Electronic Supplementary Material (ESI) for RSC Advances.

Catalytic dehydration of fructose to 5-hydroxymethylfurfural over mesoscopically assembled sulfated zirconia nanoparticles catalyst in organic solvent

Supplementary data

Contents

1. Particles Size Calculation
2. Reactor Studies
3. Supporting figures

1. Particles Size Calculation:

Here, we calculated the particle size by using Scherrer equation based on PXRD result.

According to the Scherrer equation size of the crystallite $D=K\lambda /(\beta\cos\theta)$ Where;

β is the full width of the peak at half maximum intensity of a specific phase in radian.

K is a constant that varies with the method of taking the breadth ($0.89 < K < 1$).

λ is the wavelength of incident X-rays.

θ is the centre angle of the peak.

D is the crystallite length.

From Fig. 2, for the MAZN-1;

$2\theta = 30.46°$; $\theta = 15.23°$; $\cos\theta = \cos(15.23°) = 0.965$; $\beta = 0.0184$; $\lambda = 0.154$ nm and $K = 0.9$

Therefore, estimated D for MAZN-1 will be 7.80 nm.

Particles size for the MAZN-2 will be calculated as follows.

$2\theta = 30.34°$; $\theta = 15.17°$; $\cos\theta = 0.9652$; $\beta = 0.0186$; $\lambda = 0.154$ nm and $K = 0.9$

D for MAZN-2 will be 7.72 nm.

Particles size calculation will be for MAZN-3

$2\theta = 30.17°$; $\theta = 15.085°$; $\cos\theta = 0.966$; $\beta = 0.0194$; $\lambda = 0.154$ nm and $K = 0.9$

D for MAZN-3 will be 7.39 nm.

Particles size calculation will be for MAZN-4

$2\theta = 30.17°$; $\theta = 15.085°$; $\cos\theta = 0.966$; $\beta = 0.0198$; $\lambda = 0.154$ nm and $K = 0.9$

D for MAZN-4 will be 7.24 nm.

Particle Size Calculation after Sulfonation:

From Fig. 3(a), for the MASZN-1;

$2\theta = 28.16°$; $\theta = 14.08$; $\cos\theta = 0.97$; $\beta = 0.0196$; $\lambda = 0.154$; $K = 0.9$

Therefore, estimated D for MASZN-1 will be 7.29 nm.

From Fig. 3(b), for the MASZN-2;

$2\theta = 28.15°$; $\theta = 14.075$; $\cos\theta = 0.97$; $\beta = 0.0179$; $\lambda = 0.154$; $K = 0.9$

Therefore, estimated D for MASZN-2 will be 7.98 nm.

From Fig. 3(c), for the MASZN-3;

$2\theta = 28.15°$; $\theta = 14.075$; $\cos\theta = 0.97$; $\beta = 0.0182$; $\lambda = 0.154$; $K = 0.9$

Therefore, estimated D for MASZN-3 will be 7.85 nm.

From Fig. 3(d), for the MASZN-4;

$2\theta = 28.15°$; $\theta = 14.075$; $\cos\theta = 0.97$; $\beta = 0.0196$; $\lambda = 0.154$; $K = 0.9$

Therefore, estimated D for MASZN-4 will be 7.29 nm.

2. Reactor Studies

Table S1. Conversion and yield following glucose dehydration over mesoscopic assembly sulfated zirconia nanoparticles.[a]

Entry	Substrate	Catalysis	*t*(min)	*T*(°C)	Conversion/%	HMF yield/%
1	Glucose	MASZN-1	300	120	81.2	12.8
2	Glucose	MASZN-2	300	120	84.3	21.5
3	Glucose	MASZN-3	300	120	83.6	12.8
4	Glucose	MASZN-4	300	120	80.4	20.3

[a] Conditions: glucose (1 mmol), each catalyst is 10mg; solvent [AMIM]Cl (3 mL).

Table S2. The effect of solvent.[a]

Entry	Solvent	Conversion(%)	HMF Yield(%)
1	DMF	73.9	35.4
2	NMP	78.5	43.6
3	DMA	64.8	22.8
4	H_2O	43.7	8.5

[a] Reaction conditions: fructose (1 mmol), Catalyst MASZN-3 (10 mg), solvent (3mL), T=110 °C, t=120 min.

