

---Supporting Information---

Adjusting the Acidity of Sulfonated Organocatalyst for the One-pot Production of 5-Ethoxymethylfurfural from Fructose

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Table S1. The results of elemental analysis of the sulfonated polymer catalysts.

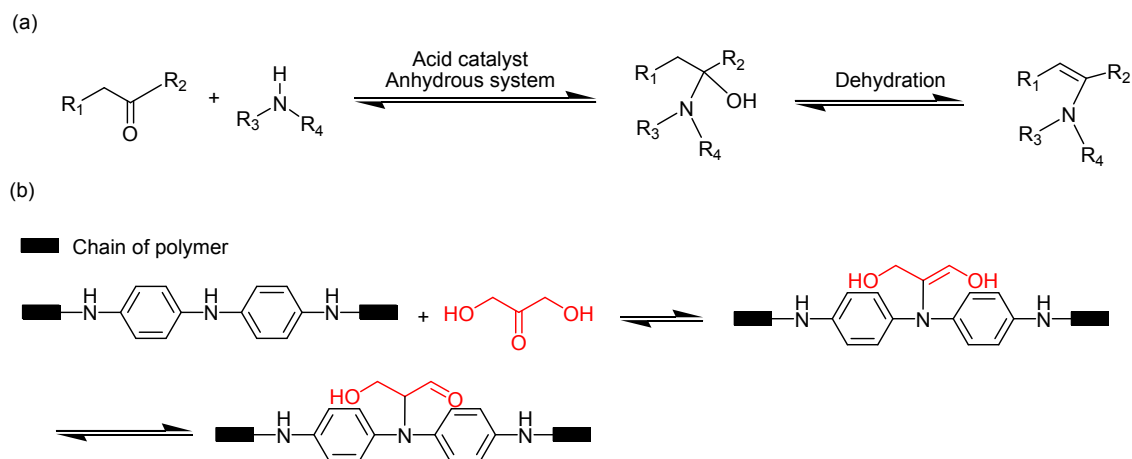
Entry	Catalysts	S/N molar ratio	C/N molar ratio	Acid density (mmol g ⁻¹) ^a
1	SPC-0.25-11/3	0.30	5.9	2.6
2	D0.5-SPC-0.25-11/3	0.29	7.3	2.5
3	SPC-0.25-11/3 (used)	0.31	10.6	2.6
4	D0.5-SPC-0.25-11/3 (after 3 rd run)	0.27	18.3	2.4
5	SPC-0.10-11/3	0.22	5.9	2.0
6	SPC-0.40-11/3	0.39	5.9	3.1
7	D-SPC-0.10-11/3	0.15	7.6	1.4
8	D-SPC-0.40-11/3	0.37	7.5	3.0
9	SPC-0.25-3/3	0.26	5.6	2.3
10	SPC-0.25-6/3	0.28	5.9	2.4
11	SPC-0.25-9/3	0.30	5.9	2.6
12	D-SPC-0.25-3/3	0.23	7.2	2.1
13	D-SPC-0.25-6/3	0.28	7.3	2.4
14	D-SPC-0.25-9/3	0.29	7.2	2.5
15	D0.125-SPC-0.25-11/3	0.31	7.5	2.6
16	D0.375-SPC-0.25-11/3	0.29	7.5	2.5
17	Amberlyst-15	-	-	6.3 ^b

^a Based on the S/N molar ratio of catalysts. ^b Based on sulfur (mmol)/ Amberlyst-15 (g).

Table S2. One-pot conversion of fructose to EMF in ethanol/THF over various SPC-x-y catalysts.

Entry	Catalysts	Conv. (mol%)	Yield of products (mol%)	
			EMF	HMF
1	SPC-0.25-3/3	100	45.5	0.3
2	SPC-0.25-6/3	100	62.4	1.8
3	SPC-0.25-9/3	100	63.1	2.4
4	SPC-0.10-11/3	65.5	1.9	16.2
5	SPC-0.40-11/3	100	59.9	1.0

Reaction conditions: 0.5 mmol of fructose, 30 mg of polymer catalysts, 3 mL of ethanol/THF solvent ($V/V=3/1$), 413 K, 18 h, under a N_2 atmosphere.



Scheme S1. (a) The cross-amination between ketone and secondary amine. (b) Possible imination reaction between DHA and benzenoid amine in SPC.

Using ketone and secondary amine as the substrates, the imination reaction could be described as Scheme S1(a), wherein the addition and dehydration steps are involved.¹ Moreover, it is widely accepted that the presence of water molecules in solvent would significantly promote the hydrolysis of enamine back to ketone and secondary amine. Therefore, the formation of enamine product from the cross-amination needs to be carried out in anhydrous solvent and in the presence of a dehydrating agent. Based on the molecular structure of SPC, the possible reaction between SPC and DHA is described in Scheme S1(b). This cross-amination reaction is unlikely to occur under the reaction conditions investigated because it should be inhibited by water. Firstly, the ethanol used for DHA treatment was utilized without further purification to remove trace amount of water. Meanwhile, water might be generated by etherification between DHA and ethanol. That is, water in the system can drive the reaction equilibrium back towards amine and ketone, which makes the cross-amination between SPC and DHA to be negligible.

