Electronic Supporting Information

ZrO_2-SBA-15 catalysts for the one-pot cascade synthesis of GVL from furfural

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Characterisation

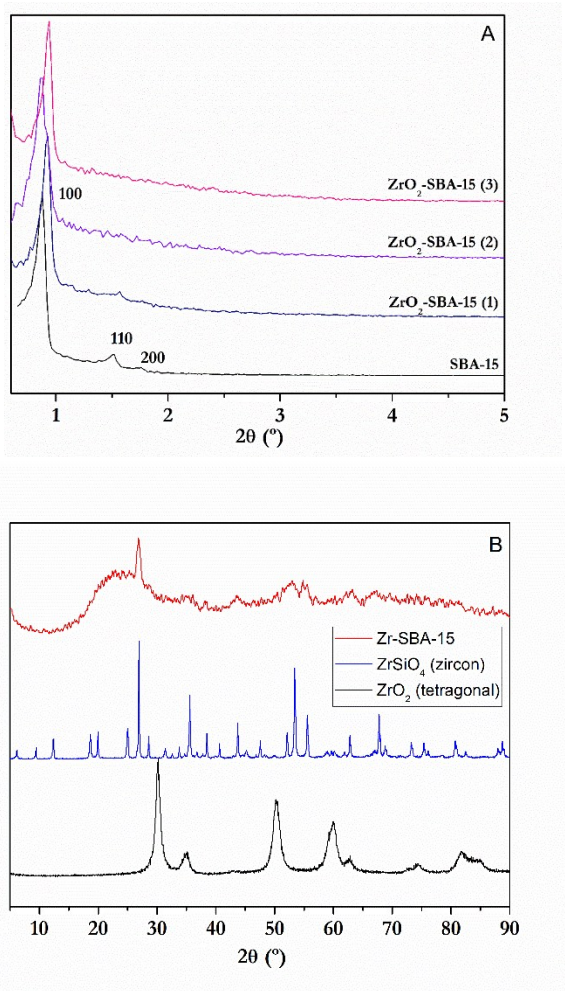


Figure ESI-1. (A) Low-angle, and (B) wide angle powder XRD patterns of ZrO_2-SBA-15, and t-ZrO_2, zircon, and Zr-SBA-15 reference materials.

