Supporting Information

Balanced distribution of Brønsted acid sites and Lewis acid sites for highly selective conversion of xylose into levulinic acid/ester over Zr-beta catalysts

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Table S1 The explication of naming of catalysts (Zr-beta-X-Y)[a]

Catalysts	Synthesis methods	X-Calcination temperature (°C)	Y-loading or concentration
Zr-beta-400-1%	Impregnation	400	1%
Zr-beta-400-2.5%	Impregnation	400	2.5%
Zr-beta-400-5%	Impregnation	400	5%
Zr-beta-400-10%	Impregnation	400	10%
Zr-beta-400-20%	Impregnation	400	20%
Zr-beta-400-30%	Impregnation	400	30%
Zr-beta-500-1%	Impregnation	500	1%
Zr-beta-500-2.5%	Impregnation	500	2.5%
Zr-beta-500-5%	Impregnation	500	5%
Zr-beta-500-10%	Impregnation	500	10%
Zr-beta-500-20%	Impregnation	500	20%
Zr-beta-500-30%	Impregnation	500	30%
Zr-beta-600-1%	Impregnation	600	1%
Zr-beta-600-2.5%	Impregnation	600	2.5%
Zr-beta-600-5%	Impregnation	600	5%
Zr-beta-600-10%	Impregnation	600	10%
Zr-beta-600-20%	Impregnation	600	20%
Zr-beta-600-30%	Impregnation	600	30%
Zr-beta 400-0.01	Ion exchange	400	0.01 mol/L
Zr-beta-400-0.05	Ion exchange	400	0.05 mol/L
Zr-beta-400-0.15	Ion exchange	400	0.15 mol/L
Zr-beta-400-0.2	Ion exchange	400	0.2 mol/L
Zr-beta 500-0.01	Ion exchange	500	0.01 mol/L
Zr-beta-500-0.05	Ion exchange	500	0.05 mol/L
Zr-beta-500-0.15	Ion exchange	500	0.15 mol/L
Zr-beta-500-0.2	Ion exchange	500	0.2 mol/L
Zr-beta 600-0.01	Ion exchange	600	0.01 mol/L
Zr-beta-600-0.05	Ion exchange	600	0.05 mol/L
Zr-beta-600-0.15	Ion exchange	600	0.15 mol/L
Zr-beta-600-0.2	Ion exchange	600	0.2 mol/L

[a]Y in impregnation method means the Zr loading; Y in ion exchanged method means the concentration of $ZrCl_4$ solution.

Table S2 Conversion of different reactants over Zr-beta-600-10 catalyst[a]

Entry	Reactants	Reaction time (min)	Con. (%)	Yield (%)				Carbon balance (%)
				FUR	IL	LA	IFE	
1	Xylose	0	51.2	3.2	3.5	0.0	−	6.7
2	Xylose	15	76.4	19.9	9.4	0.0	−	29.3
3	Xylose	30	95.6	20.4	22.9	17.0	−	60.3
4	Xylose	45	99.8	15.5	34.0	23.4	−	72.9
5	Xylose	60	100.0	11.4	43.7	22.4	−	77.5
6	Xylose	90	100.0	8.1	52.1	26.4	−	86.6
7	Xylose	120	100.0	3.6	46.3	18.6	−	68.5
8	Furfural	0	25.3	0.0[b]	1.4	0.0	12.9	14.3
9	Furfural	15	44.9	1.3[b]	4.0	0.0	22.2	27.5
10	Furfural	30	54.8	1.6[b]	8.0	0.0	28.0	37.6
11	Furfural	45	62.3	1.8[b]	11.2	0.0	29.8	42.8
12	Furfural	60	67.7	2.0[b]	12.0	0.0	30.6	44.6
13	Furfural	90	73.2	2.0[b]	14.2	0.0	31.9	48.1
14	Furfural	120	77.0	1.6[b]	12.4	2.4	32.2	48.6
15	FA	0	23.9	−	0.0	−	25.5	25.5
16	FA	15	46.1	−	0.3	−	39.8	40.1
17	FA	30	58.5	−	5.6	−	47.3	52.9
18	FA	45	74.3	−	6.9	−	56.5	63.4
19	FA	60	85.1	−	7.9	−	62.0	69.9
20	FA	90	90.0	−	8.9	−	69.1	78.0
21	FA	120	100.0	−	8.0	−	58.3	66.3
22	FA[c]	0	49.1		6.7	0.0	28.1	34.8
23	FA[c]	15	66.1	−	18.1	3.3	31.3	52.7
24	FA[c]	30	75.2	−	23.5	5.4	36.4	65.3
25	FA[c]	45	88.8	−	30.0	7.0	33.0	70.0
26	FA[c]	60	90.3	−	38.0	11.5	31.2	80.7
27	FA[c]	90	93.6	−	41.7	15.0	30.5	87.2
28	FA[c]	120	100.0	−	42.1	19.6	27.4	89.1

