Dehydration of Xylose to Furfural in a Biphasic System: Catalyst Selection and Kinetic Modelling Discrimination

Dominik Soukup-Carne [a], Ben Hillman[b], Christopher M. A. Parlett [a,c,d,e] , Xiaolei Fan [a,f], and Jesús Esteban[g a]*

[a] *Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*

[b] *Department of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*

[c]*Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire OX11 0FA, United Kingdom*

[d]*Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom*

[e]*University of Manchester at Harwell, Diamond Light Source, Didcot, Oxfordshire OX11 0DE, United Kingdom*

[f]*Nottingham Ningbo China Beacons of Excellence Research and Innovation Institute, Ningbo, 315100, China*

[g]*Department of Chemical Engineering and Materials, Faculty of Chemical Sciences, Complutense University of Madrid, Madrid 28040, Spain*

*Corresponding author: E-mail address: jesus.estebanserrano@manchester.ac.uk; jeesteba@ucm.es (Jesús Esteban)

Table of Contents

S1: Sulfated Zirconia preparation

Table S1: Sulfated Zirconia preparation details supplied by LuxferMEL.

Sample	Dopant	Calcination Temperature (°C)	Calcination Time (h)	Dopant Loading (%)
SO_4/ZrO_2-1	SO_3	650	2	6.0
SO_4/ZrO_2-2	SO_3	650	2	8.1
SO_4/ZrO_2-3	SO_3	610	2	6.0

S2: Statistical metrics for modelling:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{N - P}} \quad S1$$

$$AIC = N.\ln\left(\frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{N}\right) + 2P \quad S2$$

$$BIC = \mathrm{N}.\ln\left(\frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{N}\right) + P\ln N \quad S3$$

$$F = \frac{\sum_{i=1}^{n}\frac{(\hat{x}_i)^2}{P}}{\sum_{i=1}^{n}\frac{(x_i - \hat{x}_i)^2}{N - P}} \quad S4$$

Where x_i is experimental value, $\hat{x}_i$ the predicted value, N is the number of observations, and P is the number of parameters.

S3: Catalyst Characterisation

Table S2: Sulfated zirconia physical properties., where [a] C_B and C_L represents the concentration of Brønsted and Lewis acid sites, respectively. [b] Based on the first peak integration in the corresponding NH_3-TPD spectra. [c] Based on the second peak integration in the corresponding NH_3-TPD spectra .[d] Determined by py-IR

Sample	C_B/C_L [a]	Medium acidity [b] (µmol g^{-1})		Strong acidity [c] (µmol g^{-1})		Total B- or L- acidity (µmol g^{-1})		Total NH_3-TPD acidity (µmol g^{-1})	Surface area (m^2 g^{-1})	Average Pore diameter (nm)	Pore Volume (cm3 g^{-1})
		Brønsted [d]	Lewis [d]	Brønsted [d]	Lewis [d]	Brønsted	Lewis				
SO_4/ZrO_2-1	14.78	535.7	36.2	26.0	1.8	561.7	38.0	599.7	98	5.9	0.14
SO_4/ZrO_2-2	6.93	595.2	85.8	27.5	4.0	622.7	89.8	712.5	113	10.1	0.29
SO_4/ZrO_2-3	4.44	723.9	163.1	3.7	0.8	727.6	163.9	891.5	153	12.4	0.47

