

**Supplementary Information**

**One-pot fructose conversion into 5-ethoxymethylfurfural using a highly active and stable heterogeneous catalyst of sulfonated hydrophobic mesoporous organic polymer**

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## Experimental section

### a. Chemicals and materials

5-Hydroxymethylfurfural (99%), 5-ethoxymethylfurfural (97%), amberlyst-15, amberlyst-16, divinylbenzene (80%), ethyl levulinate (99%), D-(-)-fructose (99%), glucose (99%), (3-Mercaptopropyl)trimethoxysilane (95%) and phosphotungstic acid were purchased from Sigma-Aldrich. Sucrose was obtained from Duksan Pure Chemical Co., Ltd. Inulin (from chicory root) was obtained from Acros Organics. Aluminium trichloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ), azobisisobutyronitrile (AIBN), ethanol (anhydrous 99.9%), phosphoric acid (85%), p-toluenesulfonic acid monohydrate (99%), sodium hydroxide, sulfuric acid (95%) and tetrahydrofuran (99.8%) were obtained from Samchun chemicals. Sodium p-styrenesulfonate (80%) was purchased from Wako chemicals. Trimethylphosphine oxide (TMPO) was purchased from Alfa Aesar.

### b. Catalyst synthesis procedure

#### Synthesis of sulfonated hydrophobic mesoporous organic polymer (MOP-SO<sub>3</sub>H)

Prior to the material synthesis, 20 mL of DVB was washed with 500 mL of 5wt% sodium hydroxide solution to remove the polymerization inhibitor. Later, the obtained DVB was washed with deionized water until the neutral pH. Finally, the purified DVB was further used for catalyst preparation.

The sulfonated hydrophobic mesoporous organic polymer (here onwards MOP-SO<sub>3</sub>H-x) was synthesized by free radical co-polymerization of DVB and sodium p-styrenesulfonate using AIBN as a radical initiator under solvothermal condition <sup>1</sup>. In a typical synthesis, 2 g of DVB was added into a solution containing 0.055 g of AIBN, 19.6 g of THF and 3 g of deionized water. Later, to the above mixture, 1.92 g SPSS (a sulfonate monomer) was added to obtain MOP-SO<sub>3</sub>Na-0.6. After stirring the mixture at room temperature for 3 h, the solution was transferred into an autoclave and solvothermally treated at 100 °C for 24 h. The obtained monolithic material was crushed and allowed for solvent evaporation at room temperature for 48 h to obtain MOP-SO<sub>3</sub>Na-0.60.

The synthesized Na<sup>+</sup> form of catalyst was converted into H<sup>+</sup> form by simple ion-exchange with 1M aqueous H<sub>2</sub>SO<sub>4</sub> at room temperature for 1 day. In the typical method, 2 g

MOP-SO<sub>3</sub>Na-x was added into 200 mL of 1M sulfuric acid and stirred for 24 h at room temperature. Then, the sample was filtered and washed with large amount of deionized water until the filtrate reached to neutral pH. Later, the sample was washed with ethanol and dried at 100 °C for overnight. The obtained sample was denoted as MOP-SO<sub>3</sub>H-x. A series of MOP-SO<sub>3</sub>H-x catalysts was synthesized by following the afore-mentioned procedure by varying the amount of SPSS (a sulfonate monomer) and amount of water until the complete dissolution of SPSS.

The acidic sites content in the sulfonated hydrophobic mesoporous organic polymer was tuned by varying the amount of DVB and SPSS monomer. During the synthesis, the amount of deionized water was varied for the complete dissolution of SPSS salt and the details are mentioned in the below table.

Catalyst	Mole ratio of DVB/SPSS	Weight (g)				
		DVB	SPSS	AIBN	THF	H <sub>2</sub> O
MOP	0.0	2	-	0.05	19.6	2.0
MOP-SO <sub>3</sub> H-0.1	0.1	2	0.32	0.05	19.6	2.0
MOP-SO <sub>3</sub> H-0.2	0.2	2	0.64	0.05	19.6	2.0
MOP-SO <sub>3</sub> H-0.3	0.3	2	0.96	0.05	19.6	2.0
MOP-SO <sub>3</sub> H-0.4	0.4	2	1.28	0.05	19.6	2.2
MOP-SO <sub>3</sub> H-0.5	0.5	2	1.60	0.05	19.6	2.5
MOP-SO <sub>3</sub> H-0.6	0.6	2	1.92	0.05	19.6	3.0
MOP-SO <sub>3</sub> H-0.7	0.7	2	2.24	0.05	19.6	3.2
MOP-SO <sub>3</sub> H-0.8	0.8	2	2.56	0.05	19.6	3.8
MOP-SO <sub>3</sub> H-0.9	0.9	2	2.88	0.05	19.6	4.0
MOP-SO <sub>3</sub> H-1.0	1.0	2	3.20	0.05	19.6	4.5

The sulfonic acid functionalized SBA-15 (SO<sub>3</sub>H-SBA-15) were synthesized according the reported literature <sup>2</sup>. To the obtained calcined SBA-15 (1 g), a 2 ml of (3-Mercaptopropyl)trimethoxysilane was used during the synthesis of SO<sub>3</sub>H-SBA-15 for grafting thiol into SBA-15 <sup>3</sup>.

### **c. Catalyst regeneration procedure**

The catalyst after 5<sup>th</sup> cycle use was stirred with DMSO (25 ml DMSO/g catalyst) at 100 °C for overnight, followed by filtration and, washing with deionized water and ethanol. Later, the obtained catalyst was further subjected to repeated washing by following the above-mentioned procedure for 4 times. Then, the catalyst was stirred with a solution containing a mixture of ethanol (35 ml) and water (15 ml) at 80 °C for overnight, followed by filtration, washing with deionized water and ethanol, and drying at 100 °C for overnight.

### **d. Adsorption studies**

Fructose and EMF adsorption on catalytic materials were obtained using a static adsorption method. Prior to the experiment, the Amberlyst-16 and MOP-SO<sub>3</sub>H-0.6 were dried in an oven at 120 °C for overnight. For adsorption studies, a known concentration (x mg/ 50 mL water) of fructose and EMF solutions were prepared (x= 10 to 400 mg). Next, the dried catalytic materials (1 g) were added into the solutions containing different concentrations of fructose and EMF. Then, the resultant mixture was kept for 24 h at room temperature under static condition. Later, the solution was filtered using a syringe membrane filter (0.2µm) and subjected to HPLC analysis for quantification.

### **e. Catalyst characterization**

The textural properties of prepared catalysts were determined from the N<sub>2</sub> sorption at 77 K using a Micromeritics Tristar II (3020) instrument. The sulfur content in catalysts was determined by Thermo Scientific FLASH EA-2000 Elemental Analyzer. The number of acidic sites in catalysts was determined by acid–base titration method using 5 mM NaOH solution. In a typical procedure, 100 mg of catalyst (pre-treated prior to experiment) was stirred with 20 ml of 2 M NaCl solution for 12 h to undergo ion exchange. Then, the mixture was centrifuged to separate out the catalyst particles from ion-exchanged solution and the filtrate containing liberated HCl was titrated against 5 mM NaOH using phenolphthalein as an indicator <sup>4</sup>. The FT-IR spectra were recorded in transmittance mode using Thermo Scientific AtFTIR 300 series. The thermogravimetric analysis of catalysts was performed using a Scinco TGA-N 1000 thermal analyzer under constant air flow of 25 min<sup>-1</sup> with the heating rate of 10 °C min<sup>-1</sup>. Transmission

electron micrograph images was obtained from Thermo Scientific Talos F200S scanning/transmission electron microscope(S/TEM). <sup>31</sup>P MAS NMR of TMPO adsorbed catalysts was recorded in Agilent 400MHz 54mm NMR DD2 instrument. Firstly, 0.1 g of catalyst was pre-treated at 150 °C in a custom made Schlenk line tube for 3 h to remove moisture. Once, the sample reached to room temperature, it was placed inside a glove box, then a known amount of TMPO (an equivalent amount referred to the acidic sites present in catalyst taken for analysis) dissolved in dichloromethane was added into the Schlenk line tube containing catalyst using a syringe. Then, the dichloromethane was evaporated at 35 °C under vacuum and further, the sample was thermally treated at 160 °C for 2 h to ensure the adsorption of probe molecules with the acidic sites. X-ray photoelectron spectroscopy measurement was performed using Thermo VG Scientific analyzer Sigma probe. Contact angles were tested on a DSA100 (Kruss Company, Germany) at 25 °C.

