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Electronic Supplementary Information

One-pot cascade transformation of xylose into γ-valerolactone (GVL) over bifunctional Brønsted-Lewis Zr-Al-Beta zeolite

1-Synthesis of materials

Commercial Al-Beta zeolite (2 wt% Al) was purchased from Zeolyst international. Partial dealumination was carried out by treatment in HNO_3 solution in the concentration range 0.1-10 M (room temperature, 1h, 20 $mL\cdot g^{-1}$). Total dealumination was accomplished using more severe conditions (100 °C, 20 h, 20 $mL.g^{-1}$). After filtration and washing with deionized water, the resulting materials were dried overnight (110 °C) before proceeding to Zr incorporation.

Zirconium incorporation was accomplished by impregnation in water suspending the pre-treated Al-Beta zeolite in deionized water followed by the addition of the appropriate amount of zirconium(IV) oxychloride octahydrate (Sigma Aldrich, 99 % w/w). The resultant slurry was heated at 110 °C to distil the water off, dried overnight and calcined in air at 200 °C for 6 h (3 $°C\cdot min^{-1}$ heating ramp) and then at 550 °C for another 6 h at the same heating rate.

Four Zr-Al-Beta zeolites were synthesised and named Zr-Al-Beta (x), x denoting their Zr wt. content. The Al free material was denoted Zr-Beta (x).

2-Characterization of materials

Zirconium and aluminium content was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with a Varian Vista AX apparatus. Textural properties of the catalyst were evaluated through nitrogen adsorption-desorption isotherms recorded at 77 K, using a Micromeritics Tristar 3000 system. Surface area values were calculated from isotherm data using the B.E.T. method and total pore volume was taken at $P/P_0 = 0.975$ single points. X-ray powder diffraction (XRD) patterns were collected in a Philips X-pert diffractometer using the Cu Kα line in the 2θ angle range from 5° to 60° (step size of 0.04°). Structural characterization was completed by transmission electron microscopy (TEM) on a Philips Tecnai-20 electronic microscope operating at 200 kV. Scanning electron microscopy (SEM) images and elemental mapping for Zr, Al and Si were obtained on a Philips XL30 ESEM electronic microscope operating at 3.5 kV.

Acidity was measured by temperature programmed desorption of NH_3 in a Micromeritics 2910 (TPD/TPR) equipment fitted with a TCD detector. Fourier Transform Infra-red (FTIR) spectra were collected in a Varian Excalibur Series 3100 apparatus (400-4000 cm^{-1}, 4 cm^{-1}, resolution, 64 scans). For the ex-situ pyridine adsorption, samples were exposed to pyridine vapour overnight. Diffuse Reflectance Infra-red Fourier Transform (DRIFT) spectra were recorded using a Nicolet Avatar 370 MCT equipment.

X-ray Photoelectron Spectroscopy (XPS) measurements were obtained using a Specs Phoibos 150 9MCD photoelectron spectrometer.

3-Catalytic tests

Catalytic runs were performed under the following reaction conditions: catalyst 0.01 g·mL^{-1}, substrate: 2-propanol (Scharlab 98 % w/w) molar ratio 1:50, substrate loading: 4 g xylose (Sigma Aldrich), 2.5 g furfural (Sigma Aldrich 99% w/w). Decane (Acros organics >99 % w/w) was used as internal standard (0.01 g·mL^{-1}).

The experiments were carried out in a stainless steel stirred autoclave (200 mL) with temperature control and pressure gauge. The reactants and catalyst, together with the internal standard, were placed within the reaction vessel to a total volume of 100 mL. After sealing the reactor, stirring was fixed at 1000 rpm and a heating rate was established to reach the desired temperature within 1 h. This point is taken as the beginning of the reaction, ignoring the time needed for heating up. Samples were taken periodically and the solution filtered into a vial.

Samples were analysed by GC-FID (Varian 3900) using a capillary column (Agilent CP-WAX 52 CB, 30 m-long, 0.25 mm-i.d., 0.25 µm thickness). Conversion of xylose was evaluated by HPLC analysis with a refractive index detector (Varian 356-LC), using a Hi-PLEX H+ column (300 mm-long, 7.7 mm-i.d., 8 µm particle size). Conversion was calculated as (mol substrate converted/mol initial substrate)x100 and products yield as (mol produced/mol initial substrate)x100.

4-Tables

Table S1. Al and Zr content, textural properties and acidity of the parent Al-Beta and modified Zr-Al-Beta zeolites.

Catalyst	Composition[a]					Surface area[b] (m^2g^{-1})	Total pore volume[c] (cm^3g^{-1})	Acid site loading[d] (mmol H^+g^{-1})
	% Al	% Zr	Si/Al	Si/Zr	Al/Zr			
Al-Beta	2.0	0.0	22	∞	-	623	0.36	0.413
Zr-Al-Beta (2.8)	1.2	2.8	35	51	1.46	571	0.24	0.351
Zr-Al-Beta (3.7)	1.0	3.7	43	38	0.88	571	0.25	0.306
Zr-Al-Beta (4.0)	0.7	4.0	62	35	0.57	560	0.26	0.233
Zr-Al-Beta (5.7)	0.4	5.7	111	24	0.22	539	0.24	0.215
Zr- Beta (6.4)	0.02	6.4	∞	22	0.00	638	0.28	0.083

[a] % Al, % Zr (w/w); Si/Al, Si/Zr, Al/Zr (atomic ratio) measured by ICP-OES. [b] Surface area calculated by the B.E.T. method. [c] Total pore volume recorded at $P/P_0 = 0.975$. [d] Acid site loading analysed by NH_3-TPD.

Table S2. Brønsted to Lewis acid sites ratio determined by FTIR using pyridine as molecular probe and total Brønsted and Lewis acid site loading.

