Supplementary Information

Zirconium-Beta zeolite as a robust catalyst for the transformation of levulinic acid to γ-valerolactone via Meerwein-Ponndorf-Verley reduction

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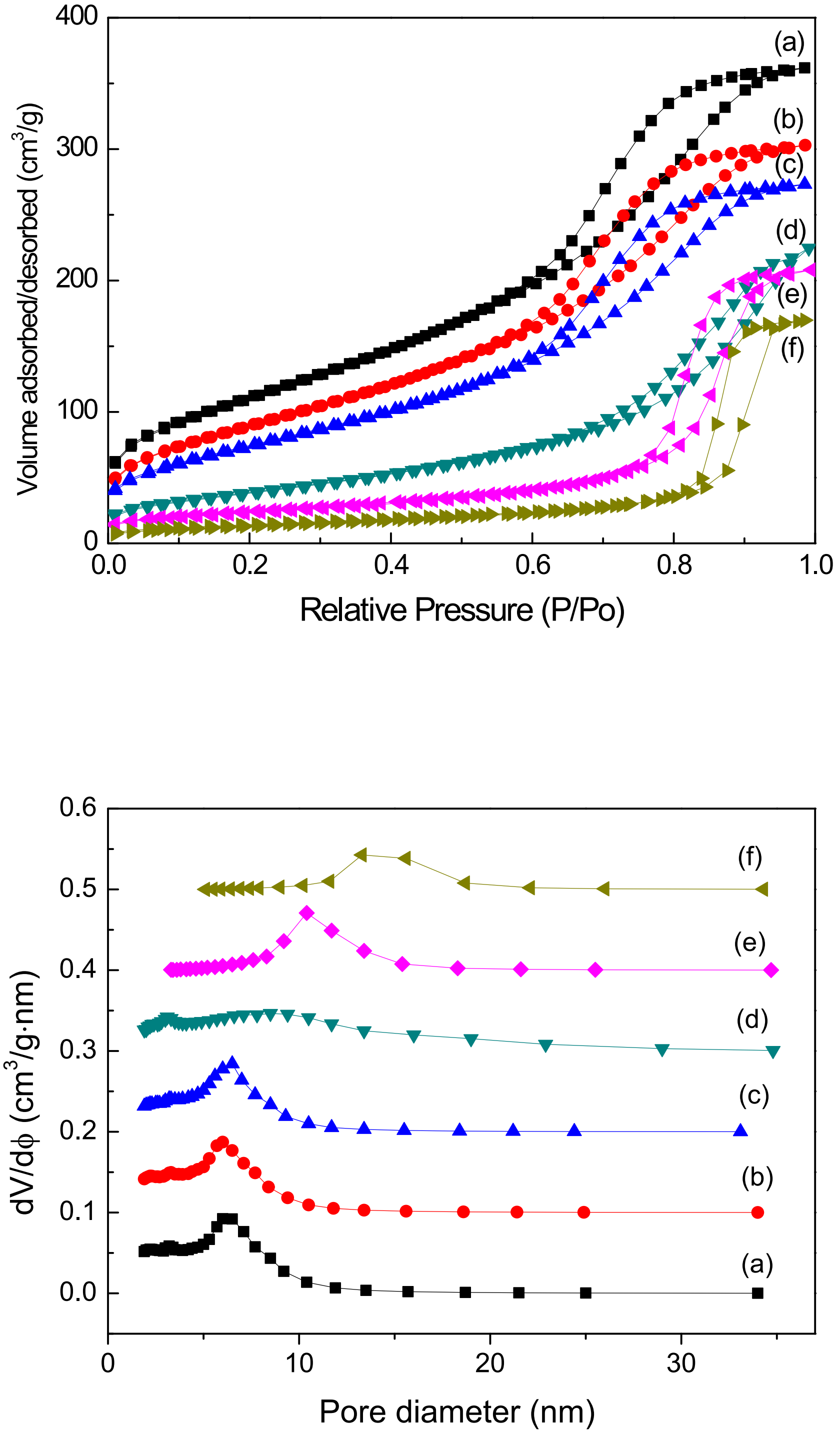