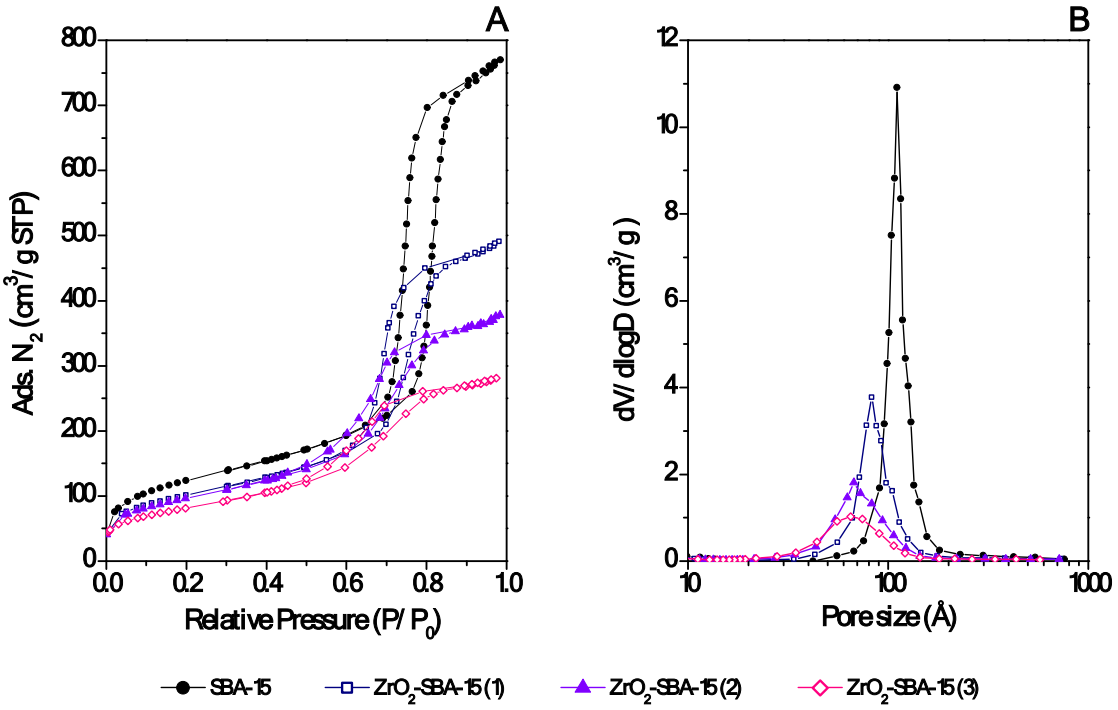


Figure ESI-2. (A) N_2 adsorption-desorption isotherms, and (B) corresponding BJH- pore size distributions for ZrO_2-SBA-15 and parent SBA-15 materials.