Catalyst	Brønsted/ Lewis acid sites ratio	Acid site loading (mmol H^+g^{-1})	
		Brønsted	Lewis
Al-Beta	0.56	0.149	0.264
Zr-Al-Beta (2.8)	0.52	0.120	0.231
Zr-Al-Beta (3.7)	0.39	0.087	0.220
Zr-Al-Beta (4.0)	0.31	0.055	0.178
Zr-Al-Beta (5.7)	0.17	0.031	0.185
Zr- Beta (6.4)	0.04	0.003	0.080

5-Figures

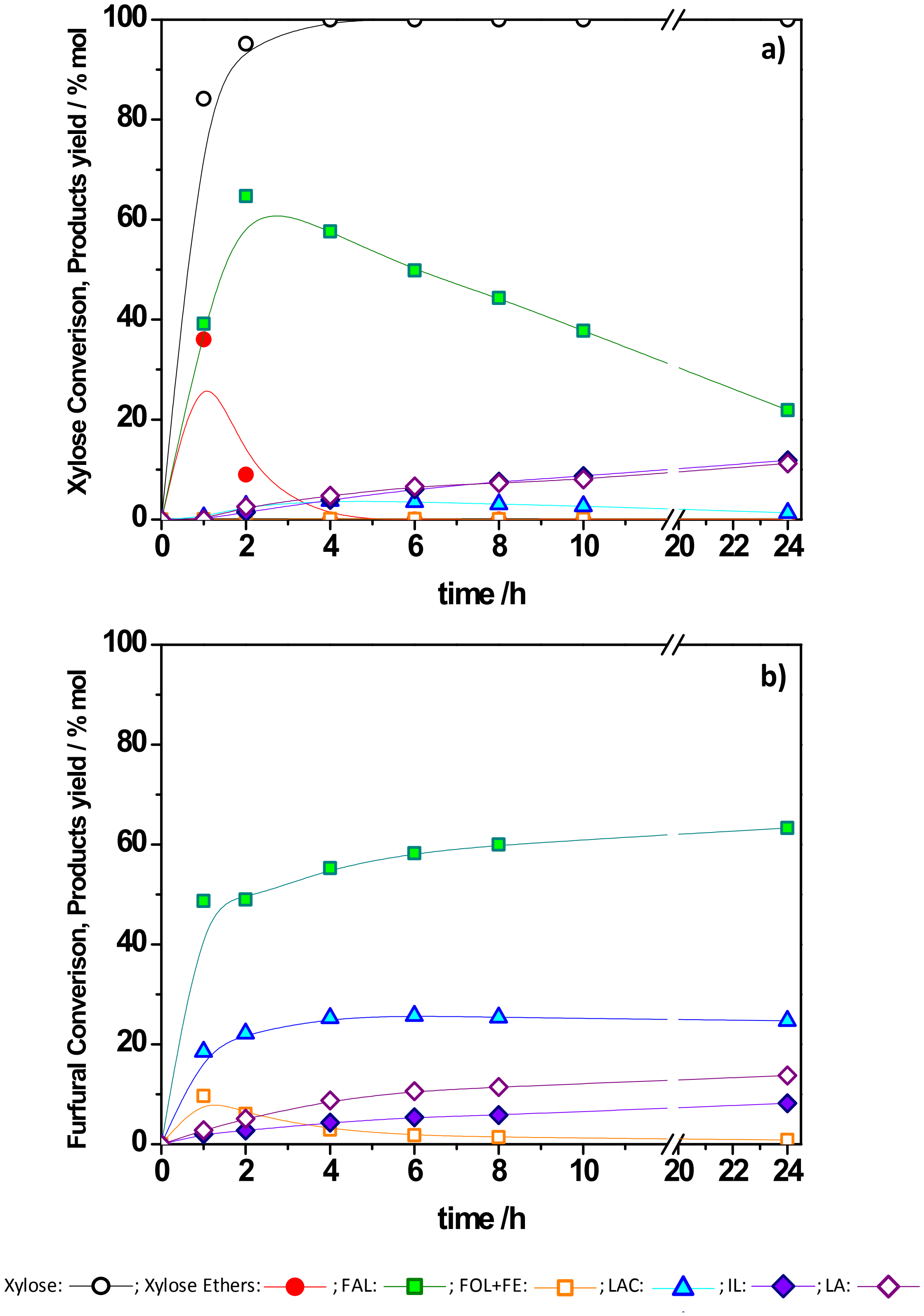


Figure S1. Catalytic performance of Al-Beta in the conversion of a) xylose and b) furfural. Reaction conditions: 170 °C, substrate:2-propanol molar ratio 1:50, catalyst 0.1 g·mL^{-1}.

