Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Bio-oil upgrading via vapour phase acetic acid ketonisation over zirconia

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Electronic Supporting Information

a) **b)**

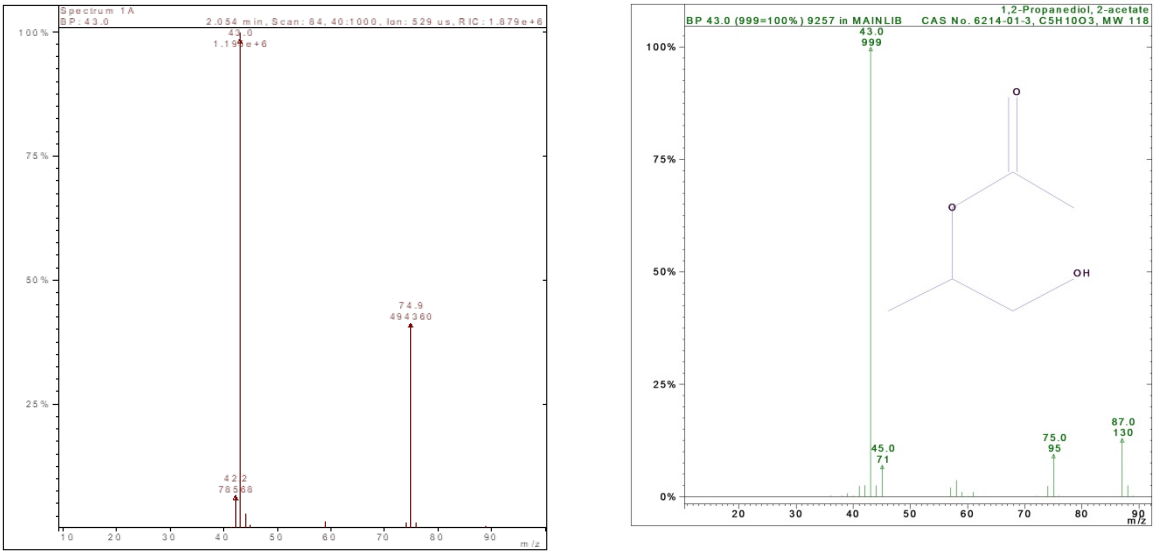

Figure S1. a) MS of main by-product formed during acetic acid ketonisation over ZrO_2 catalysts; and b) library MS of 1,2,propanediol-2-acetate.

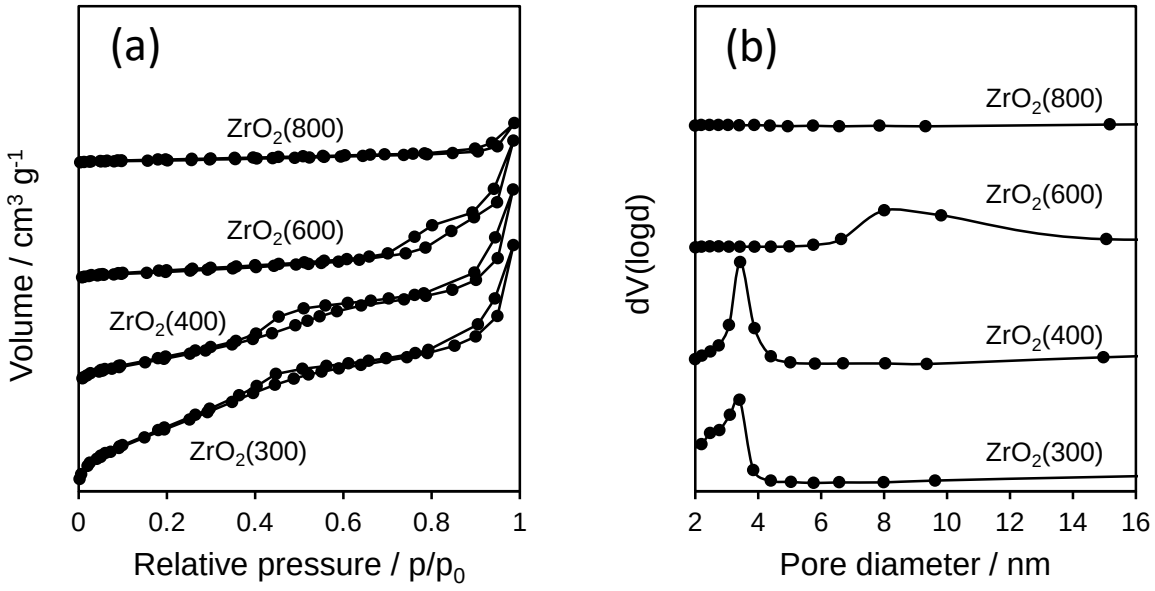

Figure S2. a) N_2 porosimetry isotherms and b) pore size distributions of $Zr(OH)_4$ as a function of calcination temperature.

