Supplementary Information

Liquid phase catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone over ZrO_2/SBA-15

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Surface and Bulk elemental analysis

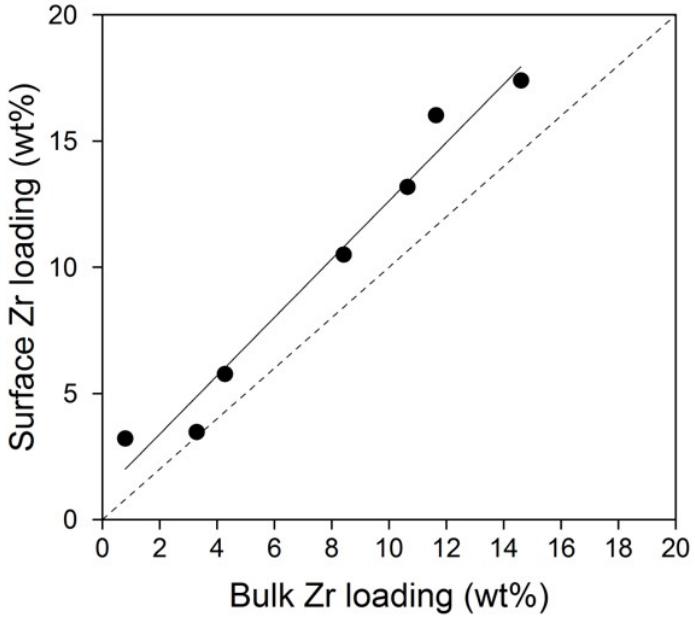

Figure S1. Surface versus bulk Zr loading of ZrO_2/SBA-15 measured by XPS and ICP-OES, respectively.

Table S1. Elemental analysis of ZrO_2/SBA-15 catalysts.

Nominal Zr surface coverage / %	Zr loading / wt% (ICP)	Surface Composition (XPS)					
		O wt%	Zr wt%	Si wt%	O at%	Zr at%	Si at%
1	0.8	38.6	3.2	58.1	53.4	0.8	45.8
5	3.3	37.7	3.5	58.8	52.5	0.9	46.7
10	4.3	34.9	5.8	59.3	50.1	1.5	48.5
20	8.4	36.6	10.5	52.9	53.3	2.7	43.9
30	10.7	36.2	13.2	50.7	53.7	3.4	42.9
50	11.6	34.3	16.0	49.7	52.5	4.3	43.2
100	14.6	33.8	17.4	48.8	52.3	4.7	42.9
ZrO_2	58.8	18.6	81.4	0	56.6	43.4	0

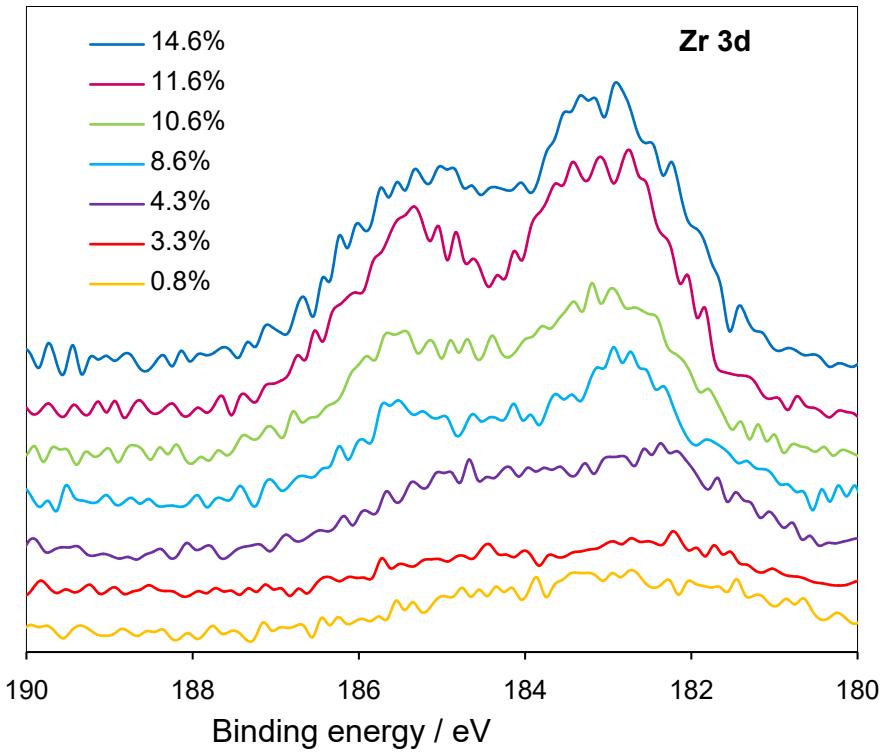

Figure S2. Zr 3d XP spectra of ZrO_2/SBA-15 as a function of Zr surface loading (wt%).