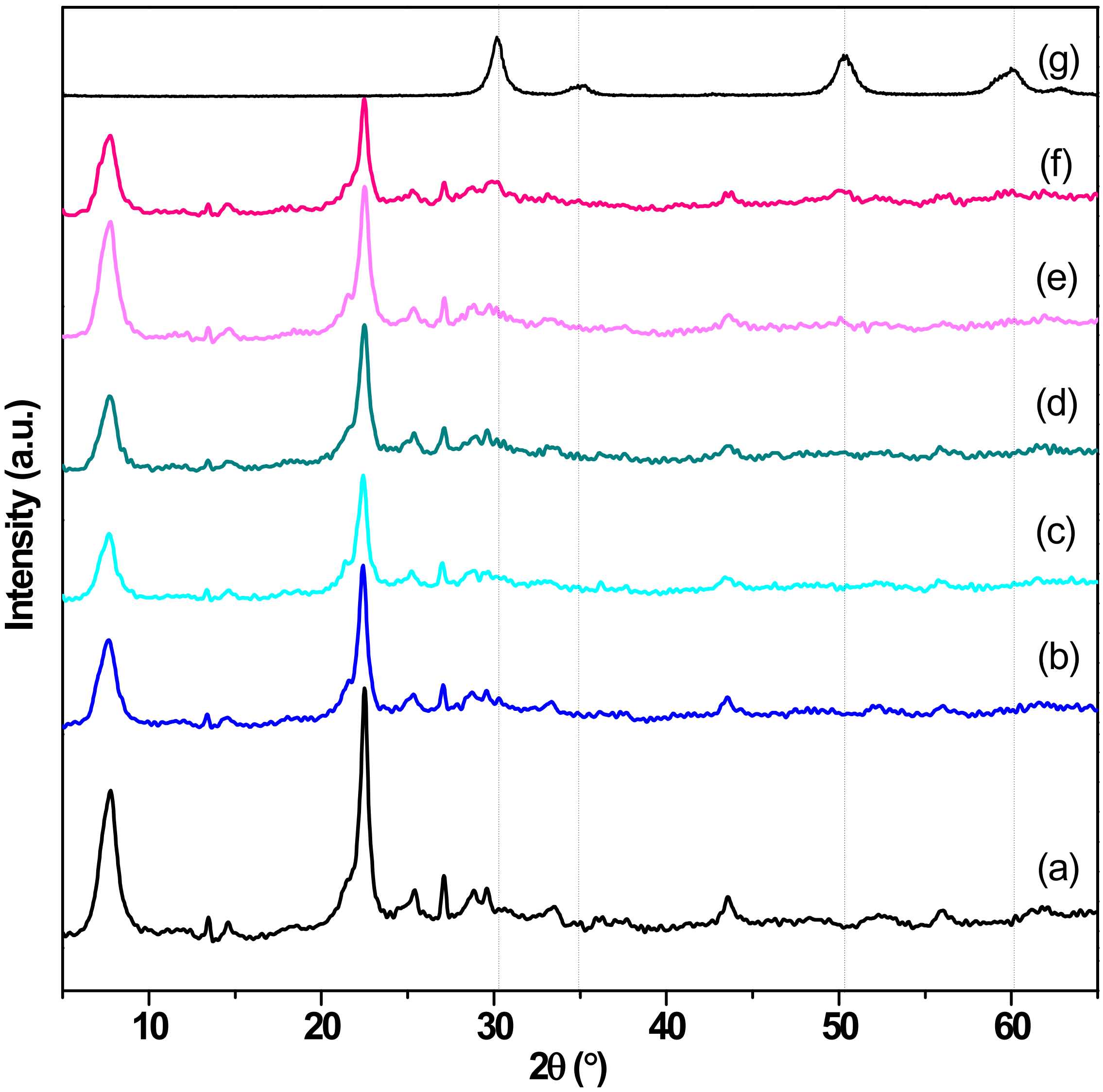


Figure S2. XRD patterns of (a) Al-Beta, (b) Zr-Al-Beta (2.8), (c) Zr-Al-Beta (3.7), (d) Zr-Al-Beta (4.0), (e) Zr-Al-Beta (5.7), (f) Zr-Beta (6.4) zeolites and (g) tetragonal ZrO_2 (different scale) for comparative purposes.

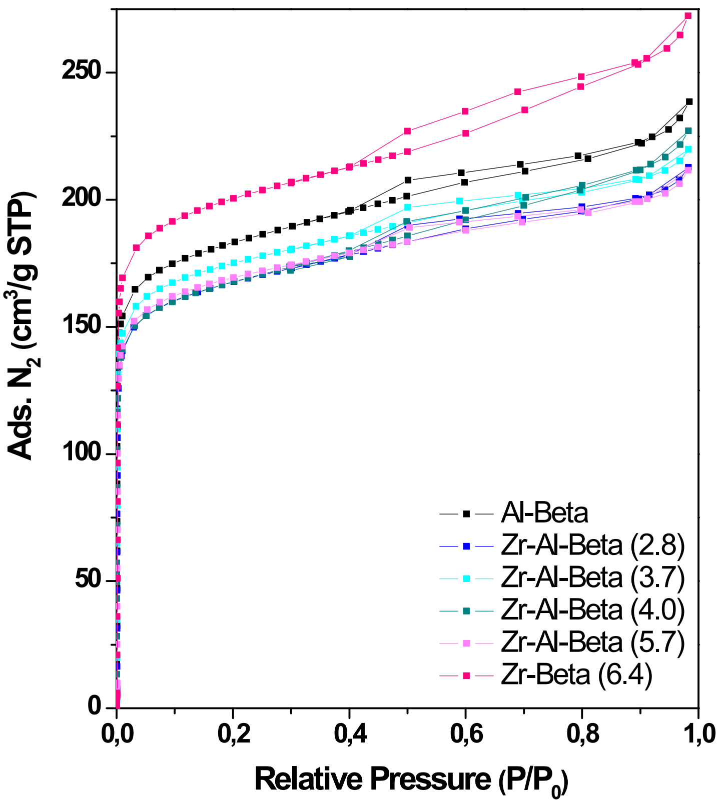


Figure S3. N_2 adsorption-desorption isotherms of Beta zeolites.

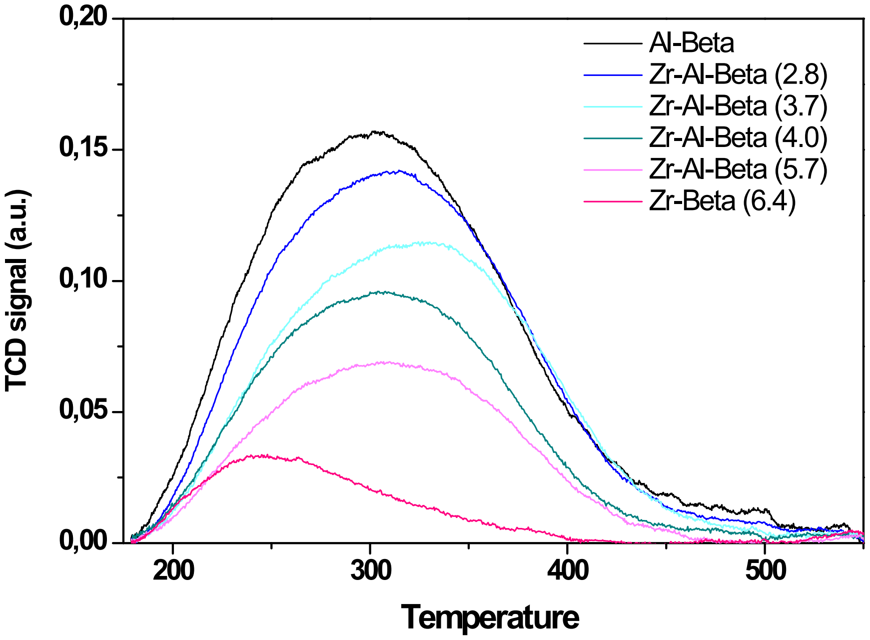


Figure S4. NH_3-TPD profiles of Beta zeolites.

