

Supporting Information

Sulfonated triazine-based covalent organic polymer supported on mesoporous material: a new and robust material for the production of 5-hydroxymethylfurfural

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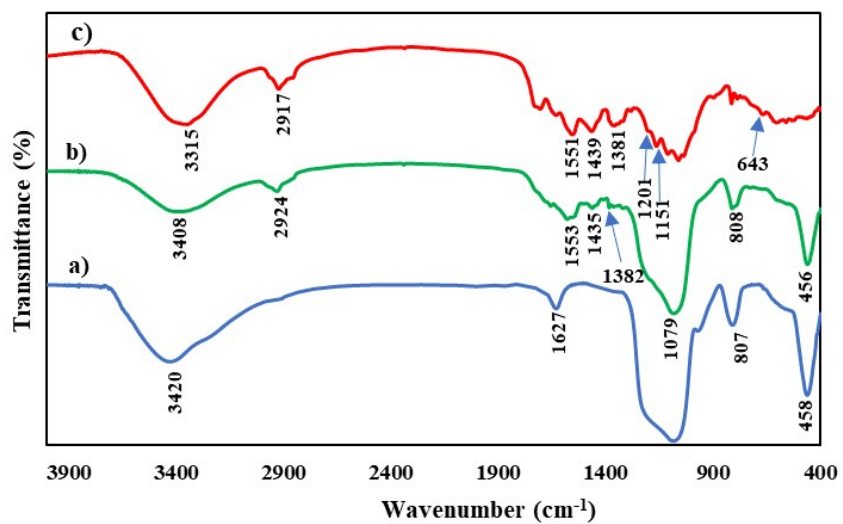


Figure S1. FT-IR spectra of a) SBA-15, b) COP-SO₃H/SB catalyst, and COP-SO₃H catalyst