The surface acid site density of H<sup>+</sup> in solid acid catalysts was calculated using the formula:

$$SASD (H^+ /nm^2) = \frac{(mmol H^+ /g) \times 6.023 \times 10^{23}}{BET \text{ surface area } (m^2/g) \times 10^{18} nm^2}$$

#### **f. Catalytic activity studies**

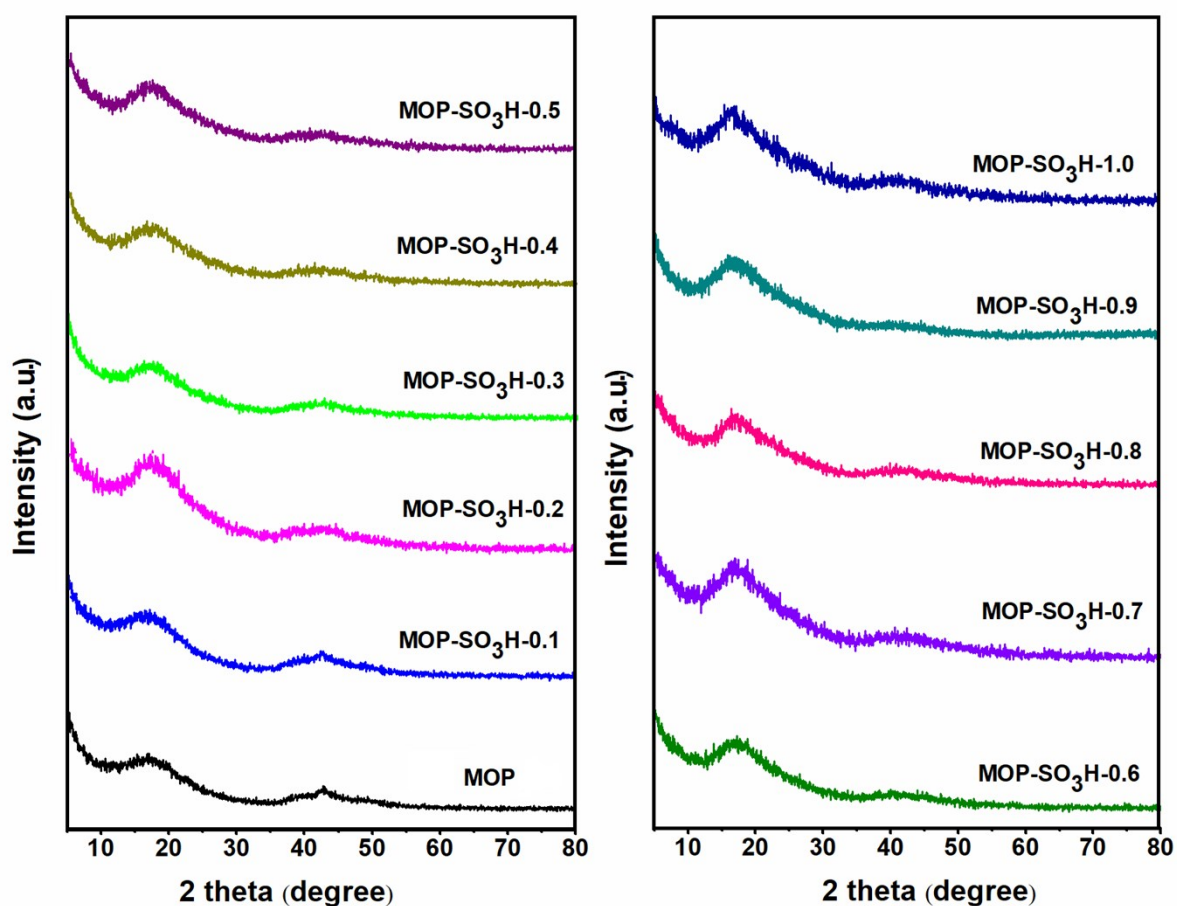
The catalytic reactions were performed in a stainless-steel stirred autoclave equipped with temperature controller and pressure gauge. In a typical experiment, 1.0 g of carbohydrate feedstock and required amount of ethanol were taken in a 50 mL stainless steel stirred autoclave with the pre-activated catalyst. Prior to the experiment, the autoclave reactor was purged with N<sub>2</sub> gas to remove air in order to avoid side reactions of 5-HMF and to maintain the ethanol in liquid phase during heating. Later, the required temperature was maintained by PID controller and the reaction mixture was stirred at 600 rpm. For multi-gram scale reactions, 100 mL stainless-steel autoclave were adopted. The progress of the reaction was monitored by Younglin HPLC equipped with an Aminex column HPX-87H column (Bio-Rad, 7.8 mm I.D. and 300 mm length) using refractive index detector by maintaining column temperature of 50 °C and 5 mM aqueous sulfuric acid solution as an eluent at a flow rate of 0.6 mL/min. The conversion and yields were calculated from an external standard calibration curve of respective molecules. The analysis was confirmed with triplicate injections and the

average result is incorporated in this work. Notably, the yields of HMF, EMF and ELV were calculated considering each monosaccharide to give an equimolar of product. Likewise, the yields of intermediates (ethyl fructoside and 2,5-anhydro-mannose) observed by HPLC were calculated using fructose as the standard. The experimental errors of conversion, selectivity and yield were estimated to be  $\pm 1\%$ .

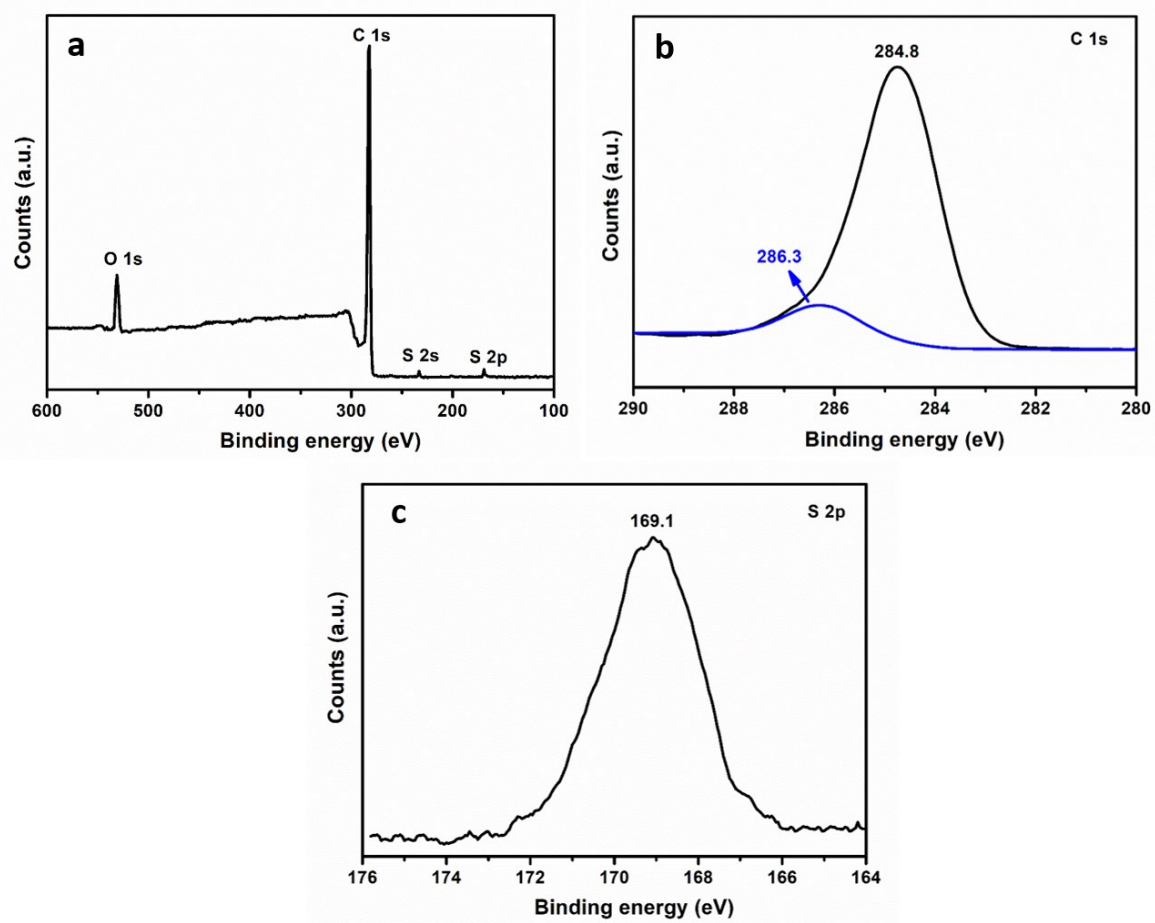
$$\text{Fructose conversion (mol\%)} = \frac{\text{moles of fructose converted} \times 100 \text{ (mol\%)}}{\text{moles of initial fructose}}$$

$$\text{Product selectivity (mol\%)} = \frac{\text{moles of product produced} \times 100 \text{ (mol\%)}}{\text{moles of fructose converted}}$$