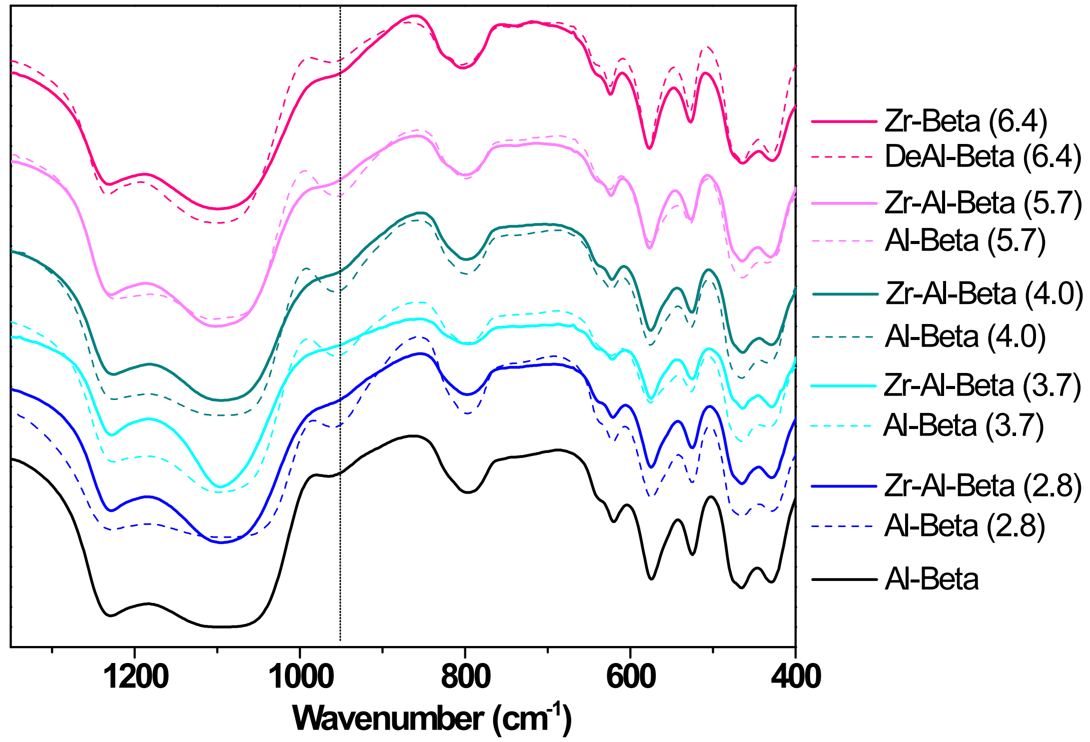


Figure S5. FTIR spectra of Zr containing Beta zeolites and their corresponding dealuminated zeolites.

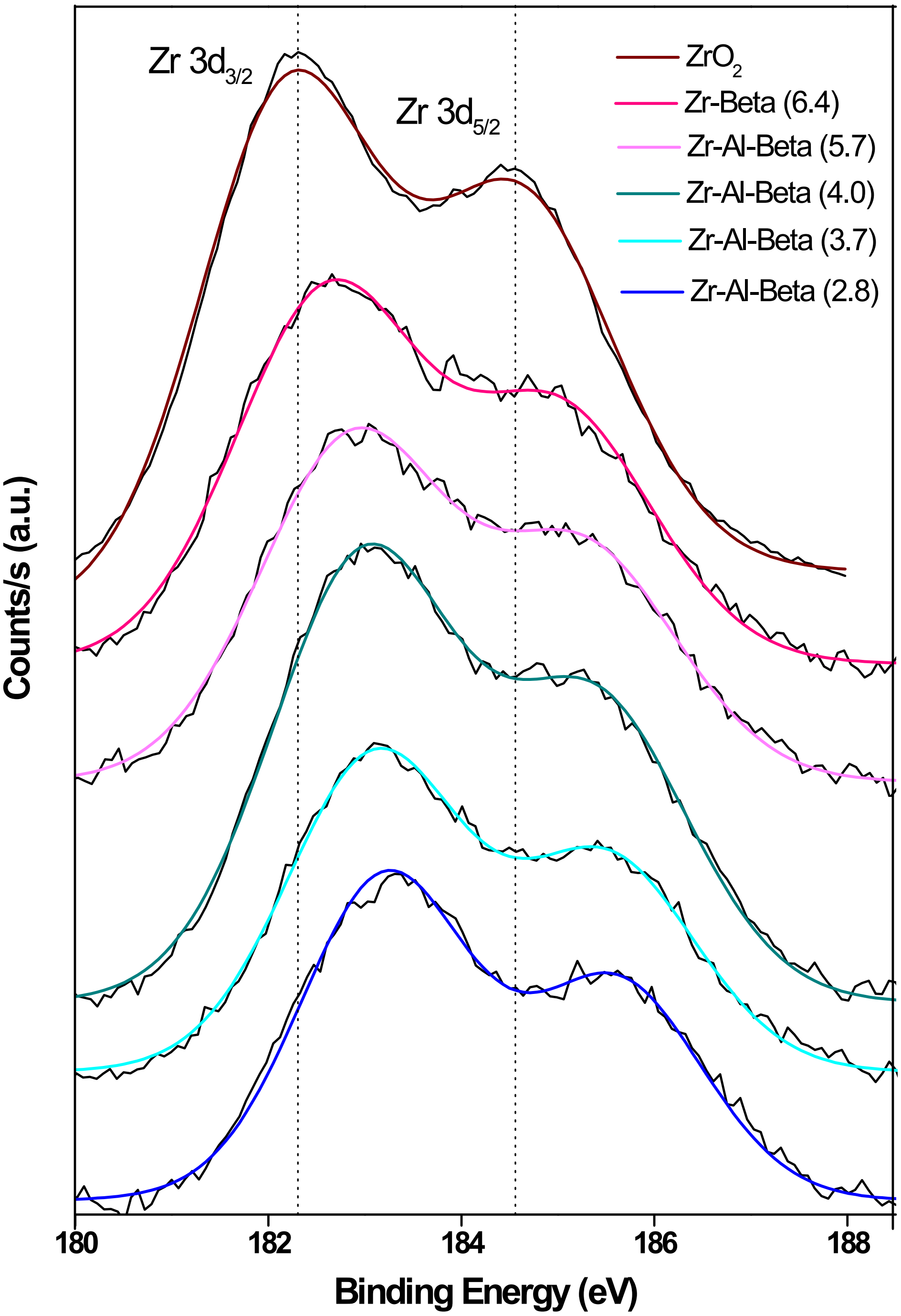


Figure S6. XPS spectra of Zr-Al-Beta zeolites.