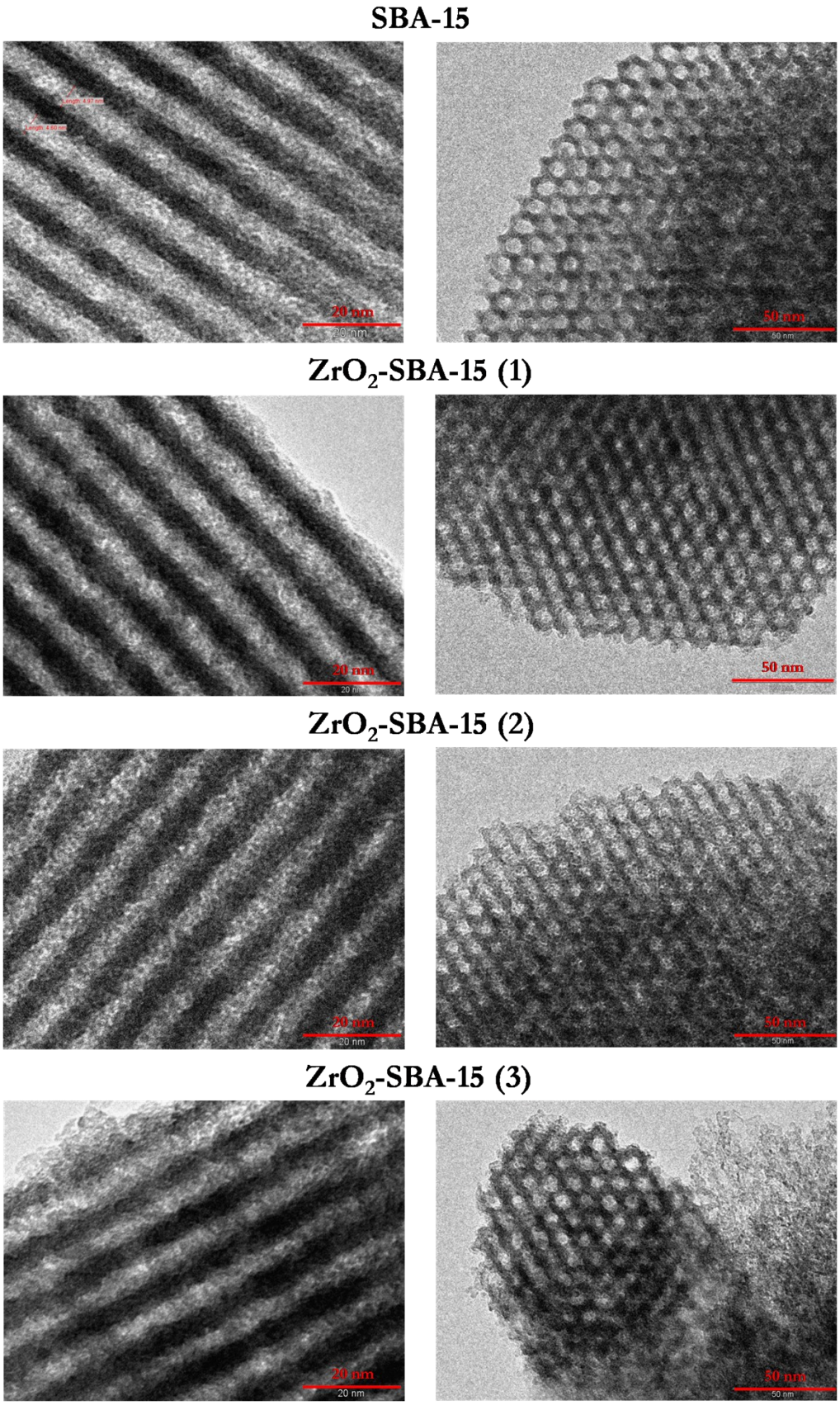


Figure ESI-3. TEM images of ZrO_2-SBA-15 and parent SBA-15 materials.

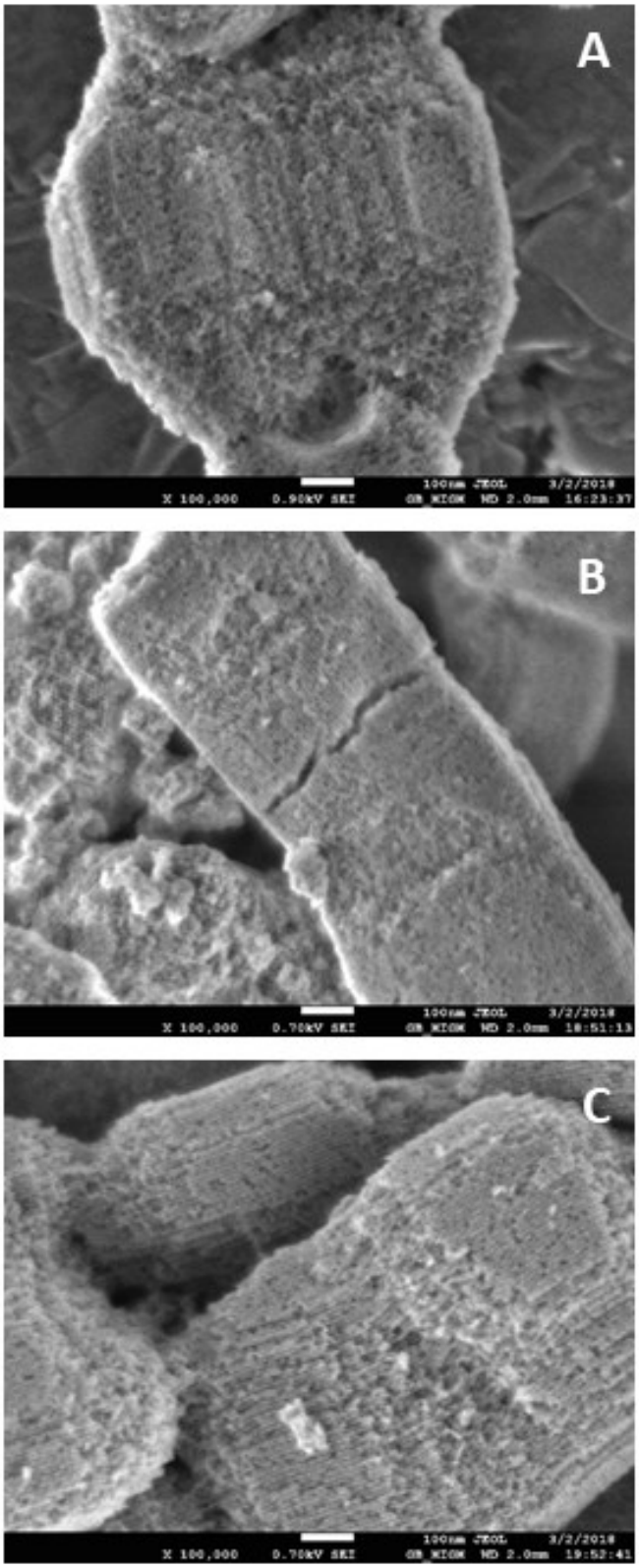


Figure ESI-4. SEM images of (A) ZrO_2-SBA-15(1), (B) ZrO_2-SBA-15(2, and (C) ZrO_2-SBA-15(3) materials.