Table S3. Fructose dehydration in various catalytic systems.

Entry	Catalysis	Solvent	*t* (min)	*T* (°C)	Conversion (%)	HMF Yield(%)	Ref.
1	Bifunctional SO_4/ZrO_2	water	360	100	25.4	8.28	32
2	TESAS-SBA-15	MIBK-2-butanol	141	130	84	71	27
3	MIL-101(Cr)-SO_3H	DMSO	60	120	99	90	28
4	a-CSS	[BMIM][Cl]	10	80	—	83	31
5	MASZN-3	DMSO	120	110	98.5	91.9	[a]

[a]:In our reasearch.

3. Supporting figures

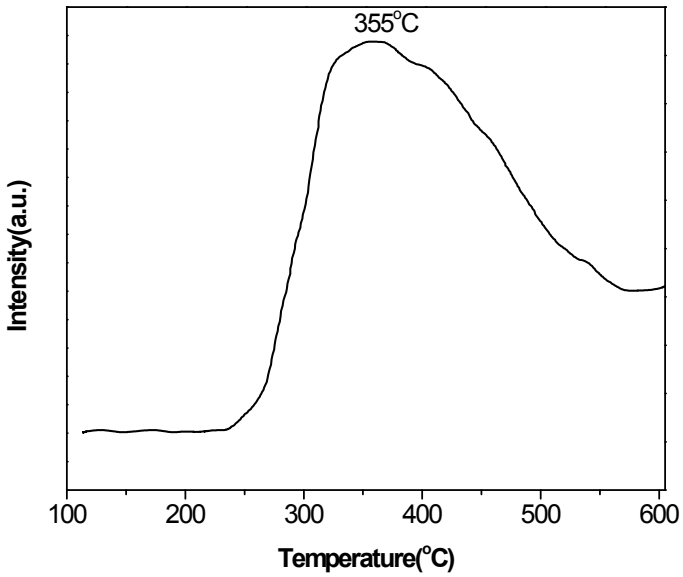


Figure S1. TPD-NH_3 profile over self-assembled mesoporous sulfated zirconia material (MASZN-3).

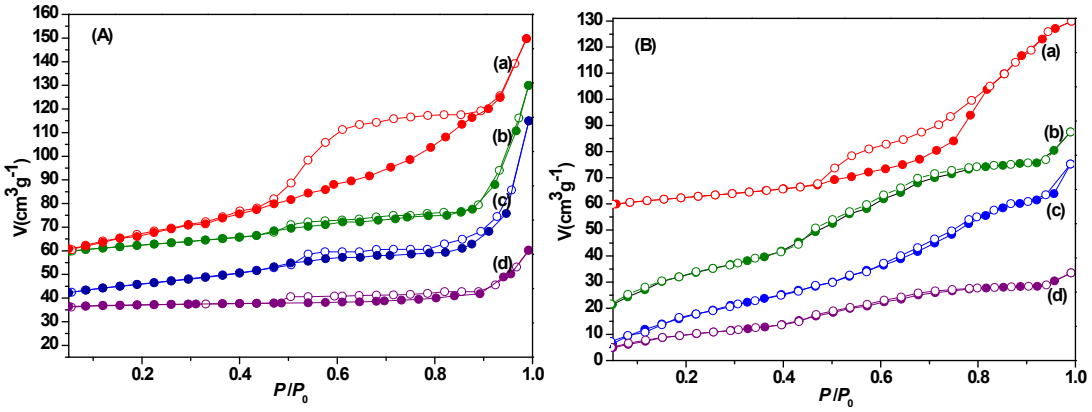


Figure S2. N_2 adsorption/desorption isotherms of A) calcined samples a) MAZN-1, b) MAZN-2, c) MAZN-3, and d) MAZN-4 ; B) calcined mesoporous sulfated samples a) MASZN-1, b) MASZN-2, c) MASZN-3, and d) MASZN-4 measured at 77 K. Adsorption points are marked by filled circles and desorption points by empty circles.

