

## Supporting Information

### **Highly efficient synthesis of 5-hydroxymethylfurfural with carbohydrates over renewable cyclopentanone-based acidic resin**

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## Experimental

### 1. Catalysts

Nafion-212 resin was supplied by Dupont. Amberlyst-15 and Amberlyst-36 resins were purchased from Sigma-Aldrich Company.

The cyclopentanone-base acidic resins were prepared by the ion-exchanging of the condensation products of sodium sulfite, cyclopentanone and aldehydes (such as formaldehyde, acetaldehyde and furfural). Taking the preparation of the sulfated cyclopentanone-formaldehyde condensate (SCFC) for example, this catalyst was prepared by following method. Typically, 8.4 g cyclopentanone was added into an aqueous solution obtained by solving 7.8 g sodium sulfite in 50 g deionized water. The mixture was stirred at 318 K for 0.5 h. Subsequently, 16.5 g formaldehyde aqueous solution (concentration 37wt.%) was added dropwise into the above mixture under vigorous stirring. After the reaction was carried out at 372 K for 3 h, the solid product was separated from the liquid phase by filtration, washed thoroughly with deionized water and dried at 353 K for 8 h. The product was ion-exchanged with 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, filtrated, washed thoroughly with deionized water and dried at 333 K to get the SCFC resin. For comparison, we also prepared two additional cyclopentanone-base acidic resins by the same method (just replacing the formaldehyde solution with acetaldehyde solution or furfural). To facilitate the comparison, 22.4 g 40wt.% acetaldehyde solution or 19.5 g furfural was used to the keep the molars of acetaldehyde or furfural same as that of formaldehyde.

## 2. Activity test

The dehydration (or hydrolysis/dehydration) reactions of different carbohydrates were carried out in a glass batch reactor. For each test, 1 g carbohydrate, 7 g solvent, 0.1 g catalyst were used. The mixture was vigorously stirred at 353 K for 1.5 h. After the reaction, the liquid products were analyzed by an Agilent 1100 HPLC equipped with a hodox SC1011 packed column ( $\text{Ca}^{2+}$ , 300 mm $\times$ 8 mm) and a RID using water as the mobile phase.

## 3. Characterization

### 3.1 $N_2$ -physisorption

The BET specific surface areas ( $S_{\text{BET}}$ ) of the catalysts were measured by nitrogen physisorption which was conducted at 77 K by ASAP 2010 (Micromeritics). Before each measurement, the sample was evacuated at 393 K to eliminate the adsorbents.

### 3.2 Chemical titration

The amounts of acidic group (*i.e.*  $-\text{SO}_3\text{H}$ ) on the surfaces of different catalysts (see Table 1 and Table S1) were measured by the acid-base titration method described in the literature.<sup>1</sup> For each test, 0.05 g catalyst was dispersed into 30 mL 8 mmol L<sup>-1</sup> NaOH solution, sonicated for 1.5 h and then centrifuged. The resulting filtrate was titrated with 1 mmol L<sup>-1</sup> potassium hydrogenphthalate solution using phenolphthalein as indicator. The molar amount of acid sites per gram of catalyst was obtained according to consumption of NaOH solution.

### 3.3 Microcalorimetric measurement of $\text{NH}_3$ adsorption

The acid strengths of the SCFC, Nafion-212, Amberlyst-15, Amberlyst-36 resin were measured by the microcalorimetric of ammonia adsorption tests which were performed at 353 K using a BT2.15 heat-flux calorimeter (France, Seteram) connected to a gas-handling and a

volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ( $\pm 0.5 \times 10^{-4}$  Torr). Before each measurement, ammonia (purity > 99.9%) was purified by successive freeze–pump–thaw cycles. The specific mass of sample with similar amount of acid sites was evacuated in a quartz cell at 353 K overnight under high vacuum to remove the physically adsorbed substance. The differential heat was measured as a function of acid site coverage by repeatedly introducing small dosage of ammonia onto the samples until the equilibrium pressure reached about 5-6 torr. Then the system was evacuated overnight to remove the physically adsorbed ammonia, and a second adsorption was performed.

