Supporting Information

Sulfonated Polyaniline as Solid Organocatalyst for Dehydration

of Fructose into 5-Hydroxymethylfurfural*

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Entry	Catalysts -		S/N molar ratio	
Entry		Fresh	Used (after first run)	Used (after fifth run)
1	Amberlyst-15	0.96 a	-	-
2	SPAN-1/3	0.141	-	-
3	SPAN-3/3	0.198	0.154	-
4	SPAN-6/3	0.209	0.174	-
5	SPAN-9/3	0.210	0.175	-
6	SPAN-12/3	0.216	0.191	-
7	SPAN-11/3	0.238	0.202	0.194

Table S1. The results of elemental analysis for fresh and used catalysts.

^a S/(C/8) molar ratio

Entry	Cat	Surface area	Pore volume	Pore width	
Ениу	Cal.	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(Å)	
1	SPAN-1/3	19.2	0.005	10.2	
2	SPAN-3/3	22.9	0.006	10.4	
3	SPAN-6/3	36.5	0.011	11.7	
4	SPAN-9/3	31.0	0.009	11.6	
5	SPAN-11/3	31.7	0.010	13.1	
6	SPAN-12/3	32.8	0.009	11.4	

Table S2. Results of BET characterization of SPAN-x/y catalysts.

All as-synthesized SPAN catalysts have surface area of about $20\sim36 \text{ m}^2 \cdot \text{g}^{-1}$. Pore volume ranges from 0.005 to 0.011 cm³ g⁻¹ while pore width is about $10\sim13 \text{ Å}$.

Entry	Solvent	Conv.	Yield	Yield of products (mol%)			
Entry	$(V_{\text{water}}/V_{1,4\text{-dioxane}})$	(mol%)	HMF	LA	FA	FF	
1	0/100	100	25	4	22	8	
2	5/95	100	46	12	27	5	
3	10/90	100	57	12	16	3	
4	15/85	91	61	6	9	2	
5	20/80	91	64	4	9	2	
6	30/70	86	63	3	10	1	
7	40/60	69	43	2	11	<1	
8	50/50	60	37	2	8	<1	

Table S3. Activity of Amberlyst-15 in water/1,4-dioxane with various volume ratios.^a

^a Reaction conditions: 0.25 mmol of fructose, 5 mg of Amberlyst-15 (0.032 mmol of S, based on elemental analysis), 1 mL of solvent, 140 °C, 3 h, N_2 .

Entry	Catalyst (mmal)	Conv.	Yield of products (mol%)			
Епиу	Catalyst (minor)	(mol%)	HMF	LA	FA	FF
1	Benzenesulfonic acid (0.032)	100	60	6	12	<1
2 ^b	Benzenesulfonic acid (0.032)	100	63	3	4	<1
3	Metanilic acid (0.032)	100	67	-	3	<1
4 ^b	Amberlyst-15 (0.032)	98	63	5	15	5
5°	Benzenesulfonic acid (0.032)	100	50	2	4	<1
6 ^d	Benzenesulfonic acid (0.032)	100	42	-	3	<1
7 ^e	Amberlyst-15 (1.2)	7	-	6	8	-

Table S4. Conversion of fructose in water/1,4-dioxane over various catalysts.^a

^a Reaction conditions: 0.25 mmol of fructose, 1 mL of water/1,4-dioxane solvent (V/V = 5/95), 140 °C, 3 h, under N₂ atmosphere. ^b Adding 0.032 mmol of diphenylamine before the reaction. ^c Adding 0.096 mmol of diphenylamine before the reaction. ^d Adding 0.096 mmol of aniline before the reaction. ^e 6.6 mmol of HMF and 7.5 mL of water/1,4-dioxane (V/V = 5/95) were used. Reaction was conducted at 95 °C for 3 h.

Entry	Solvents(5/95, V/V)	Conv.	Yield of products (mol%)			
		(mol%)	HMF	LA	FA	FF
1	Water/1,4-dioxane	99	71	-	4	2
2	Methanol/1,4-dioxane	100	51	-	4	4
3	Ethanol/1,4-dioxane	100	46	-	4	4
4	Hexane/1,4-dioxane	100	40	-	3	4
5	Acetonitrile/1,4-dioxane	100	41	-	4	5
6	Diethyl ether/1,4-dioxane	100	39	-	5	4
7	Chloroform/1,4-dioxane	100	40	-	4	5

Table S5. Dehydration of fructose over SPAN-11/3 in various solvents.^a

 a Reaction conditions: 0.025 mmol of fructose, 15 mg of SPAN-11/3, 1 mL of solvent, 140 °C, 3 h, $N_2.$

Protic solvents (water, methanol and ethanol) gave out higher HMF yields than polar aprotic or weakly polar solvent (hexane, acetonitrile, ethyl ether, and chloroform) as the latter stabilize the hydrogen-bonded species to a less extent.