Fig. S1 N_2 adsorption/desorption isotherms and pore distributions of (a) $ZrO(OH)_n$-100 (b) $ZrO(OH)_n$-200 (c) $ZrO(OH)_n$-300 (d) $ZrO(OH)_n$-400 (e) $ZrO(OH)_n$-500 and (f) $ZrO(OH)_n$-600. The pore size distribution curves are offset by 0.1

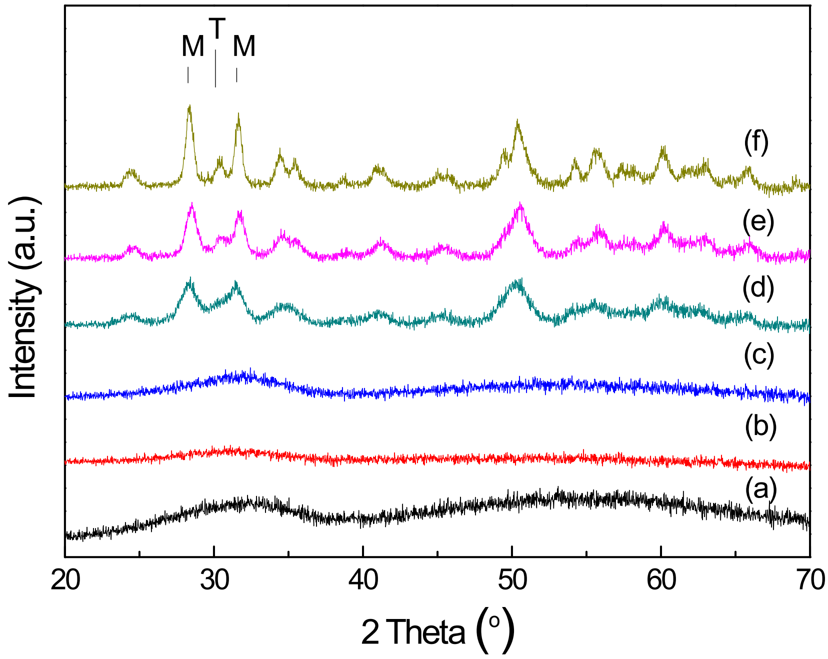


Fig. S2 X-ray diffraction patterns of (a) $ZrO(OH)_n$-100 (b) $ZrO(OH)_n$-200 (c) $ZrO(OH)_n$-300 (d) $ZrO(OH)_n$-400 (e) $ZrO(OH)_n$-500 and (f) $ZrO(OH)_n$-600. The percentage of monoclinic phase (M %) in the crystallized zirconia was measured according to the equation:[S1] $\% M = 1.6I_M / (1.6I_M + I_T)$, where I_M and I_T are the integrated intensities of the monoclinic $(11\bar{1})$ ($2\theta = 28.5^o$) and tetragonal (111) ($2\theta = 30.4^o$) reflexes, respectively.