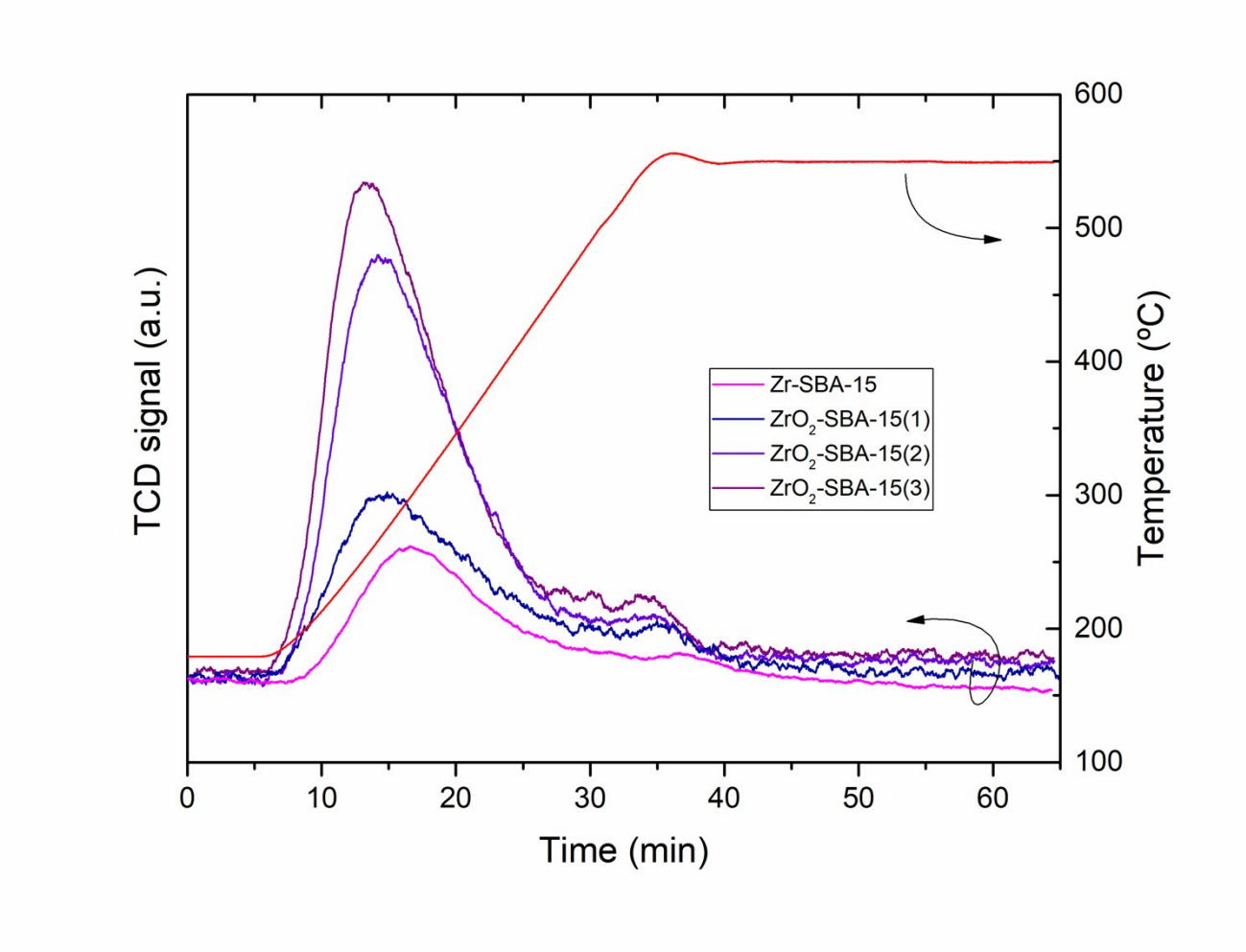


Figure ESI-5. NH_3 TPD profiles for Zr- and ZrO_2-SBA-15 materials.

