Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Bifunctional SO_4/ZrO_2 catalysts for 5-hydroxymethylfufural (5-HMF) production from glucose

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Electronic Supplementary Information

Table S1: Calibration of surface sulfate coverage for SZ catalysts

H_2SO_4 conc[n] /M	Bulk S Content[a] / wt%	Surface S content[b] / w%	SO_4 coverage[c] / ML
$Zr(OH)_4$	-	0.0	0.0
0.010	0.07	0.73	0.1
0.015	0.30	0.99	0.2
0.020	0.40	1.53	0.3
0.025	0.51	2.04	0.4
0.050	1.10	3.26	0.6
0.075	1.66	3.43	0.7
0.100	2.26	4.05	0.8
0.25	2.92	5.09	1.0
0.5	3.55	5.51	1.1

From [a]EDX; [b]XPS; [c]Assuming 1 ML corresponds to 5 wt% surface S content

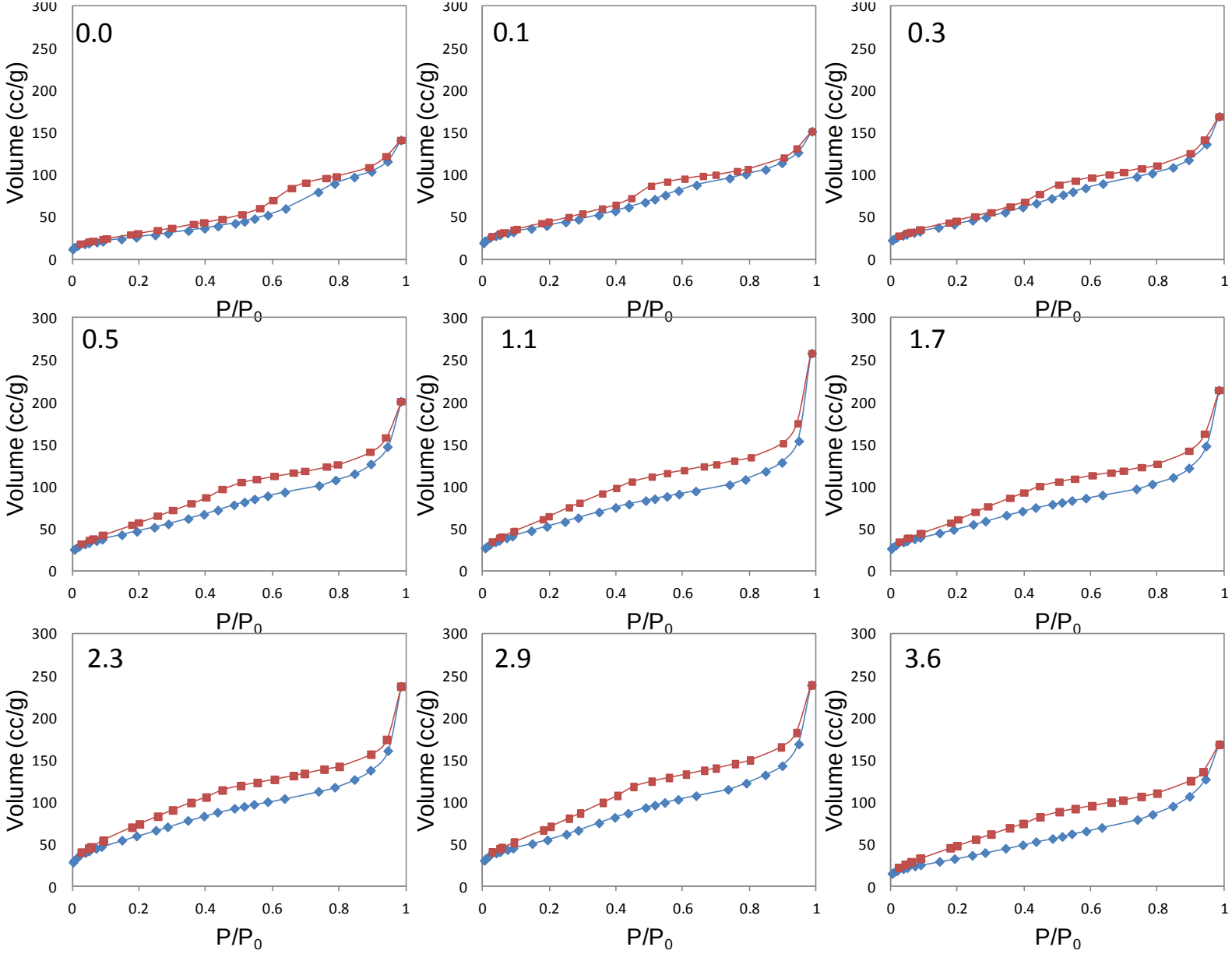

Figure S1 N_2 Porosimetry on the series of calcined SZ catalysts prepared from impregnation of $Zr(OH)_4$ with 0.01-0.5M $H2SO_4$