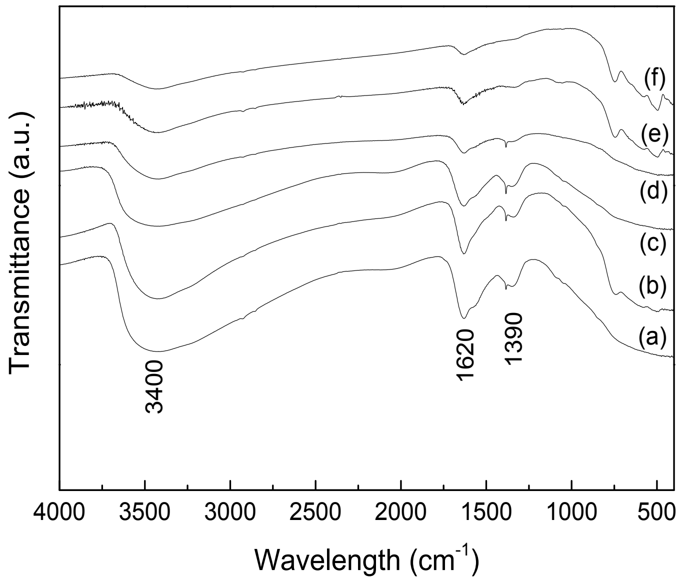


Fig. S3 FT-IR spectra of (a) $ZrO(OH)_n$-100 (b) $ZrO(OH)_n$-200 (c) $ZrO(OH)_n$-300 (d) $ZrO(OH)_n$-400 (e) $ZrO(OH)_n$-500 and (f) $ZrO(OH)_n$-600. The band at *ca.* 1390 cm^{-1} due to atmospheric CO_2 adsorbed on the sample forming a bicarbonate-like species.

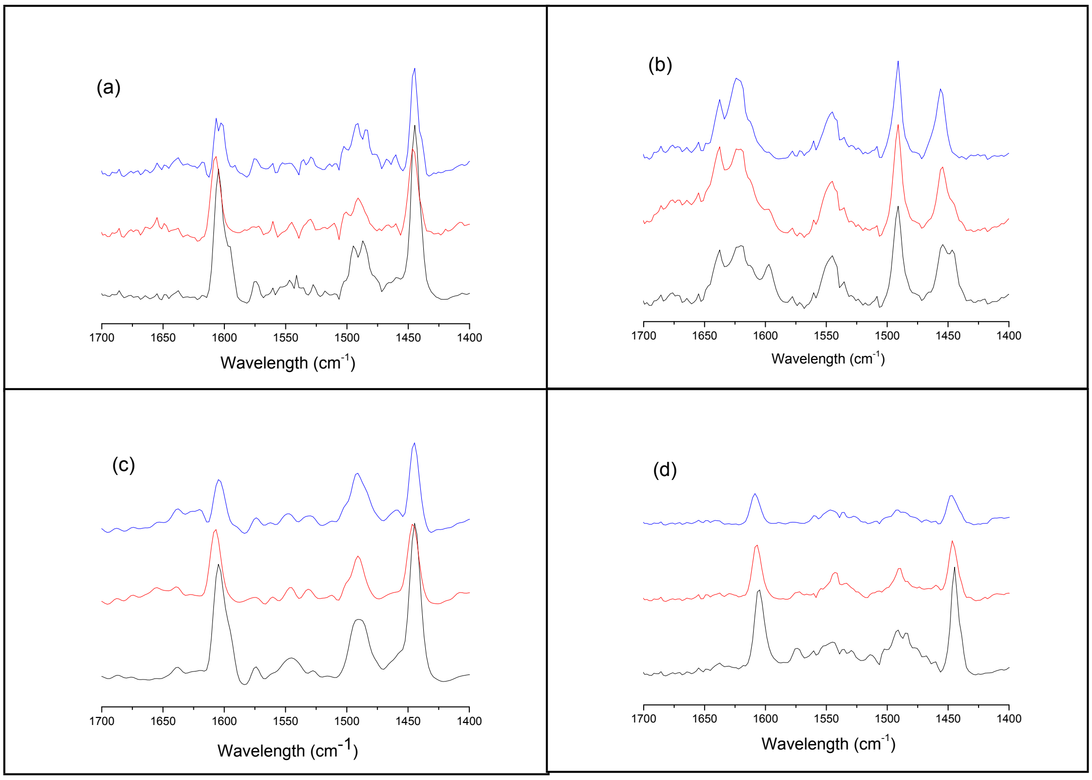


Fig. S4 Pyridine IR spectra of (a) Zr-Beta-100 (b) ZrAl-Beta-25 (c) $ZrO(OH)_n$-300 and (d) $ZrO(OH)_n$-400 after evacuation at 100 ^oC (—), 200 ^oC (—) and 300 ^oC (—).