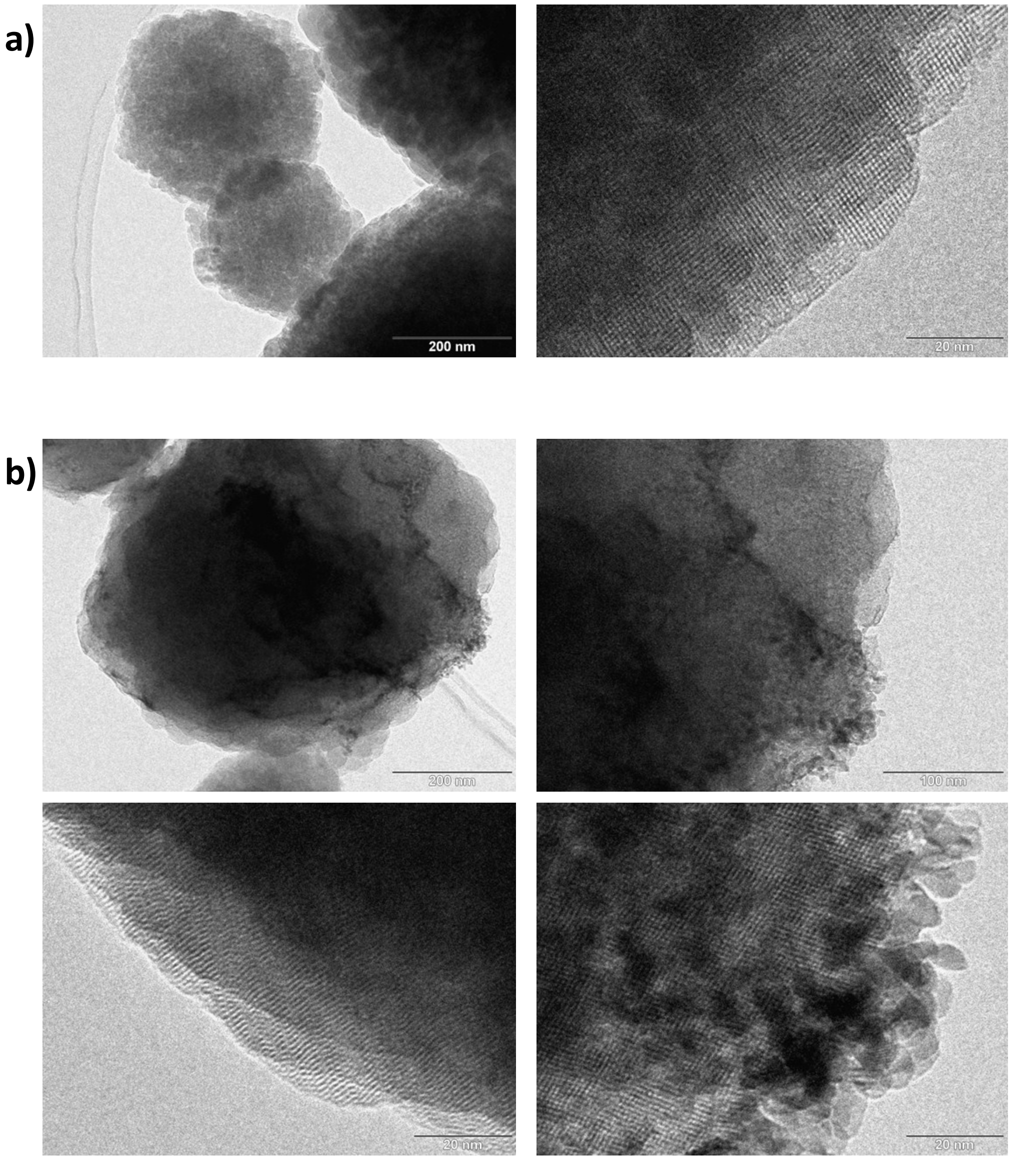


Figure S7. TEM of (a) parent Al-Beta and (b) Zr-Al-Beta (5.7) zeolites.

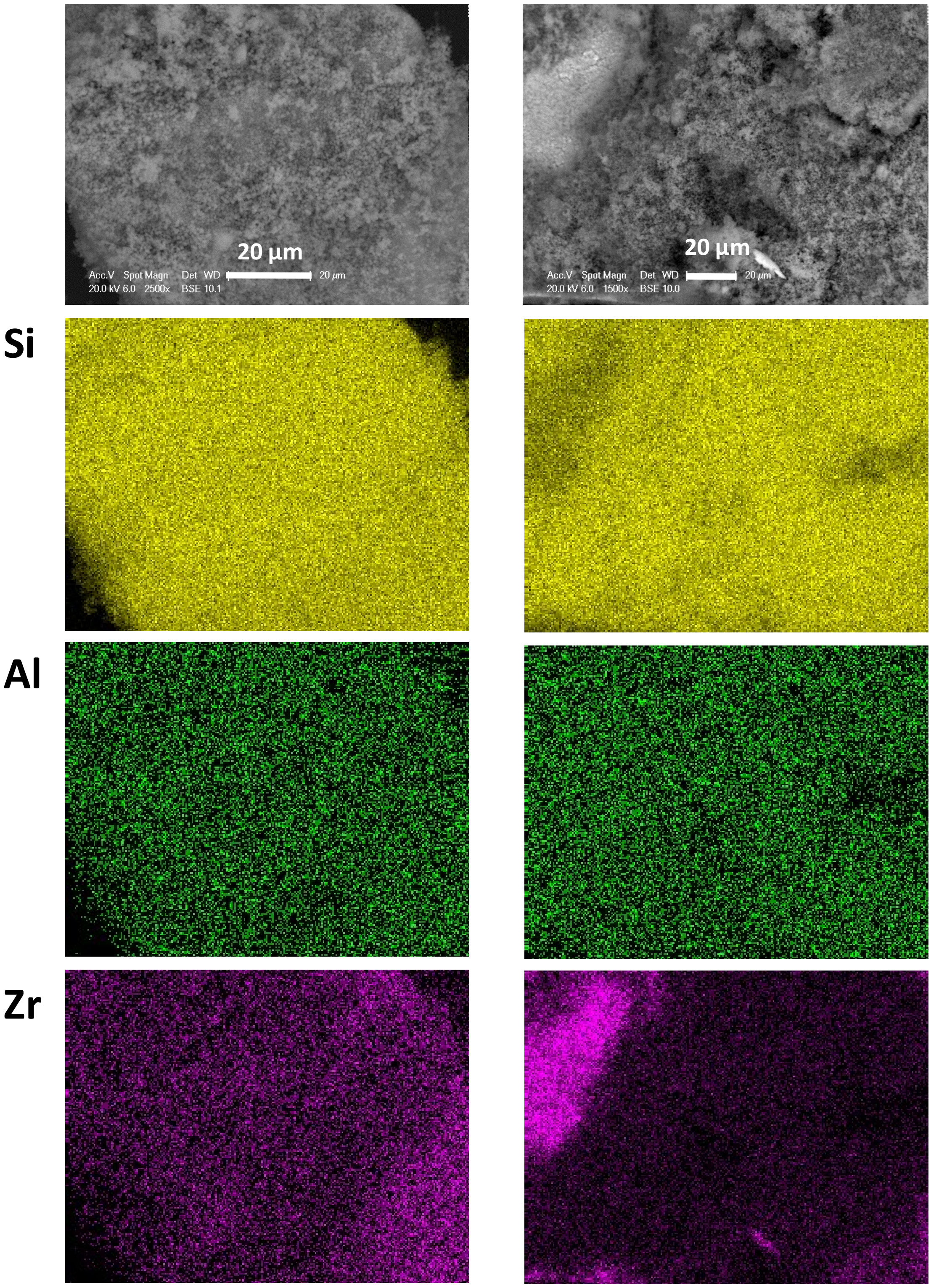


Figure S8. SEM and mapping of Si, Al and Zr for Zr-Al-Beta (5.7) zeolite.