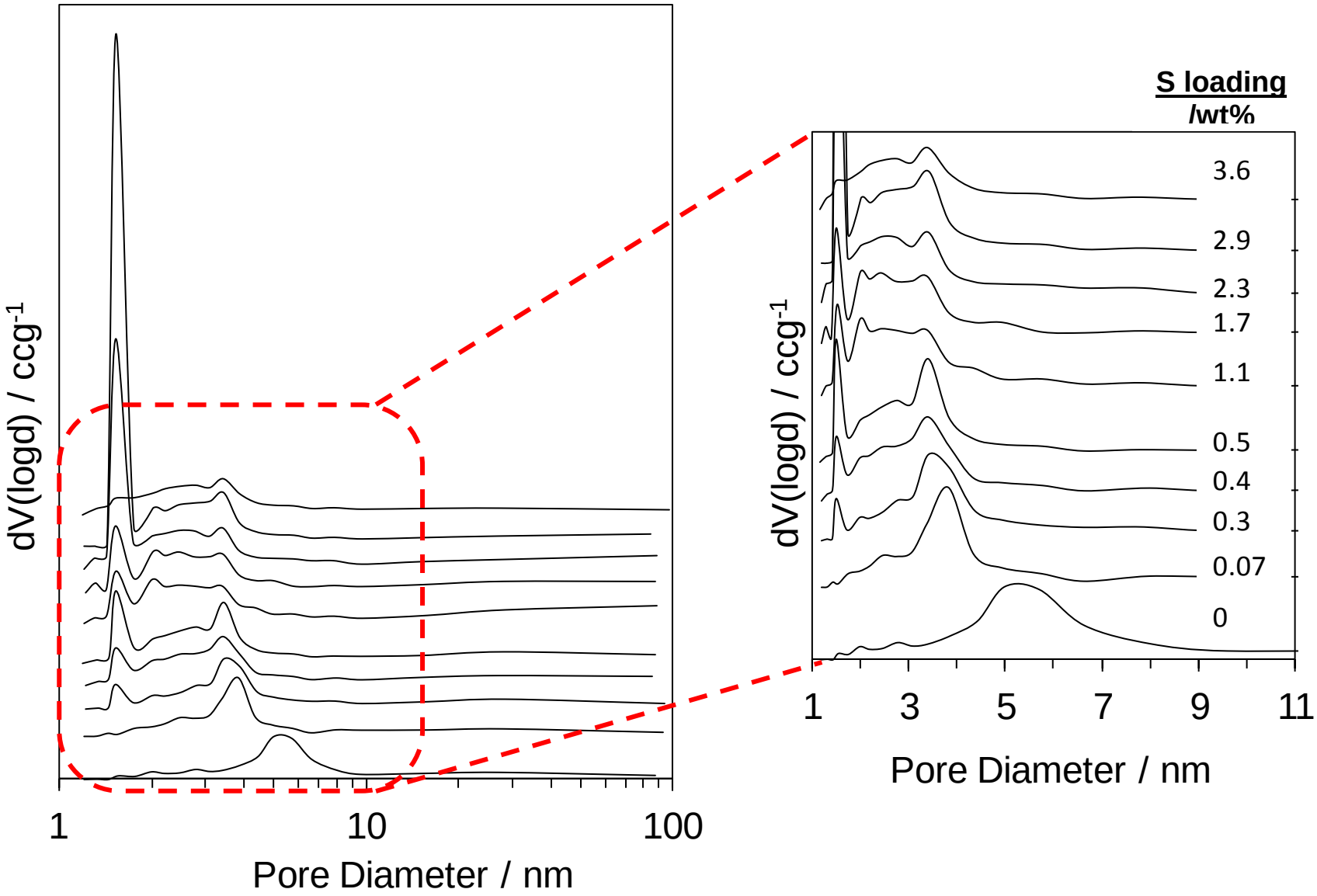

Figure S2 BJH pore size distributions for the calcined SZ catalyst series prepared from impregnation of $Zr(OH)_4$ with 0.01-0.5M H_2SO_4