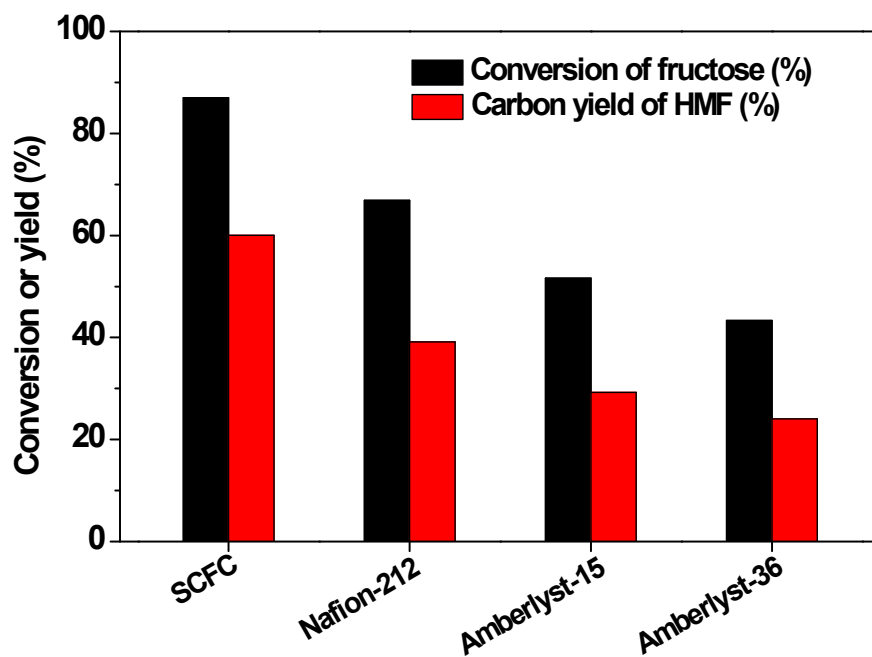
#### *3.4 Fourier Transform Infrared Spectroscopy (FT-IR)*

The FT-IR spectrum of the SCFC resin was collected by a Bruker Equinox 55 spectrometer which was equipped with a deuterated triglycine sulphate (DTGS) detector and extended KBr beam splitter. The spectrometer was operated in the absorbance mode at a resolution of  $4 \text{ cm}^{-1}$ . Before the test, the SCFC resin was mixed with KBr at a mass ratio of 1/100 and pressed to self-supporting tablets.

**Table S1.** Specific BET surface areas ( $S_{\text{BET}}$ ) and the amounts of acid sites on the surfaces of the cyclopentanone-based acidic resins which were prepared by the ion-exchanging of the sulfated cyclopentanone-aldehyde condensates.

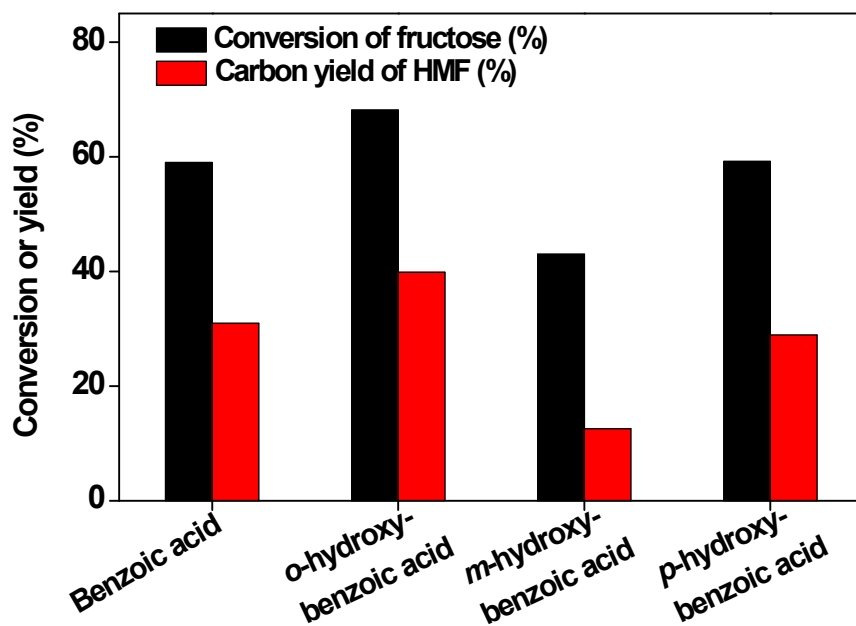
Catalyst	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Amount of acid sites on the catalyst ( $\text{mmol g}^{-1}$ )
Sulfated cyclopentanone-formaldehyde condensate	4.56	2.83
Sulfated cyclopentanone-acetaldehyde condensate	0.98	0.36
Sulfated cyclopentanone-furfural condensate	-	0.04

According to results listed in Table S1, we can see that the specific BET surface areas and the amounts of acid sites on the surfaces of different cyclopentanone-based acidic resins decrease in the order of sulfated cyclopentanone-formaldehyde condensate (SCFC) > sulfated cyclopentanone-acetaldehyde condensate > sulfated cyclopentanone-furfural condensate. This sequence is consistent with the activity sequence of these catalysts for the dehydration of fructose.



**Figure S1.** Conversions of fructose and the carbon yields of HMF over different acidic resins.

Reaction conditions: 1 g fructose, 7 g DMSO, 0.1 g catalyst; 353 K, 1.5 h.



**Figure S2.** Conversions of fructose and the carbon yields of HMF over different carboxylic acid catalysts. Reaction conditions: 1 g fructose, 7 g DMSO, 1 mmol catalyst; 353 K, 1.5 h.