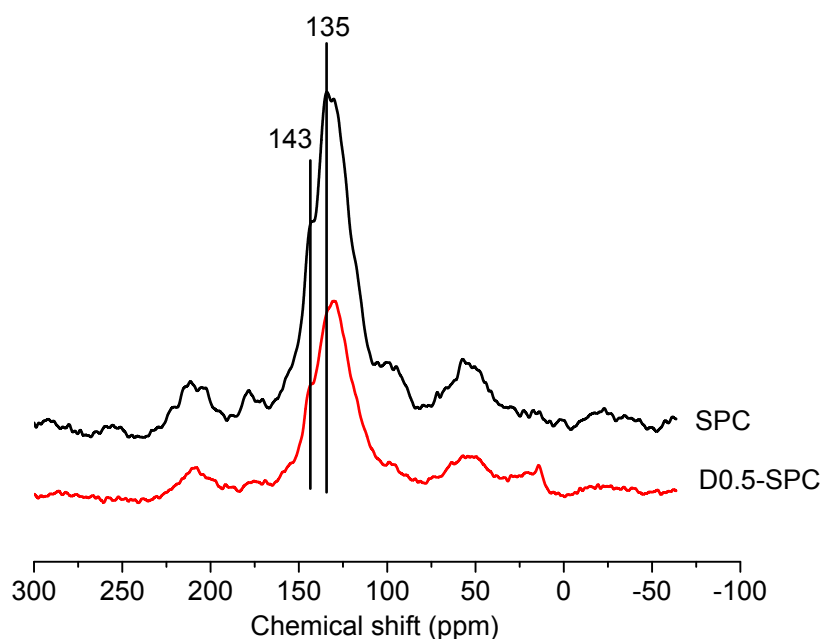


Figure S1. ^{13}C CP-MAS NMR spectra of SPC and D0.5-SPC catalysts.

The ^{13}C CP-MAS NMR signal at 135 ppm was ascribed to aromatic carbon in the polymer catalysts. The signal at 143 ppm is most possibly the overlap chemical shifts derived from the aromatic carbon bound to nitrogen and sulfur, because the aromatic carbons bound to nitrogen or sulfur show similar chemical shifts (*i.e.*, 148.2 ppm for C(-N), and 146.8 ppm for C(-S)).² However, the N-bonded carbon contributes much more to the peak at 143 ppm because of the low C(-S)/C ratio (2/42) in the as-prepared SPC and D-SPC catalysts.

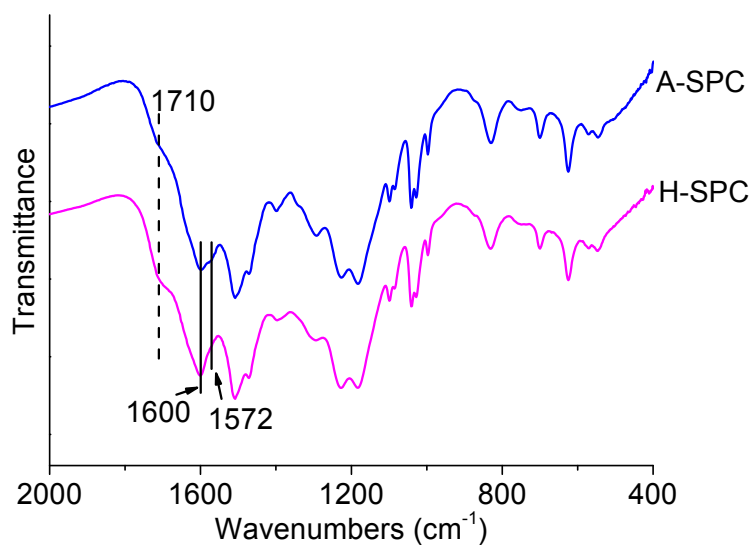


Figure S2. FTIR spectra of A-SPC and H-SPC

A-SPC and H-SPC catalysts were prepared by treating SPC with acetone and hydroxyacetone, respectively. Interestingly, the FT-IR spectra of both catalysts give a new IR band at 1710 cm^{-1} , as the band appears in the FTIR spectrum of D-SPC. Considering the co-existence of carbonyl group in molecules of DHA, acetone, and hydroxyacetone, we infer that this new band at 1710 cm^{-1} is attributed to the stretching vibration of carbonyl group.

