Sulfated zirconia catalysts for D-sorbitol cascade cyclodehydration to isosorbide: impact of zirconia phase

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Supporting Information

13 pages comprising 12 Figures and 2 tables

1: Characterisation

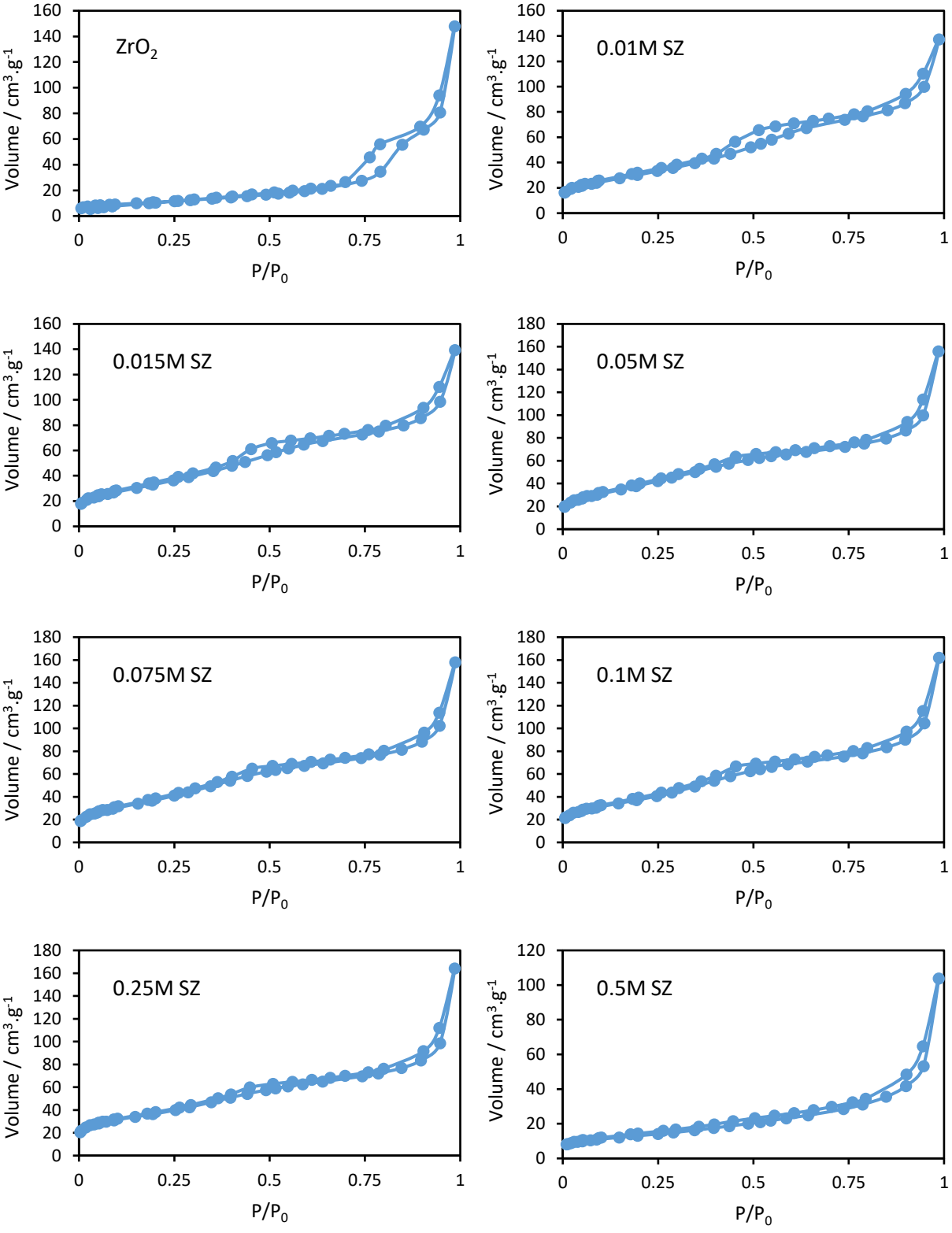

Figure S1. Isotherms of SZ prepared from $Zr(OH)_4$ impregnation, as a function of $[H_2SO_4]$

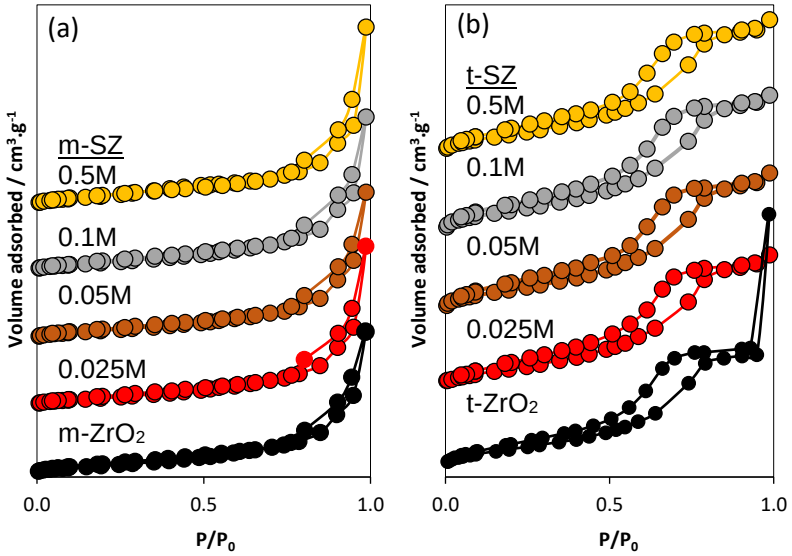

Figure S2: N_2-isotherms of (a) *m*-SZ catalysts and (b) *t*-SZ catalysts.