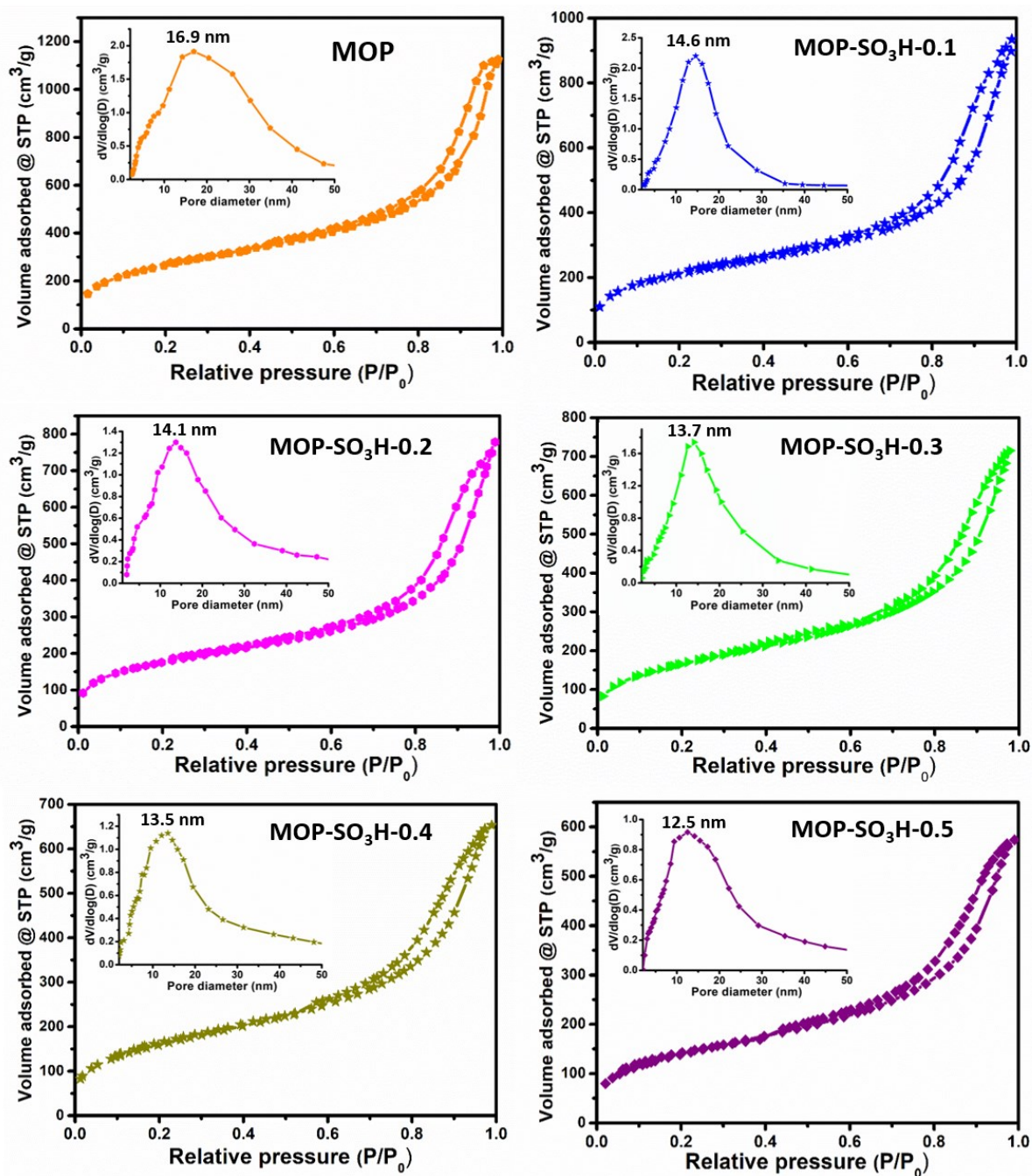
$$\text{Product yield (mol\%)} = \frac{\text{moles of product produced} \times 100 \text{ (mol\%)}}{\text{moles of initial fructose}}$$



**Fig. S1.** XRD pattern of MOP and MOP-SO<sub>3</sub>H-x



**Fig. S2.** XPS measurements of (a) survey, (b) C 1s and (c) S 2p spectra of MOP-SO<sub>3</sub>H-0.6 sample.



**Fig. S3.** N<sub>2</sub> sorption isotherms and pore size distributions (insert) of MOP and MOP-SO<sub>3</sub>H-x



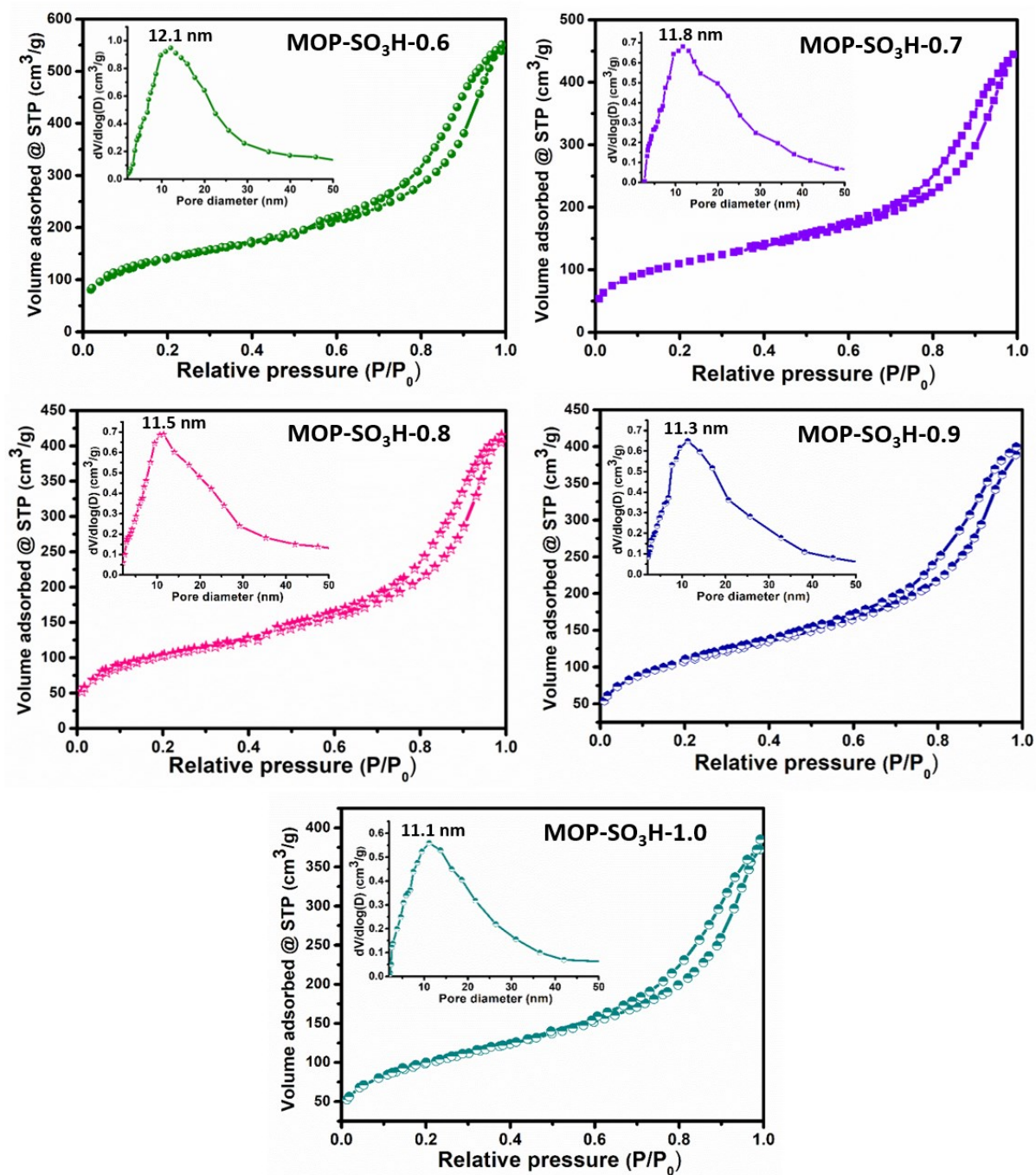
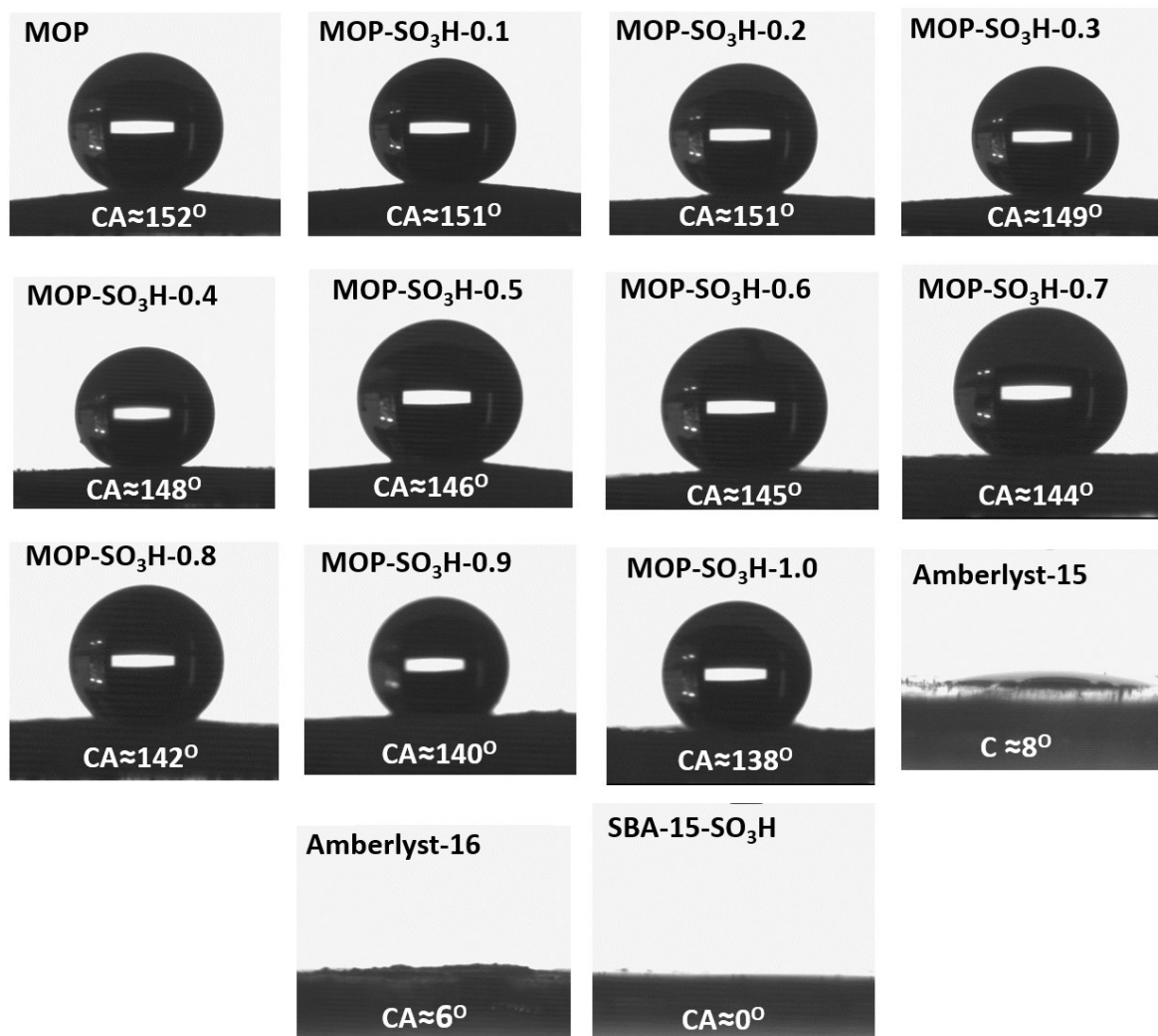
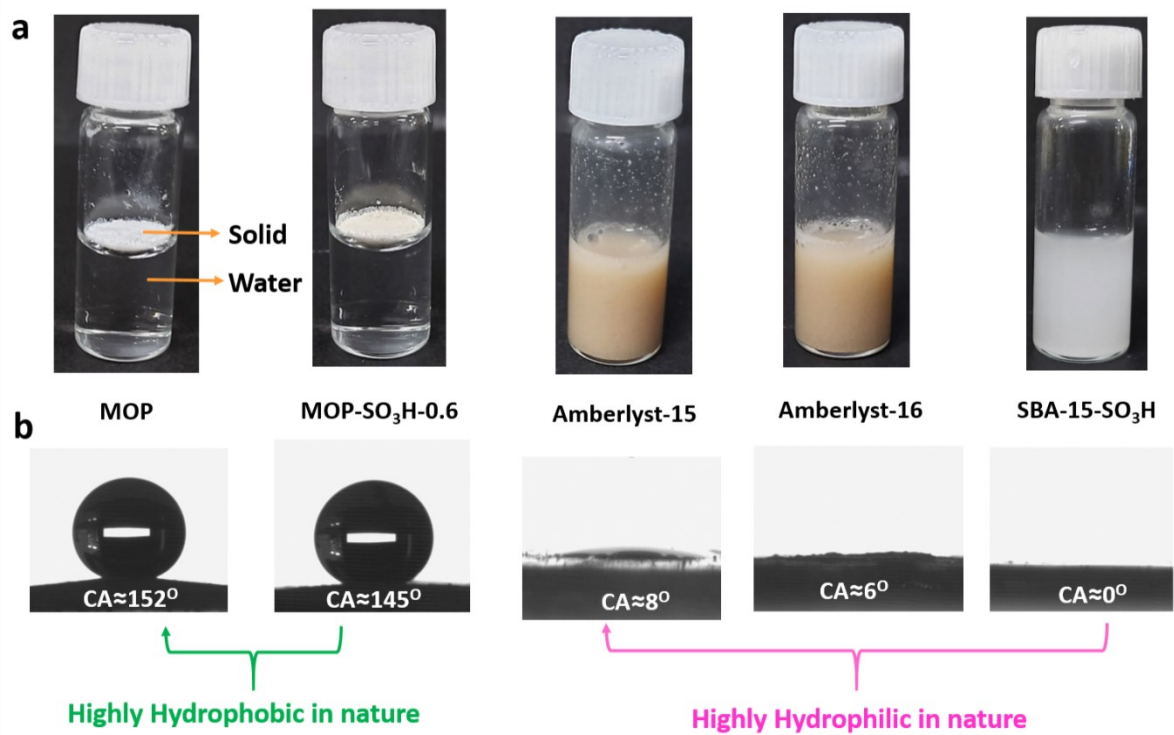