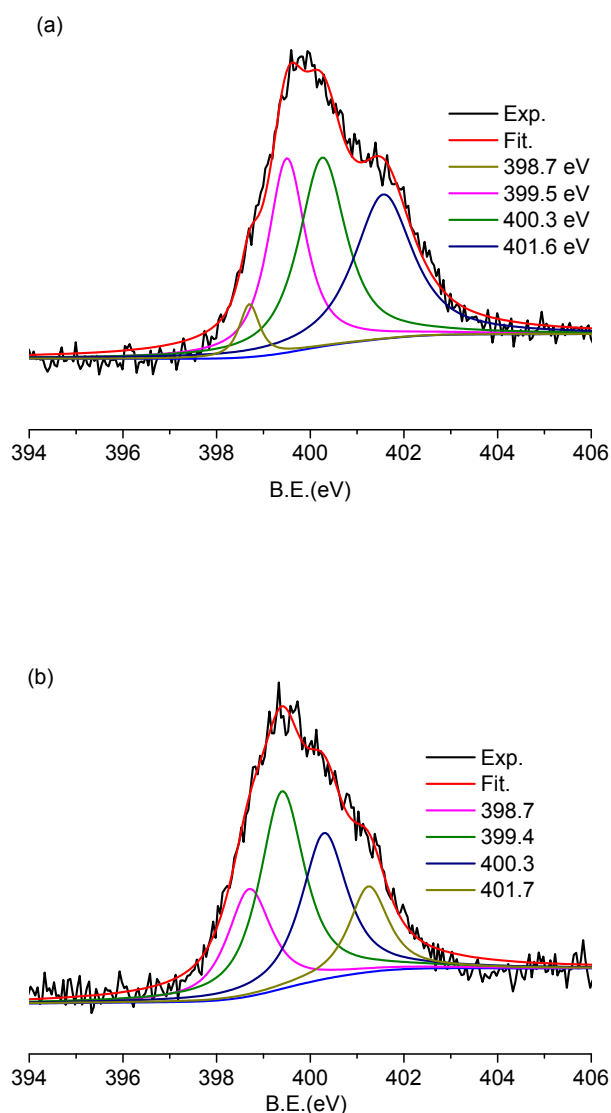


Figure S3. Deconvoluted N 1s XPS spectra of (a) SPC, and (b) D0.5-SPC.

Four peaks are resolvable for the N 1s spectra of SPC and D0.5-SPC. The two peaks with lower binding energy at 398.7 ± 0.1 eV and 399.4 ± 0.1 eV are assigned to quinoid imine and benzenoid amine nitrogens, respectively. The other two peaks centered at 400.3 ± 0.1 eV and 401.6 ± 0.1 eV are related to doped structures, that is, the polarized quinoid imine ($-N^{+\bullet}=\text{C}$) and protonated amine/imine ($-\text{NH}_2^+/-\text{NH}^+=\text{C}$), respectively.

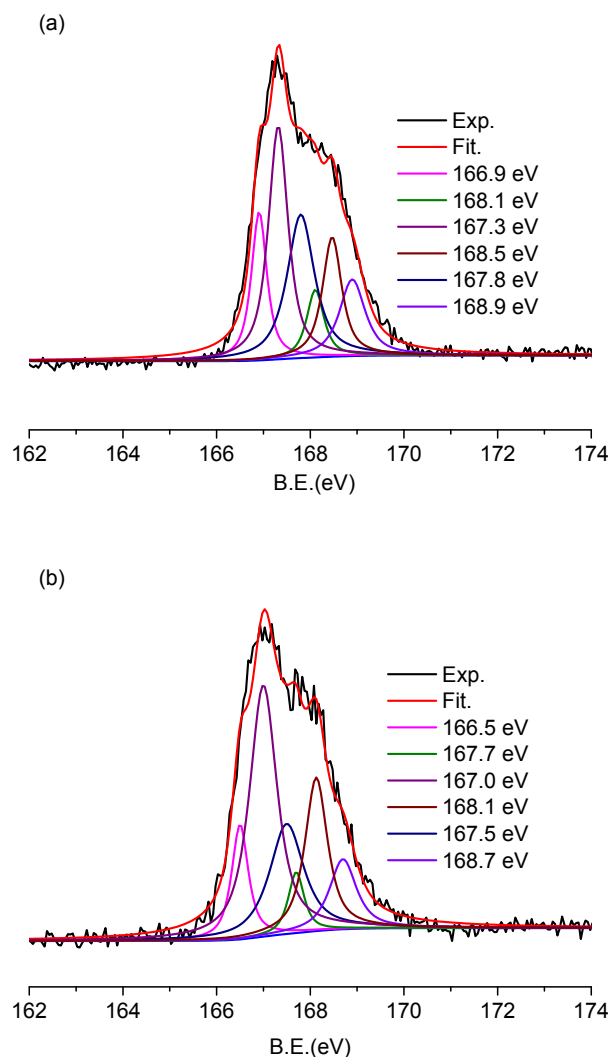


Figure S4. Deconvoluted S 2p XPS spectra of (a) SPC, and (b) D0.5-SPC.