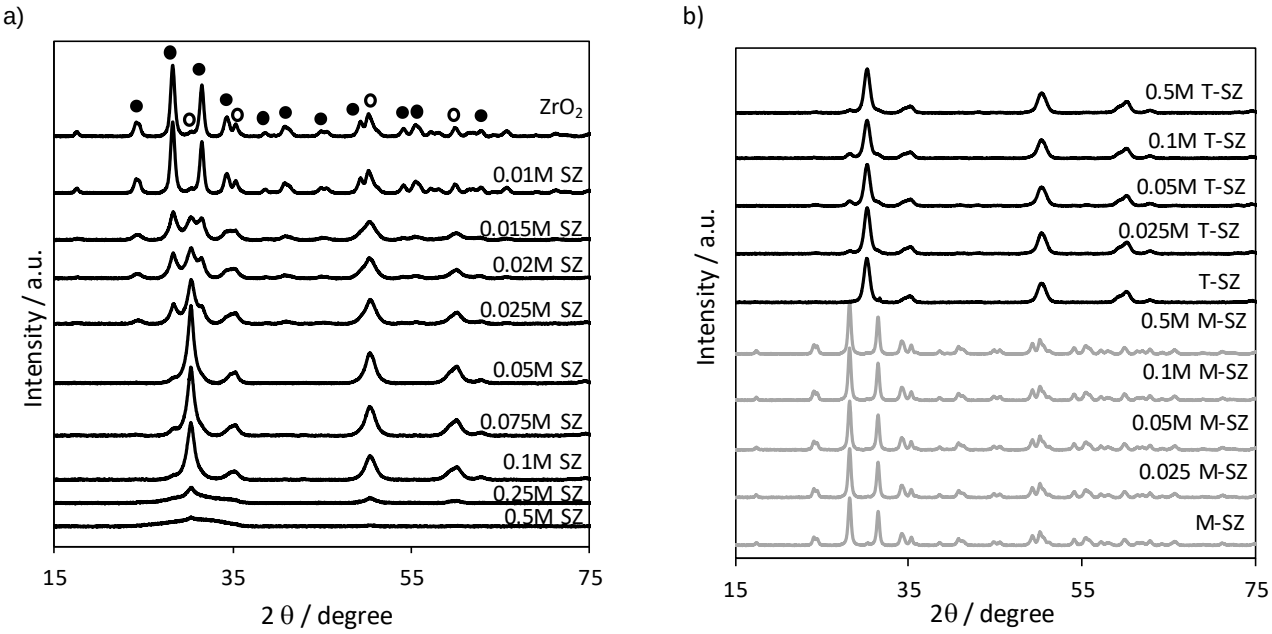

Figure S3. Powder XRD of xM a) SZ and b) *m*-SZ and *t*-SZ family of catalysts as a function of [H_2SO_4]. Main moncolinic peaks (2θ = 24.3°, 28.3°, 31.5°, and 34.3 according to the JCPDS 37-1484 reference patterns) (●) and tetragonal peaks (2θ = 30.3°, 35.3°, 50.6°, and 60.2° according to the JCPDS 80-0965 reference patterns) (○).