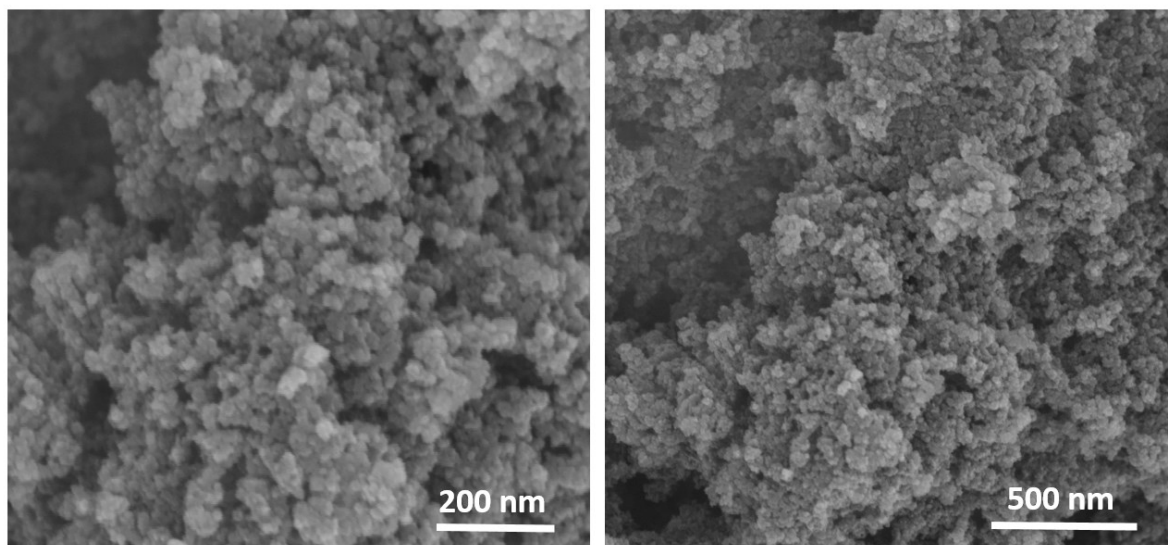
Fig. S4. N<sub>2</sub> sorption isotherms and pore size distributions (insert) of MOP-SO<sub>3</sub>H-x



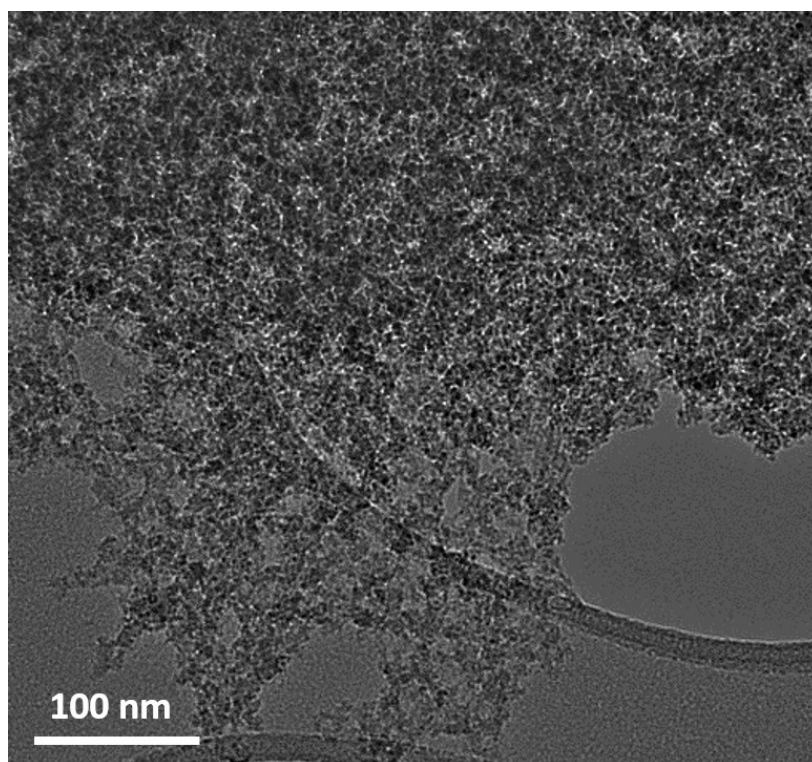
**Fig. S5.** Contact angles of water droplets on the surface of MOP, MOP-SO<sub>3</sub>H-x and other conventional catalysts.