Table ESI-1. Results from NH3-TPD analysis performed on Zr- and ZrO_2-SBA-15 materials.

Sample	Acid loading ($mmoles_{eq}H^+/g$)	T_{max}[a] (°C)
Zr-SBA-15	0.205	285
ZrO_2-SBA-15(1)	0.227	269
ZrO_2-SBA-15(2)	0.320	264
ZrO_2-SBA-15(3)	0.357	251

[a]Maximum desorption temperature in NH_3 TPD

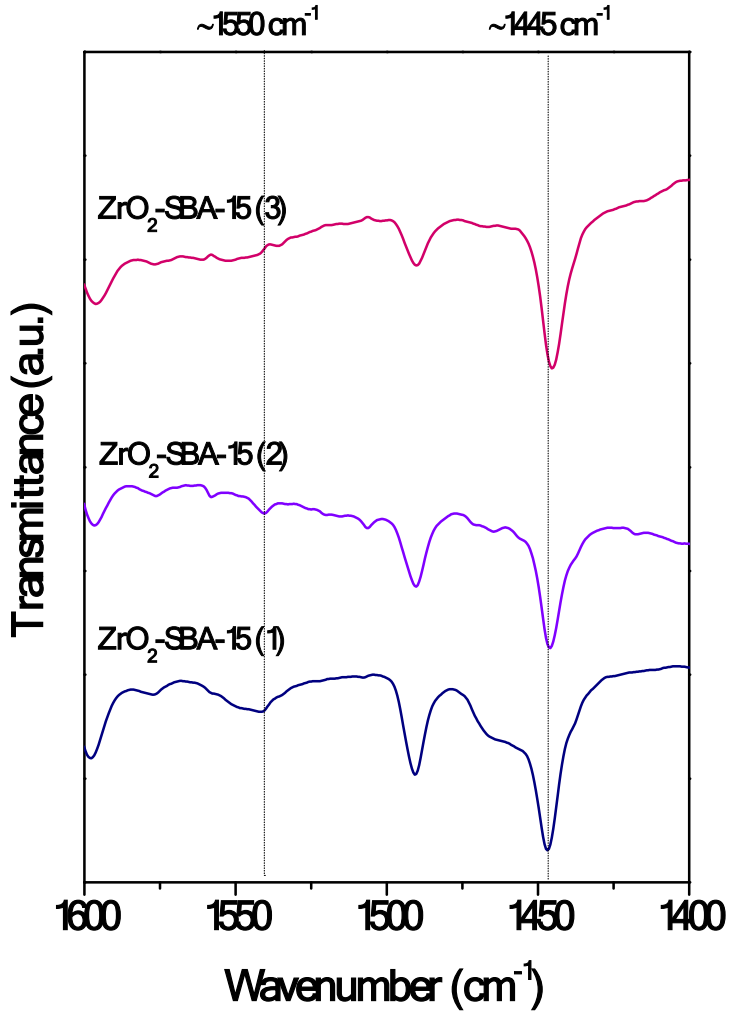


Figure ESI-6. DRIFT spectra of adsorbed pyridine on ZrO_2-coated SBA-15.

Table ESI-2. Lewis:Brønsted acid ratio for ZrO_2-coated SBA-15 from pyridine adsorption and subsequent in vacuo DRIFTS analysis.