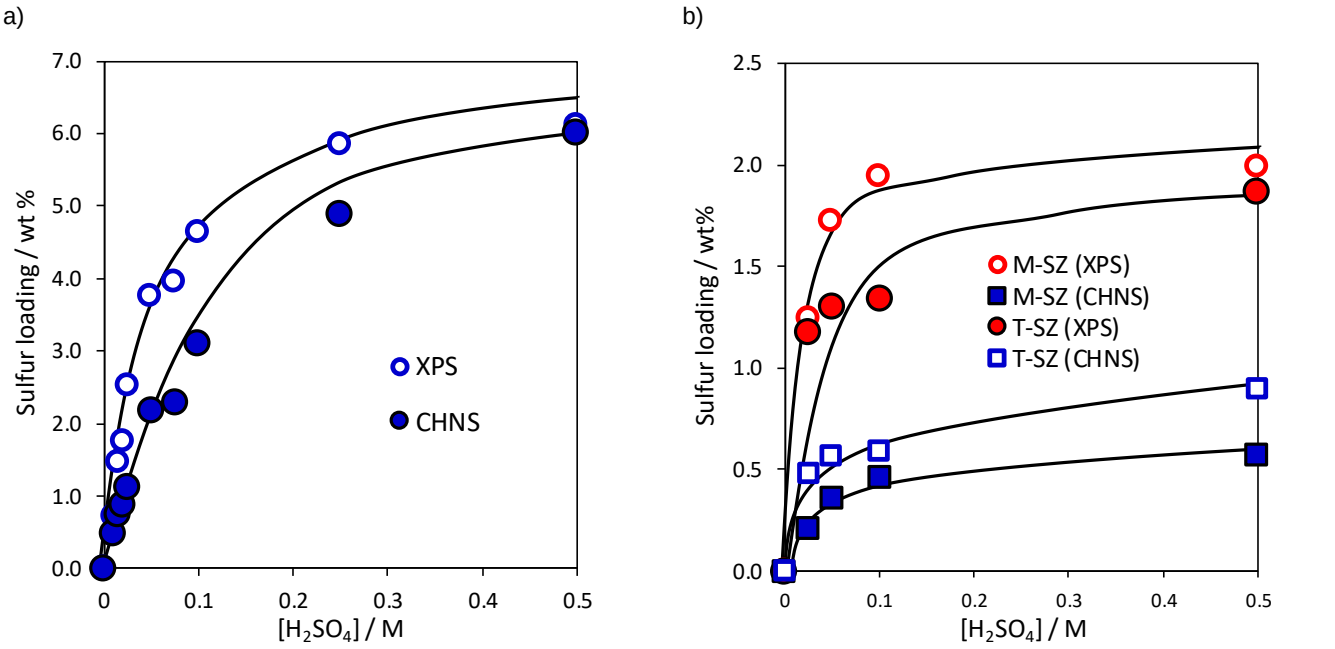

Figure S4. Comparison of the bulk and the surface sulfur content from HCNS elemental analysis and XPS respectively for xM a) SZ and b) *m*-SZ and *t*-SZ families as a function of [H_2SO_4] used during impregnation.

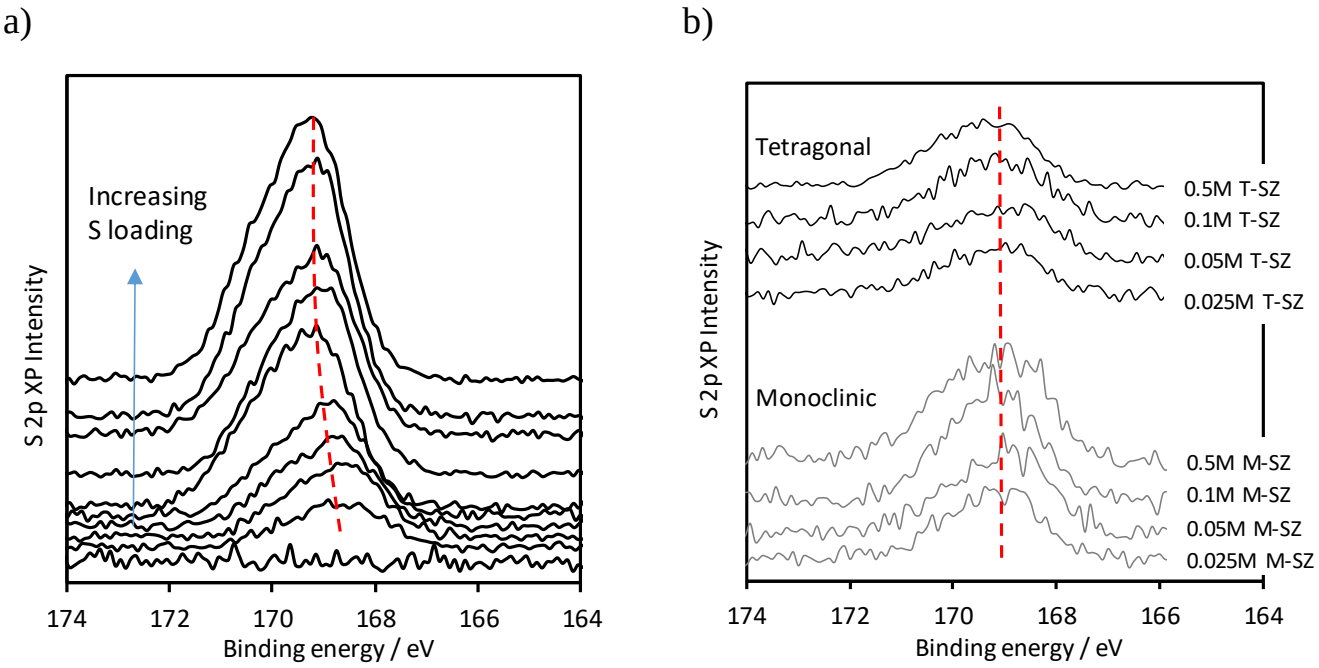

Figure S5. S 2p XP spectra for xM a) SZ and b) *m*-SZ and *t*-SZ families as a function of [H_2SO_4] used during impregnation.