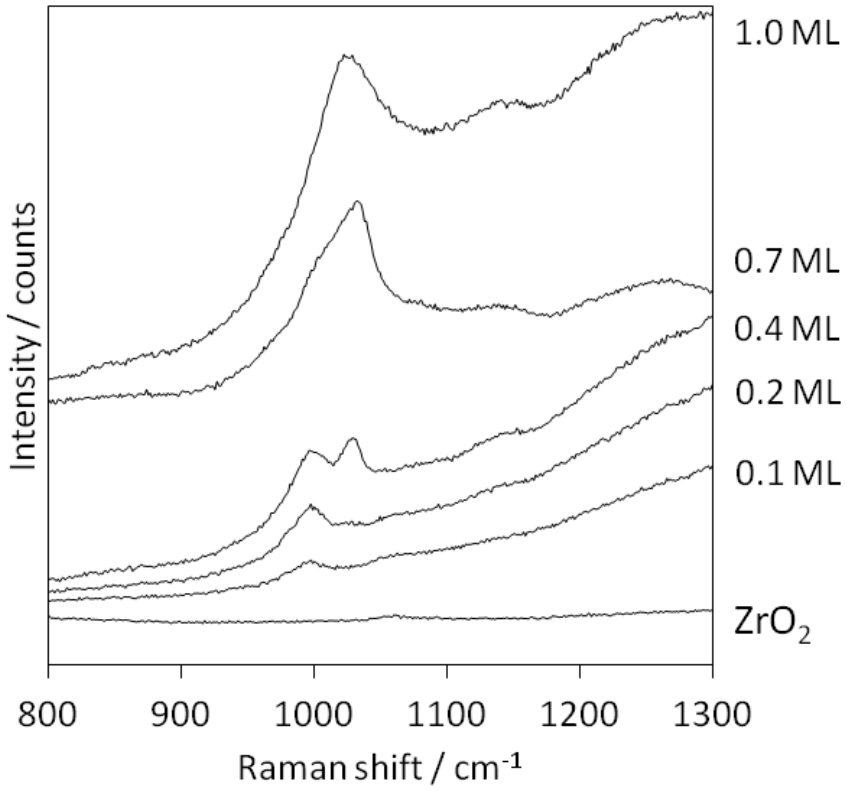

Figure S3 Raman of SZ catalyst series prepared showing evolution of symmetric stretching mode of sulfate with coverage. Splitting of peaks is attributed to a transition from SO_4 coordinated on monoclinic and tetragonal phases of ZrO_2

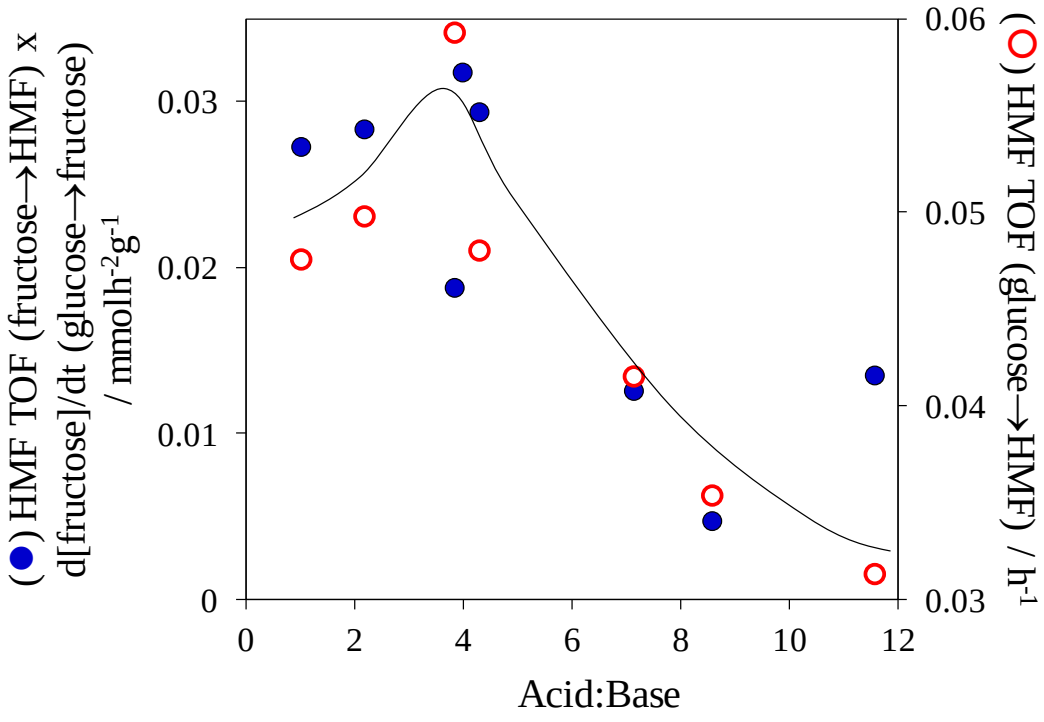

Figure S4 Correspondence between the overall rate of glucose conversion to 5-HMF, and the product of the independently calculated rates of glucose isomerisation to fructose and fructose dehydration to 5-HMF, as a function of Acid:Base character over SZ catalysts.