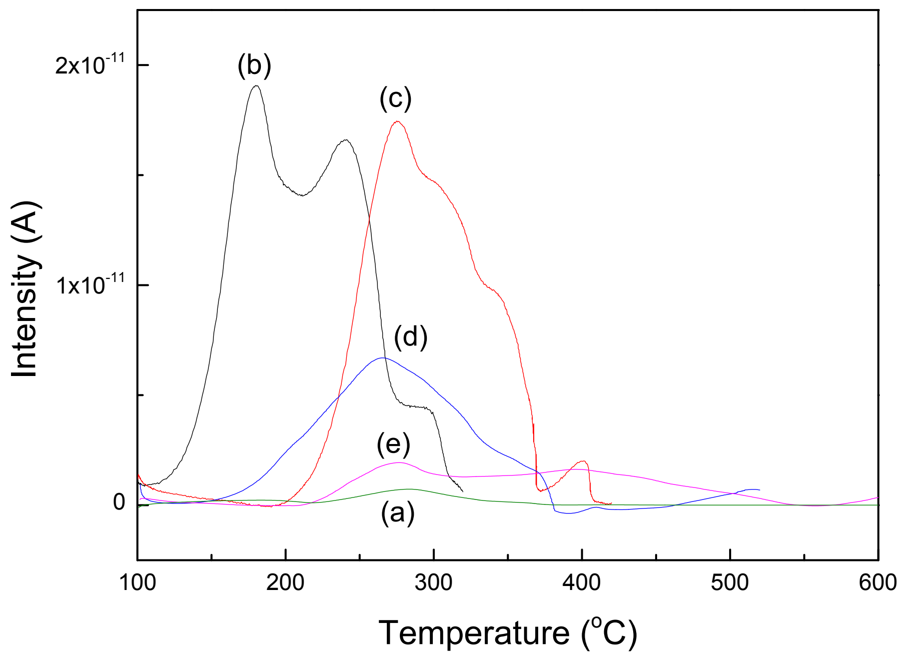


Fig. S5 CO_2-TPD profiles for: (a) Zr-Beta-100 (b) $ZrO(OH)_n$-300 (c) $ZrO(OH)_n$-400 (d) $ZrO(OH)_n$-500 (e) $ZrO(OH)_n$-600.

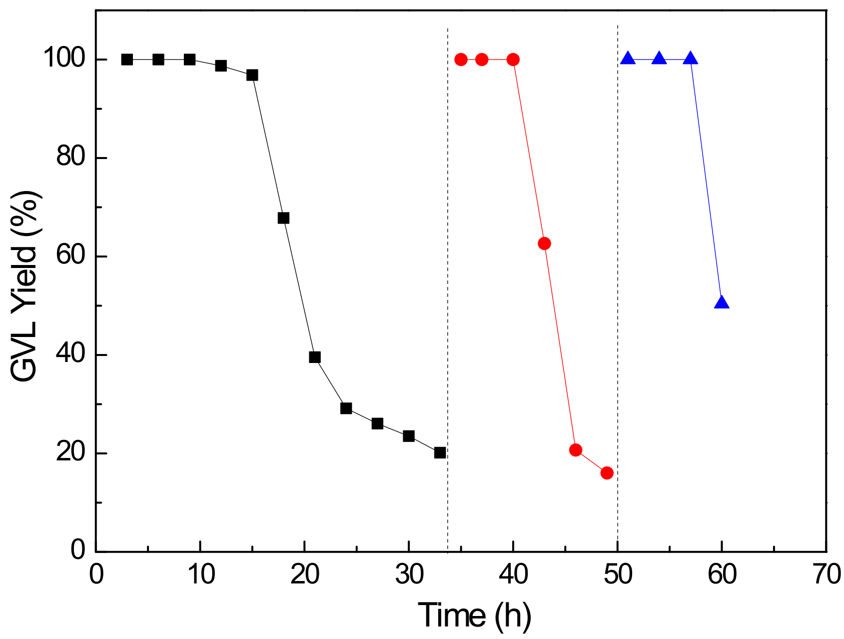


Fig. S6 Yield of GVL versus time-on-stream for the MPV of LA over Zr-Beta-100 at 150 ^{o}C in a continuous flow reactor with WHSV = 0.16 h^{-1}. Catalyst was regenerated at 34 h and 50 h by *in-situ* calcination in air at 500 ^{o}C for 3 h.