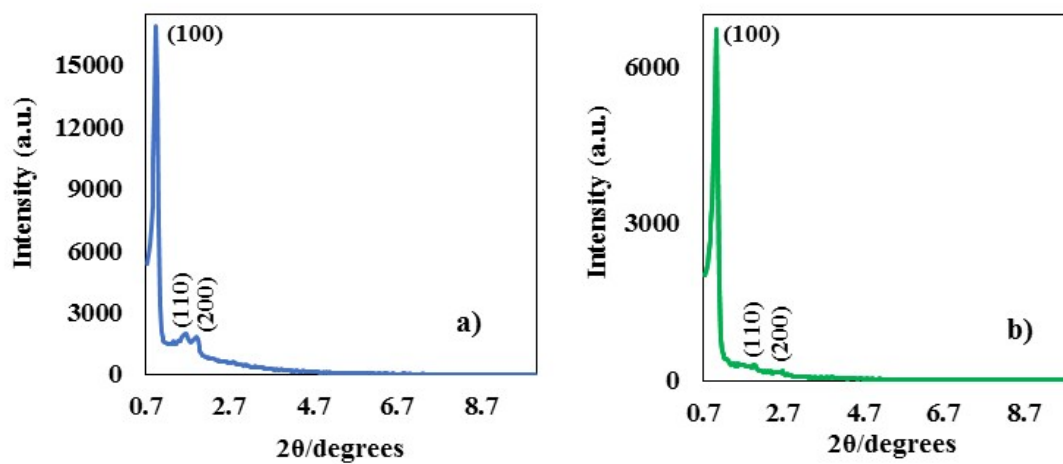


Figure S2. The low-angle XRD patterns of a) SBA-15, and b) COP-SO₃H/SB catalyst

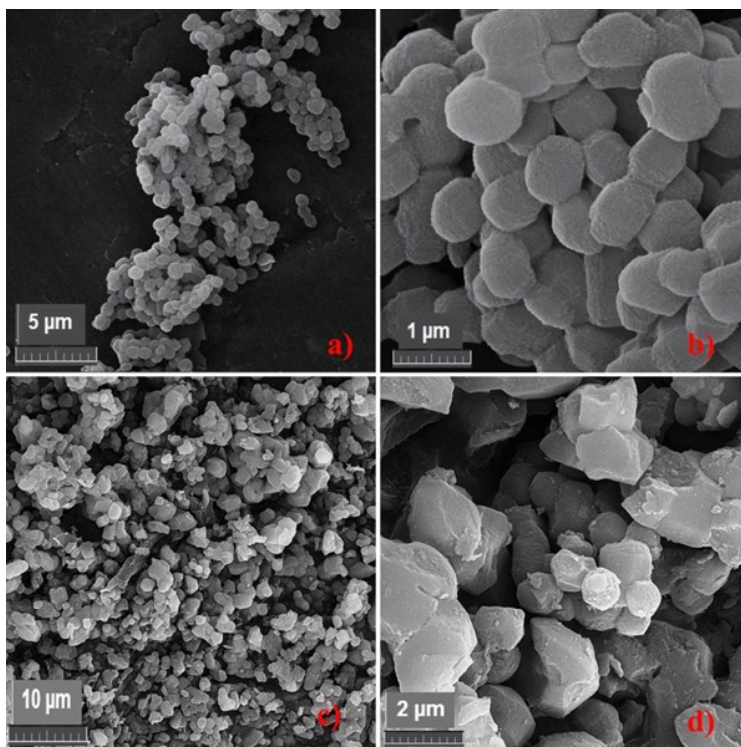


Figure S3. The SEM analysis of a, b) pure SBA-15, and c, d) COP-SO₃H/SB catalysts

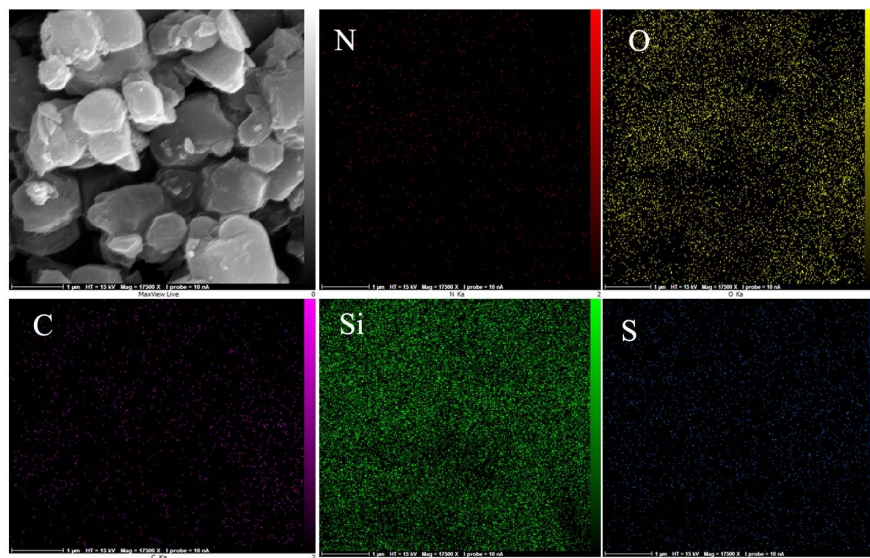


Figure S4. Elemental mapping analysis of elements existence and dispersion in COP-SO₃H/SB catalyst