For SPC, three doublets (six peaks) were resolvable. The bands at B.E.s of $166.9 \pm 0.1 / 168.1 \pm 0.1$ eV, $167.4 \pm 0.1 / 168.6 \pm 0.1$ eV, $167.8 \pm 0.1 / 168.9 \pm 0.1$ eV were ascribed to the sulfurs in the ring-attached sulfonic acid groups that protonate the imine and/or amine nitrogen, sulfonic acid groups H-bonded with quinoid imine, and sulfonic acid groups H-bonded with benzenoid amine, respectively. For D0.5-SPC, the S 2p XPS band ascribing to sulfonic acid groups H-bonded with amine disappeared and sulfonic acid groups H-bonded with imine decreased significantly. Meanwhile, a new doublet with B.E.s of $166.5 \pm 0.1 / 167.7 \pm 0.1$ eV ascribed to newly-formed sulfonic acid groups H-bonded with DHA molecules was observed. There is one possibility that APS was incorporated into the SPC catalyst, thereby the S 2p spectra with BE of 167.1/168.3 eV should be resolvable.³ However, this assumption is reasonably excluded because the increase of the amount of APS in the D-SPC catalyst (from 21% to 55%, in Table 1, entry 3 and 4) is incompatible to the fact that APS is

deemed to decompose during the treatment of SPC catalyst with DHA at 140 °C (p.s., the decomposition temperature of APS is 120 °C). Therefore, the S 2p XPS spectra confirmed the destruction of existing H-bonds on SPC catalyst and the generation of new H-bonds on D0.5-SPC catalyst.

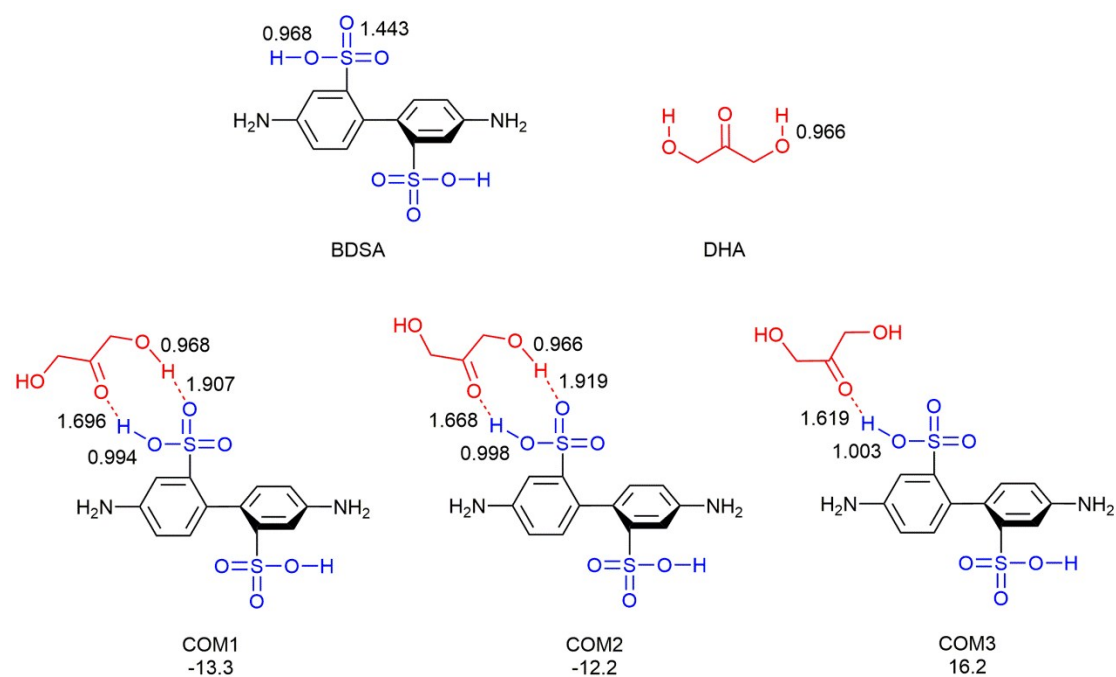


Figure S5. Theoretical simulation of selected fragments in D0.5-SPC catalyst. Optimized geometric structures and the relative Gibbs free energies (G_r , kJ mol⁻¹) for the three complexes relative to the discrete BDSA and DHA obtained at the M06-2x/6-311++G(d,p) level are shown. Bond lengths are reported in Å. The COM1 species is the thermodynamically most stable among the three species. The interaction of BDSA and DHA is existed *via* two intermolecular H-bonds.

Computational details

All calculations were performed with the Gaussian 09 program package.¹ Geometry optimizations were carried out to locate all the stationary points using M06-2x density functional theory method with the 6-311++G(d, p) basis set for all atoms, namely M06-2x/6-311++G(d, p).^{4, 5} Systematic harmonic frequency calculations were performed to ensure all the structures obtained are true minima on the potential energy surfaces. Unless otherwise mentioned, the Gibbs free energy of formation (ΔG) is relative to the initial reactants obtained at M06-2x/6-311++G(d, p) level under atmospheric pressure and room temperature (1 atm and 298.15 K).