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N_2 porosimetry

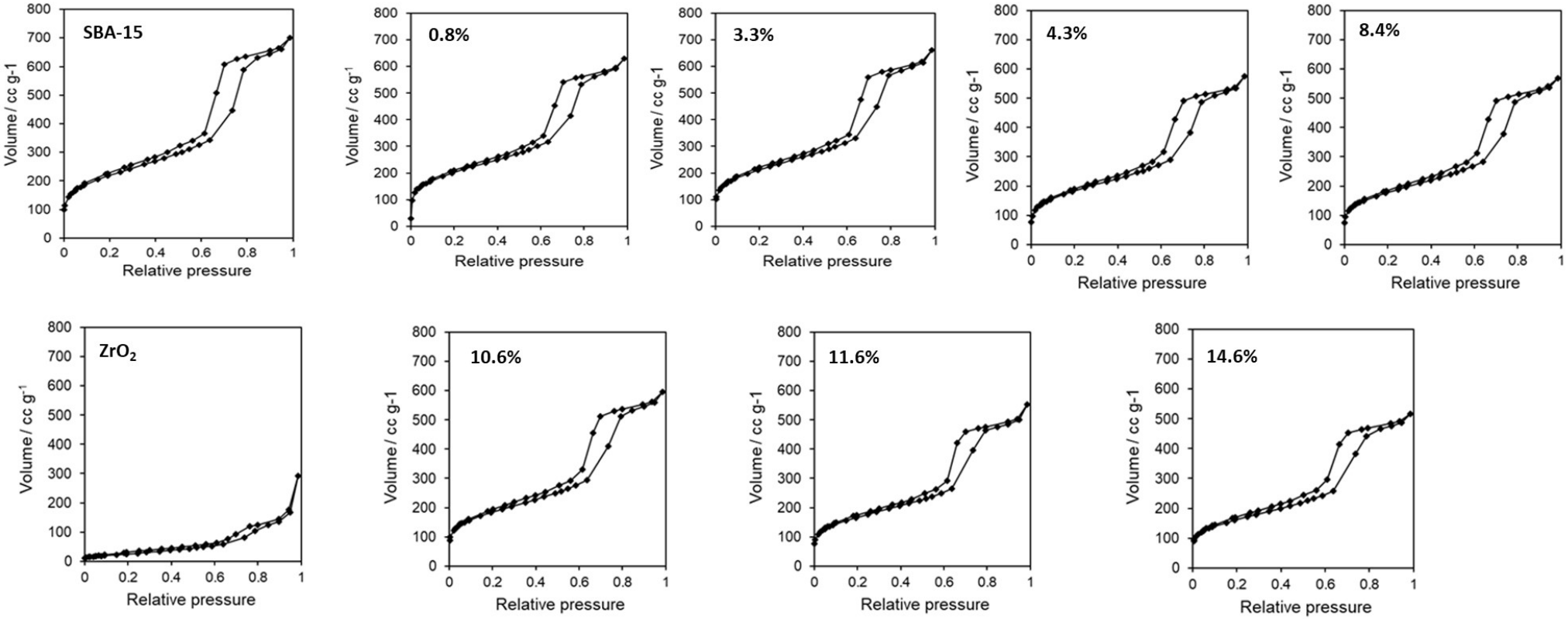

Figure S3. N_2 adsorption-desorption isotherms of ZrO_2/SBA-15.

Transmission electron microscopy

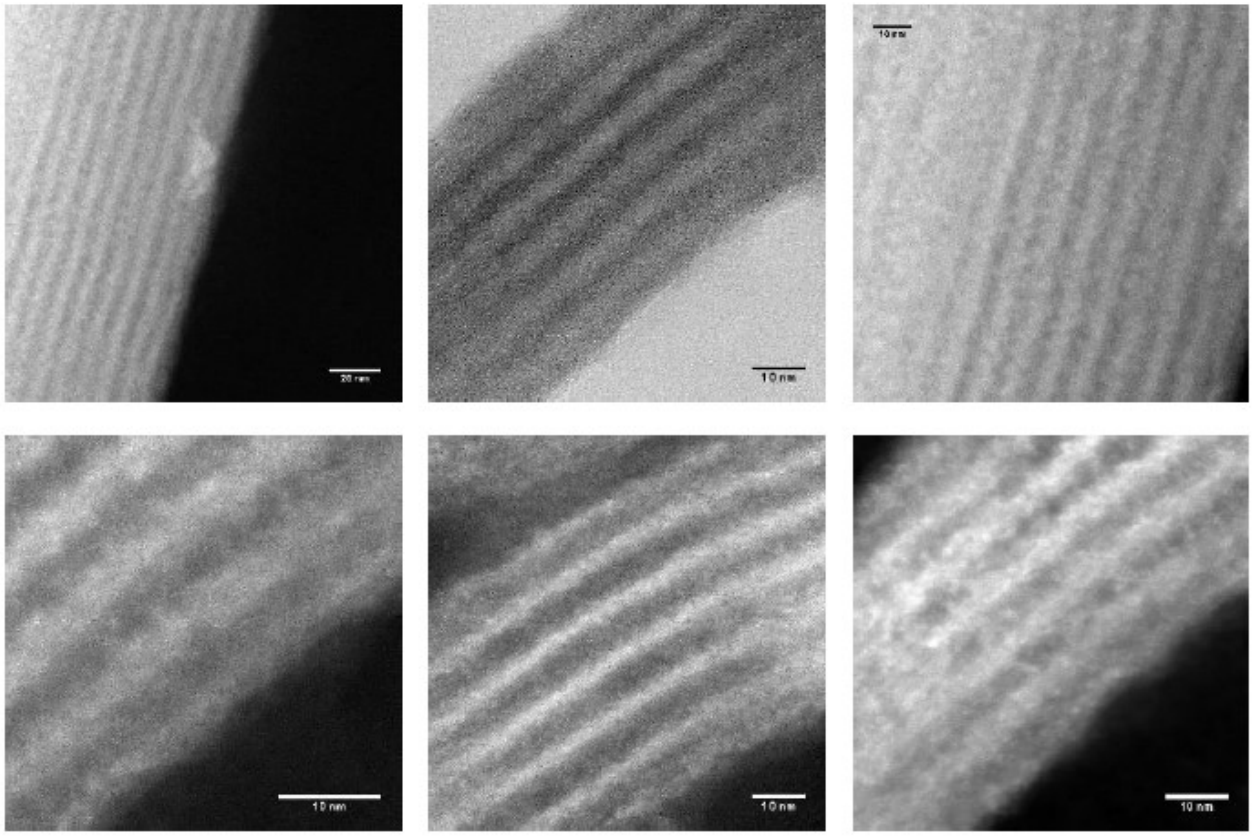

Figure S4. TEM micrographs of 11.6 wt% Zr/SBA-15 illustrating 2D parallel pore channels.

X-ray Powder Diffraction (XRD)