S4: HPLC Chromatogram of xylose and intermediate

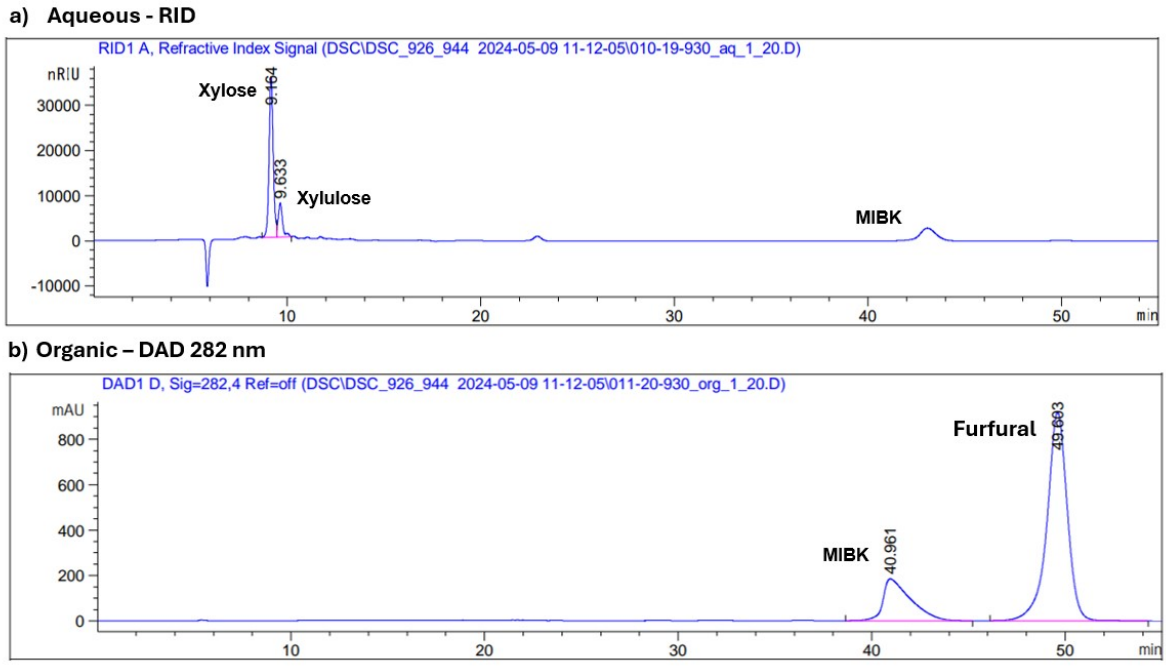

Figure S1:a) HPLC RID Chromatogram of aqueous phase and b) organic phase post-reaction at 160 °C after 10 min, 10 wt.% xylose loading and 2 wt.% SO_4/ZrO_2-1 loading.