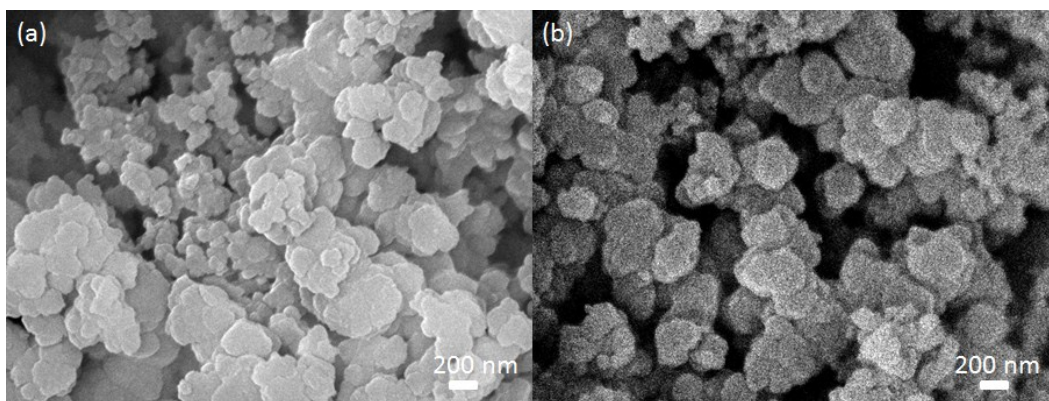


Figure S6. SEM images of fresh (a) SPC, and (b) D0.5-SPC catalysts.

The SEM images of SPC and D0.5-SPC show similar morphology of nanoplate with average diameters of 296 and 358 nm, respectively, indicating that the polymeric catalyst just swells to a larger size without morphology change during DHA treatment.

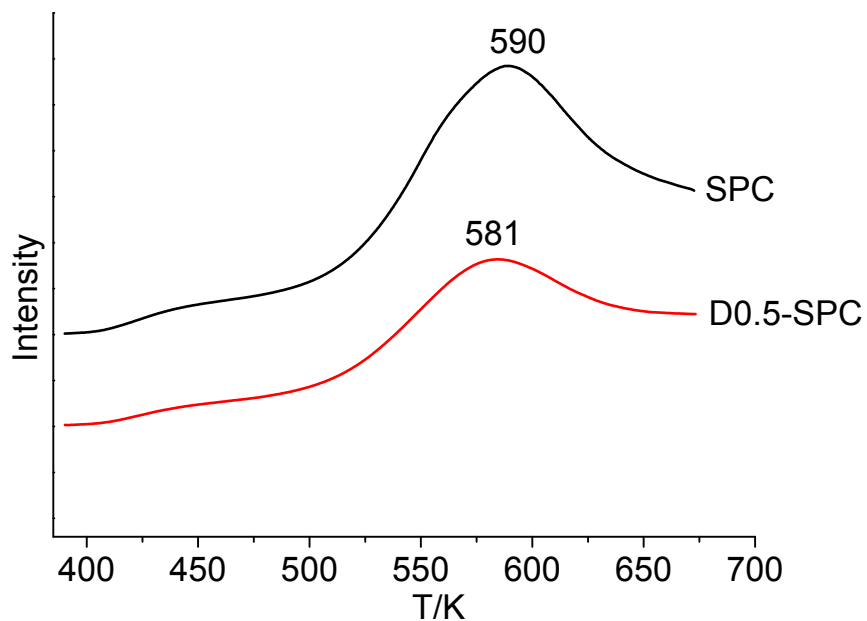


Figure S7. NH₃-TPD profiles of SPC and D0.5-SPC catalysts.

The NH₃-TPD profile of D0.5-SPC shows a lower desorption temperature (581 K) than that of SPC (590 K), which implies that DHA treatment weakens the acidity strength of the polymeric catalyst. We infer that the decrease in acidity strength of D0.5-SPC should be induced by the existence of stronger double H-bonds between sulfonic acid groups and DHA molecules, which provides a confinement to the protons on the organocatalyst.