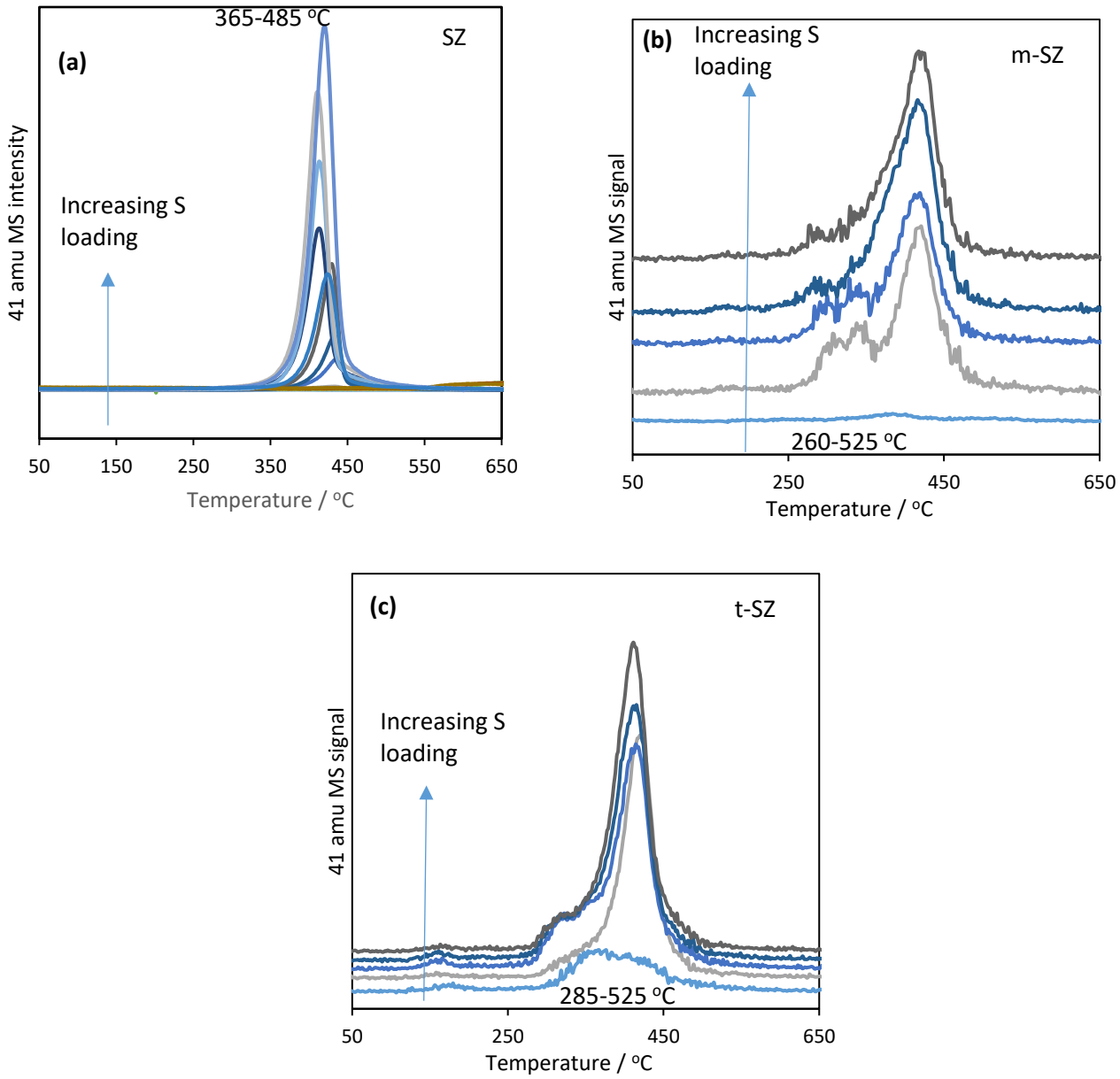

Figure S6: Propene desorption profile during TGA-MS of propylamine thermal decomposition. (a) SZ, (b) *m*-SZ catalysts and (c) *t*-SZ catalysts.