[a]Other reaction conditions: reactant = 0.5 g; solvent: 19.5 g; catalyst loading: 100 mg; T = 190°C; P_{N2} = 3 MPa (at room temperature). IFE represents isopropyl furfuryl ether, and FUR represents furfural. Carbon balance was determined based on the products identified with GCMS. “0 min” in the x-axis represented the setting reaction

temperature just reached, and “120 min” in the x-axis represented the reactor was cooled to room temperature.

[b]The yield represents the yield of FA.

[c]Water of 2 g was used.

[d]The carbon balance was calculated according to the total amounts of the products generated divided by the xylose converted. It needs to note that the unidentified organic products were not included in the calculation of carbon balance.

Table S3 Particle sizes of H-beta and modified beta zeolite catalysts

Entry	Samples	Particle sizes of beta (nm)
1	H-beta	11.70
2	Fe-beta	11.62
3	Ni-beta	11.77
4	Sn-beta	11.55
5	Zr-beta	10.93
6	Zr-beta-400-10	11.46
7	Zr-beta-500-10	11.35
8	Zr-beta-600-10	11.16
9	Zr-beta-400-0.05	11.55
10	Zr-beta-500-0.05	11.40
11	Zr-beta-600-0.05	11.27

Table S4 Physicochemical properties of H-beta and Zr-beta catalysts

Samples	$S_{BET}/m^2 \cdot g^{-1}$	Median pore width/Å	$V_{micro}/cm^3 \cdot g^{-1}$
H-beta	442.9	26.3	0.58
Zr-beta-400-10	389.0	28.2	0.55
Zr-beta-500-10	381.0	26.2	0.49
Zr-beta-600-10	394.5	29.4	0.58
Zr-beta-400-0.05	380.5	26.3	0.50
Zr-beta-500-0.05	418.1	23.3	0.49
Zr-beta-600-0.05	378.9	27.2	0.51

Table S5 Chemical composites of Zr-beta-600-10 catalyst[a]

Sample	O (at%)	Al (at%)	Si (at%)	Zr (at%)	Zr (wt%)	Atomic ratio	
						Si/Al	Si/Zr
H-beta	72.0	2.7	25.3	–	–	9.4	–
Zr-beta-600-10	79.0	1.9	18.5	0.67	3.2	9.7	27.6

[a]Chemical composites were determined based on energy-dispersive X-ray spectrometry.