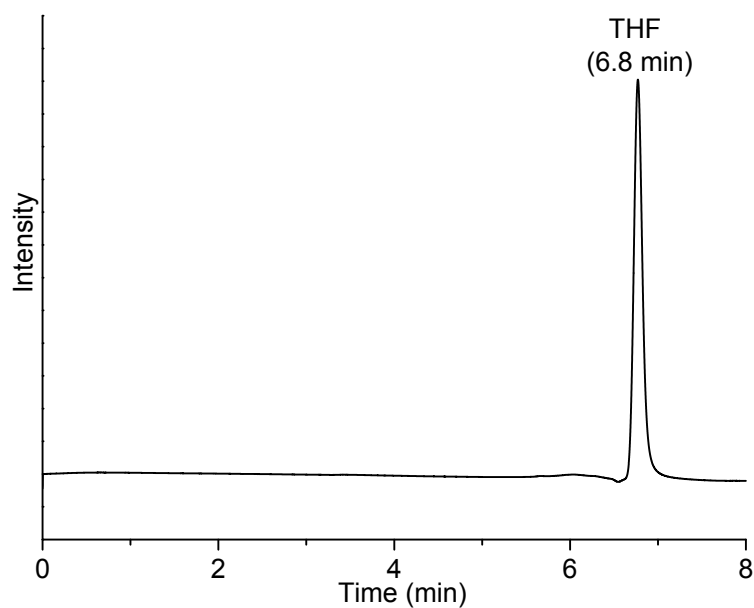


Figure S8. GPC analysis of the liquid mixture after treating D0.5-SPC (30.0 mg) in ethanol/THF ($V/V=3/1$, 3 mL) in the presence of water (27 mg) at 413 K for 6 h.

The possible hydrolysis of the polymer catalyst was studied by treating D0.5-SPC catalyst (30.0 mg) in an ethanol/THF ($V/V=3/1$, 3 mL) mixed solvent in the presence of 27 mg of water at 413 K for 6 h, wherein the water content in solvent was equivalent to that formed from fructose-to-EMF transformation (based on 75% yield of EMF). The gel permeation chromatography (GPC) analysis of the resulting liquid revealed that no oligomers formed during the treatment. In addition, the solid catalyst was collected by centrifugation, washed with ethanol and dried at 353 K. The weight of the recovered D0.5-SPC was 29.6 mg, which was very close to that before treatment.

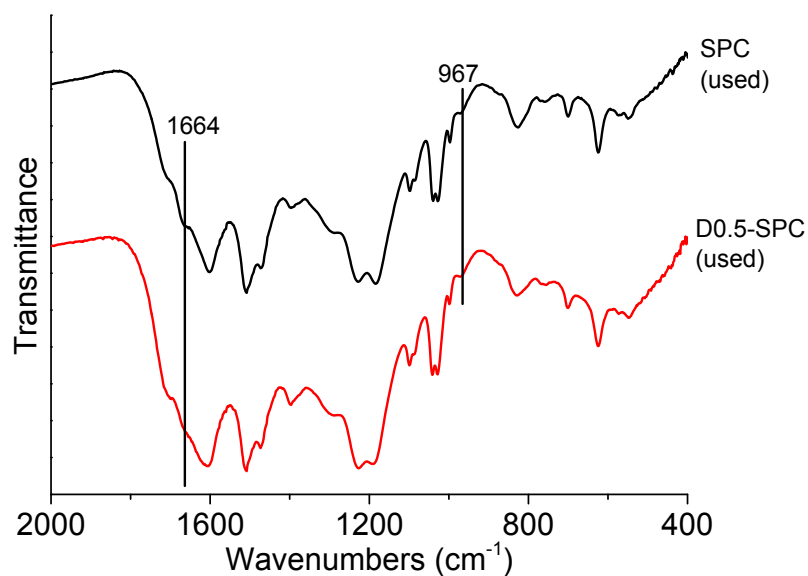


Figure S9. FT-IR spectra of used SPC and D0.5-SPC catalysts.

The FT-IR spectra of used SPC and D0.5-SPC catalysts exhibit two bands at 1664 and 967 cm^{-1} , assigned to the characteristic stretching vibrations of carbonyl groups and symmetrically multiple rocking of C-O-C bonds,⁶ respectively, which imply the deposition of HMF, EMF, or oligomerized products on the used catalysts. For the SPC catalyst, the upshift from 1572 cm^{-1} on fresh catalyst to 1600 cm^{-1} on used catalyst suggests the de-protonation of the polymer chain after catalytic reaction, which makes us reasonable to assume that HMF or EMF might have absorbed on the solid catalyst *via* interaction between carbonyl groups and the released sulfonic acid groups. However, the FT-IR spectrum of the used D0.5-SPC is similar with the fresh one.

