary Materials) were carried out to gain further insights into the mechanism for the transformation of glucose to 5-HMF in the systems of SO<sub>3</sub>H-SPPS and [EMIM]Br. According to previous experimental<sup>36-40</sup> and theoretical studies<sup>38-44</sup> on the catalytic conversion of glucose to HMF by Brønsted acids and Lewis acidic metal salts, It is generally acknowledged that the first step is the formation of an enediol intermediate (IM) from glucose, and then the enediol intermediate converts into fructose and further to 5-HMF. Based on our DFT calculation, we suppose that the reaction may follow the mechanism shown in Scheme 1 and Figure 5-8 with SPPS acting as Brønsted acid catalyst and [EMIM]Br as solvent. Firstly, the H atom of sulfonic acid attacks the ring O of the glucose 6-

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member ring structure, resulting in the protonation of the ring O and the breakage of  $C_1$ - $O_6$  bond (intermediate IM1), which has a very low barrier with only about 10.7 kcal/mol. Subsequently, the open-ring aldehyde form is transformed in to 1,2-enol by a ketone-enol isomerization, which is slowly elementary step with an energy barrier of 21.5 kcal/mol. Then, the 1,2-enol to ketose occurs via the second enol-ketone isomerization step with an barrier of 17.4 kcal/mol. The ketose form closes the ring structure to form a 5-member ring fructose with an energy barrier of 9.3 kcal/mol. The results indicates that it is relatively difficult for the formation of 1,2-enediol to ketoneenol isomerization reaction. Generally, the transformation of fructose to 5-HMF includes three dehydration processes. The calculated dehydration mechanism details are shown in Figure 6-7. Along the reaction coordinate, the first dehydration process is key step with a barrier of 13.6 kcal/mol, leading to C-OH bond cleavage. Throughout the whole reaction pathway, we found that the ketol-isomerization and the first dehydration are two rate-determining elementary steps to be carried out under thermal conditions.

#### (Scheme 1) and (Figure 5-8)

To verify the role of SPPS, sulfonated polysulfone (SPSF), benzenesulfonic acid (BSA) and acidic ion-exchange resin (AIER) were used to catalyze the synthesis of 5-HMF from fructose and glucose, respectively. As expected, SPSF, BSA and AIER displayed higher activity in fructose conversion to 5-HMF than in glucose conversion. In contrast SPPS showed much better activity in glucose conversion to 5-HMF

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(Figure S5). Moreover, the unique structure of the SPPS catalyst is believed to contribute to the high 5-HMF selectivity. The catalyst possesses a hydrophobic backbone matrix and hydrophilic  $SO_3H$  sites. The hydrophobic backbone matrix minimizes the attraction to the nearby SPPS catalyst of H<sub>2</sub>O molecules formed in the reaction, and thus avoids further reaction to form the by-product levulinic acid (Figure S2 and S6).

The SPPS catalyst also possesses a number of advantages for practical application in biomass conversion. For instance, the SPPS catalyst can be well dispersed in an ionic liquid though the ion-exchange of [BMIM]Cl with SO<sub>3</sub>H, and can be readily separated after the reaction simply by filtration, sedimentation, or centrifugation (Figure S7). The synthesis of the SPPS catalyst can be scaled up without difficulty because of the facile sulfonation of commercial PPS bulky particles. More importantly, the SPPS catalyst could be recycled and displayed no decline in activity after 5 recycles (Figure S8). Therefore, SPPS is an ideal heterogeneous catalyst for the conversion of a biomass (glucose) into a fine chemical (5-HMF).

#### Conclusions

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This study demonstrates that SPPS are highly efficient for the direct conversion of glucose or cellulose to 5-HMF. The environmentally benign conversion involves some new mechanism and is feasible for the practical valorization of glucose and cellulose. Thus, knowledge acquired in this study may inspire further research on new catalysts for this purpose.

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#### LEGEND

Figure 1 | XPS and FTIR survey spectra of SPPS. The sulfonation degree was calculated from Figure 1A, and S binding energy (eV) located at around 164 eV, while the S binding energy of  $SO_3H$  is located at 168-169 eV.

Figure 2 | 5-HMF synthesis from fructose, glucose and cellulose. A: 0.9 g carbohydrate, 0.09 g SPPS (26.2% sulfation degree), 5 mL [EMIM]Br, 4 h; B: 0.9 g carbohydrate, 0.09 g SPPS (26.2% sulfation degree), 5 mL [EMIM]Br. C: Glucose conversion to 5-HMF over SPPS in different solvent (reaction condition: 0.18 g SPPS with 26.2 mol% sulfonation degree, solvent10 ml, 140  $^{\circ}$ C for 4 h)

**Figure 3** | **5-HMF yield from different carbohydrates.** (Condition: SPPS catalyst 0.09 g, carbohydrate 0.9 g, 5 ml [EMIM]Br)

Figure 4 | 5-HMF yield from fructose over different catalysts in [EMIM] Br. (Conditions: A: 0.9 fructose, 0.09 g catalyst, SPPS with 40.5% sulfation degree, 5mL [EMIM]Br, 100  $^{\circ}$ C, 4 h); B: 5-HMF yield from glucose over different catalysts in [EMIM]Br (Conditions: 0.9 g glucose, 0.09 g catalyst, SPPS with 26.2% sulfation degree, 5 mL [EMIM]Br, 140  $^{\circ}$ C,4 h); C: 5-HMF yield from celluloseover different catalysts in [EMIM]Br (Conditions: 0.9 g catalyst, 0.09 g catalyst, SPPS with 21.8% sulfation degree, 5 mL [EMIM]Br, 180  $^{\circ}$ C, 2 h).

Scheme 1. The mechanism of glucose conversion in the presence of SPPS

**Figure 5**. The computed Gibbs free energy profile of intermediates and transition states for the formation of the 1,2-enediol intermediate (IM3). Solvent effects were considered by polarizable continuum model (PCM) single-point calculations in water. **Figure 6**. The computed Gibbs free energy profile of the enol-ketone isomerization and ring-closing reactions to form fructose. Solvent effects were considered by polarizable continuum model (PCM) single-point calculations in water.

**Figure 7**. The computed Gibbs free energy profile of the continuous dehydration process to form 5-HMF. Solvent effects were considered by polarizable continuum model (PCM) single-point calculations in water.

**Figure 8**. Transition states for the reaction of Glucose to 5-HMF. Red: oxygen, yellow: sulfur, gray: carbon, white: hydrogen.

Figure 1



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Figure 3



#### Figure 4



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Scheme 1



Figure 5



Figure 6





Figure 8

