Supplementary Information

Dehydration of fructose to 5-hydroxymethylfurfural over a mesoporous sulfonated high-crosslinked polymer in different solvents

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**Synthesis of SKB-G and SXC-72:** The activated carbon materials (KB-G and XC-72) were dried at 100 °C in a vacuum overnight to eliminate impurities such as water and gas adsorbed in the material channels before making sulfonated activated carbon materials (SKB-G and SXC-72). The SKB-G and SXC-72 both have the same sulfonation process. Specifically, 0.5 g material (KB-G or XC-72) was added to 5 mL of concentrated sulfuric acid, and stirred at 70 °C for 1 h. Then, the resulting sample was washed with H₂O until no SO₂⁻ ions were detected by BaCl₂ in the filtrate. The catalyst was dried at 90 °C in a vacuum overnight.

**Table S1** Physical and chemical properties of HCP and SHCP.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP</td>
<td>846</td>
<td>0.70</td>
<td>3.74</td>
</tr>
<tr>
<td>SHCP</td>
<td>234</td>
<td>0.17</td>
<td>3.91</td>
</tr>
</tbody>
</table>
Fig. S1 TG-DTA-DTG curves of (a) HCP and (b) SHCP under the air atmosphere.

Fig. S2 Possible reaction mechanism between DMSO and SHCP.\textsuperscript{1}
Fig. S3 Equation for reaction of DMF with acid.²

\[
\text{Eqn.} \quad \text{N} = \text{O} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H} \text{O} \text{H} + \text{H} = \text{N}
\]

Fig. S4 Recycles of SHCP in the dehydration of fructose reaction. Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL H₂O, 120 °C, 120 min.

Fig. S5 Photographs of the reaction liquid. Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL DIO, 120 °C.
**Fig. S6** MALDI-TOF spectra of reaction mixture with different reaction time (a: 15 min, b: 120 min). Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL DIO, 120 °C.

**Fig. S7** The possible path of 5-HMF polymerization to soluble oligomers and humin.
Fig. S8 Photographs of the reaction liquid. Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL H₂O, 120 °C.

Fig. S9 FTIR spectra of SHCP recycles in the repeat degradation reaction.
Fig. S10 HAADF-STEM image (a), line scan image (b) and line sum spectrum (c) of fresh SHCP.
The effect of reaction temperature on dehydration of fructose was illustrated in Fig. S12. It was found that the conversion of fructose increased with the increasing temperature, achieving 97.4 % at 120 °C. When the temperature was higher than 120 °C, the selectivity of 5-HMF decreased slightly because side reactions were more favorable to occur at higher temperatures. Fig. S13 presented the time course of dehydration of fructose over SHCP at 120 °C. The conversion of fructose increased with the prolonged time and reached a maximum of 120 min, and it was also interesting to note the selectivity of 5-HMF only dropped slightly to 71.6 % even prolonging the reaction time to 180 min.
**Fig. S12** Dehydration of fructose under varied reaction temperature.

Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL of a 9.75/0.25 v/v mixture of DIO/H$_2$O, 120 min.

**Fig. S13** The performance of SHCP for dehydration of fructose with prolonged time.

Reaction conditions: 0.5 g fructose, 0.05 g SHCP, 10 mL of a 9.75/0.25 v/v mixture of DIO/H$_2$O, 120 °C.
References