Sample	B (1550 cm^{-1})	L (1445 cm^{-1})	B+L	B:L
ZrO_2-SBA-15 (1)	0.067	0.160	0.227	0.42
ZrO_2-SBA-15 (2)	0.023	0.297	0.320	0.08
ZrO_2-SBA-15 (3)	0.004	0.371	0.375	0.01

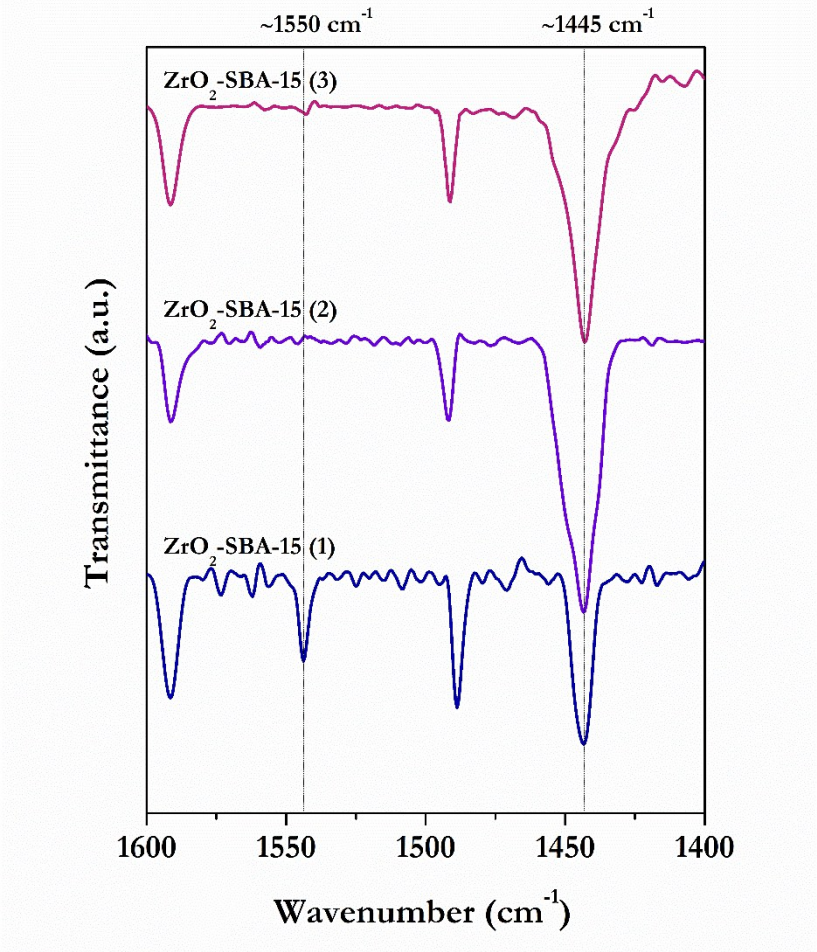


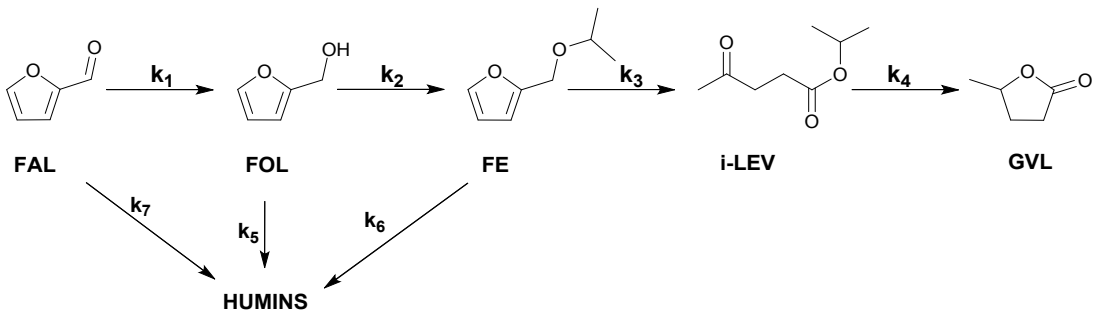
Figure ESI-7. ATR-IR spectra of adsorbed pyridine on ZrO_2-coated SBA-15 in i-PrOH.

Table ESI-3. Lewis:Brønsted acid ratio for ZrO_2-coated SBA-15 from pyridine adsorption and ATR-IR analysis in i-PrOH.