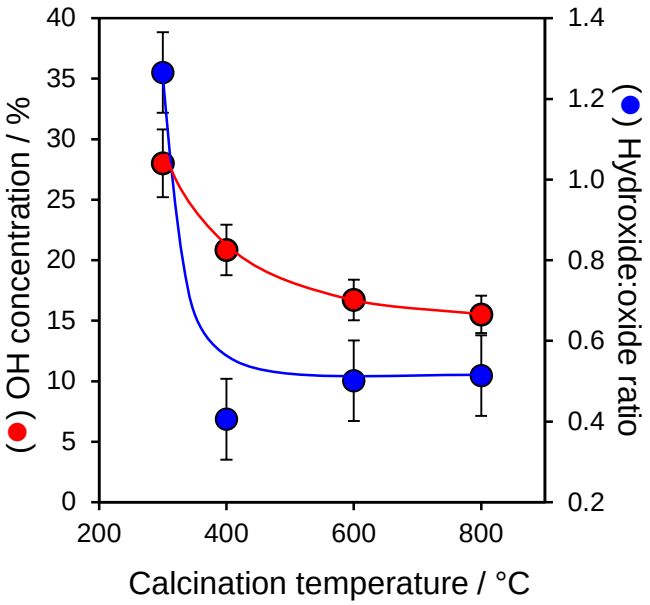

Figure S3. Surface O species in the form of OH with respect to total surface O content (●) and hydroxide:oxide ratio calculated from the corresponding Zr 3*d* peaks (●) of $Zr(OH)_4$ as a function of calcination temperature.

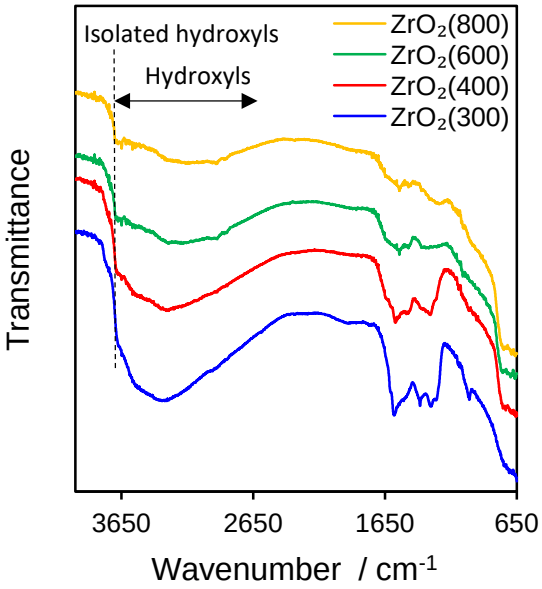

Figure S4. DRIFT spectra of $Zr(OH)_4$ as a function of calcination temperature.

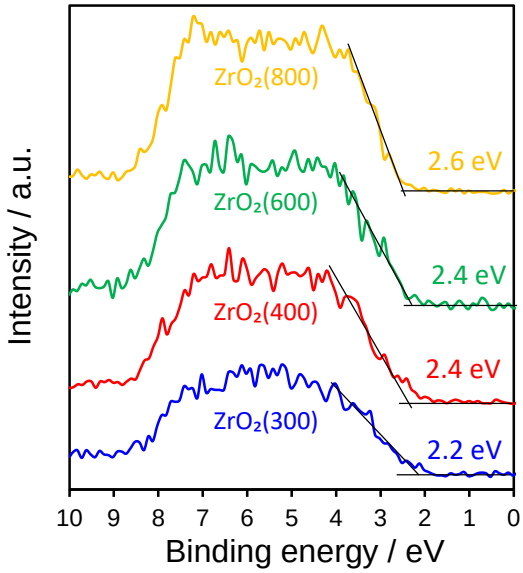

Figure S5. Valence band XP spectra of $Zr(OH)_4$ as a function of calcination temperature.

Table S1. Surface composition of $Zr(OH)_4$ as a function of calcination temperature from XPS.