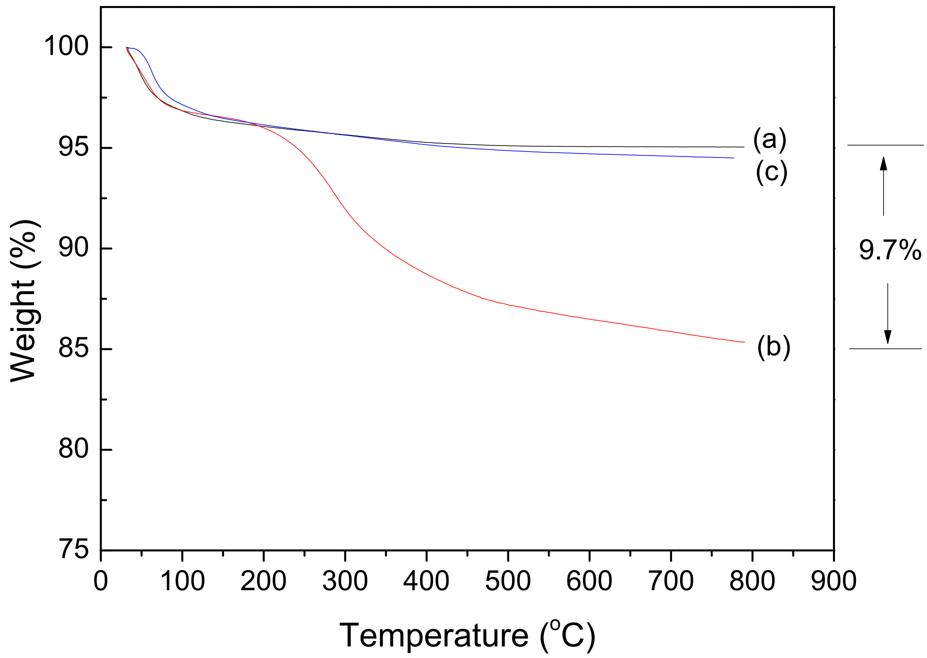


Fig. S7 Thermogravimetry of (a) fresh Zr-Beta-100 (b) Zr-Beta-100 after 34 h of reaction at 150 °C and (c) regenerated Zr-Beta-100.