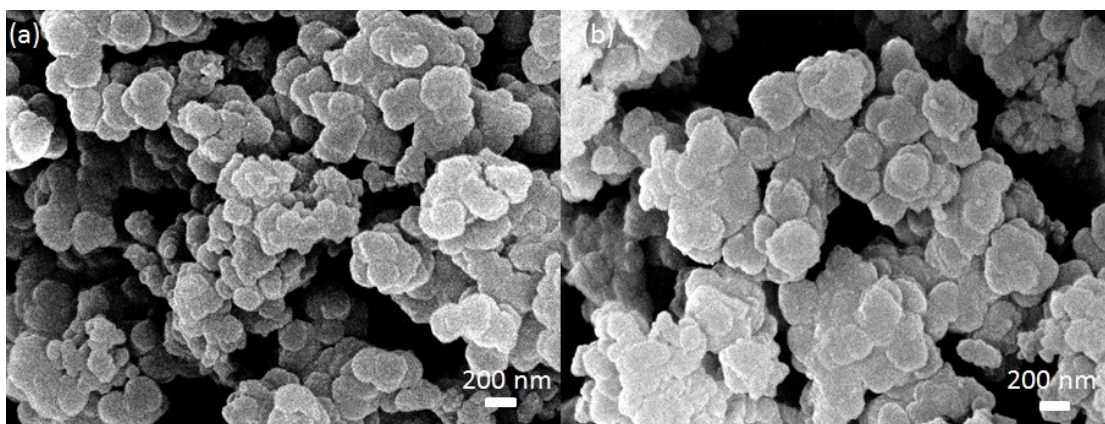


Figure S10. SEM images of used (a) SPC, and (b) D0.5-SPC catalysts.

The SEM images of both used catalysts exhibit a morphology of nanoplate with smaller average diameter than the fresh catalysts, possibly resulting from the mechanical stirring during the reaction.

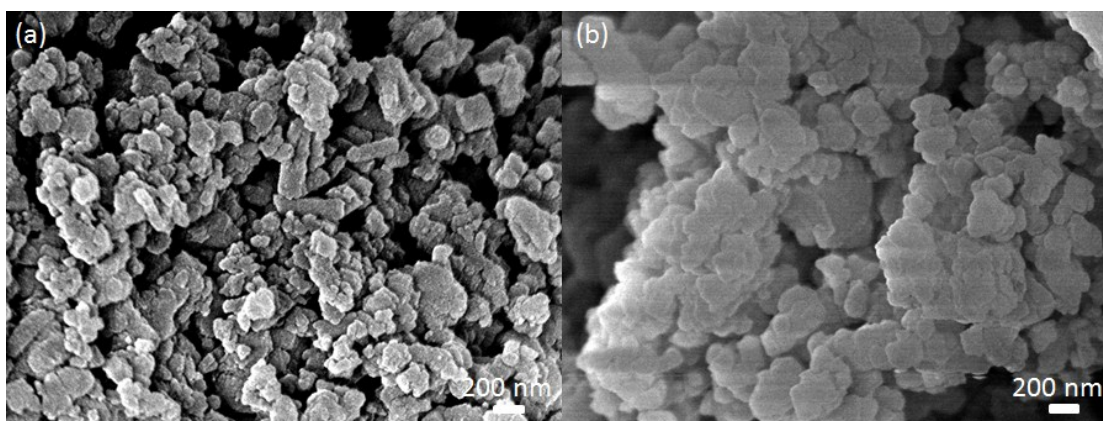


Figure S11. SEM images of (a) SPC-0.1-11/3, and (b) SPC-0.4-11/3 catalysts.

With increasing the molar ratio of monomers in catalyst preparation, the morphology changed from nanorod (SPC-0.10-11/3) to nanofibers (SPC-0.40-11/3), which may be impacted by the chain conformation of the doping acid/monomer salts in the aqueous solution.⁷ A relatively rigid and straight conformation will be formed after BDSA interacts with AN to produce salts, followed by parallel aggregation to form nanoplate structure.

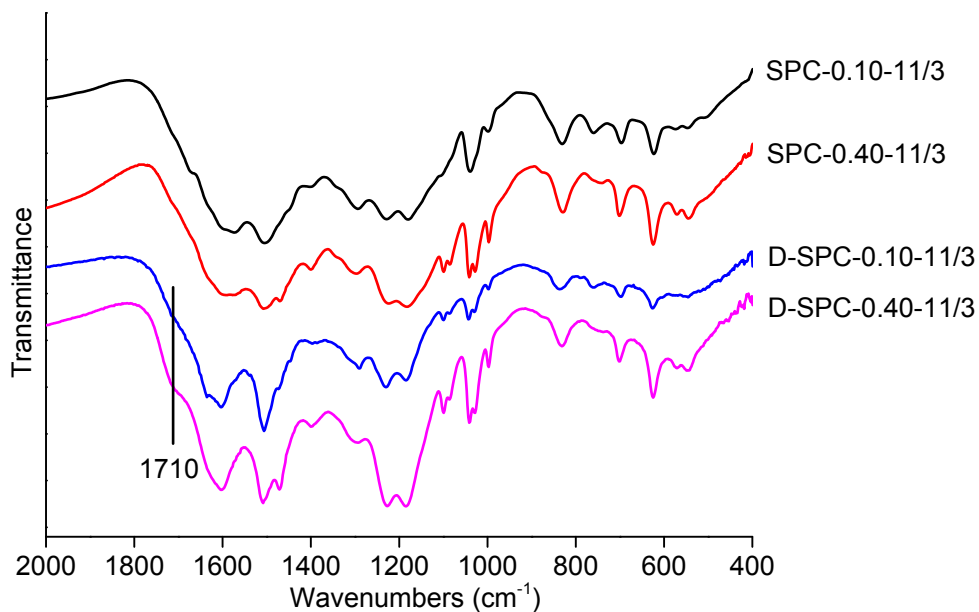


Figure S12. FT-IR spectra of SPC-0.1-11/3, SPC-0.4-11/3, D-SPC-0.1-11/3, and D-SPC-0.4-11/3 catalysts.