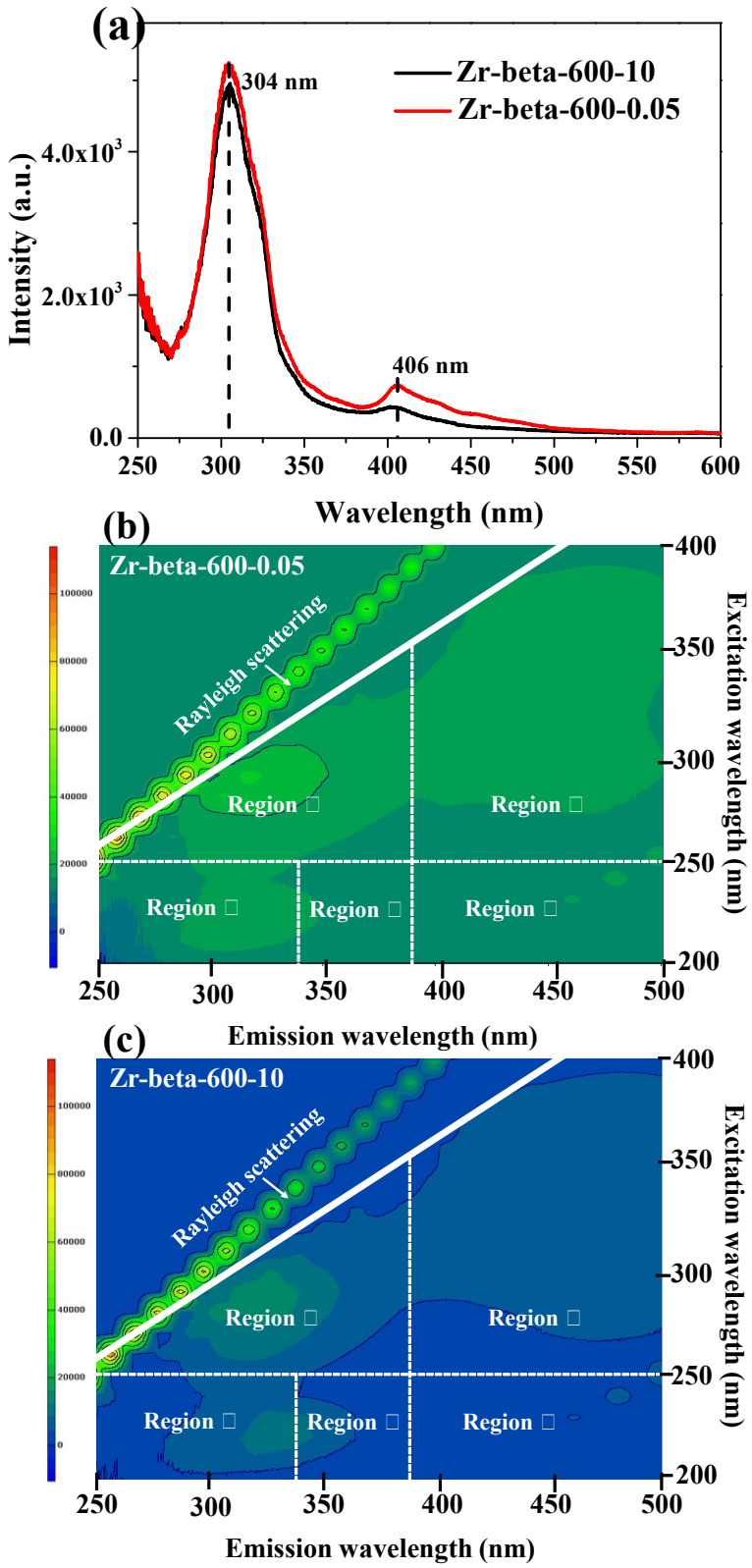

Fig. S1 UV fluorescence spectra in 2D (a) and 3D (b) and (c) of liquid products over Zr-beta-600-10 and Zr-beta-600-0.05 catalysts, these liquid products were diluted to 400 ppm before analysis.