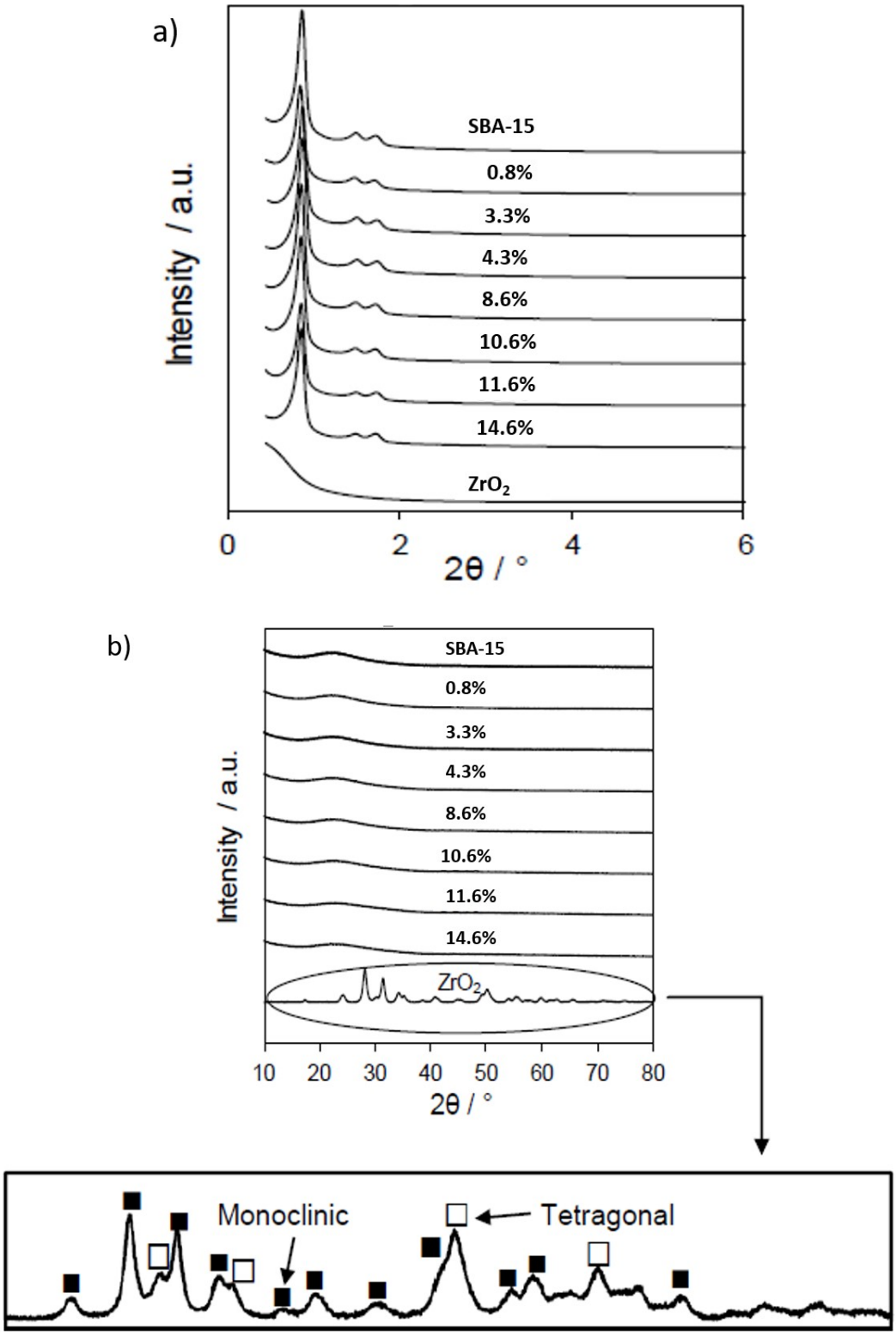

Figure S5. Powder X-ray diffractograms of ZrO_2/SBA-15 as a function of Zr loading (wt%): (a) low angle patterns; and (b) wide angle patterns including parent SBA-15 support and bulk ZrO_2.

Acidity measurement

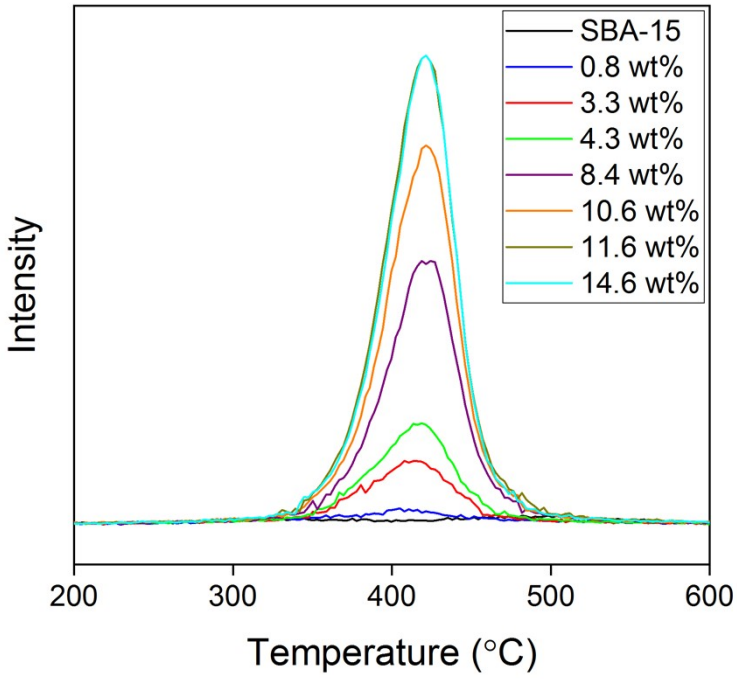

Figure S6. Propylamine TPD showing 41 amu mass spectrometer signal for reactively formed propene from ZrO_2/SBA-15 as a function of Zr loading.

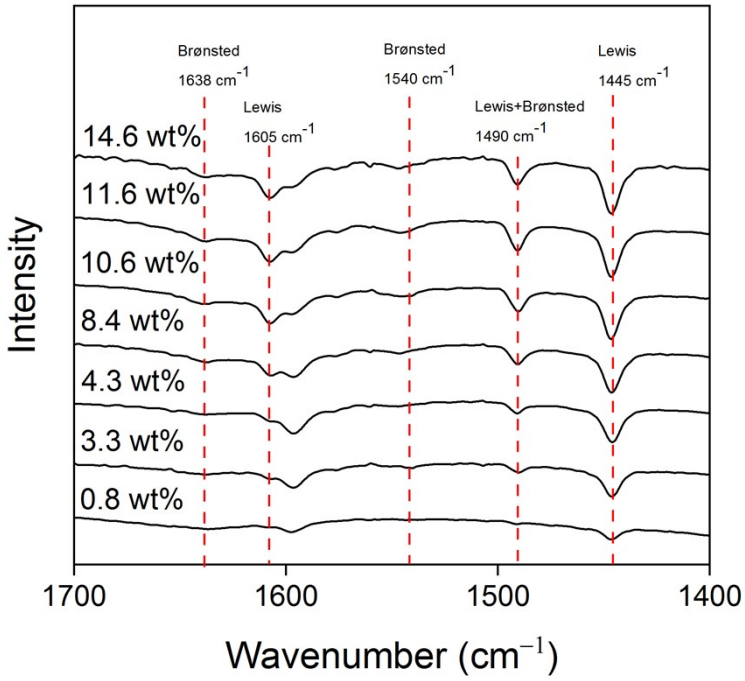

Figure S7. DRIFTS spectra of absorbed pyridine on pure ZrO_2 and ZrO_2/SBA-15.