**Fig. S6.** (a) Photographs of solid samples treated with water and (b) Contact angles of water droplets on the surface of MOP, MOP-SO<sub>3</sub>H-0.6 and various solid acid catalysts



**Fig. S7.** SEM image of MOP-SO<sub>3</sub>H-0.6



**Fig. S8.** TEM image of MOP-SO<sub>3</sub>H-0.6



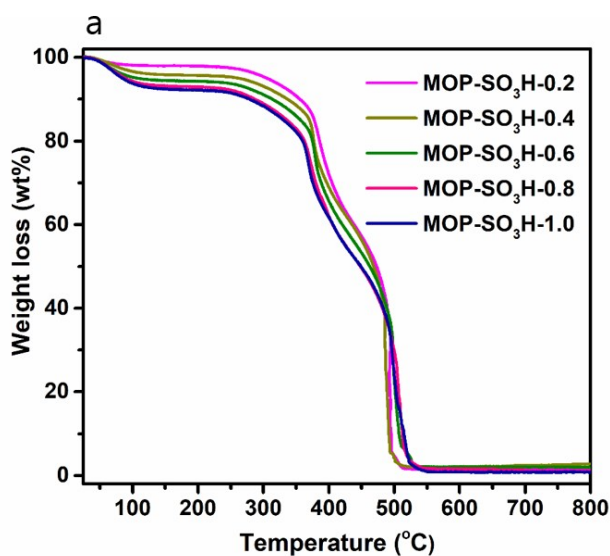


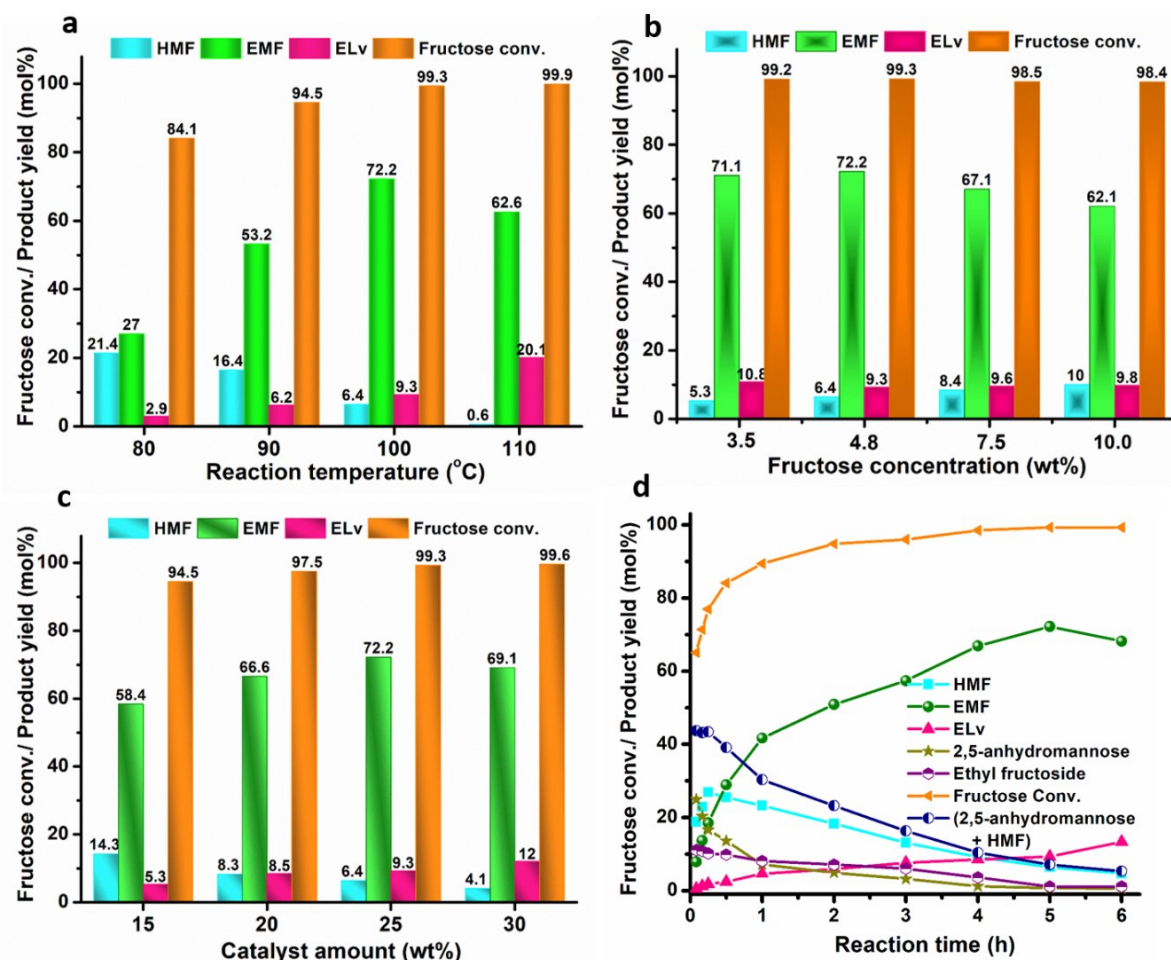
Figure S9(b) is a table comparing the H<sub>2</sub>O desorption and contact angle of MOP-SO<sub>3</sub>H-x catalysts.

Catalysts	H <sub>2</sub> O desorption (wt%) (25 -120 °C) [a]	Contact angles of water droplets [b]
MOP-SO <sub>3</sub> H-0.2	2.0	151°
MOP-SO <sub>3</sub> H-0.4	2.0	148°
MOP-SO <sub>3</sub> H-0.6	5.3	145°
MOP-SO <sub>3</sub> H-0.8	6.5	142°
MOP-SO <sub>3</sub> H-1.0	7.2	138°

[a] TGA, weight loss related to H<sub>2</sub>O desorption, [b] Contact angle measurements

Fig. S9. (a) Thermogravimetric analysis of MOP-SO<sub>3</sub>H catalysts and (b) Comparison of H<sub>2</sub>O desorption and Contact angle of MOP-SO<sub>3</sub>H-x.

### Influence of reaction conditions



**Figure S10.** (a) Effect of reaction temperature: fructose (1.0 g), ethanol (20.0 g), MOP-SO<sub>3</sub>H-0.6 (0.25 g), reaction time (5 h); (b) Effect of fructose concentration: ethanol (20.0 g), MOP-SO<sub>3</sub>H-0.6 (0.25 g), temperature (100 °C), reaction time (5 h); (c) Effect of catalyst amount: fructose (1.0 g), ethanol (20.0 g), MOP-SO<sub>3</sub>H-0.6 catalyst, reaction temperature (100 °C), reaction time (5 h); (d) Effect of reaction time: fructose (1.0 g), ethanol (20.0 g), MOP-SO<sub>3</sub>H-0.6 (0.25 g), temperature (100 °C).

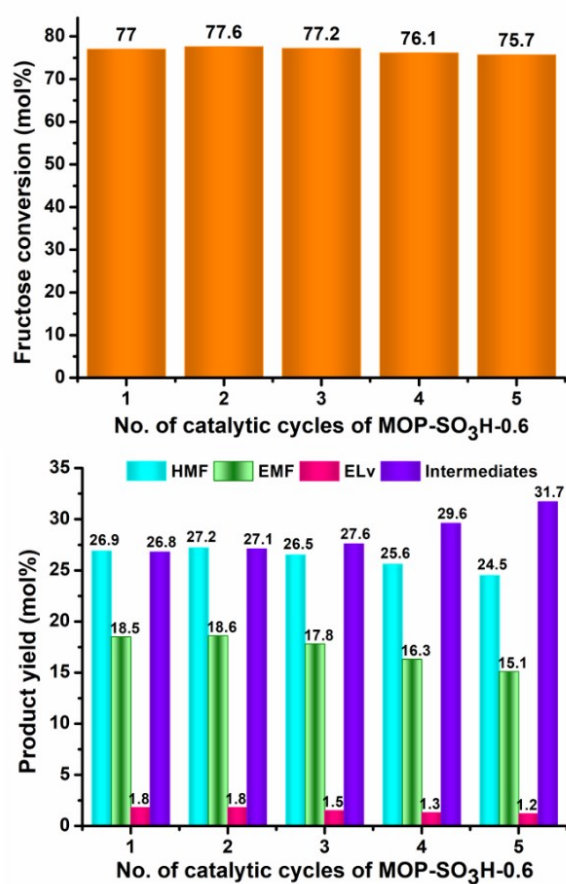
Next, we optimized the reaction conditions to achieve the highest EMF yield using the MOP-SO<sub>3</sub>H-0.6 catalyst. First, the effect of reaction temperature was investigated at a fixed reaction time of 5 h (Fig. S10a). At 80 °C, the fructose conversion was 84.1%, but the EMF yield was as low as 27.0%. This low EMF yield was ascribed to the formation of a large amount of HMF, AHM, and EFS. At 90 °C, the fructose conversion slightly increased to 94.5%, while the EMF yield significantly increased to 53.2% with a decrease in HMF and other intermediates. At 100 °C, the fructose conversion was almost complete (99.3%), where a 72.2% EMF and 6.4% HMF yield were obtained. However, a further increase in reaction temperature to 110 °C reduced the EMF yield to 62.6%. The ELV yield improved to 20.1%, but a negligible HMF yield was observed. These results indicated that the hydrolysis of EMF and hydrolysis-esterification of HMF increased at high reaction temperatures (> 110 °C), as shown in Scheme 2. Thus, 100 °C was the optimum reaction temperature to produce EMF from fructose using the MOP-SO<sub>3</sub>H-0.6 catalyst.