The DHA treatment generates a new peak at 1710 cm⁻¹ in the FT-IR spectra of D-SPC-0.1-11/3 and D-SPC-0.4-11/3, which is originated from the stretching vibration of carbonyl group. Therefore, we infer that double H-bonded structure also formed in catalysts D-SPC-0.1-11/3 and D-SPC-0.4-11/3.

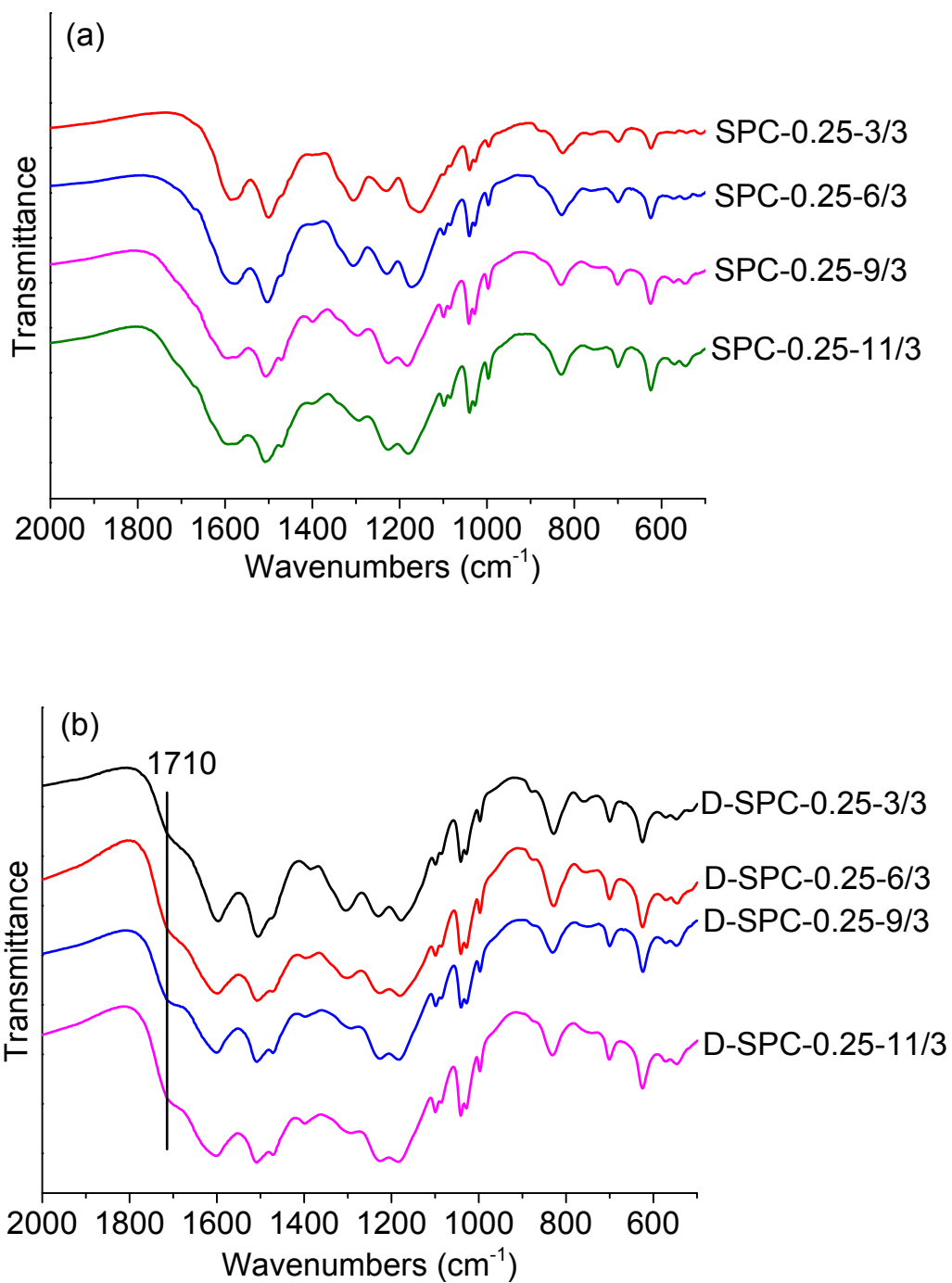


Figure S13. FT-IR spectra of (a) SPC-0.25-y, and (b) D-SPC-0.25-y catalysts.

Reference:

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