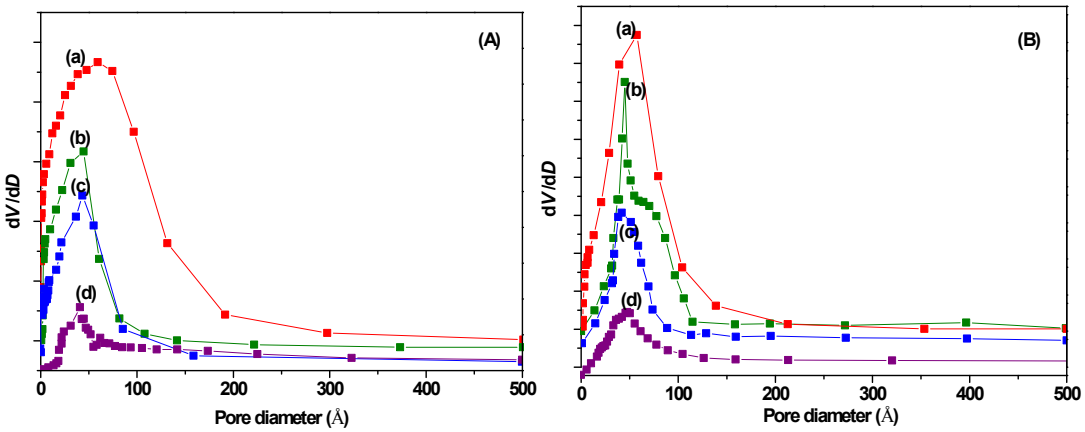


Figure S3. BJH pore size distribution curves of A) calcined samples a) MAZN-1, b) MAZN-2, c) MAZN-3, and d) MAZN-4; B) calcined mesoporous sulfated samples a) MASZN-1, b) MASZN-2, c) MASZN-3, and d) MASZN-4.

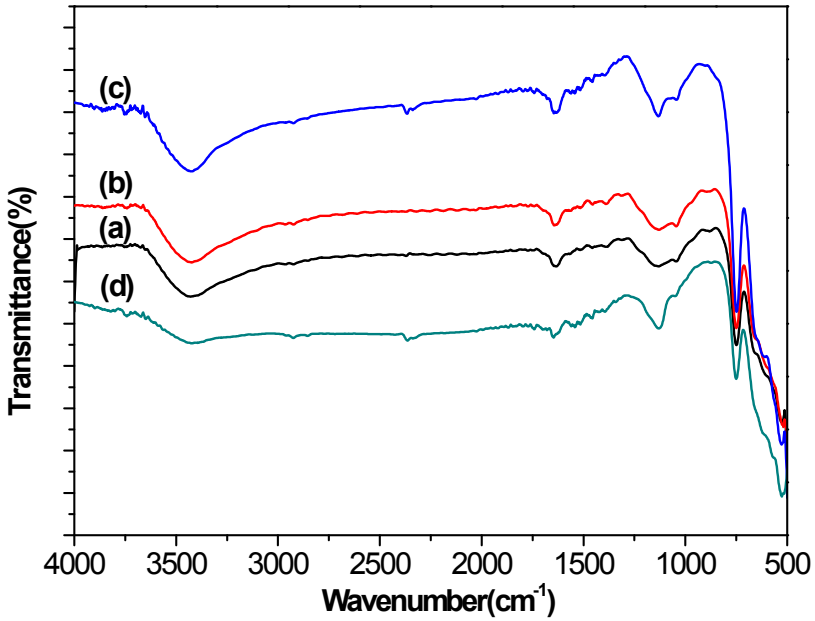
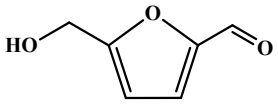


Figure S4. FTIR spectra of the mesoporous ZrO_2 samples: (a) MAZN-1, (b) MAZN-2, (c) MAZN-3 and (d) MAZN-4.