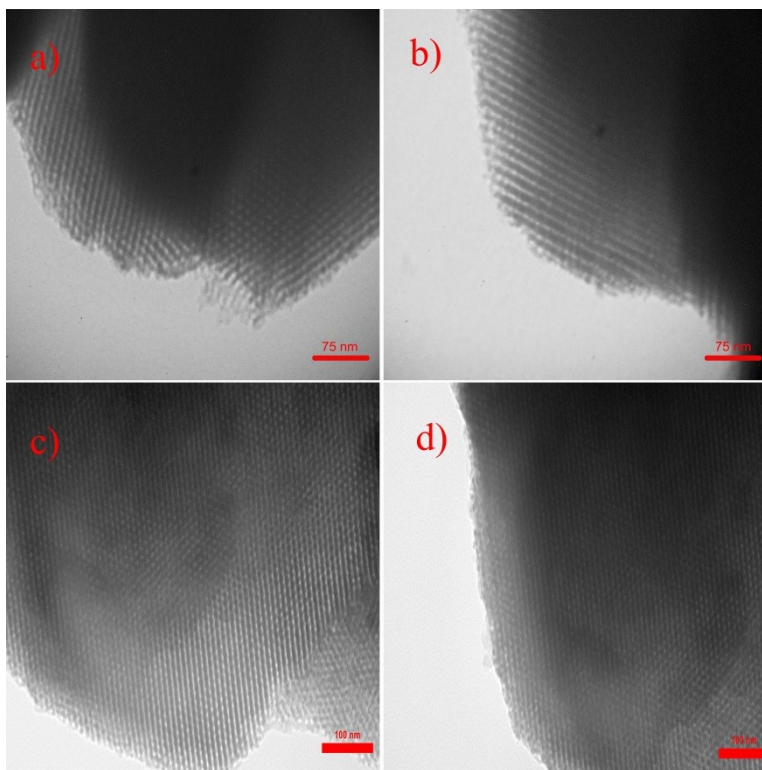


Figure S5. The TEM images of a, b) the pure SBA-15, and c, d) COP-SO₃H/SB catalyst

Acid capacity measurement of catalysts

For COP-SO₃H/SB and COP-SO₃H catalysts, pyridine test was not investigated due to the existence of triazine rings in the structure of these catalysts. therefore, back titration with HCl (0.01 M) using phenolphthalein as an indicator was used for calculation of their Bronsted acid capacity (Table S1). Also, for the SBA-15/SO₃H catalyst was done back titration. The acid capacity of SBA-15/Zr, SBA-15/Al, and SBA-15/Zn was calculated by pyridine test and the following equations ¹:

$$[C_B] = 1.88 A_B r^2 / W \quad (1)$$

$$[C_L] = 1.42 A_L r^2 / W \quad (2)$$

C_B and C_L are concentration of Brønsted acid sites and Lewis acid sites, respectively. Also, A_B and A_L are integrated absorbance of 1550 cm^{-1} (related to the Bronsted acid sites), 1490 cm^{-1} (related to the Bronsted acid and Lewis acid sites), and 1581 and 1445 cm^{-1} (related to the Lewis acid sites) ² in the final data of FT-IR spectra, W is the weight of catalyst disk and r is the radius of catalyst disk.

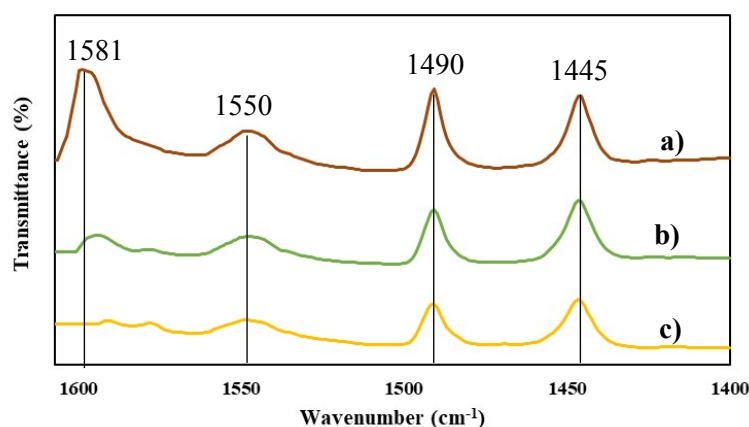


Figure S6. FT-IR spectra of pyridine adsorption for a) SBA-15/Zr, b) SBA-15/Al, and c) SBA-15/Zn catalysts

Table S1. The result of the acid capacity measurement of catalysts

Sample	Back titration method		Pyridine test method	
	B ^a acid (mmol. g ⁻¹)	L ^b acid (mmol. g ⁻¹)	B acid (mmol. g ⁻¹)	Total acid (mmol. g ⁻¹)
COP-SO ₃ H/SB	3.5	-	-	-
COP-SO ₃ H	3.2	-	-	-
SBA-15/SO ₃ H	2	-	-	-
SBA-15/Zr	-	0.26	0.24	0.5
SBA-15/Al	-	0.44	0.36	0.8
SBA-15/Zn	-	0.63	0.57	1.2