Batch reactor studies

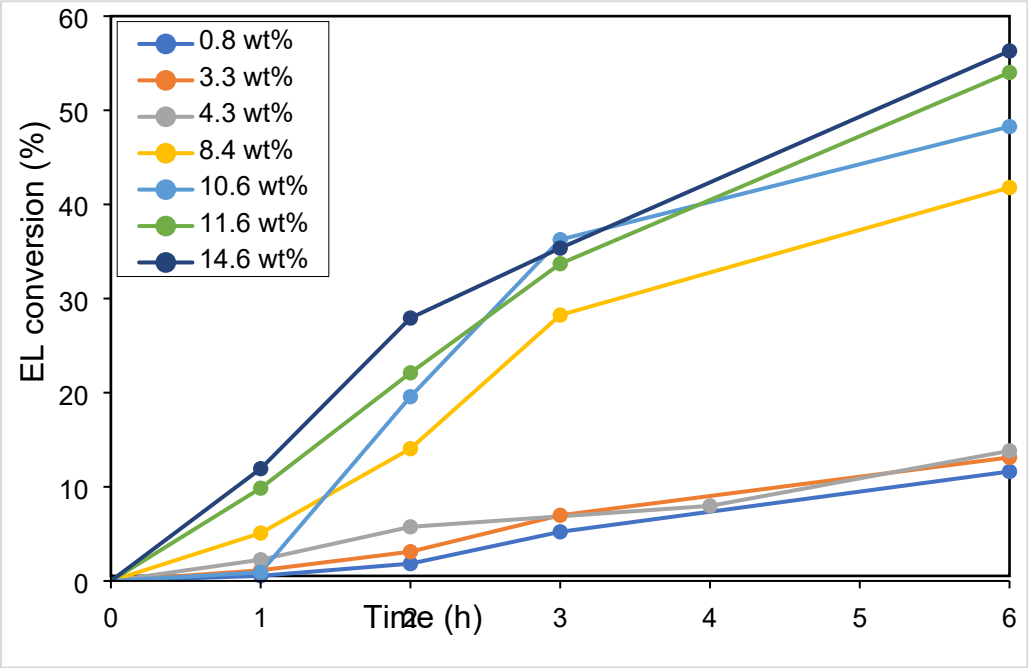

Figure S8. EL conversion as a function of reaction time over ZrO_2/SBA-15. Reaction conditions: 5 mmol EL:250 mmol IPA, 100 mg catalyst, 170 °C, 5 bar N_2.

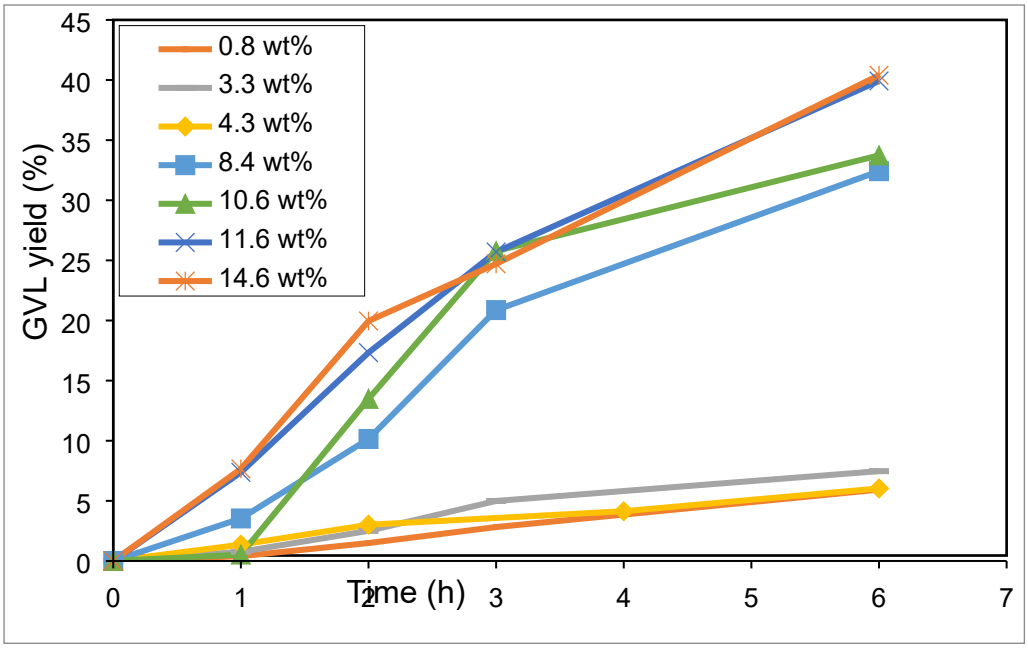

Figure S9. GVL yield as a function of EL reaction time over ZrO_2/SBA-15. Reaction conditions: 5 mmol EL:250 mmol IPA, 100 mg catalyst, 170 °C, 5 bar N_2.

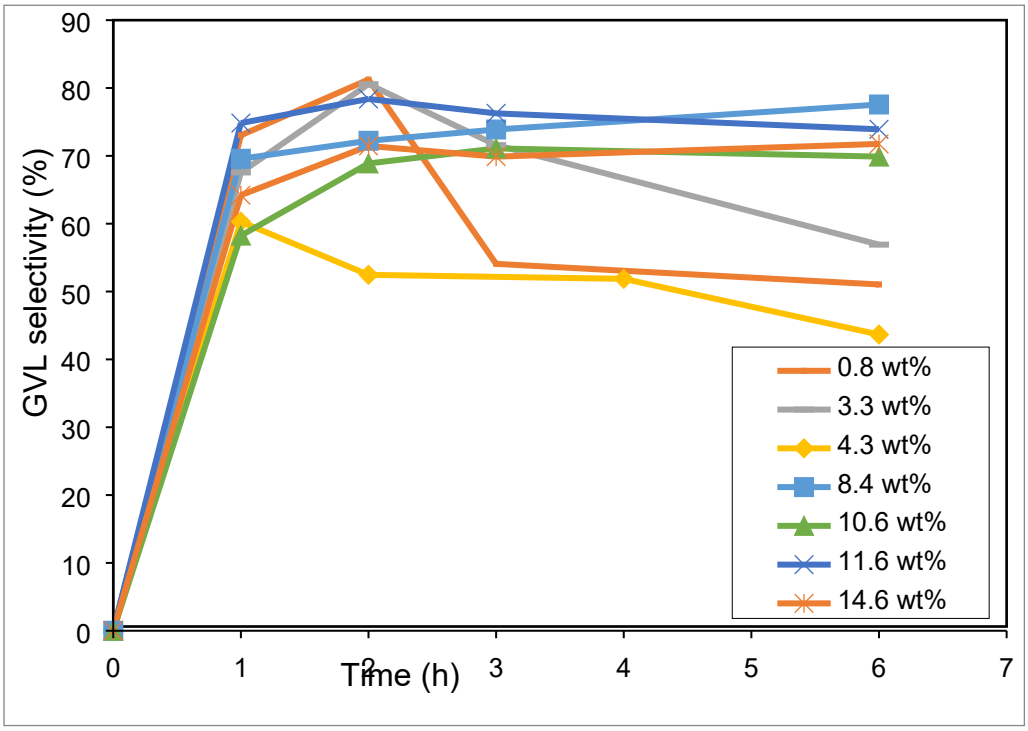

Figure S10. GVL selectivity as a function of EL reaction time over ZrO_2/SBA-15. Reaction conditions: 5 mmol EL:250 mmol IPA, 100 mg catalyst, 170 °C, 5 bar N_2.