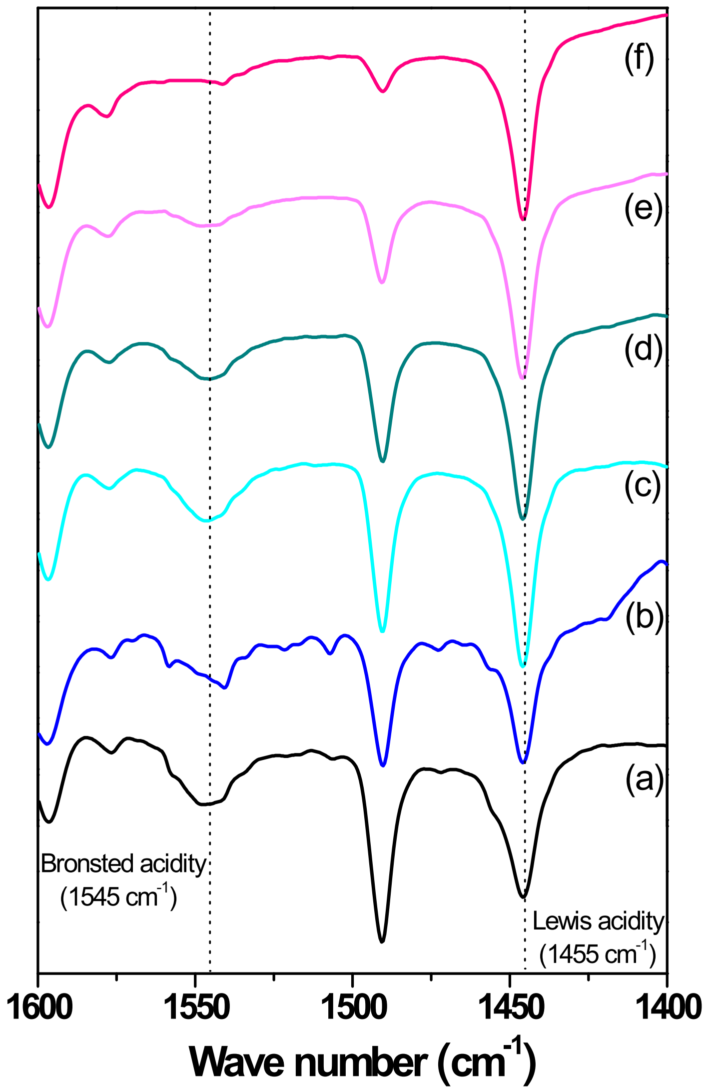


Figure S9. DRIFT signal of adsorbed pyridine on (a) Al-Beta, (b) Zr-Al-Beta (2.8), (c) Zr-Al-Beta (3.7), (d) Zr-Al-Beta (4.0), (e) Zr-Al-Beta (5.7), (f) Zr-Beta (6.4) zeolites.