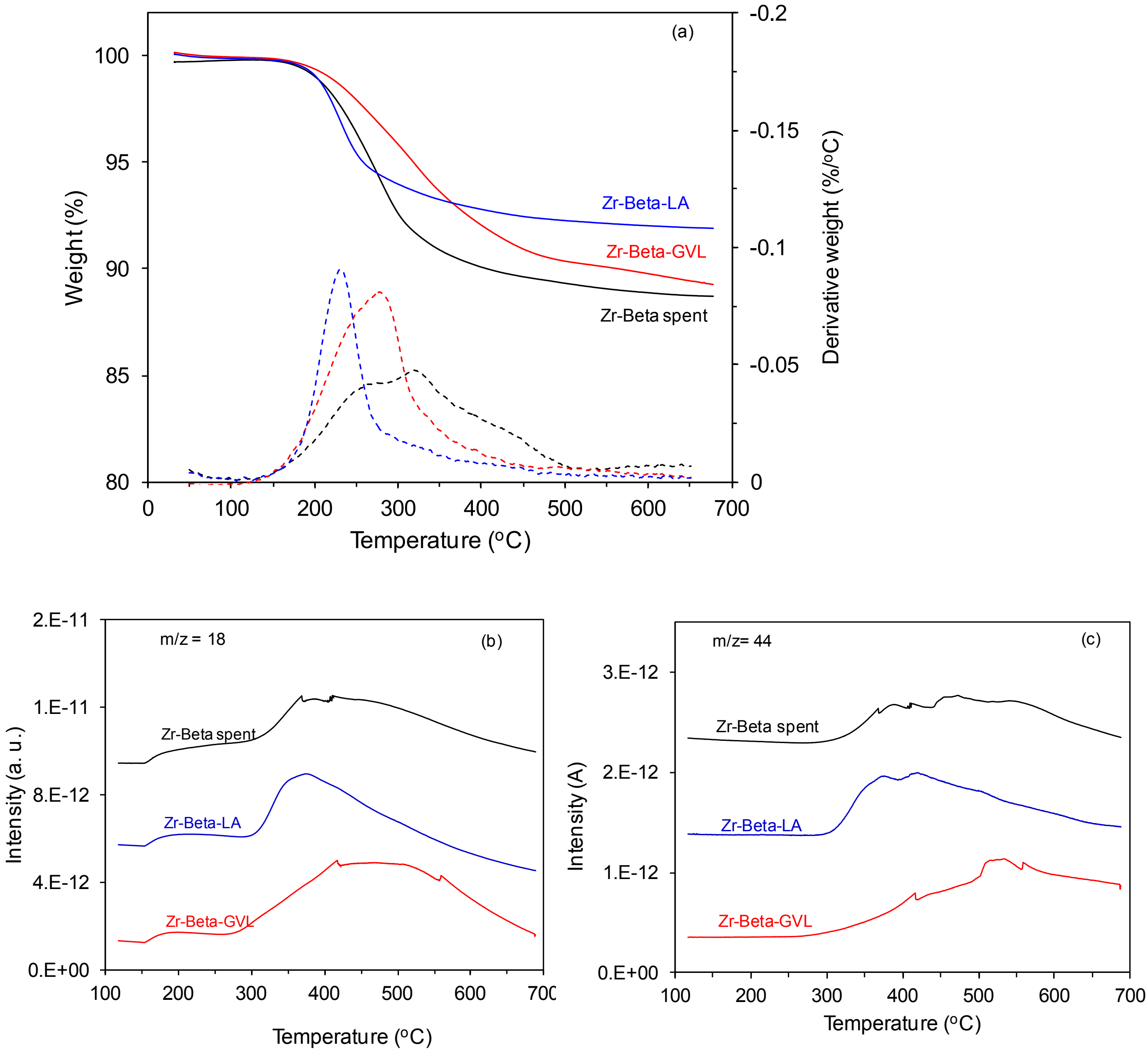
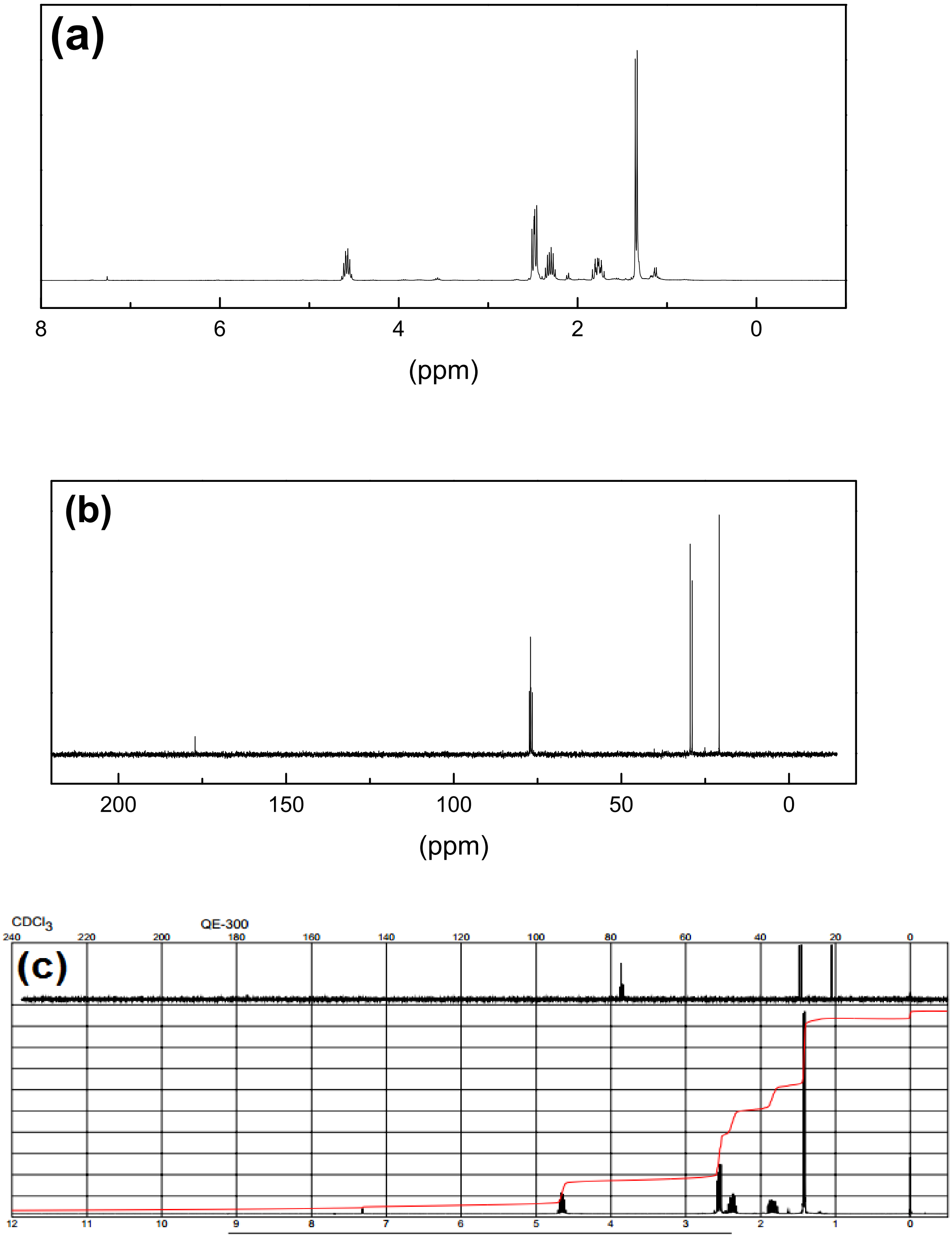