HMF

Chemical Formula: $C_6H_6O_3$ Molecular Weight: 126.11

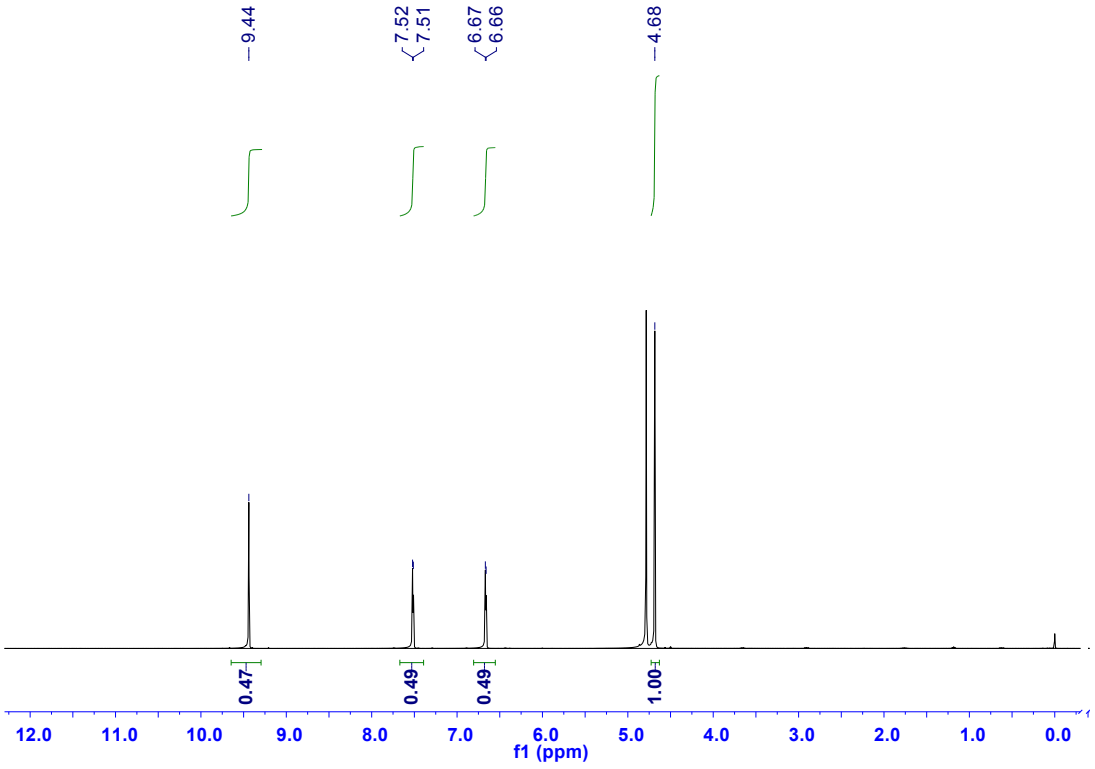


Figure S5. ^{1}H NMR spectra of synthetic HMF.

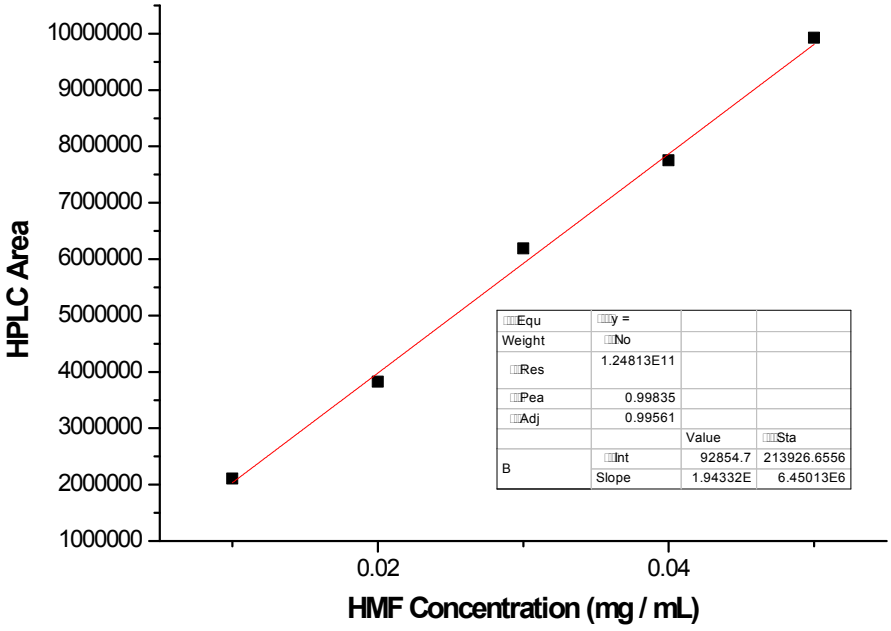


Figure S6. Standard curve of authentic HMF in H_2O.