The influence of fructose concentration (wt% in ethanol) on fructose conversion and EMF yield at 100 °C is depicted in Fig. S10b. At 3.5 wt% fructose, the fructose conversion and EMF yield were 99.2% and 71.1%, respectively. The fructose conversion and EMF yield did not change significantly at a 4.8 wt% fructose concentration. However, a further increase of fructose concentration to 7.5 wt% and 10.0 wt% reduced the EMF yield to 67.1% and 62.1%, respectively, while the fructose conversion almost remained unchanged. The decrease in EMF yield was related to the increase in HMF yield and the formation of other reaction intermediates. These results suggest that the reaction intermediates can be effectively converted into the desired EMF product at fructose concentrations less than 4.8 wt%.

The catalyst amount determines the concentration of active sites in the reaction medium and subsequently influences the substrate conversion and product distribution. The

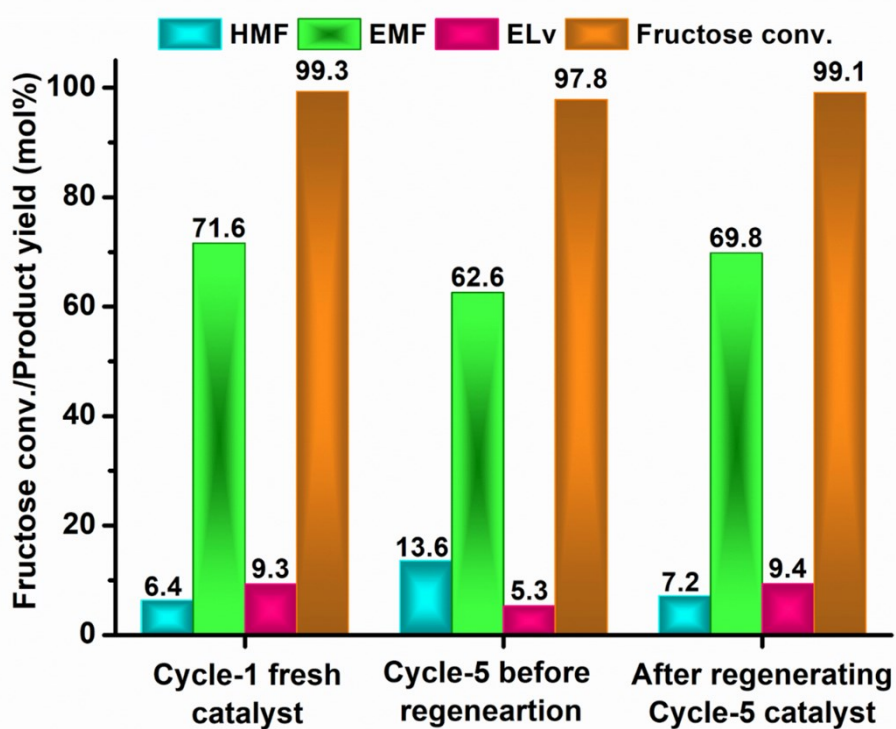
effect of catalyst amount on fructose conversion at 100 °C was investigated in the range of 15–30 wt% (Fig. S10c). As the catalyst amount increased from 15 to 25 wt%, the EMF yield gradually increased from 58.4 to 72.2%. The fructose conversion also increased from 94.5% to 99.3% because more active sites were available. However, further increasing the catalyst amount to 30 wt% resulted in a lower EMF yield (69.1%) but a higher ELV yield (12.0%), while the fructose conversion insignificantly changed. These results indicated that the EMF hydrolysis, as well as hydrolysis-esterification of HMF to form ELV, improved at a high catalyst-to-fructose ratio. Hence, 25 wt% was the optimum catalyst concentration to obtain the highest EMF yield.

The effect of reaction time on catalytic activity was investigated at 100 °C (Fig. S10d). After 15 min, the fructose conversion reached 77.0% to yield 18.5% EMF. However, it was notable that the formation of AHM and HMF by fructose dehydration and EFS by fructose etherification was significant. After 5 h, the fructose conversion and EMF yield increased to 99.3% and 72.2%, respectively, while the intermediates AHM, HMF, and EFS decreased gradually. After 6 h, the EMF yield decreased to 68.5%, which was mainly caused by an increase in ELV yield.



**Figure S11.** Reaction conditions: 1<sup>st</sup> run reaction condition: fructose (3.0 g), ethanol (60.0 g), catalyst (0.75 g), reaction temperature (100 °C), and reaction time (15 minutes); from 2<sup>nd</sup> run the fructose amount was adjusted to maintain the catalyst to fructose ratio (25wt%).