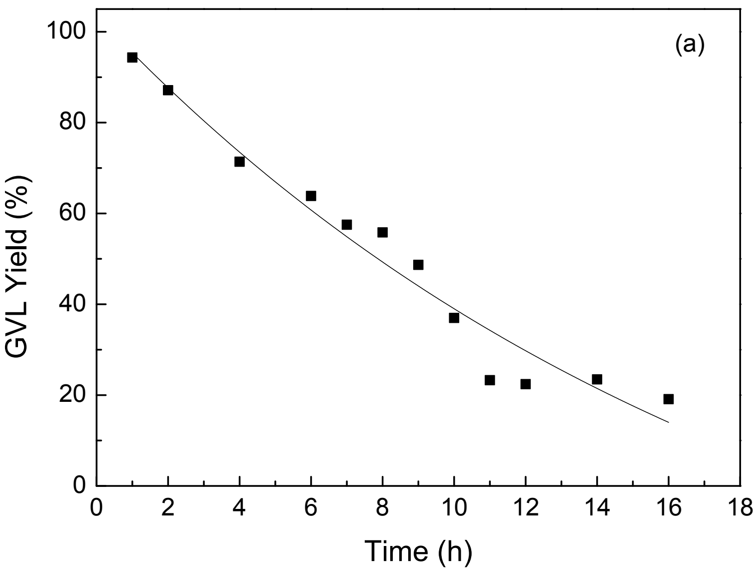