Entry	Substrate	Yield of products (mmol%)						
		HMF	Fructose	Glucose	FA	LA	FF	
1	Inulin	59	<1	-	7	-	2	
2	Glucose	11	-	14	17	-	<1	
3	Sucrose	41	-	6	23	-	2	

Table S6. Catalytic conversion of various carbohydrates over SPAN-11/3 catalyst.^a

^a Reaction conditions: 0.25 mmol of carbohydrates (based on monosaccharide), 15 mg of SPAN-11/3, 1 mL of water/1,4-dioxane solvent (V/V = 5/95), 140 °C, 3 h, N₂.

SPAN catalyst was active for the conversion of inulin and sucrose, giving out HMF yields of 59% and 41%, respectively. However, only 11% of HMF yield was obtained when glucose was used as the substrate, suggesting that this polymer catalyst was less active for glucose-to-fructose isomerization.



Fig. S1 XRD patterns of SPAN-x/y catalysts.

The XRD patterns show typical amorphous structure with a single broad diffraction peak centered at 20 of ca. 23.9° except SPAN-3/3 and SPAN-6/3 wherein larger 20 at ca. 25.8° and smaller crystallographic spacing (*d*) indicate the obvious presence of external dopants on these two polymer catalysts.



Fig. S2 TEM images of a) SPAN-6/3, b) SPAN-9/3, c) SPAN-11/3, and d) SPAN-12/3.

TEM images of the SPAN-x/y catalysts reveal the formation of nanorod structures for SPAN-6/3, SPAN-9/3, and SPAN-11/3. For SPAN-12/3, irregular nanogranules formed. These results are consistent with that observed in their SEM images.



Fig. S3 Deconvoluted S 2p XPS of a) SPAN-1/3, b) SPAN-3/3, c) SPAN-6/3, d) SPAN-9/3, e) SPAN-11/3, and f) SPAN-12/3.

Six peaks (three doublets) are resolvable for the S 2p spectra of all catalysts except SPAN-1/3. The doublet with binding energies (BEs) of $167.0(\pm 0.1 \text{ eV})$ and $168.1 (\pm 0.1 \text{ eV})$ is from the sulfur in the ring-attached sulfonic acid group that protonates the imine and/or amine nitrogen.^[1] However, the two doublets with higher BEs of $167.4(\pm 0.1 \text{ eV})/168.6(\pm 0.1 \text{ eV})$ and $167.9(\pm 0.1 \text{ eV})/169.0(\pm 0.1 \text{ eV})$ are lower than that reported as the sulfur in free sulfonic acid group.^[1] which are tentatively ascribed to the sulfur in the sulfonic acid groups that hydrogen-bonded with benzenoid amine (-NH-) and quinoid imine (-N=) nitrogen, respectively. That is, all of the sulfonic acid groups in SPAN catalysts interact with adjacent nitrogen atom. As a result, no free sulfonic acid group exists.







Fig. S4 Theoretical simulation of selected fragments of SPAN catalyst at M06-2x/def2-tzvpp level showing the distance between H atom in sulfonic acid group and adjacent (a, b) quinoid imine N, and (c) benzenenoid amine N atoms.

The N-H distances in a, b and c were simulated to be 1.798, 1.981 and 2.140 Å, respectively. The results reveal that the ring-attached sulfonic acid group would interact with the benzenoid amine and quinoid imine nitrogen *via* hydrogen bonding, among which the interaction with quinoid imine N is thermodynamically more favored.



Fig. S5 Schematic showing the internal and external doping of SPAN. The green dashed line bracketed regions indicate the internal doping of SPAN by H-bonding between the ring-attached sulfonic acid group and the benzenoid amine/quinoid imine nitrogen. The pink dashed line bracketed regions indicate the external doping of SPAN by salification of metanilic acid by the benzenoid amine/quinoid imine nitrogen.



Fig. S6 Deconvoluted N 1s XPS of a) SPAN-1/3, b) SPAN-3/3, c) SPAN-6/3, d) SPAN-9/3, e) SPAN-11/3, and f) SPAN-12/3.

For the six SPAN-x/y catalysts, the N 1s XPS spectra are deconvoluted to four components at BEs of $398.6(\pm0.1)$, $399.3(\pm0.1)$, $400.3(\pm0.1)$, and $401.6(\pm0.1)$ eV, which are assigned to quinoid imine N, benzenoid amine N, polarized quinoid imine (-N⁺⁻=) N and protonated amine/imine (-NH⁺-/-NH⁺=) N, respectively. The latter two components are originated from acid-base interactions in the solid SPAN catalysts.