^a Bronsted acid

^b Lewis acid

For more evaluation of activity of COP-SO₃H catalyst in fructose dehydration reaction its performance was compared to a series of the catalysts based on SBA-15 including SBA-15/Al, SBA-15/Zn, SBA-15/Zr, and SBA-15/SO₃H catalysts which in each case the mesoporous SBA-15 was modified by Al(NO₃)₃, Zn(NO₃)₂, ZrOCl₂, and propyl sulfonic acid groups (Figure S7). First, the reaction was carried out under optimal conditions without any catalyst and only 40% HMF yield, and 82% conversion of fructose was observed. Then, the reaction was performed using SBA-15/Zr (1.2 mmol. g⁻¹), SBA-15/Al (0.8 mmol. g⁻¹), and SBA-15/Zn (0.5 mmol. g⁻¹) and 63.8, 61.7 and 44.6% of HMF, was obtained, respectively. According to Figure S7, the conversion of fructose is almost constant (> 99%) for these experiments. These results indicated that with increasing the oxidation number of Zr (4), Al (3) and Zn (2) active sites, the performance of the catalysts was improved probably due to the acidity of the samples is increased. Also, the yield of HMF was obtained 68.1% in the presence of SBA-15/SO₃H (2 mmol. g⁻¹) catalyst while COP-SO₃H/SB (3.5 mmol. g⁻¹) catalyst produces 78% yield for HMF. This 10% increase in HMF yield can be related to the stronger acidity of COP-SO₃H/SB catalyst due to the higher concentration of -SO₃H groups. At last, this reaction was done using COP-SO₃H (3.2 mmol. g⁻¹) catalyst without SBA-15 as the supported and 70% HMF yield was observed. In comparison with the performance of COP-SO₃H/SB catalyst, this reduction of the HMF yield can be attributed to the uniform dispersion of the COP-SO₃H catalyst on the larger surface of the SBA-15.

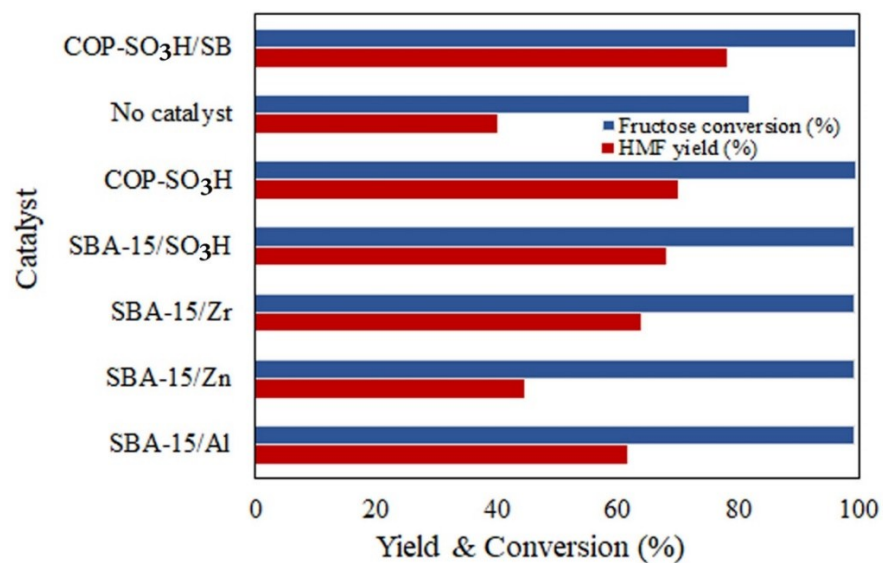


Figure S7. The effect of the different catalysts on the synthesis of HMF. Condition of reaction: fructose (100 mg), 2 ml DMSO, catalyst (55 mg), reaction temperature 120 °C, reaction time 60 min.

Reference

- 1 C. A. Emeis, *J. Catal.*, 1993, **141**, 347–354.
- 2 M. V. Zakharova, F. Kleitz and F. G. Fontaine, *Dalt. Trans.*, 2017, **46**, 3864–3876.