Identification of Propyl Levulinate

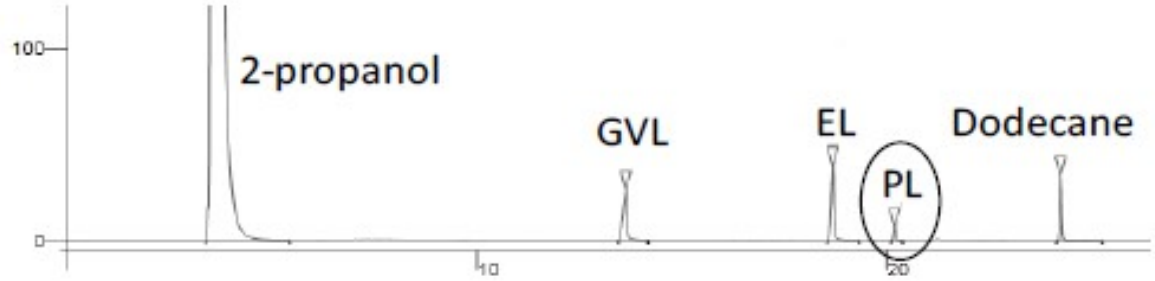

Figure S11. Gas chromatogram of reaction mixture for EL conversion to GVL over 11.6 wt% Zr/SBA-15 at 170 °C evidencing reactively-formed propyl levulinate (PL) intermediate.

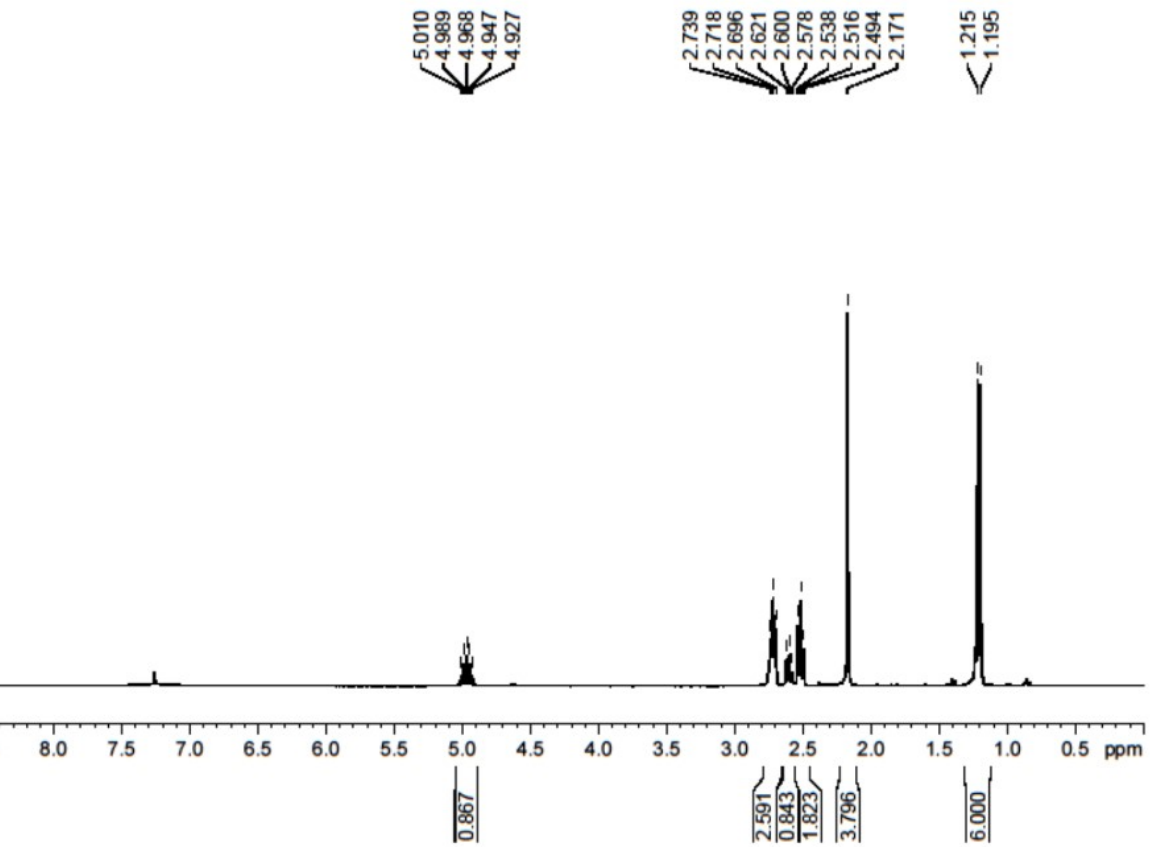

Figure S12. ^{1}H NMR in $CDCl_3$ of isopropyl levulinate (PL) formed during EL conversion to GVL over 11.6 wt% Zr/SBA-15 at 170 °C. NMR spectra were recorded on a Bruker Avance3 spectrometer operating at 300.14 MHz for ^{1}H and referenced to residual solvent peaks.

Batch reactor studies at 150 °C

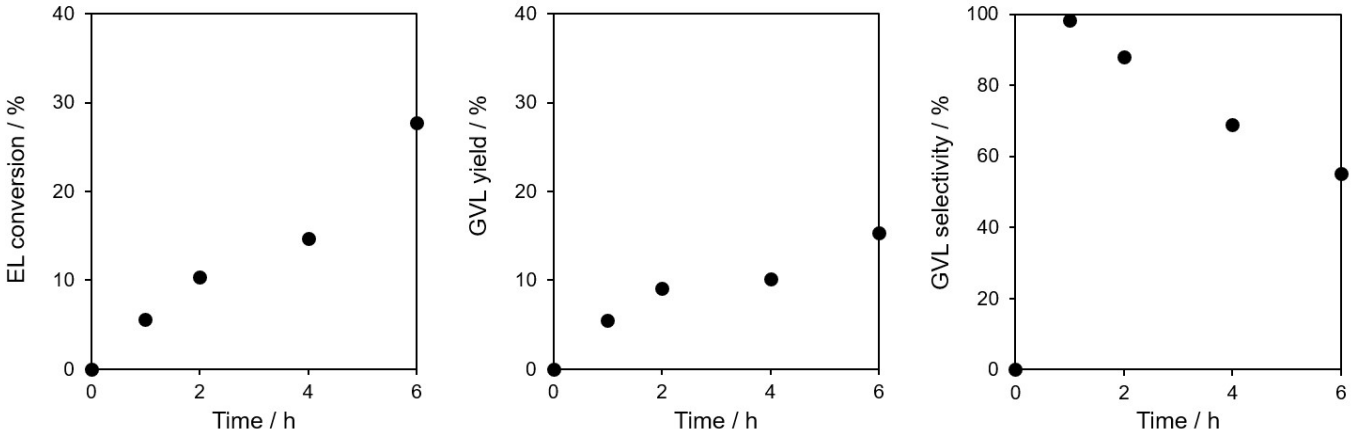

Figure S13. EL conversion, GVL yield and selectivity as a function of time for 11.6 wt% Zr/SBA-15. Reaction conditions: 5 mmol EL:250 mmol IPA, 100 mg catalyst, 150 °C, 5 bar N_2.