Sample	B ($1550\ cm^{-1}$)	L ($1445\ cm^{-1}$)	B+L	B:L
ZrO_2-SBA-15 (1)	0.0077	0.0256	0.0333	0.3
ZrO_2-SBA-15 (2)	0	0.0730	0.0730	0
ZrO_2-SBA-15 (3)	0	0.0674	0.0674	0

Table ESI-4. Basicity loadings calculated for ZrO_2-coated SBA-15 from CO_2-TPD profiles.

Sample	Basicity loading ($\mu mol \cdot g^{-1}$)
ZrO_2-SBA-15 (1)	2.4
ZrO_2-SBA-15 (2)	4.9
ZrO_2-SBA-15 (3)	11.1



Scheme ESI-1 Proposed reaction network for the transformation of furfural in alcohol media over ZrO_2-grafted SBA-15. FAL, furfural; FOL, furfuryl alcohol; FE, isopropyl furfuryl ether; i-LEV, isopropyl levulinate; GVL, γ-valerolactone; HUMINS, degradation product

Table ESI-5 First-order pseudo-homogeneous apparent kinetic constants (k_i) of the modelled overall reaction of furfural in 2-propanol over ZrO_2-SBA-15 catalysts, at 130, 150 and 170 °C. See Scheme ESI-1 for the reaction steps.

Catalyst		**ZrO_2-SBA-15 (1)**			**ZrO_2-SBA-15 (2)**			**ZrO_2-SBA-15 (3)**		
T / °C		**130**	**150**	**170**	**130**	**150**	**170**	**130**	**150**	**170**
k_i / h^{-1}	**1**	0.881	1.472	1.986	0.913	1.523	2.126	0.949	1.588	2.510
	2	0.603	1.857	4.622	0.197	0.791	4.548	0.257	1.099	1.193
	3	0.051	0.086	0.219	0.047	0.055	0.192	0.044	0.052	0.064
	4	0.068	0.150	0.268	0.145	0.325	0.421	0.158	0.381	0.793
	5	0.126	0.287	0.703	0.010	0.042	0.412	0.055	0.195	0.125
	6	0.003	0.015	0.150	0.004	0.025	0.107	0.005	0.011	0.025
	7	0.002	0.007	0.019	0.003	0.024	0.095	0.003	0.009	0.021