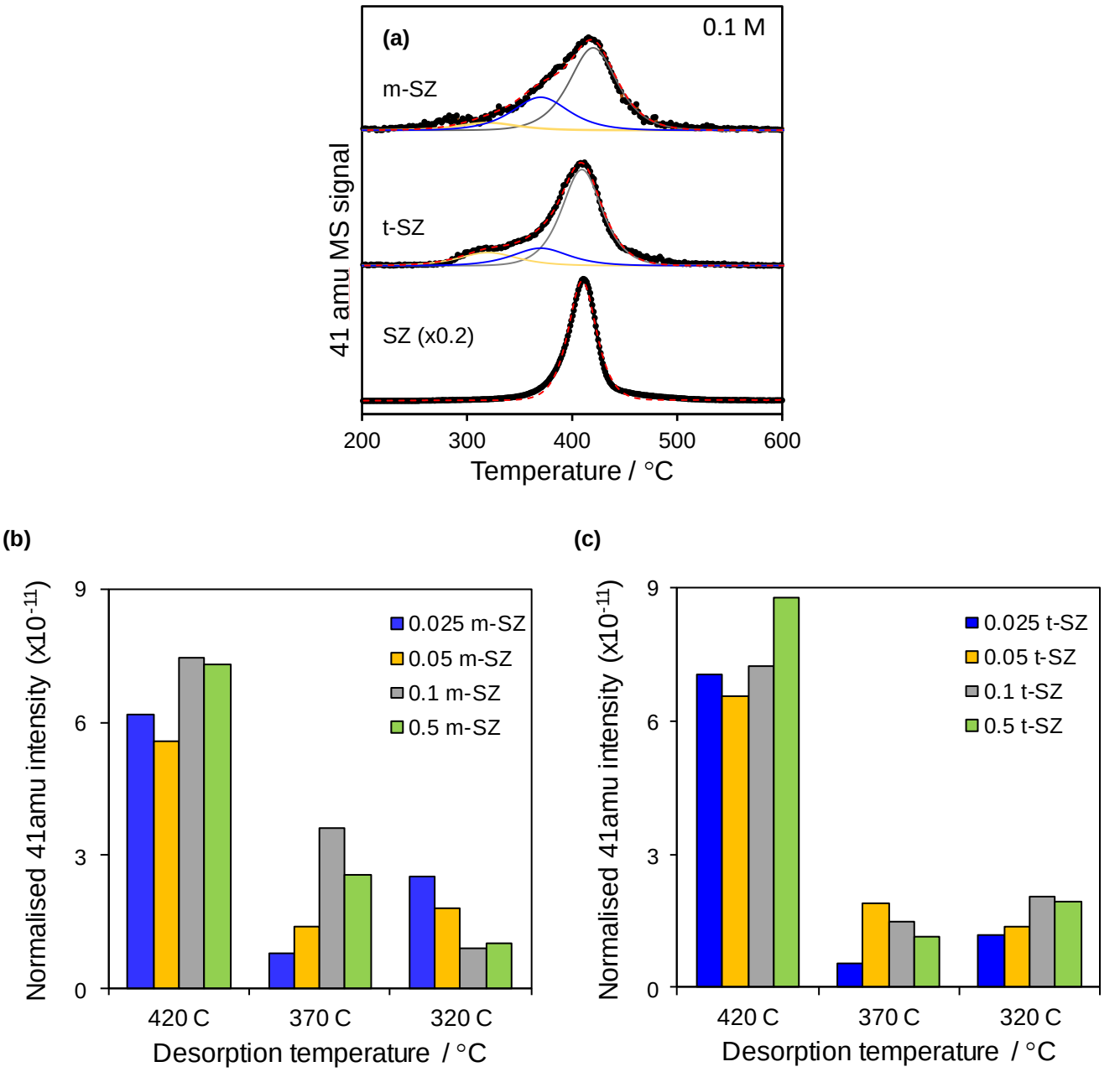

Figure S7: (a) Fitted propene desorption from propylamine thermal decomposition over 0.1SZ, 0.1*t*-SZ and 0.1*m*-SZ; (b) Surface area normalized fitted 41amu (propene) desorption peak intensities for 420, 370 and 320 °C components for *m*-SZ and *t*-SZ series as a function of [H_2SO_4].

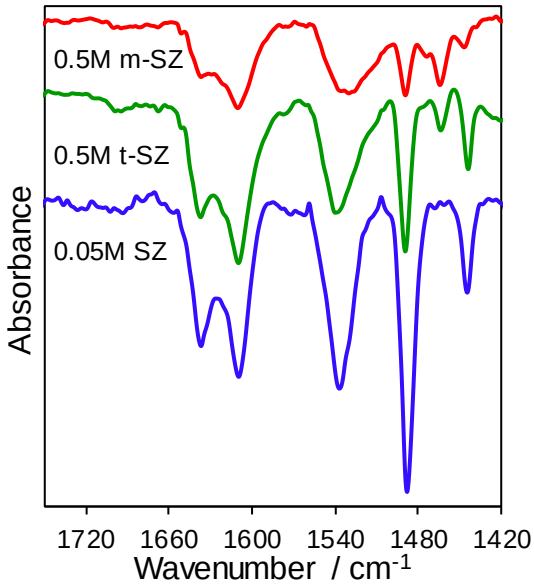

Figure S8: DRIFTS of adsorbed pyridine for (a) SZ, (b) m-SZ catalysts and (c) t-SZ catalysts having similar surface sulfate density (2.5-3.5 SO_4/nm^{-2}).