Fig. S8 TGA-MS results of (a) weight loss (b) H_2O signal (m/e 18) and (c) CO_2 signal (m/e 44) for spent Zr-Beta (—), Zr-Beta adsorbed with pure levulinic acid (—) and Zr-Beta adsorbed with pure γ-valerolactone (—). The calculated H/C ratios are 1.57, 1.63 and 1.60, respectively. The theoretical H/C ratio for levulinic acid and γ-



valerolactone are 1.60.

Fig. S9 (a) ^{1}H and (b) ^{13}C NMR profiles for the isolated GVL. Comparison with ^{1}H from(c) standard PDF file http://www.sigmaaldrich.com/spectra/fnmr/FNMR011623.PDF) supplied by Sigma-Aldrich. For further information of NMR for levulinic acid and possible by-products, please refer to literature S2, S3.



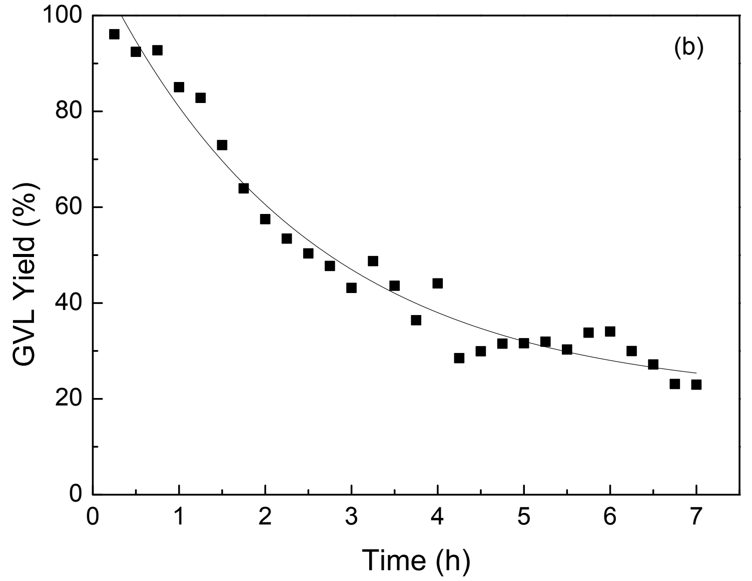


Fig. S10 Yield of GVL versus time-on-stream over Zr-Beta-100 at 250 ^{o}C in a continuous flow reactor at a high WHSV of (a) 2.0 h^{-1} and (b) 4.0 h^{-1}

Table S1 MPV over Zr-Beta-100 with different concentration of levulinic acid.

Catalyst (mg)	LA (mmol)	2-Pentanol (mL)	LA conc. (wt. %)	Temp. (°C)	Time (h)	Conv. (%)	GVL sel. (%)
200	1	2	7.2	118	6	82	77
					8	100	75
200	1	4	3.6	118	6	59	94
200	1	5	2.9	118	6	46	98
200	1	10	1.4	118	6	38	100

Table S2 Esterification of different concentration of levulinic acid without catalyst after 4 h

LA (mmol)	2-Pentanol (mL)	LA conc. (wt. %)	T (°C)	Conv. (%)	Ester	
					Sel. (%)	Yield (%)
1	2	7.2	118	11	85	9.4
1	4	3.6	118	5.2	91	4.7
1	5	2.9	118	4.6	>99	4.6
1	10	1.4	18	3.1	>99	3.1

References:

[S1] D. L. Porter, A. H. Heuer, *J. Am. Ceram. Soc.,* 1979, **62**, 298.

[S2] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horváth, *Top. Catal.*, 2008, **48**, 49-54.

[S3] J. M. Tukacs, D. Király, A. Strádi, G. Novodarszki, Z. Eke, G. Dibó, T. Kégl and L. T. Mika, *Green Chem.,* 2012, **14**, 2057-2065.