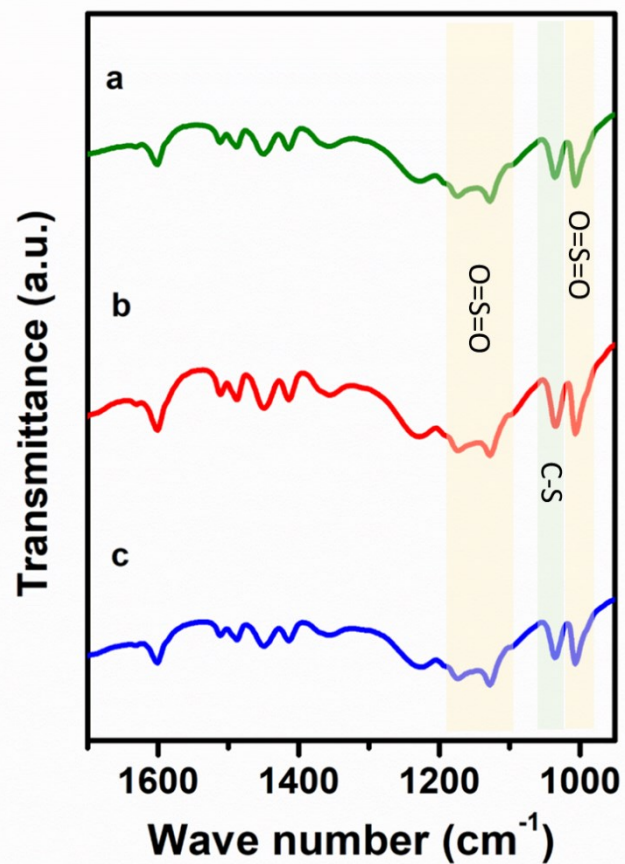




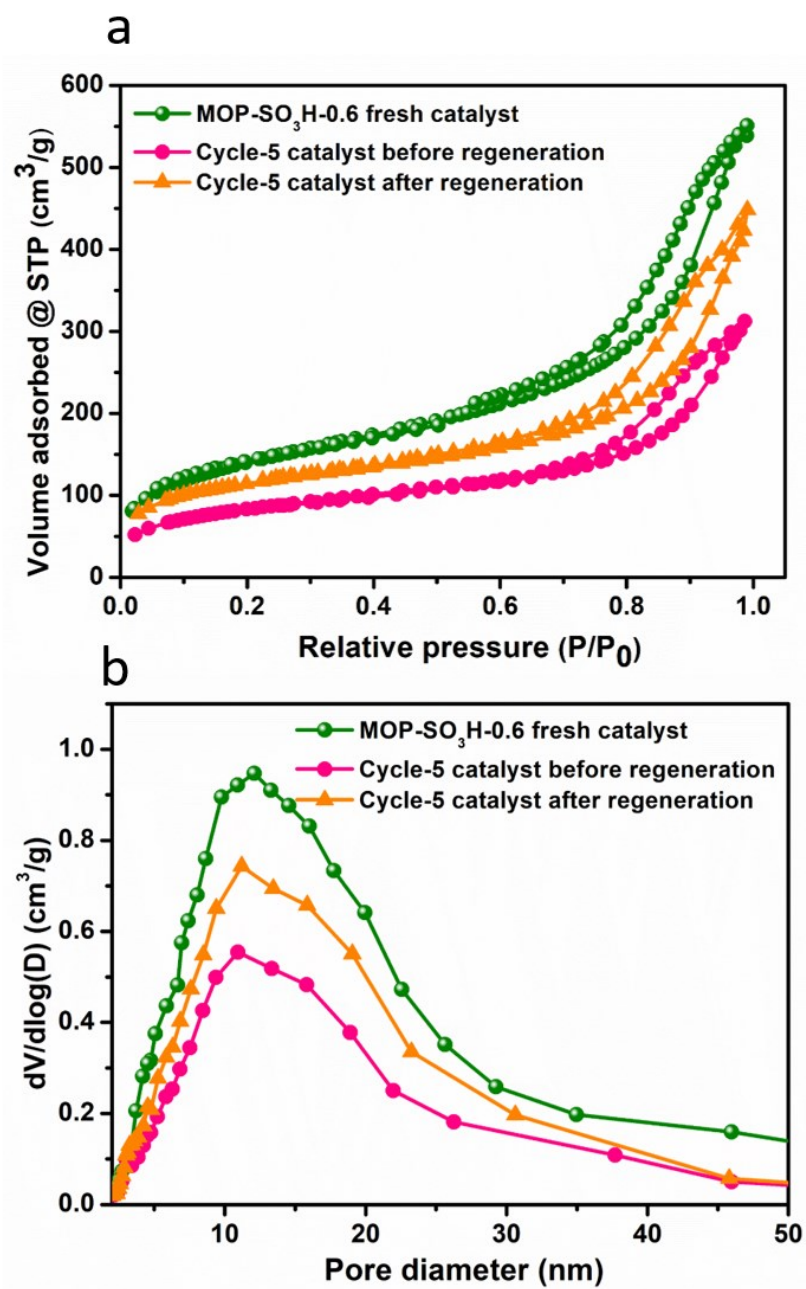
**Fig. S12.** Catalyst recycle and regeneration studies: Conditions: fructose (3.0 g), ethanol (60.0 g), MP-SO<sub>3</sub>H-0.6 catalyst (0.75 g), reaction temperature (100 °C), and reaction time (5 h); After each cycle, the reactant concentration was maintained referred to 25wt% of catalyst amount to fructose weight.

## Study on the spent catalysts

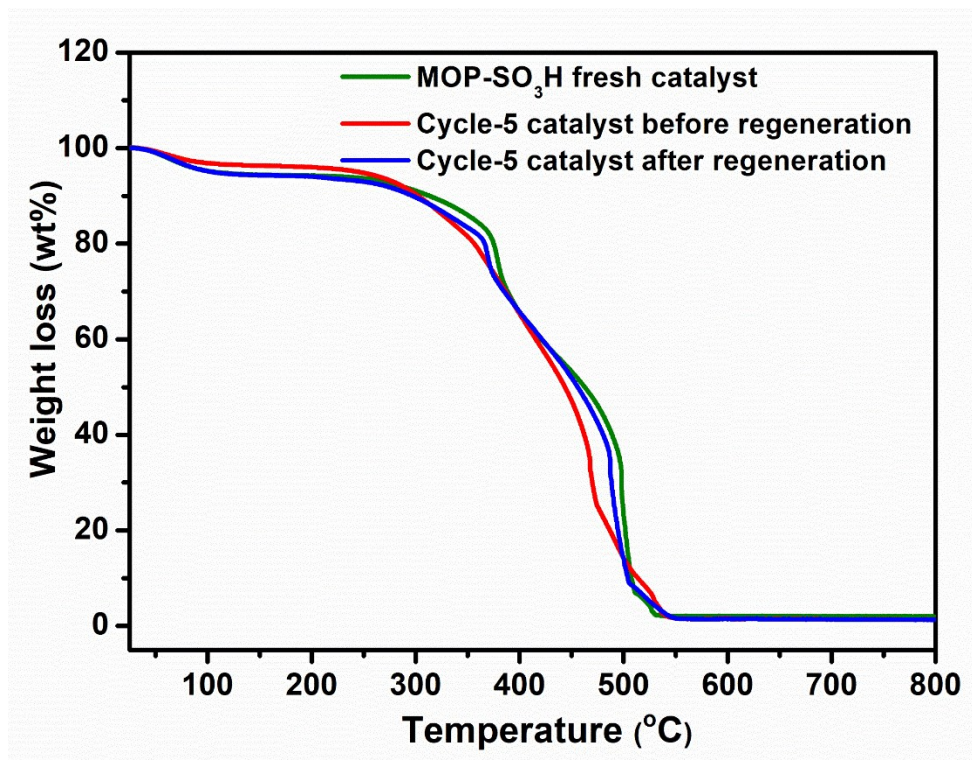
The spent MOP-SO<sub>3</sub>H-0.6 catalyst after 5 runs was characterized by FTIR, nitrogen sorption, TGA and acid-base titration techniques. The FTIR analysis of used catalyst shows no changes compared with that of fresh catalyst confirming that the spent catalyst retains its functional groups (ESI Fig. S14). The nitrogen sorption analysis (Table S4 and ESI Fig. S15) of spent catalyst cycle-5 before regeneration showed a drastic decrease in surface area (~225 m<sup>2</sup>/g), pore size (~1.2 nm) and pore volume (~0.36 cm<sup>3</sup>/g) compared to the fresh catalyst indicating that the accumulation of inevitably formed humins in the pore structure of the catalyst. Importantly, a phenomenal change in structural properties of used catalyst was observed after regeneration. It showed a remarkable improvement by increasing the surface area from 295 to 410 m<sup>2</sup>/g with pore volume from 0.49 to 0.70 cm<sup>3</sup>/g along with the pore size of 11.1 nm. The acid-base titration showed a marginal decrease in amount of acidity (by 0.25 mmol H<sup>+</sup>/g) compared to fresh catalyst (ESI Table S4). The thermogravimetric analysis of spent and regenerated cycle-5 catalysts showed an interesting information (ESI Fig. S16). The 3<sup>rd</sup> step decomposition in spent catalyst started at earlier temperature 420-480 °C compared to the fresh and regenerated catalysts and that indicates the deposition of humins/oligomeric products on the catalyst surface which could be the reason for decrease of activity in the fifth cycle. Thus, physico-chemical properties of the used catalysts prove that the catalyst can be effectively utilized and regenerated with extent durability under the reaction conditions.



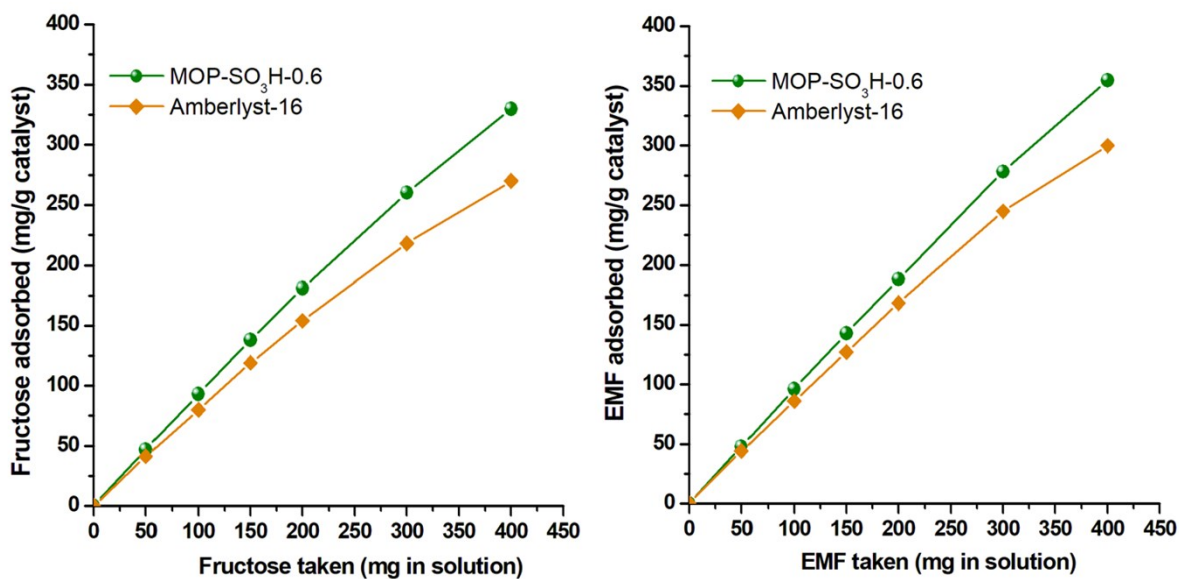
**Fig. S13.** FTIR spectra of (a) MP-SO<sub>3</sub>H-0.6 fresh catalyst, (b) Cycle-5 catalyst before regeneration and (c) Cycle-5 after regeneration



**Fig. S14.** (a) Nitrogen sorption isotherms and (b) Pore size distribution of spent catalysts



**Fig. S15.** Thermogravimetric analysis of fresh, used and regenerated MOP-SO<sub>3</sub>H-0.6 catalysts.



**Fig. S16.** Adsorption isotherms of fructose and EMF over amberlyst-16 and MOP-SO<sub>3</sub>H-0.6 catalysts at 20 °C.

Interestingly, the adsorption amount of fructose and EMF over MOP-SO<sub>3</sub>H-0.6 catalyst was about 20% higher than Amberlyst-16. The higher adsorption property of MOP-SO<sub>3</sub>H-0.6 catalyst could be attributed to its high surface area containing a large quantity of readily accessible acid sites. This discussion was included in the revised manuscript.