2. D-Sorbitol Cyclodehydration

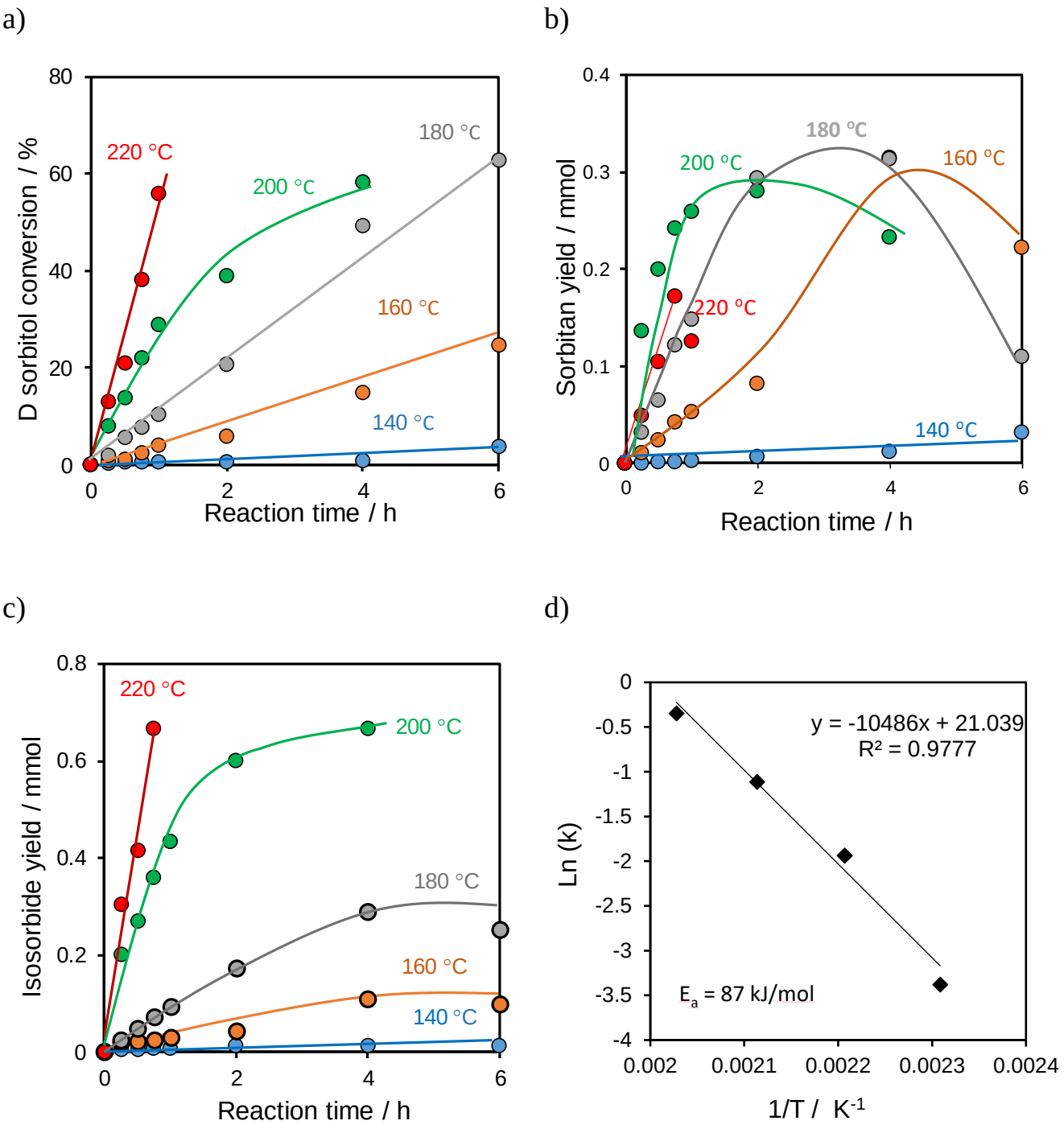

Figure S9: Effect of reaction temperature during D-sorbitol cyclodehydration over 0.1SZ. a) Sorbitol conversion, b) 1,4-sorbitan and d) isosorbide yield. d) Arrhenius plot and activation energy calculation. Conditions 0.4g catalyst, 0.4 g D-sorbitol, 40 ml water, 0.1 ml DMSO internal standard.

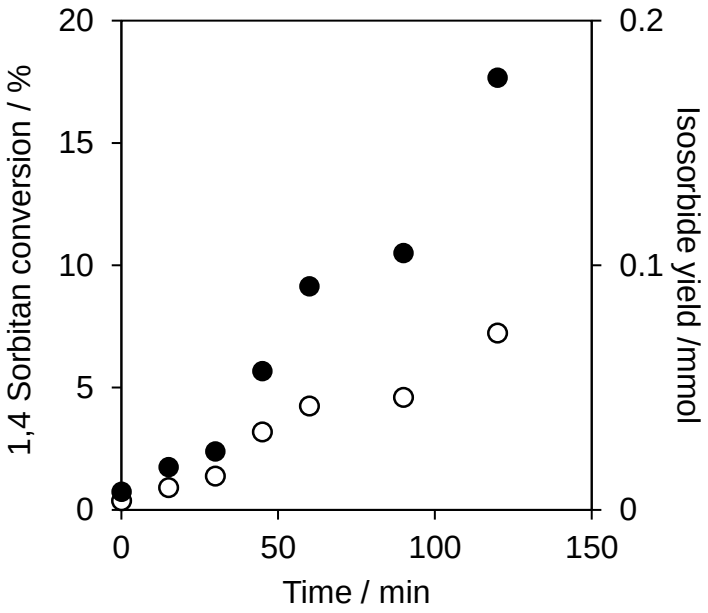

Figure S10: Reaction profiles for 1.4-sorbitan cyclodehydration over 0.1SZ. Conditions: 0.2 g catalyst; 0.1 g 1,4 Sorbitan (0.66 mmol); 40 ml water; 180°C and 0.1 ml DMSO internal standard.

