Electronic Supplementary Information

Catalytic dehydration of fructose to HMF over sulfonic acid functionalized periodic mesoporous organosilicas: role of the acid density

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Materials preparations:

All air sensitive operations were carried out using standard Schlenk techniques under a nitrogen atmosphere. Octadecyltrimethylammonium bromide (ODTMA, 98%), trimethylchlorosilane (98%), 4,4'-bis-(triethoxysilyl)biphenyl (BTEBP, 95%) and 3-mercaptopropyltrimethoxysilane (MPTMS, 95%) were obtained from Aldrich and used as received. 1,4-bis(triethoxysilyl)benzene (BTEB) was prepared via a Grignard reaction and distillated in vacuum as reported by Shea *et al.*²⁷ Solvents were dried by standard procedures, distilled under nitrogen and kept over 4 Å molecular sieves.

PMO1a-d were prepared by co-condensation of different molar ratios of BTEB and 3-MPTMS in the presence of ODTMA. The molar ratios of BTEB/MPTMS were 0.5:0.5 (PMO-1a), 0.7:0.3 (PMO-1b), 0.8:0.2 (PMO-1c) and 0.9:0.1 (PMO1-d). The conversion of the thiol groups to sulfonic acid-derivatized mesoporous material was accomplished by reaction with nitric acid (HNO₃, Panreac, 65 wt%).²³ PMO-2 was obtained using similar methodology but substituting the BTEB for 4,4'-bis-(triethoxysilyl)biphenyl (BTEBP, Aldrich, 95%). The molar ratio of BTEBP/MPTMS in the initial mixture was 0.5:0.5.

For comparative proposes, the residual silanol groups of PMO-1 materials were silylated by reaction with trimethylchlorosilane of the extracted materials. Each powder (0.3 g) was dried under vacuum at 70 °C for 3 hours. After, it was added dried toluene (7.5 mL) and chlorotrimethylsilane (1 mL), under N₂ atmosphere. The mixture was stirred for 20 hours, at room temperature. Then, the samples were washed several times with 6 mL aliquot of acetone (6 mL) followed by washing with dried CH_3Cl_2 and dried under vacuum. Afterwards, the thiol groups were oxidized as previously described.

For the synthesis of PMO-**3**, first it was prepared the Ph-PMO using the method described in 29.The sulfonation of the aromatic ring was achieved by reacting Ph-PMO powder with sulfuric acid (Aldrich, 98%) and stirring at 75 °C for 24 hours.²⁵ The final product washed with water till neutral pH and dried under vacuum.

<u>Titration</u>: typically, 30 mg of each material was added to 20 mL of KCl (0.1 M) solution and was left to equilibrate under stirring for 30 minutes. The solution was then titrated with a 0.01 M KOH to produce the titration curve.

Materials characterization:

Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert MPD diffractometer (Cu-K α X-radiation, $\lambda = 1.54060$ Å) fitted with a graphite monochromator and a flat plate sample holder, in a Bragg-Brentano para-focusing optics configuration. Samples were step-scanned in $0.02^{\circ} 2\theta$ steps with a counting time of 2 s per step. TEM images were recorded by a 300eV Hitachi H9000-NA instrument. FTIR spectra were obtained on a FTIR Mattson-7000 infrared spectrophotometer with 2 cm-1 resolution, using KBr pellets. Solidstate magic-angle spinning (MAS) NMR spectra were recorded at 79.49 MHz for 29Si and 125.76 MHz for ¹³C on a Bruker Avance 400 and 500 spectrometers, respectively. 29Si MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0 kHz and 60 s recycle delays. 29Si CP MAS NMR spectra were recorded with 4.0 µs 1H 90° pulse, a contact time of 8 ms, a spinning rate of 5 kHz and 5 s recycle delays. ¹³C cross-polarisation (CP) MAS NMR spectra were recorded with 4.5 μ s ¹H 90° pulses, a contact time of 2 ms, a spinning rate of 7.0 kHz and 4 s recycle delays. 31P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired for all samples on a Bruker Avance III 400 spectrometer operating at a B0 field of 9.4 T with ³¹P Larmor frequency of 161.98 MHz. All spectra were recorded using a double tuned 4 mm probe employing a rotation speed of 12 kHz, using a 3.5 us radio-frequency excitation pulse length with a radio-frequency field strength of 70 kHz (90° flip-angle). Recycle delays between 15 and 60 s were used in a series of single-pulse excitation ³¹P experiments and no difference in the relative intensities of the different ³¹P resonances were observed. Therefore, the reported ³¹P spectra were acquired using a recycle delay of 15 s. Chemical shifts are quoted in ppm and were referenced from the external standard, 85 % H₃PO₄ solution, which was set at 0.0 ppm. ¹H two-pulse phase modulated (TPPM) decoupling was used during acquisition with a pulse length of 6.5 µs at a radiofrequency field strength of 70 kHz.