Flow reactor studies

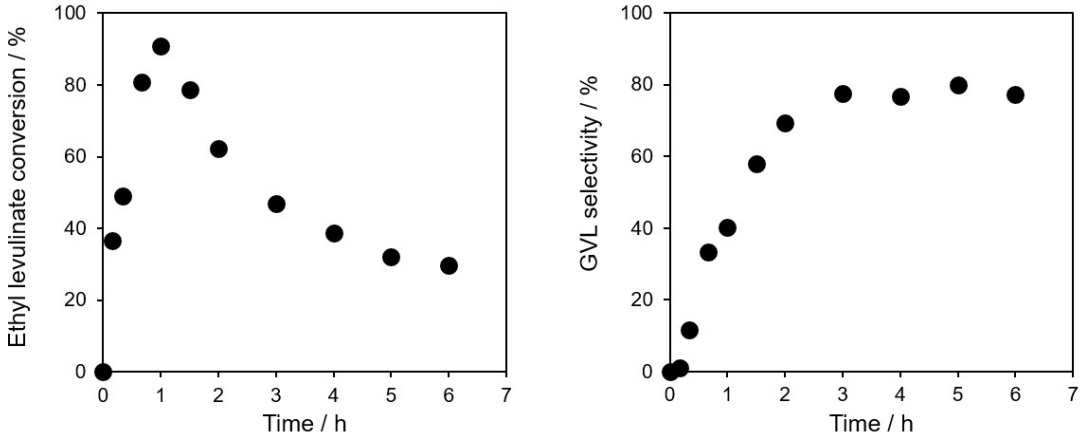

Figure S14. EL conversion and GVL selectivity as a function of reaction time for 11.6 wt% Zr/SBA-15. Reaction conditions: 0.25 M EL in IPA liquid feedstream, 100 mg catalyst, 150 °C, 0.1 ml/min, 27.5 min residence time.

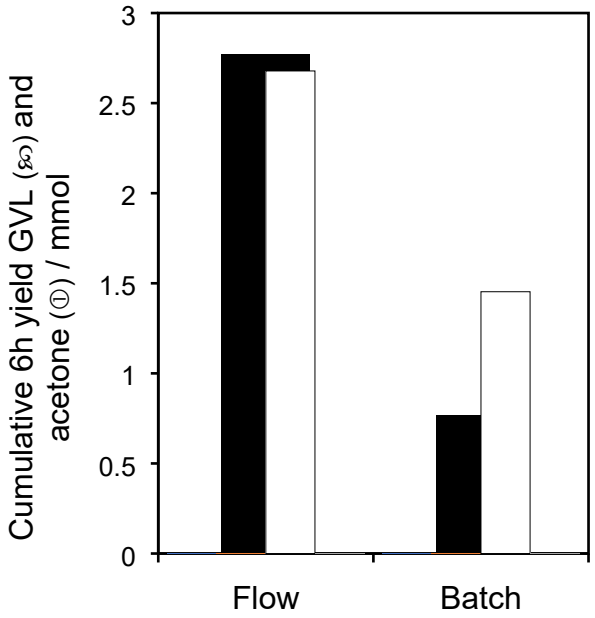

Figure S15. Comparison of cumulative GVL and acetone yields for 11.6 wt% Zr/SBA-15 in continuous flow versus batch operation. Reaction conditions: (**Flow)** 0.25 M EL in IPA liquid feedstream, 100 mg catalyst, 150 °C, 0.1 ml/min, 27.5 min residence time, over 6 h; (**Batch**) 5 mmol EL:250 mmol IPA, 100 mg catalyst, 150 °C, 5 bar, 6 h reaction.

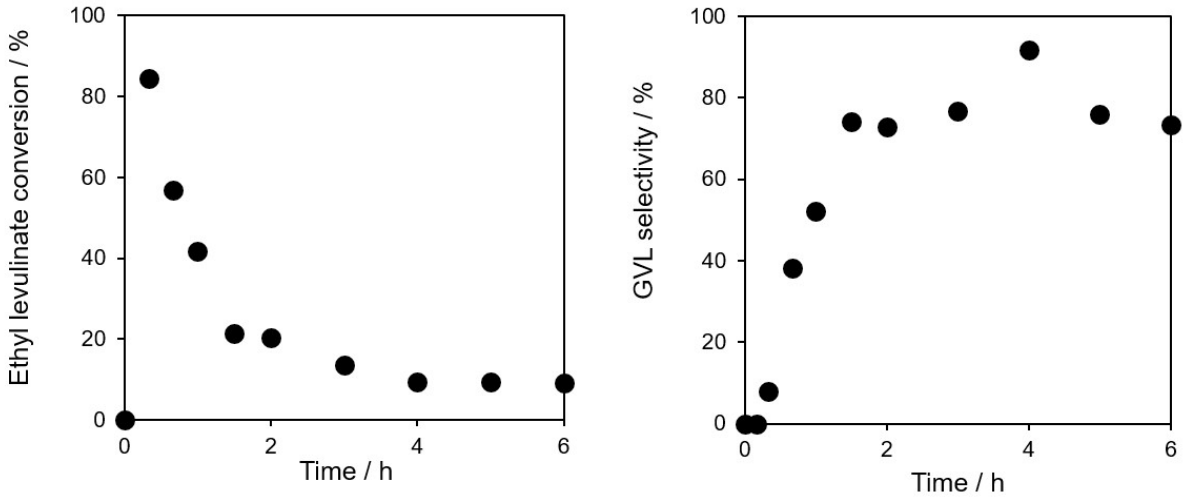

Figure S16. EL conversion and GVL selectivity as a function of reaction time for 11.6 wt% Zr/SBA-15. Reaction conditions: 0.25 M EL in IPA liquid feedstream, 100 mg catalyst, 150 °C, 0.18 ml/min, 17.5 min residence time.