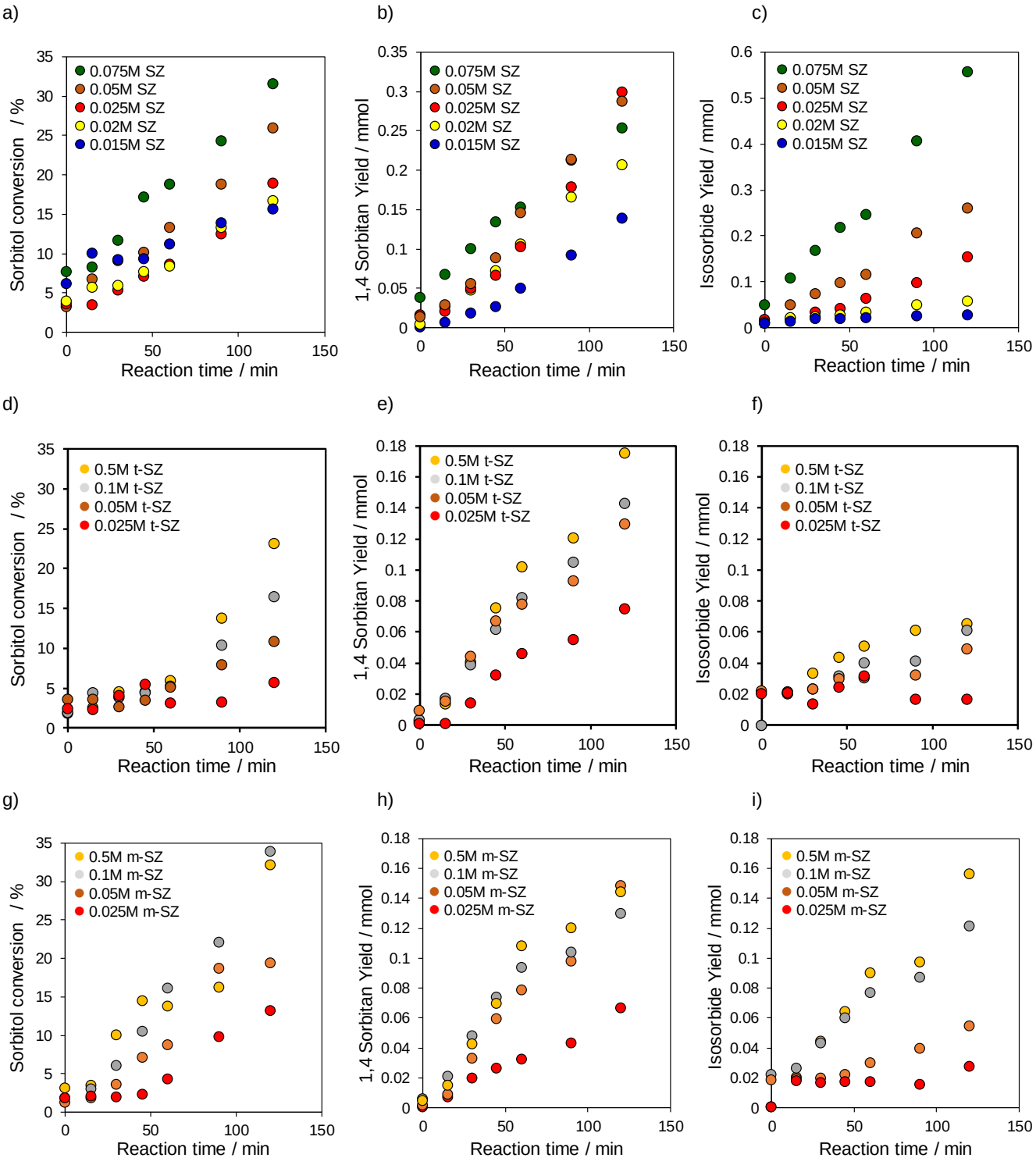

Figure S11: Reaction profiles for D-sorbitol cyclodehydration showing D-sorbitol conversion, 1,4-sorbitan and isosorbide yield for: a-c) SZ; d-f) t-SZ and g-i) m-SZ catalysts. Conditions 0.4g catalyst, 0.4 g D-sorbitol, 40 ml water, 0.1 ml DMSO internal standard at 180°C

Table S1. D-sorbitol conversion and yields of 1,4-sorbitan and isosorbide following 2h cyclodehydration at 180 °C using SZ, *m*-SZ and *t*-SZ catalysts.