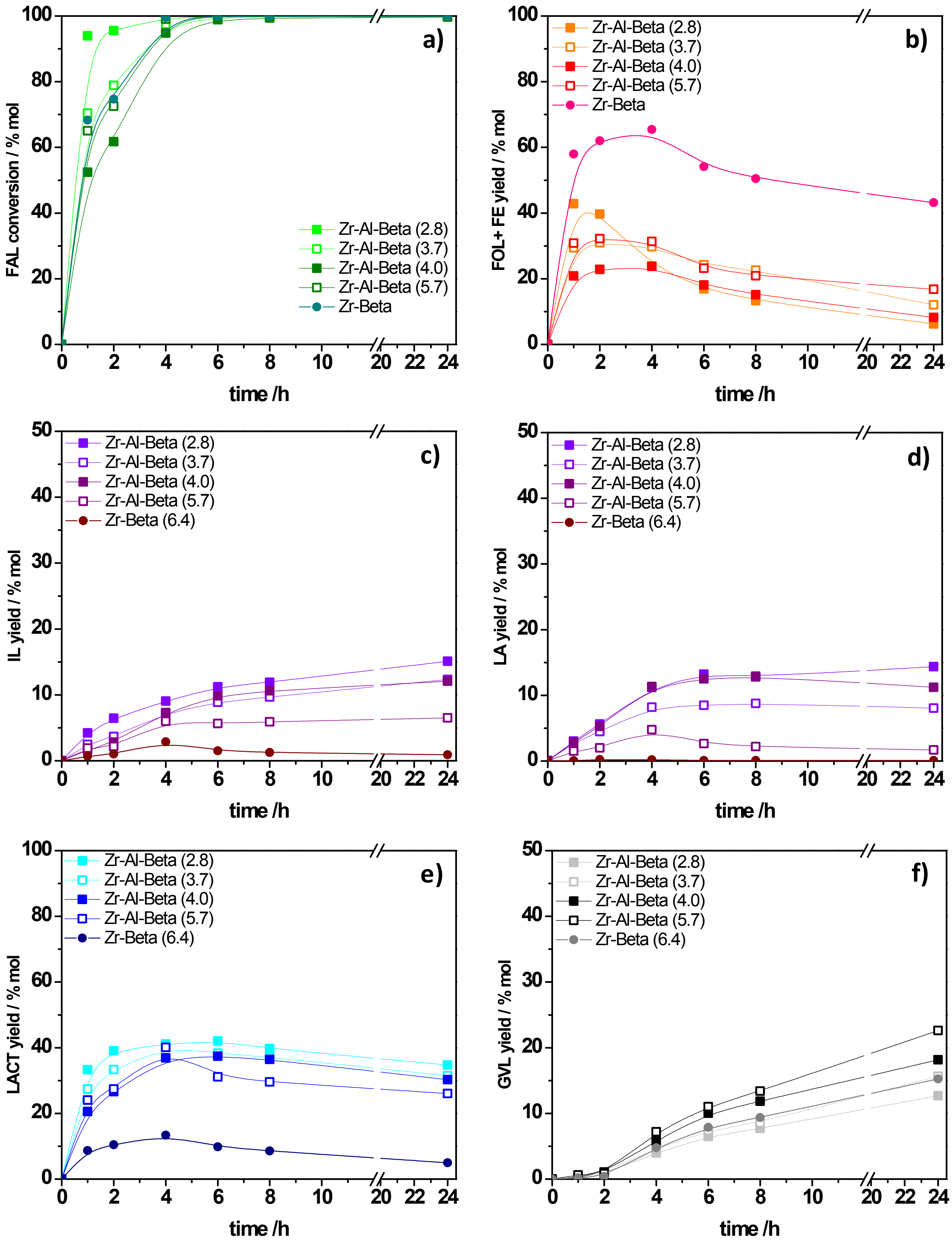


Figure S10. Catalytic performance of Zr-Al-Beta zeolites in the conversion of furfural. a) FAL conversion; b)FOL+FE; c) IL; d) LA; e) LACT and f) GVL yield. Reaction conditions: 170 °C, furfural:2-propanol molar ratio 1:50, catalyst 0.1 g·mL^{-1}.

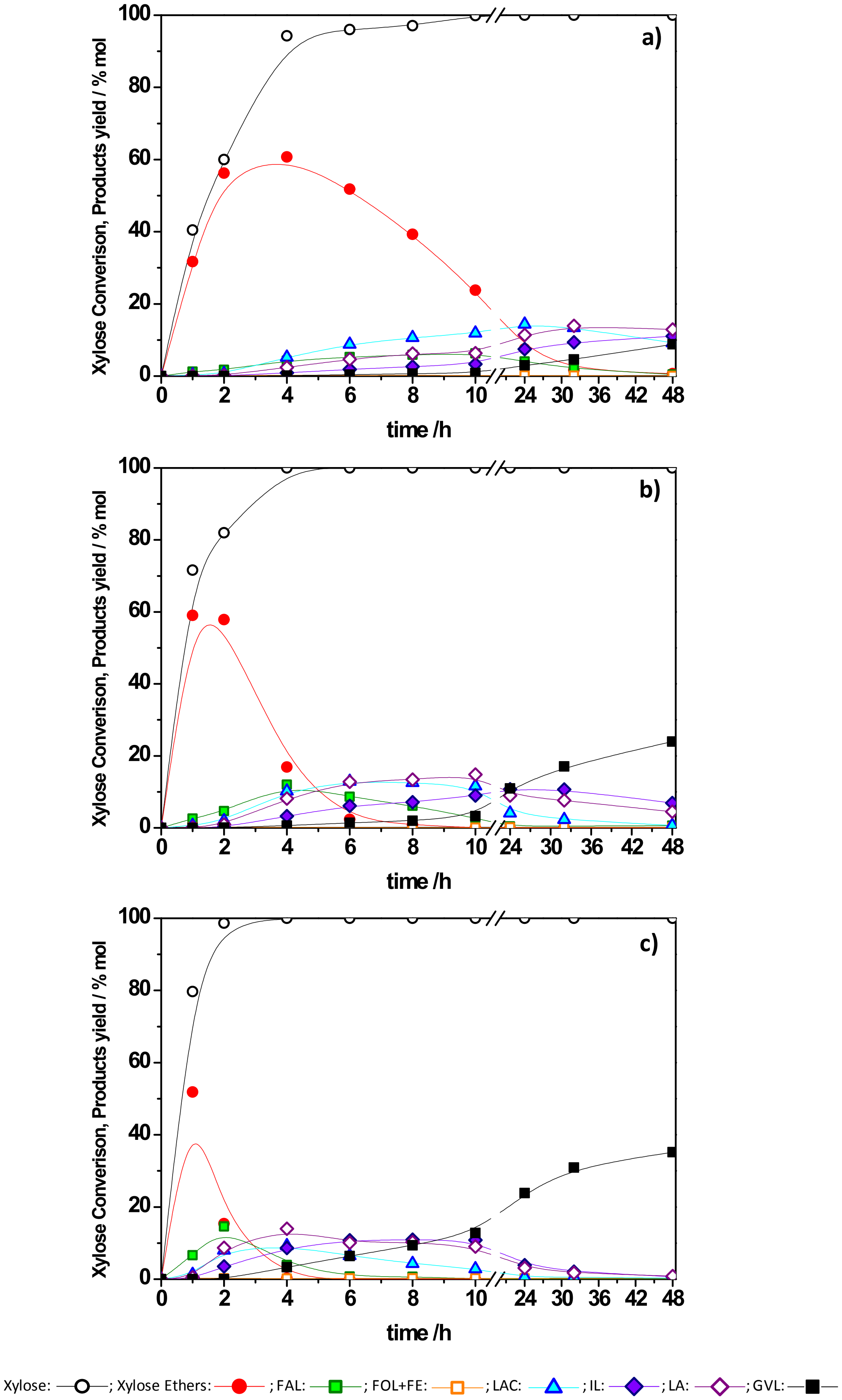


Figure S11. Catalytic performance of Zr-Al-Beta (5.7) zeolite in the conversion of xylose at different temperatures: a) 150 °C; b) 170 °C; c) 190 °C. Reaction conditions: xylose:2-propanol molar ratio 1:50, catalyst 0.1 g·mL^{-1}.