<u>Chemisorption of TEPO</u>: It was inspired from previous procedures. 0.010 g of TEPO (Aldrich) was dissolved into 5 mL of dry pentane (Aldrich) and then 0.050 g of activated material (dried 8 hours in vacuum at 200 °C) was added to the solution under nitrogen. The mixture was allowed to equilibrate for 25 minutes and the solvent was evaporated in vacuum at 50 °C. The powders were transferred into a NMR rotor in a glove box.

Characterization of materials



Figure S1. X-ray diffraction patterns of PM0-1a, PMO-1b, PMO-1c, PMO-1d and Si-PMO-1c



Figure S2. X-ray diffraction patterns of PM0-2 and PMO-3.

Sample	d_{100}	$S_{\rm BET}$	$V_{ m P}$	$d_{ m P}{}^{ m a}$	b^{b}	
	nm	$m^2 g^{-1}$	cm ³ g ⁻¹	nm	nm	
PMO-1a	4.42	650	0.58	3.8	1.30	
PMO-1b	4.45	975	0.72	2.9	1.74	
PMO-1c	4.49	830	0.63	3.1	2.08	
PMO-1d	4.54	823	0.65	3.2	2.04	
Si-PMO-1c	4.54	813	0.64	3.0	2.24	
PMO-2	4.78	664	0.63	2.7	5.60	
PMO-3	4.83	760	0.81	3.6	1.98	

Table S1. Textural properties of PMO-1a-d, PMO-2 and PMO-3.

^aPore width obtained from the maximum on the BJH pore size distribution calculated on the basis of adsorption data. ^bPore wall thickness calculated as $(2d_{100}/\sqrt{3} - d_P)$, where the first term is the unit cell parameter.



Figure S3. ¹³C CP-MAS NMR spectra of PMO-1a, PMO-1b, PMO-1c, PMO-1c and Si-PMO-1c.



Figure S4. ¹³C CP-MAS NMR spectra of PMO-2 and PMO-3.



Figure S5. ²⁹Si CP-MAS and MAS NMR spectra of PMO-1a, PMO-1b, PMO-1c and Si-PMO-1c.



Figure S6. ²⁹Si CP-MAS and MAS NMR spectra of PMO-2 and PMO-3.



Figure S7. Selected TEM images for PMO-1c and PMO-2 (lateral view)



Figure S8. -196 °C N₂ isotherms of PMO-1a, PMO-1b, PMO-1c, PMO-1d, PMO2 and PMO-3. Open symbols are used for adsorption patterns and close symbols for desorption curve. The pore size distributions are displayed as inset for each material.

Selected and typical kinetic profiles

<u>Caution</u>: all kinetic profiles were performed using 16 wt% of solid catalyst to avoid any discrimination due to diffusional problems. However, note that the proton loading is rather different between all tested PMOs so all comparison between kinetic profiles should be done carrefully.



Fig. S9: selected kinetic profiles (16 wt% of **PMO-1a**, **PMO-1b**, **PMO-3**) performed at 160°C from a 44 wt% aqueous solution of fructose



Fig. S10. Kinetic profiles of PMO-1a (a) using an aqueous solution of 44wt% and 10 wt% of fructose and (b) at 130°C and 160°C