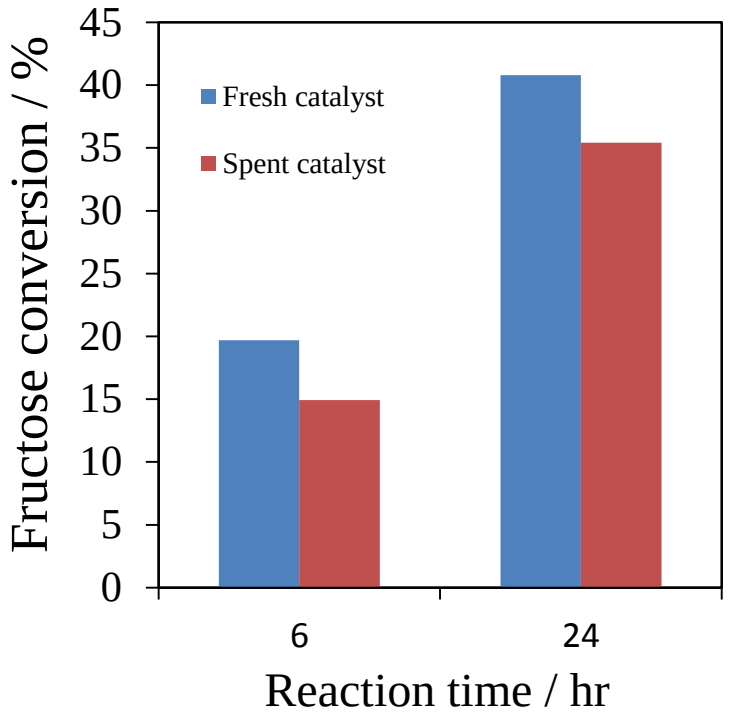

Figure S5 Comparison of fructose conversions in water at 100°C for fresh and recycled 0.2 ML SZ catalyst (re-calcined at 550°C before reaction)

Table S2 Conversion and selectivity data after 6 h reaction for SZ catalysts in fructose and glucose conversion.

Sulfur Coverage	Substrate	Conversion	Carbon balance	HMF selectivity	Fructose selectivity	Glucose selectivity	Other sugars selectivity	Furfural selectivity
ML		%	%	%	%	%	%	%
0	Fructose	14.7	96.4	11.7	-	25.0	48.7	14.6
	Glucose	20.9	98.2	1.9	84.2	-	11.7	2.3
0.1	Fructose	16.2	92.0	13.3	-	26.4	44.9	15.3
	Glucose	22.7	99.9	3.0	81.3	-	11.8	3.8
0.2	Fructose	18.6	88.4	17.9	-	17.8	43.7	20.6
	Glucose	23.3	99	3.7	81.0	-	10.7	4.6
0.3	Fructose	19.1	94.1	19.9	-	16.2	40.9	22.9
	Glucose	20.9	99.5	4.8	78.2	-	10.9	6.0
0.4	Fructose	18.2	97.0	19.3	-	20.0	38.5	22.2
	Glucose	17.8	99.3	4.6	79.8	-	9.8	5.8
0.6	Fructose	20.8	93.3	29.9	-	8.1	27.6	34.3
	Glucose	7.5	99.7	10.5	63.9	-	12.5	13.2
0.7	Fructose	19.8	91.9	23.8	-	7.4	41.4	27.4
	Glucose	5.4	99	9.9	65.3	-	12.2	12.5
0.8	Fructose	25.4	89.4	32.6	-	8.1	21.9	37.4
	Glucose	7.2	98	10.0	77.2	-	12.7	0.1
1.0	Fructose	23.3	89.3	26.6	-	8.4	32.0	33.0
	Glucose	11.6	99	9.4	70.2	-	8.6	11.8
1.1	Fructose	16.6	88.3	28.2	-	9.0	27.8	35.1
	Glucose	5.5	99.2	7.7	81.5	-	10.7	0.1