Fig. S7 Effect of SPAN-11/3 amount on fructose dehydration. Reaction conditions: 0.25 mmol of fructose, 1 mL of water/1,4-dioxane (V/V = 5/95), 140 °C, 3 h, N₂.

With increasing SPAN-11/3 dosage, the yield of HMF increased and reached a maximum of 71% when 15 mg of SPAN-11/3 was used. A further increase of the catalyst dosage to 30 mg decreased the HMF yield to 57% accompanied with the increase of FA yield to \sim 8%. The yield of FF was kept at about 2% in all catalyst dosage. Notably, no LA formed, revealing that the rehydration of HMF was completely inhibited by SPAN-11/3 catalyst.



Fig. S8 Effect of reaction temperature on fructose dehydration. Reaction conditions: 0.25 mmol of fructose, 15 mg of SPAN-11/3, 1 mL of water/1,4-dioxane solvent (V/V =5/95), 3 h, N₂.

With increasing the reaction temperature, the yield of HMF increased and reached a maximum of 71% when reaction was performed at 140 °C. A further increase of the temperature to 170 °C decreased the HMF yield to 50% accompanied with the increase of FA yield to ~10% and FF yield to 4%. Significantly, no LA formed even at high temperature (170 °C), revealing that the rehydration of HMF was completely inhibited by SPAN-11/3 catalyst.



Fig. S9 Effect of reaction time on fructose dehydration. Reaction conditions: 0.25 mmol of fructose, 15 mg of SPAN-11/3, 1 mL of water/1,4-dioxane solvent (V/V =5/95), 140 °C, N₂.

As reaction progressed, HMF formed with time, giving out a maximum yield of 71% at 3 h. Further increase of the reaction time to 5 h did not lead to the improvement of HMF yield. The yield of FF was always no more than 2%, and FA yield increased to 6%. It should be noted that the rehydration of HMF was still completely restrained by SPAN-11/3 in the whole process of reaction.



Fig. S10 In situ ATR-IR spectra of a) HMF at 95 °C in the presence of SPAN-11/3. b) Magnified view of the bracketed regions in a). Blank in a) and b) represents the ATR-IR spectra of HMF in water/1,4-dioxane solvent (V/V = 5/95) at 95 °C in the absence of catalysts. Reaction conditions: 6.6 mmol of HMF, 1.2 mmol of SPAN-11/3, 7.5 mL of water/1,4-dioxane solvent (V/V = 5/95), 95 °C.

ATR-IR spectra were collected at 95 °C on the ReactIR iC10 system (Mettler Toledo) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector with a resolution of 4 cm⁻¹. The characteristic IR bands of HMF kept almost invariable within 3 h except that a weak band at 1731 cm⁻¹ appeared at 2 h. This new IR band corresponded to the carboxylic C=O stretching vibration of FA or LA.^[2] The result of HPLC revealed that only FA (2 mol%) formed after 3 h's reaction, therefore, the appearance of the IR band at 1731 cm⁻¹ belonged to the C=O stretching vibration of FA. The *in situ* ATR-IR spectra indicate that HMF is stable towards rehydration to LA after mixing with SPAN catalyst.



Fig. S11 In situ ATR-IR spectroscopy of a) HMF at 95 °C in the presence of Amberlyst-15. b) Magnified view of the bracketed regions in a). Blank represents the ATR-IR spectra of HMF in water/1,4-dioxane solvent (V/V = 5/95) at 95 °C in the absence of catalysts. Reaction conditions: 6.6 mmol of HMF, 1.2 mmol of Amberlyst-15 (based on S), 7.5 mL of water/1,4-dioxane solvent (V/V = 5/95), 95 °C.

ATR-IR spectra were collected at 95 °C on the ReactIR iC10 system (Mettler Toledo) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector with a resolution of 4 cm⁻¹. The band at 1346 cm⁻¹ originates from hydroxymethyl O-H stretching vibration in HMF.^[3] A downshift from 1346 to 1340 cm⁻¹ revealed that the interaction between Amberlyst-15 and HMF occurred. Furthermore, a new IR band at 1731 cm⁻¹ was observed after 0.5 h's reaction, which corresponded to the carboxylic C=O stretching vibration of FA or LA. Both LA (6%) and FA (8%) were detected by HPLC. The *in situ* ATR-IR spectra and the result of HPLC indicate that the rehydration of HMF to LA and FA resulted from the interaction of hydroxymethyl -OH in HMF with Amberlyst-15.



Fig. S12 SEM images of a) fresh SPAN-11/3, and b) used SPAN-11/3 after the fifth catalytic run.

Reference:

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