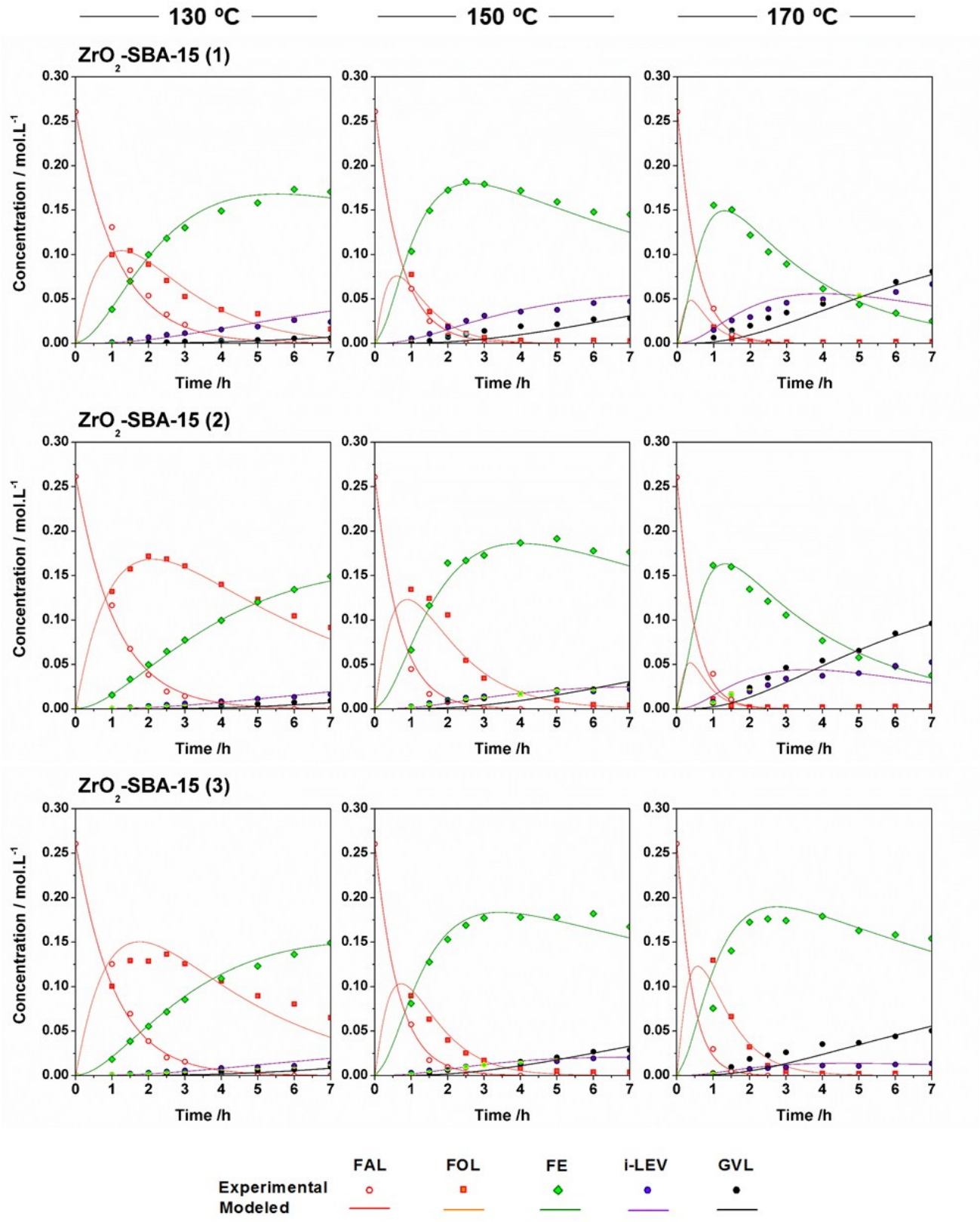


Figure ESI-8. Experimental (symbol) and modelled (solid lines) products concentration for furfural transformation to GVL in 2-propanol over ZrO_2-SBA-15 catalysts. Reaction conditions: furfural:2-propanol=1:50 (by mols); furfural:catalyst=2.5:1 (by weight).

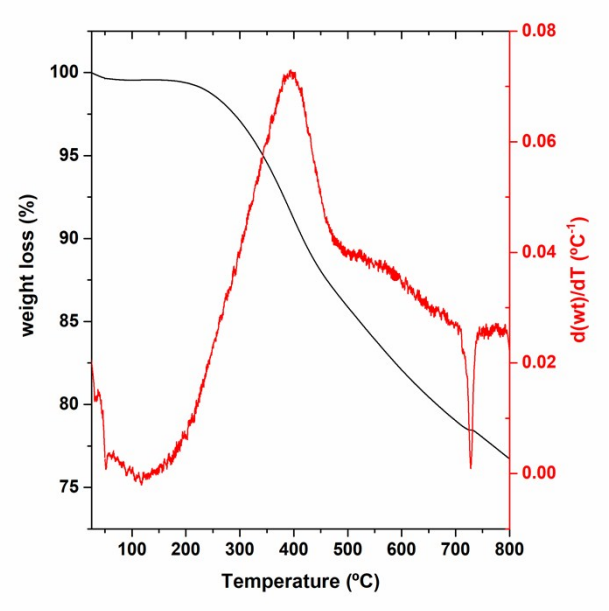


Fig ESI-9. TG analysis curves recorded for sample ZrO2-SBA-15 used during 3 consecutive reutilization cycles in the cascade transformation of furfural to GVL. Reaction conditions: 170 °C; 7 h; furfural:2-propanol=1:50 (by mols); furfural:catalyst=2.5:1 (by mass).