Support	Catalyst[a]	S loading / wt%	D-Sorbitol conversion / %	1,4 sorbitan yield / μmol	1,4 sorbitan yield / mol%	Isosorbide yield / μmol	Isosorbide yield / mol%	Mass Balance / %
$Zr(OH)_4$	0.015M SZ	0.73	15.6	140	6.3	26	1.2	89.6
	0.02M SZ	0.88	16.6	206	9.4	56	2.5	91.6
	0.025M SZ	1.11	18.8	299	13.6	153	7.0	94.7
	0.05M SZ	2.18	25.9	286	13.0	259	11.8	91.0
	0.075M SZ	2.28	31.5	252	11.5	555	25.2	92.2
	0.1M SZ	3.10	37.0	272	12.4	647	29.4	89.1
	0.25M SZ	4.08	26.3	461	21.0	218	9.9	93.9
	0.5M SZ	6.02	19.7	382	17.3	168	7.6	97.0
m-ZrO_2	0.025M m-SZ	0.21	13.1	66	3	27	1.2	90.2
	0.05M m-SZ	0.36	19.3	148	6.7	54	2.4	87.8
	0.1M m-SZ	0.46	33.8	129	5.9	121	5.5	75.1
	0.5M m-SZ	0.57	32.1	144	6.5	156	7.1	78.6
t-ZrO_2	0.025M t-SZ	0.48	5.7	75	3.4	16	0.7	97.5
	0.05M t-SZ	0.57	10.8	130	5.9	49	2.2	95.5
	0.1M t-SZ	0.59	16.5	143	6.5	61	2.8	90.8
	0.5M t-SZ	0.90	23.1	175	8.0	65	3.0	85.5

[a] Catalysts are named xSZ, x*m*-SZ or x*t*-SZ where x is the molarity of H_2SO_4 used in impregnation. (Conditions 0.4g catalyst, 0.4 g D-sorbitol, 40 ml water, 0.1 ml DMSO internal standard at 180°C). Mass balance calculated using $\frac{\text{Moles of carbon in (unreacted D}-\text{sorbitol} + \Sigma\text{products)}}{\text{Moles of carbon in D}-\text{sorbitol}_{\,t=0}} \times 100$

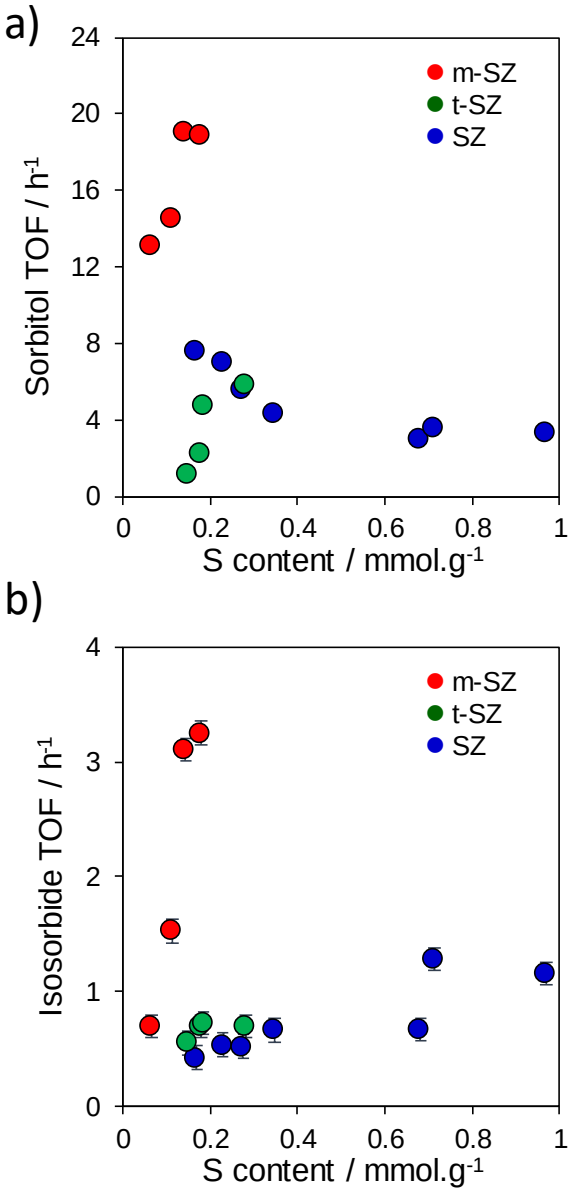

Figure S12. D-sorbitol cyclodehydration to isosorbide over xM SZ, m-SZ and t-SZ catalysts: a) TOF for D-sorbitol conversion and b) TOF for isosorbide production. Conditions: 0.4 g catalyst; 0.4 g D-sorbitol; 40 ml water; 0.1 ml DMSO internal standard; 180°C.

Table S2. D-sorbitol conversion and yields of 1,4-sorbitan and isosorbide following recycle of SZ prepared from 0.1M H_2SO_4.

Catalyst[a]	S[b] loading / wt%	D-Sorbitol conversion[c] / %	1,4 sorbitan yield[c] / μmol	Isosorbide yield[c] / μmol
0.1SZ fresh	3.1	37	272	647
0.1SZ recycled	1.8	25	143	407

[a] Similar changes were observed for 0.1*m*-SZ; [b]From CHNS analysis; [c]After 2h reaction. Conditions: 0.4 g catalyst; 0.4 g D-sorbitol; 40 ml water; 0.1 ml DMSO internal standard; 180°C.