S5: TGA of catalysts post-recycling

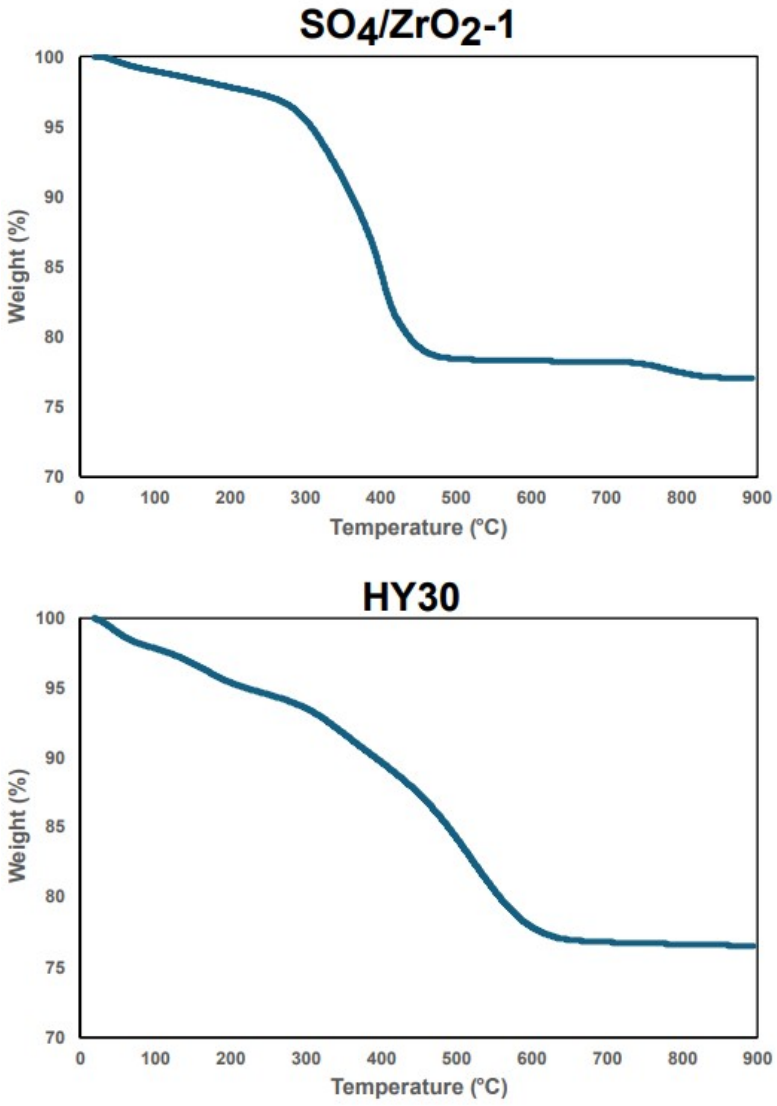

Figure S2: TGA analysis of SO_4/ZrO_2-1 and HY30 after 5 recycle runs

S6: Catalyst recycling

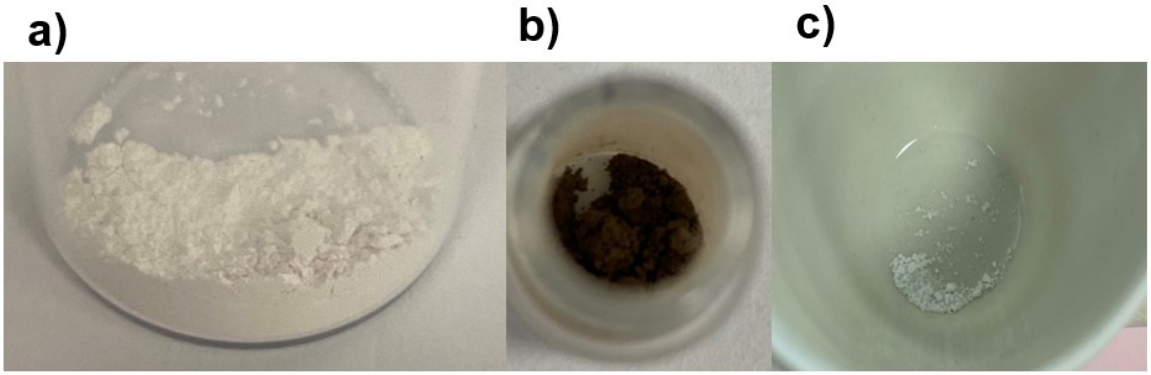

Figure S3: a) Fresh SO_4/ZrO_2-1, b) SO_4/ZrO_2-1 after six total reaction and recycle runs, c) SO_4/ZrO_2-1 regenerated through calcination in air at 550 °C

S7: Mass transfer limitations

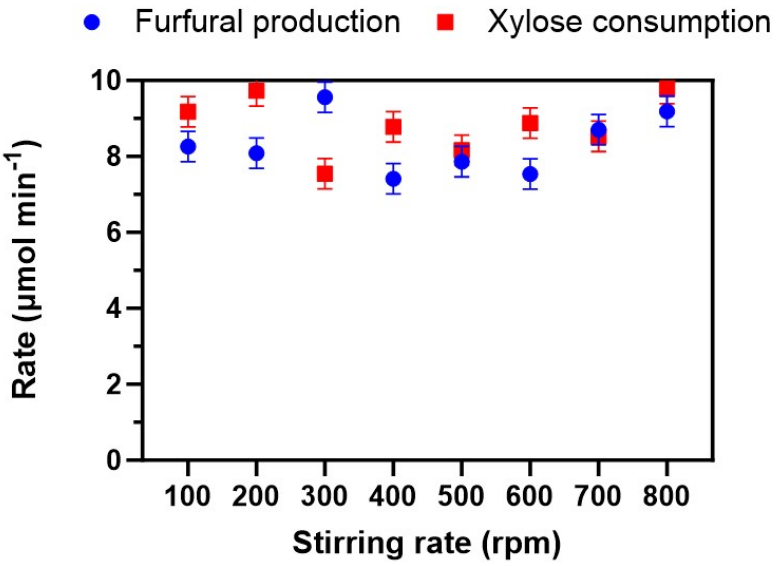

Figure S4:External mass transfer limitations in SO4/ZrO2-1 through variation of agitation rate on xylose conversion a) and b) total Fur yield (circle markers) with PR (square markers) at 160 °C.

S8: Volume changes with respect to temperature

Table S3:Fitting parameters for water-MIBK phase ratio changes obtained from Guo et al. [1]

Phase (-)	Initial (Org:Aq) (-)	u^1 (-)	v^1 (-)	w^1 (-)
Aq	2	0.898	0.092	0.003
Org	2	0.781	0.193	0.006

The actual phase ratios were calculated using eq. 5 and the paramteters in Table S2, with results for 140-170 °C presented in Table S3.

Table S4: Temperature specific phase ratios for 1:2 water-MIBK system.