Optimisation studies

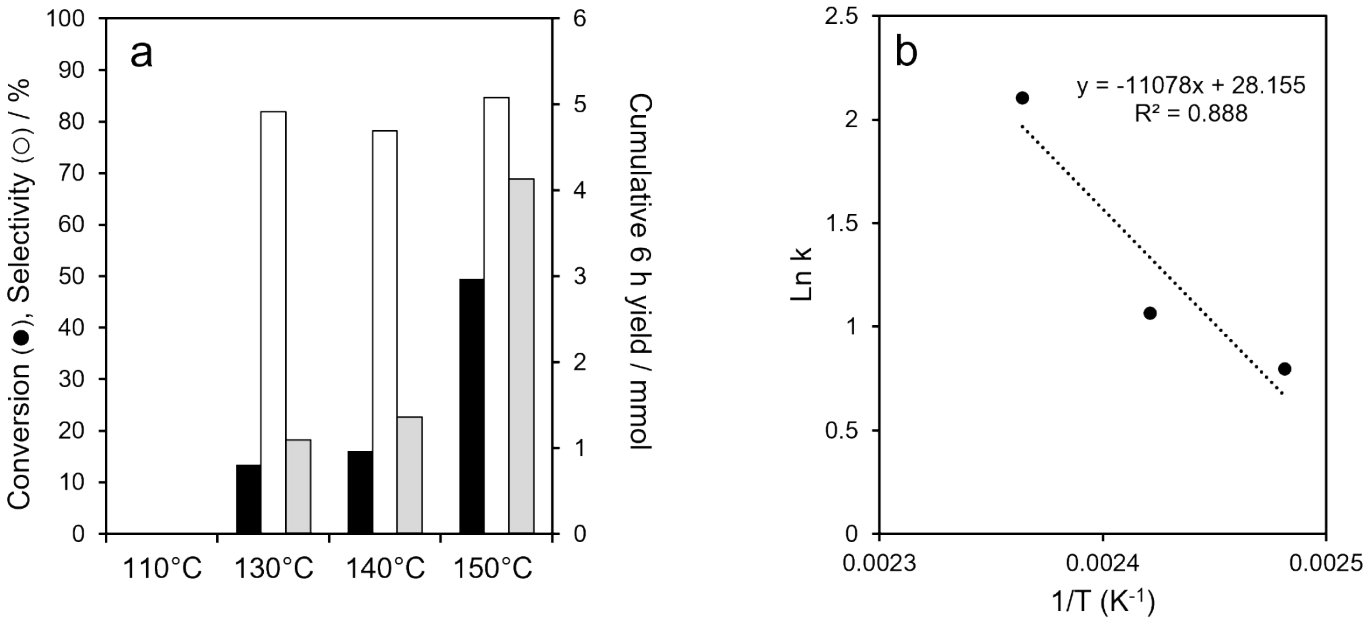

Figure S17. (a) Influence of reaction temperature on EL transformation to GVL in continuous flow over 12 wt% ZrO_2/SBA-15. EL conversion and GVL selectivity are average over 6 h reaction. Reaction conditions: 100 mg catalyst, 27.5 min residence time, over 6 h, liquid stream of ethyl levuliate (0.25 M) and isopropyl alcohol. (b) Arrhenius plot of rate of EL conversion versus reaction temperature between 130-150 °C. Note these experiment were performed with a new catalyst batch which delivered slightly higher GVL selectivity.

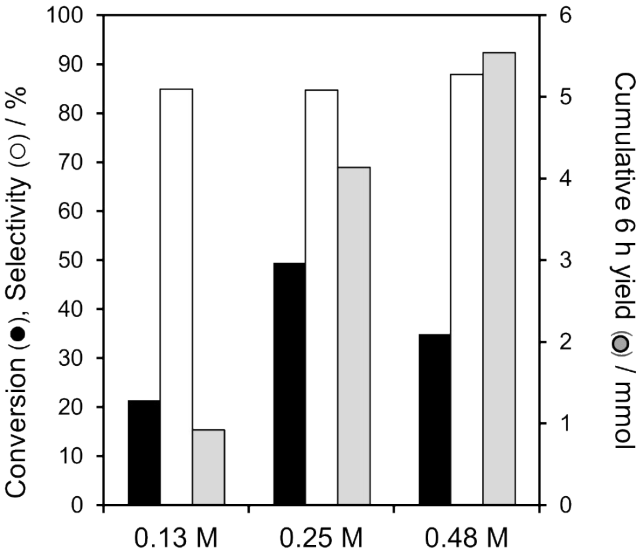

Figure S18. Influence of EL concentration on transformation to GVL under continuous flow over 12 wt% ZrO_2/SBA-15. EL conversion and GVL selectivity are average over 6 h reaction. Reaction conditions: 100 mg catalyst, 27.5 min residence time, liquid stream of ethyl levulinate and isopropyl alcohol (0.13-0.48 M), 150°C. . Note these experiment were performed with a new catalyst batch which delivered slightly higher GVL selectivity.

Spiking studies in continuous flow

Three reaction conditions were performed in the spiking studies, i) pre-treatment of the catalyst bed with acetone or GVL for 30 minutes at 150 °C prior to flowing reaction mixture over catalyst bed ii) stoichiometric (1:1) and iii) excess (5:1) poisoning of reaction mixture relative to EL.

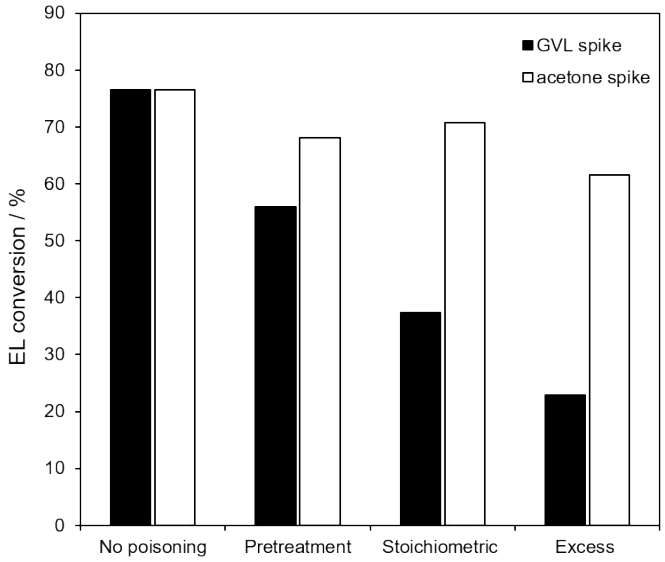

Figure S19. EL conversion averaged over 2 h reaction for 11.6 wt% Zr/SBA-15. Reaction conditions: (**Flow**) 0.25 M EL in IPA liquid feedstream, 100 mg catalyst, 150 °C, 0.1 ml/min, 27.5 min residence time, over 2 h. Pretreatment: Stream of GVL or acetone (0.1 ml/min) was passed over the catalyst bed for 30 minutes prior to starting reaction. Stoichiometric: GVL or acetone (1:1) was introduced in standard reaction mixture. Excess: GVL or acetone (5:1) was introduced in standard reaction mixture.