#### 4. Reusing of DMSO

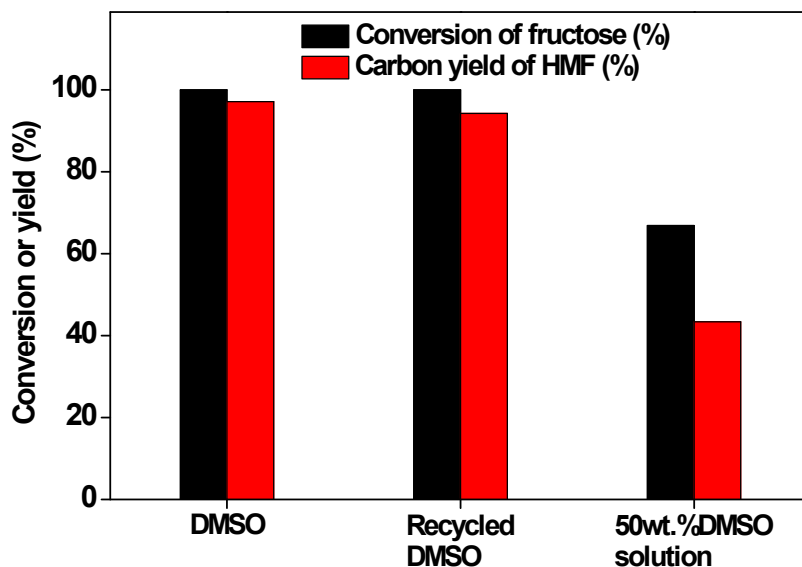
DMSO has high boil point (462 K). Therefore, it is hard to separate HMF from it by distillation. As a solution to this problem, we developed a new method for the separation of DMSO and HMF: 8.8 g dehydration product (DMSO/HMF mass ratio = 10.3), 20 mL water and 20 mL organic solvent (such as ethyl ether and methyl isobutyl ketone (MIBK)) were added into a flask. The mixture was stirred at room temperature for 5 mins and became two phases after we stopped stirring. According to analysis of HPLC (see Table S2), the DMSO/HMF mass ratio in organic phase is lower than that in the dehydration product. In contrast, the DMSO/HMF mass ratio in aqueous phase is higher than that in the dehydration product. This result indicates that the DMSO was extracted into water and HMF was extracted into organic phase at the same time. Compared with ethyl ether, MIBK has better extracting effect for HMF. In future application, we can separate the DMSO and HMF by repeatedly extraction with water and MIBK.

**Table S2.** Separation effects of different bi-phase solvent systems on the dehydration product.

Bi-phase solvent system	DMSO/HMF mass ratio			$C_{\text{HMF}}$ in organic phase <sup>d</sup>
	Dehydration product	Aqueous phase <sup>a</sup>	Organic phase <sup>b</sup>	$C_{\text{HMF}}$ in aqueous phase <sup>c</sup>
Ethyl ether/H <sub>2</sub> O	10.3	11.1	4.1	0.27
MIBK/H <sub>2</sub> O	10.3	12.7	2.4	0.55

<sup>a</sup> The DMSO/HMF mass ratio in aqueous phase. <sup>b</sup> The DMSO/HMF mass ratio in organic phase. <sup>c</sup> The ratios of HMF concentrations in organic phase to HMF concentrations in aqueous phase.





**Figure S3.** Fructose conversions and the carbon yields of HMF over the SCFC resin using pure DMSO, recycled DMSO and 50wt.% DMSO solution as the solvents. Reaction conditions: 1 g fructose, 7 g solvent, 0.1 g catalyst; 393 K, 1.5 h.

Moreover, we also explored the reusability of the DMSO which can be extracted from the dehydration product with water. To do this, we removed the water in the aqueous phase (which has been extracted with MIBK for 8 times) by vacuum distillation and used the recycled DMSO for the dehydration of fructose. From the results illustrated in Figure S3, we can see that high carbon yield (up to 94.3%) of HMF was obtained when we used the recycled DMSO as the solvent. Compared with the one which was achieved with pure DMSO (97.1%), this value is slightly lower. This can be explained by the negative effect of water in the recycled DMSO (According to the measurement of a Mettler Toledo DL39 Karl Fischer Titrator, the water content in the recycled DMSO was measured as ~3.8wt.%). To verify this speculation, we investigated the dehydration of fructose using 50wt.% DMSO solution under the same conditions. As we expected, evidently lower carbon yield of HMF (43.3%) was achieved in that case.

## References

1. X. Zhang, Z. Zhang, F. Wang, Y. Wang, Q. Song and J. Xu, *J. Mol. Catal. A: Chem.*, 2013, **377**, 102-107; S. Li, N. Li, G. Li, L. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2015, **17**, 3644-3652.