Catalyst	O / wt%	Zr / wt%	Non-hydroxyl O:Zr	Valence band / eV
ZrO_2(300)	32.5	67.5	2.0	2.2
ZrO_2(400)	28.4	71.6	1.8	2.4
ZrO_2(600)	28.2	71.9	1.9	2.4
ZrO_2(800)	27.5	72.5	1.8	2.6

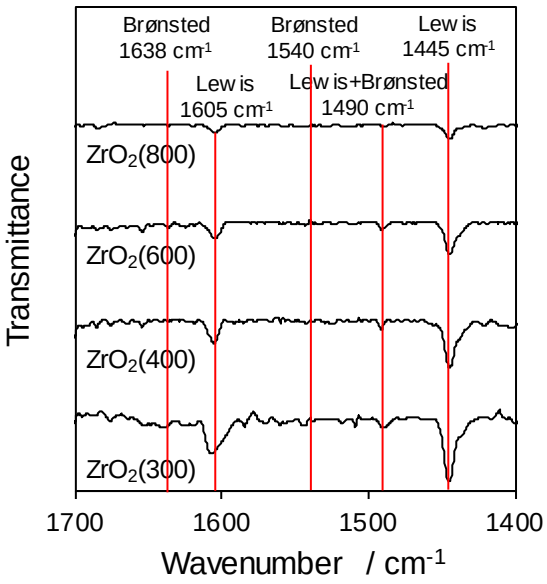

Figure S6. DRIFT spectra of pyridine titrated $Zr(OH)_4$ as a function of calcination temperature.

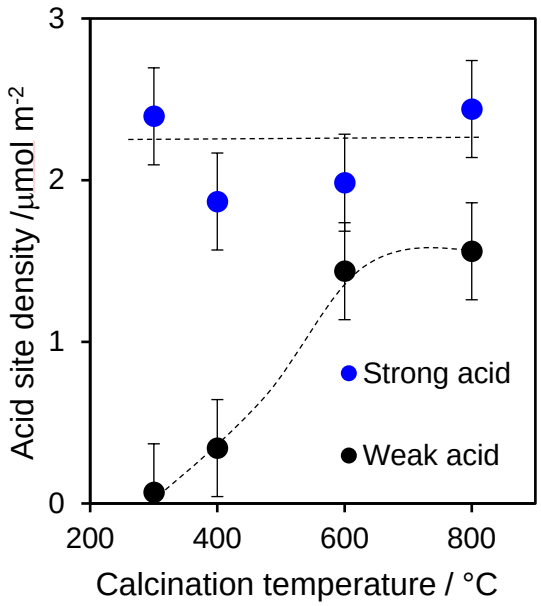

Figure S7. Density of strong and weak acid sites $Zr(OH)_4$ as a function of calcination temperature determined from propylamine TPD.

Table S2. Base site loading of $Zr(OH)_4$ as a function of calcination temperature from CO_2 chemisorption.

Catalyst	Base site loading / $mmolg^{-1}$	Base site surface loading / $\mu.molm^{-2}$	Acid:Base loading
ZrO_2(300)	0.03	0.15	16.7
ZrO_2(400)	0.08	0.72	3.1
ZrO_2(600)	0.03	0.90	3.8
ZrO_2(800)	0.02	2.09	1.9

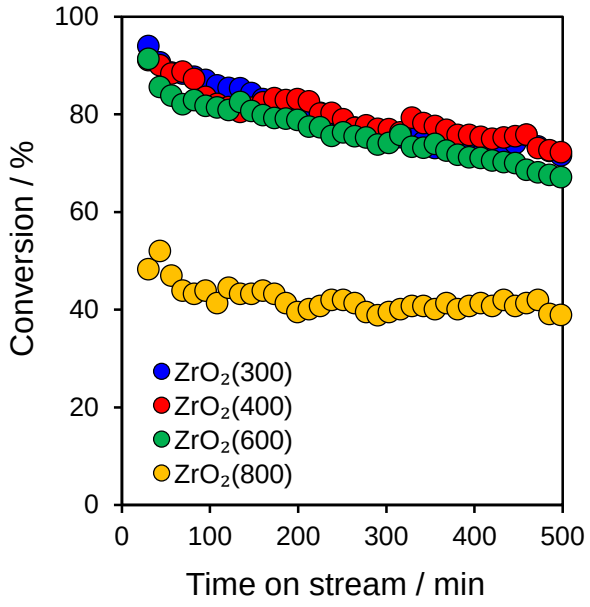

Figure S8. Acetic acid conversion over $Zr(OH)_4$ as a function of calcination temperature and time on-stream. Reaction conditions: 200 mg catalyst, at 400 °C, 0.2 ml min^{-1} acetic acid, ambient pressure, 50 ml min^{-1} N_2.