**Table S1.** Catalytic activities of various catalysts for one-pot synthesis of EMF from fructose.

Catalysts	Acidity (mmol H <sup>+</sup> /g)	Fructose Conv. (mol%)	Product Yield (mol%)							TON
			HMF	EMF	ELV	AHM	EFS	LA	HMF + EMF	
MOP [a]	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Amberlyst-15 [a]	4.70	66.9	14.8	20.4	3.1	13.5	6.3	0.3	35.2	1.0
Amberlyst-16 [a]	4.80	66.8	16.7	24.9	3.8	9.8	4.6	0.4	41.6	1.2
MOP-SO <sub>3</sub> H-0.6 [a]	2.15	86.0	20.0	36.1	3.1	10.3	10.5	0.3	56.1	3.7
SBA-15-SO <sub>3</sub> H [b]	0.55	59.3	17.4	5.4	0.9	24.8	8.4	0	22.8	2.2
MOP-SO <sub>3</sub> H-0.6 [c]	2.15	78.3	24.8	17.8	2.1	19.8	10.3	0.1	42.6	0.9
H <sub>2</sub> SO <sub>4</sub> [d]	20.40	79.5	15.8	17.6	1.7	16.7	12.1	0.0	32.4	1.8
TsOH [d]	5.25	82.0	19.9	23.4	2.7	11.0	11.4	0.5	43.3	2.4
H <sub>3</sub> PO <sub>4</sub> [d]	8.67	2.5	0.2	0.0	0.0	0.7	1.5	0.0	0.2	0.0
AlCl <sub>3</sub> .6H <sub>2</sub> O [d]	4.14	93.5	36.4	21.4	2.4	6.0	6.5	0.6	57.8	2.1
H <sub>3</sub> PO <sub>4</sub> [e]	8.67	9.3	0.9	0.0	0.0	1.6	5.5	0.4	0.9	0.0
PWA [f]	0.347	75.9	6.9	19.3	2.7	21.4	15.7	0.0	26.2	4.1

Reaction conditions: [a] fructose (1.0 g), ethanol (20.0 g), catalyst (0.25 g), reaction temperature (90 °C), N<sub>2</sub> pressure (10 bar), reaction time (2 h); [b] catalyst (0.5 g); [c] catalyst (0.125 g, equivalent to 0.5 g of SBA-15-SO<sub>3</sub>H); [d] 0.54 mmol of acid sites equivalent to 0.25 g of MOP-SO<sub>3</sub>H-0.6; [e] H<sub>3</sub>PO<sub>4</sub> (0.105 g); [f] phosphotungstic acid (0.25 g); HMF = 5-hydroxymethylfurfural, EMF = 5-ethoxymethylfurfural, ELV = ethyl levulinate, AHM = 2,5-anhydro-mannose, EFS = ethyl fructoside, LA = levulinic acid. TON (Turnover number) = moles of EMF formed per mole of acidic sites.

**Table S2.** Catalytic activities of MOP-SO<sub>3</sub>H catalysts for one-pot synthesis of EMF from fructose.

Catalysts	SASD (H <sup>+</sup> /nm <sup>2</sup> )	Acidity (mmol H <sup>+</sup> /g)	Fructose Conv. (mol%)	Product Yield (mol%)							TON
				HMF	EMF	ELV	AHM	EFS	LA	HMF + EMF	
MOP	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MOP-SO <sub>3</sub> H-0.1	0.38	0.52	71.1	24.0	8.3	0.0	22.5	10	0.2	32.3	3.5
MOP-SO <sub>3</sub> H-0.2	0.86	0.96	77.7	24.5	15.3	1.0	20	10.4	0.3	39.8	3.5
MOP-SO <sub>3</sub> H-0.3	1.36	1.39	82.1	20.7	27.5	2.7	13.9	11.1	0.3	48.2	4.4
MOP-SO <sub>3</sub> H-0.4	1.76	1.72	84.5	21.9	31.2	2.3	13.6	10.1	0.2	53.1	4.0
MOP-SO <sub>3</sub> H-0.5	2.13	1.91	85.5	20.5	34.2	2.8	12.5	10.5	0.4	54.7	4.0
MOP-SO <sub>3</sub> H-0.6	2.50	2.15	86.0	20.0	36.1	3.1	10.3	10.5	0.3	56.1	3.7
MOP-SO <sub>3</sub> H-0.7	3.10	2.35	86.6	19.1	36.4	3.2	11	10.6	0.2	55.5	3.4
MOP-SO <sub>3</sub> H-0.8	3.70	2.51	87.1	18.8	36.4	3.6	9.7	10.2	0.2	55.2	3.2
MOP-SO <sub>3</sub> H-0.9	4.27	2.64	85.7	18.3	36.6	3.4	10.8	10.7	0.2	54.9	3.1
MOP-SO <sub>3</sub> H-1.0	5.00	2.82	85.8	18.4	36.4	3.3	10.1	10.5	0.2	54.8	2.9

Reaction conditions: [a] fructose (1.0 g), ethanol (20.0 g), catalyst (0.25 g), reaction temp (90 °C), time (2 h); SASD = Surface acid site density; HMF = 5-hydroxymethylfurfural, EMF = 5-ethoxymethylfurfural, ELV = Ethyl levulinate, AHM = 2,5-anhydro-mannose, EFS = Ethyl fructoside, LA = Levulinic acid. TON (Turnover number) = moles of EMF formed per mole of acidic sites.



**Table S3.** Catalytic activities of MOP-SO<sub>3</sub>H catalysts for one-pot synthesis of EMF from fructose.

Catalysts	SASD (H <sup>+</sup> /nm <sup>2</sup> )	Acidity (mmol H <sup>+</sup> /g)	Fructose Conv. (mol%)	Product Yield (mol%)							TON
				HMF	EMF	ELV	AHM	EFS	LA	HMF + EMF	
MOP	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MOP-SO <sub>3</sub> H-0.1	0.38	0.52	85.9	25.9	24.8	1.9	14.5	11.2	0.2	50.7	10.6
MOP-SO <sub>3</sub> H-0.2	0.86	0.96	89.0	21.5	37.4	2.3	9.7	10.0	0.3	58.9	8.7
MOP-SO <sub>3</sub> H-0.3	1.36	1.39	92.6	16.2	50.5	3.2	5.1	9.0	0.3	66.7	8.1
MOP-SO <sub>3</sub> H-0.4	1.76	1.72	93.5	12.9	54.4	5.4	4.2	7.9	0.3	67.3	7.0
MOP-SO <sub>3</sub> H-0.5	2.13	1.91	94.1	11.9	56.5	7.2	3.4	6.7	0.3	68.4	6.6
MOP-SO <sub>3</sub> H-0.6	2.50	2.15	96.0	11.3	59.7	7.3	2.4	6.4	0.3	71.0	6.2
MOP-SO <sub>3</sub> H-0.7	3.10	2.35	96.0	9.8	58.2	9.2	2.4	6.0	0.4	68.0	5.5
MOP-SO <sub>3</sub> H-0.8	3.70	2.51	96.2	9.1	57.2	10.1	2.3	5.6	0.4	66.3	5.1
MOP-SO <sub>3</sub> H-0.9	4.27	2.64	96.1	9.0	56.7	11.0	2.0	5.7	0.5	65.7	4.8
MOP-SO <sub>3</sub> H-1.0	5.00	2.82	95.4	8.0	56.1	11.9	1.9	5.5	0.5	64.1	4.4

Reaction conditions: fructose (1.0 g), ethanol (20.0 g), catalyst (0.25 g), reaction temp (90 °C), N<sub>2</sub> pressure (10 bar), time (6 h); SASD, surface acid site density; HMF = 5-hydroxymethylfurfural, EMF = 5-ethoxymethylfurfural, ELV = Ethyl levulinate, AHM = 2,5-anhydro-mannose, EFS = Ethyl fructoside, LA = Levulinic acid. TON (Turnover number) = moles of EMF formed per mole of acidic sites.

**Table S4.** Textural and chemical properties of fresh and used MOP-SO<sub>3</sub>H-0.6 catalysts

<b>Catalysts</b>	<b>Surface area (m<sup>2</sup>/g) <sup>[a]</sup></b>	<b>Pore volume (cm<sup>3</sup>/g) <sup>[a]</sup></b>	<b>Pore size (nm) <sup>[b]</sup></b>	<b>Acidity (mmol H<sup>+</sup>/g) <sup>[c]</sup></b>
Fresh	520	0.85	12.1	2.15
Cycle-5 before regeneration	295	0.49	10.9	1.75
Cycle-5 after regeneration	420	0.70	11.2	2.00

[a] from nitrogen sorption analysis, [b] from BJH pore size distribution,  
[c] from acid-base titration.

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