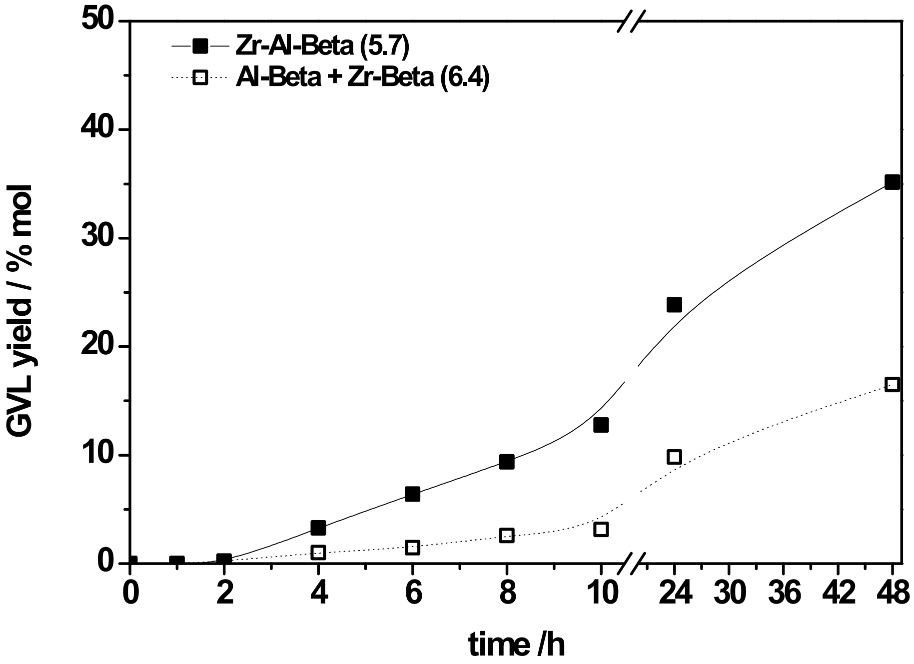


Figure S12. Comparison of GVL yield obtained for xylose conversion in presence of: Zr-Al-Beta (5.7) and a mixture of Al-Beta and Zr-Beta (6.4). The amount of each catalyst in the mixture was calculated to match the Al and Zr content of the bifunctional catalyst Zr-Al-Beta (5.7). Reaction conditions: 190 °C, xylose:2-propanol molar ratio 1:50, total amount of the single catalyst or the mixture 0.1 g·mL^{-1}.

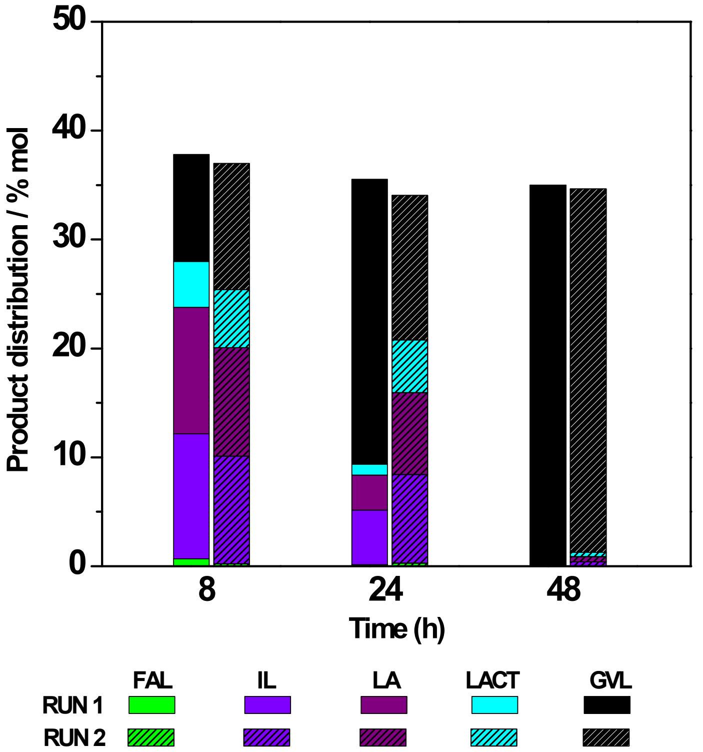
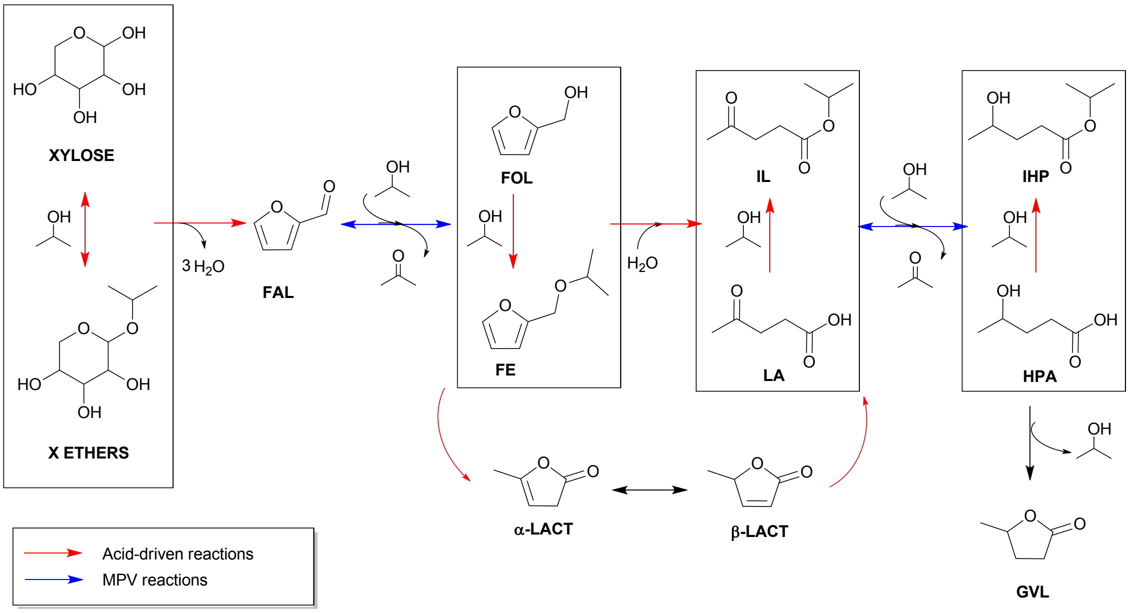


Figure S13. Reusability of Zr-Al-Beta (5.7) zeolite in the conversion of xylose. The catalyst was re-calcined after run 1 at 550 °C in air for 5 h. Reaction conditions: 190 °C, xylose:2-propanol molar ratio 1:50, catalyst 0.1 g·mL^{-1}.

6-Schemes



Scheme S1. Proposed reaction network for the cascade conversion of xylose into GVL considering side reactions. Products: X ETHERS. xylose ethers; FAL, furfural; FOL, furfuryl alcohol; FE, isopropyl furfuryl ether; IL, isopropyl levulinate; LA, levulinic acid; α/β-LACT, α/β-angelica lactone; IHP, isopropyl 4-hydroxypentanoate; HPA, 4-hydroxypentanoic acid; GVL, γ-valerolactone.