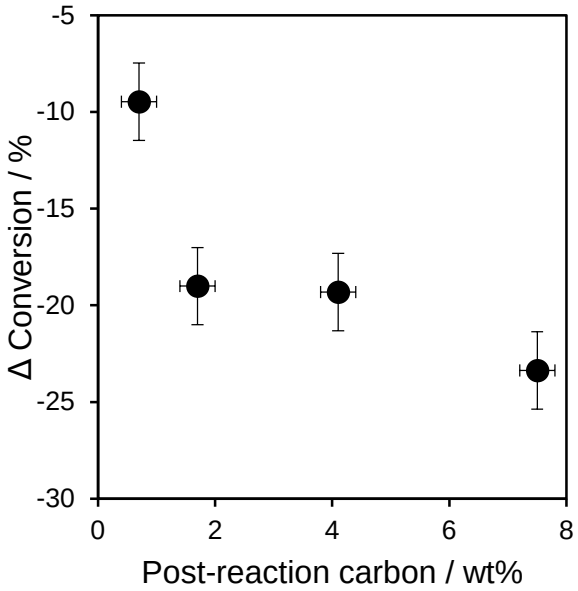

Figure S9. Relative decrease in acetic acid conversion as a function of post-reaction carbon after 8.5 h on-stream over $Zr(OH)_4$ as a function of calcination temperature Reaction conditions: 200 mg catalyst, 400 °C, 0.2 ml min^{-1} acetic acid, ambient pressure, 50 ml min^{-1} N_2.

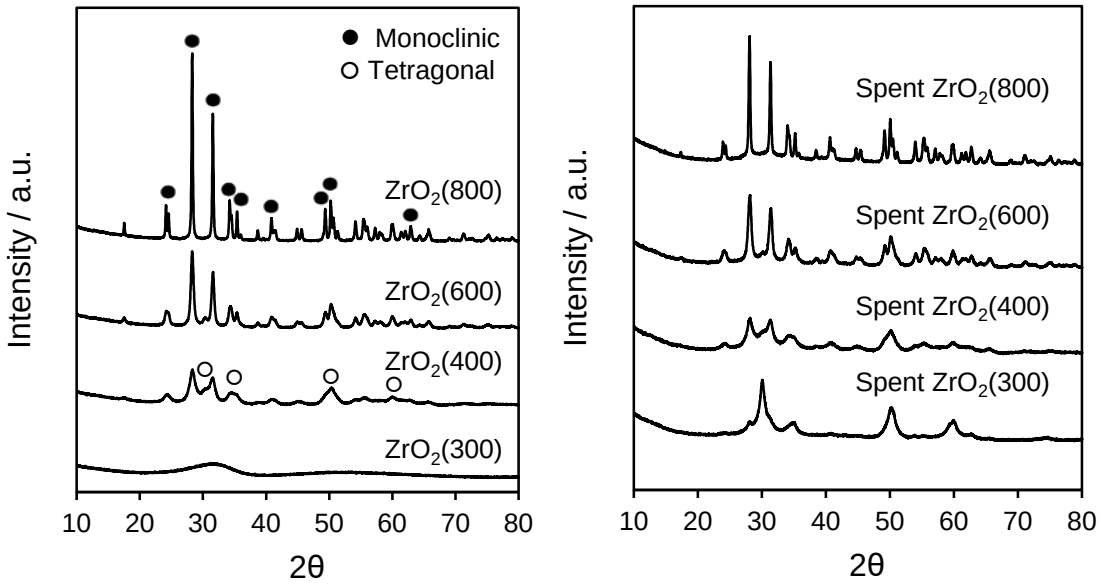

Figure S10. XRD patterns for (*left*) fresh and (*right*) spent $Zr(OH)_4$ as a function of calcination temperature after ketonisation at temperature 400 °C.

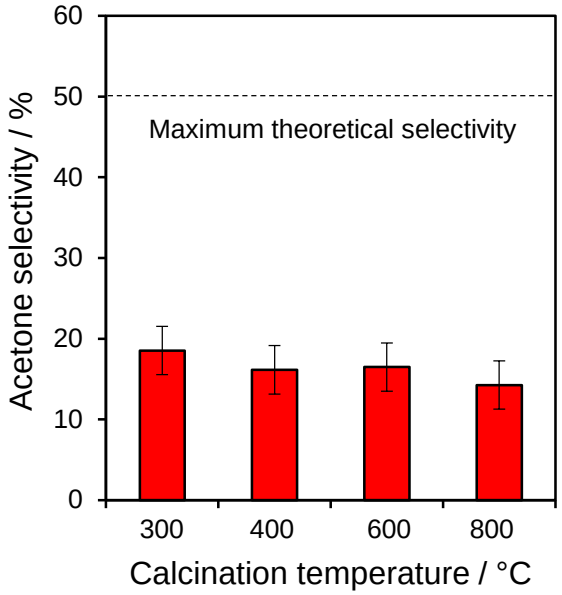

Figure S11. Acetone selectivity from acetic acid ketonisation at 50 % ico-conversion as a function of $Zr(OH)_4$ calcination temperature. Reaction conditions: 200 mg catalyst, 400 °C, 0.1-0.4 ml.min^{-1} acetic acid, 50 ml.min^{-1} N_2, and ambient pressure