Spent Catalyst Characterisation

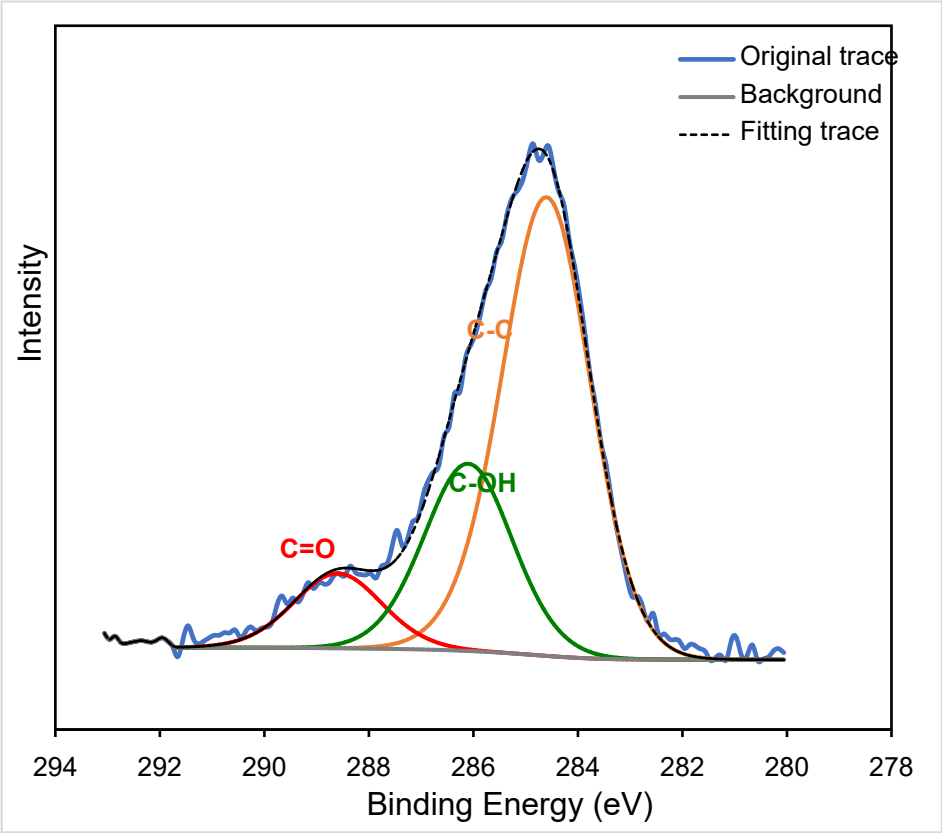

Figure S20. C 1s XP spectra of post-reaction 11.6 wt% Zr/SBA-15 following 2 h EL conversion under continuous flow. Reaction conditions: Flow, 0.25 M EL in IPA liquid feedstream, (5:1) GVL spiking, 100 mg catalyst, 150 °C, 0.1 ml/min, 27.5 min residence time, over 2 h.

Table S2. Surface composition of as-prepared and post-reaction 11.6 wt% Zr/SBA-15.

Catalyst	Surface composition							
	wt%				at%			
	O	C	Zr	Si	O	C	Zr	Si
As-prepared	51.3	3.2	12.1	33.4	64.2	5.9	3.0	26.9
Post-reaction	43.6	10.5	13	32.9	55.49	17.8	2.9	23.81

Recyclability test

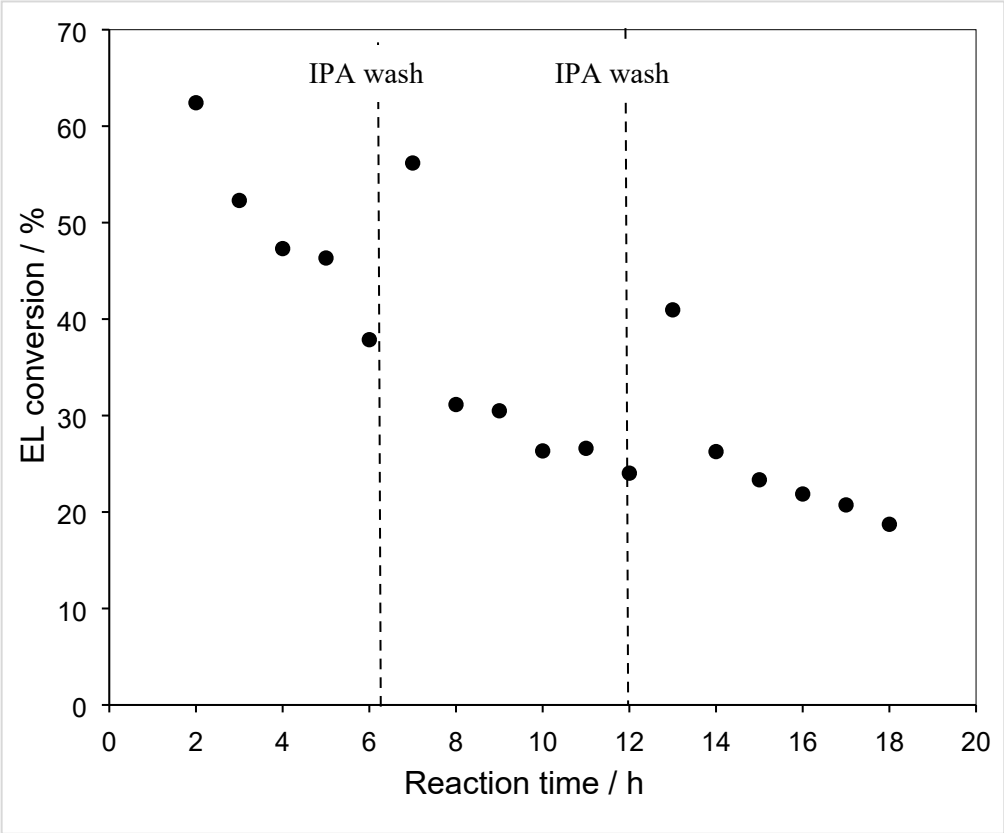

Figure S21. EL conversion as a function of time for three consecutive 6 h reactions in continuous flow over 12 wt% ZrO_2/SBA-15; 2-isopropanol washes at indicated time intervals to attempt in-situ catalyst regeneration.