T (°C)	γ_{aq}	γ_{org}	*(Org:Aq)*
140	1.038	1.228	2.366
150	1.042	1.256	2.410
160	1.047	1.285	2.455
170	1.051	1.316	2.504

S9: Partition ratio of Fur in a water-MIBK biphasic system

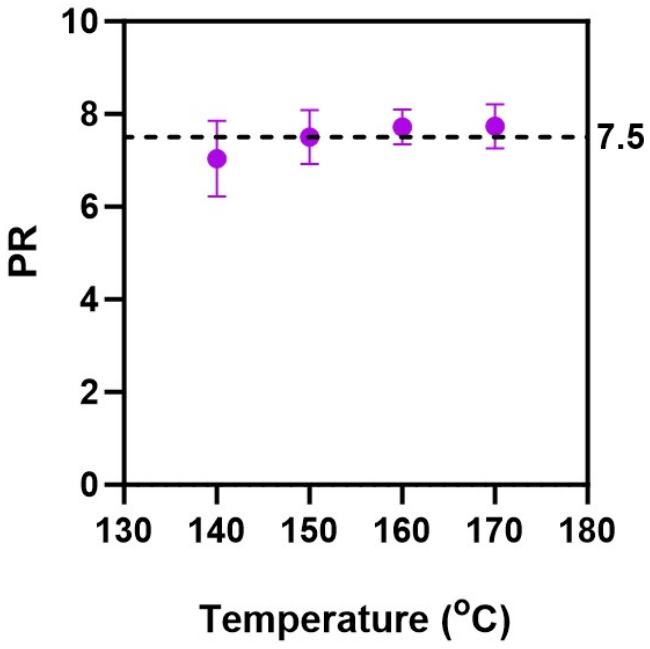

Figure S5: Partition ratio of Fur in a 1:2 water-MIBK system at 10 wt. xylose loading and 2 wt.% SO_4/ZrO_2-1loading, averaged values from 0-180 mins at temperatures 140-170 °C.

S10: Model discrimination

Table S5: True values for the statistical model discrimination.

	Including Humins				Excluding Humins			
Model	**RMSE**	**AIC**	**BIC**	**F-stat**	**RMSE**	**AIC**	**BIC**	**F-stat**
PH-1	0.0880	-1845.45	-1771.56	70.11149	0.0337	-2567.07	-2497.07	469.0008
PH-2	0.0880	-1934.79	-1860.91	86.00239	0.0627	-2427.44	-2357.44	424.4671
PH-2a	0.0880	-1839.04	-1765.15	67.8553	0.0331	-2564.92	-2494.92	463.0457
PH-2b	0.0880	-1935.07	-1861.18	86.20412	0.0630	-2423.68	-2353.68	419.4291
PH-2c	0.0880	-1854.75	-1780.86	73.89529	0.0340	-2573.9	-2503.9	481.3725
PH-2d	0.0880	-1932.31	-1858.42	85.09418	0.0623	-2427.12	-2357.12	420.8326
PH-2e	0.0880	-1839.82	-1765.93	68.14509	0.0332	-2563.07	-2493.07	460.6618
PH-2f	0.0880	-1934.18	-1860.29	85.76331	0.0628	-2426.32	-2356.32	422.5267
ER-1	0.1210	-1913.32	-1816.1	79.07691	0.0550	-2628.27	-2534.94	444.7985
LHHW-1	0.1232	-1916.35	-1819.12	82.4266	0.0455	-2664.15	-2570.82	478.6492
ER-2	0.1217	-1916.51	-1827.07	82.4917	0.0588	-2586.46	-2500.91	437.2772
LHHW-2	0.1217	-1916.51	-1827.07	82.4917	0.0588	-2586.46	-2500.91	437.2772
ER-3	0.1217	-1916.52	-1827.08	82.49361	0.0588	-2586.45	-2500.9	437.2691
LHHW-3	0.1217	-1916.51	-1827.07	82.49107	0.0588	-2586.47	-2500.92	437.2924
ER-4	0.1209	-1907.72	-1810.5	77.28441	0.0534	-2628.26	-2534.92	437.2251
LHHW-4	0.1215	-1914.73	-1817.51	78.99855	0.0549	-2610.27	-2516.94	412.0037
ER-5	0.1209	-1934.51	-1837.29	98.0439	0.0534	-2628.84	-2535.5	438.0154
LHHW-5	0.1227	-1915.09	-1817.87	82.51953	0.0544	-2661.9	-2568.56	473.0897

References

(1) Guo, W.; Zhang, Z.; Hacking, J.; Heeres, H. J.; Yue, J., Selective fructose dehydration to 5-hydroxymethylfurfural from a fructose-glucose mixture over a sulfuric acid catalyst in a biphasic system: Experimental study and kinetic modelling. *Chem. Eng. J.* **2021,** *409*, 128182.