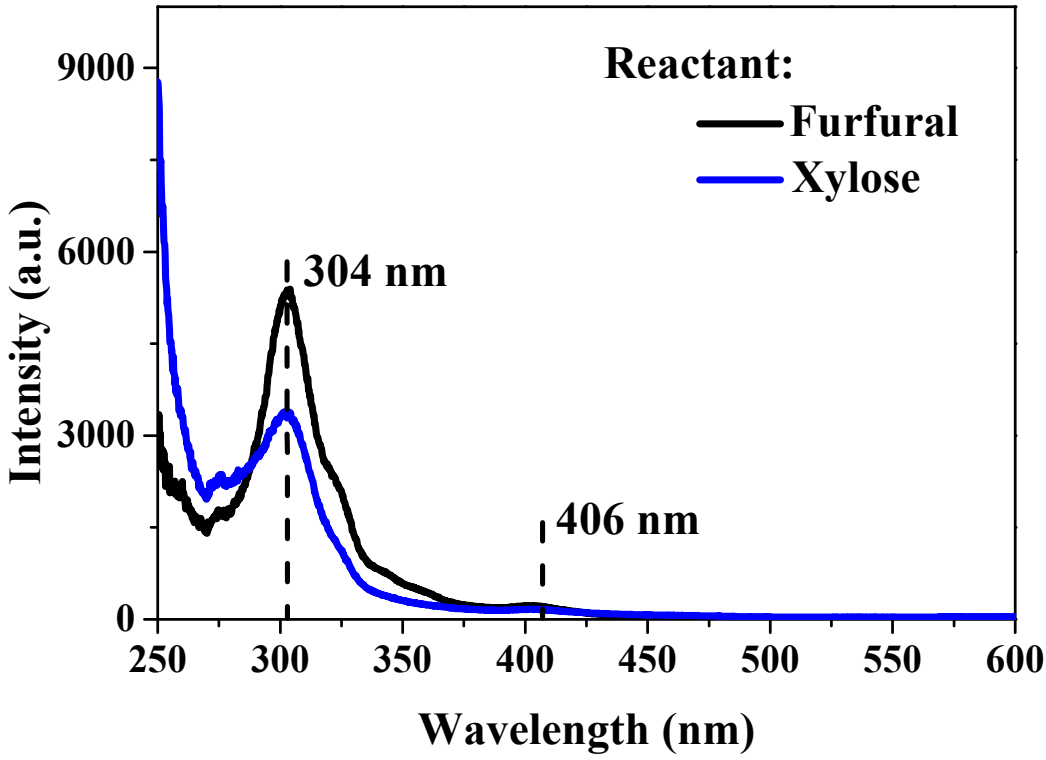

Fig. S2 UV fluorescence spectra of liquid products with different reactants, these liquid products were diluted to 400 ppm before analysis.

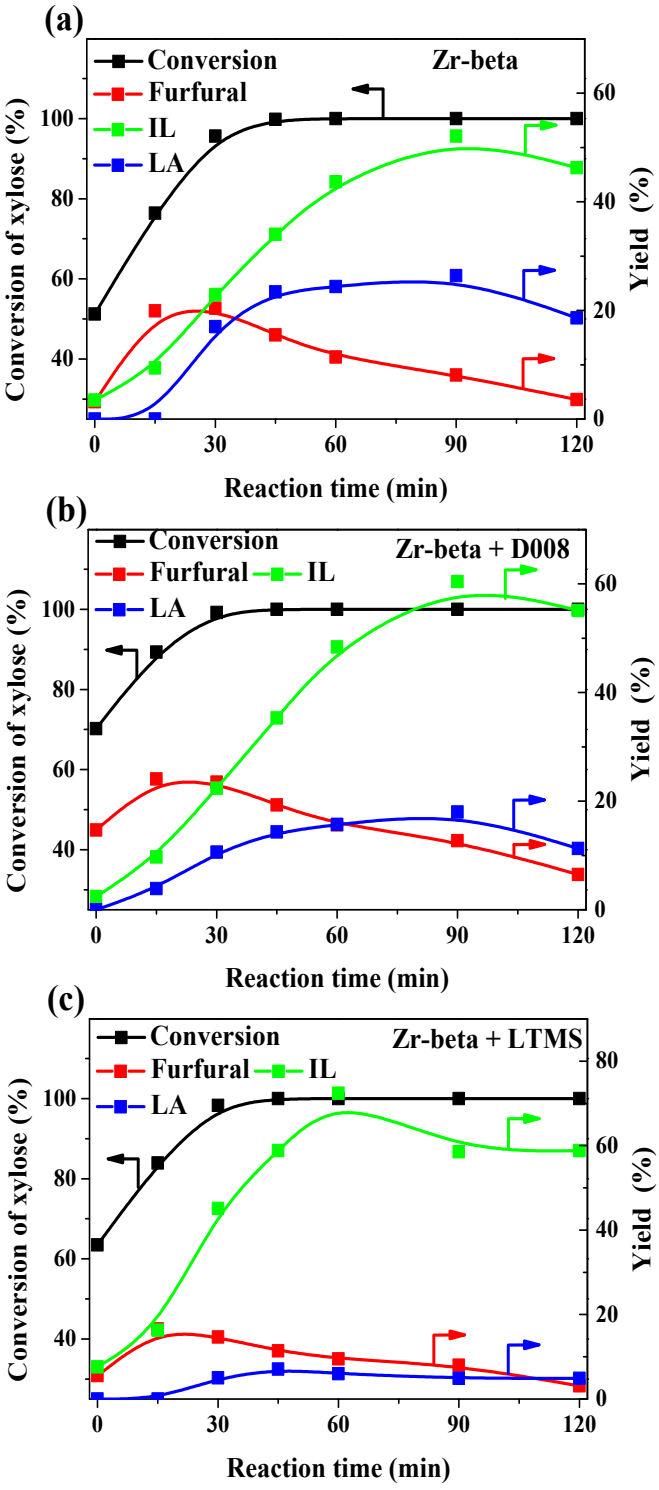

Fig. S3 Conversion of xylose over Zr-beta catalyst and co-catalysts. Other reaction conditions: reactant = 0.5 g; solvent: 19.5 g; catalyst loading: 100 mg; T = 190°C; P_{N2} = 3 MPa (at room temperature). D008: a commercial solid acid catalyst; lanthanum trifluoromethane sulfonate (LTMS), a commercial Lewis acid catalyst. "0 min" in the x-axis represented the setting reaction temperature just reached, and "120 min" in the x-axis represented the reactor was cooled to room temperature.

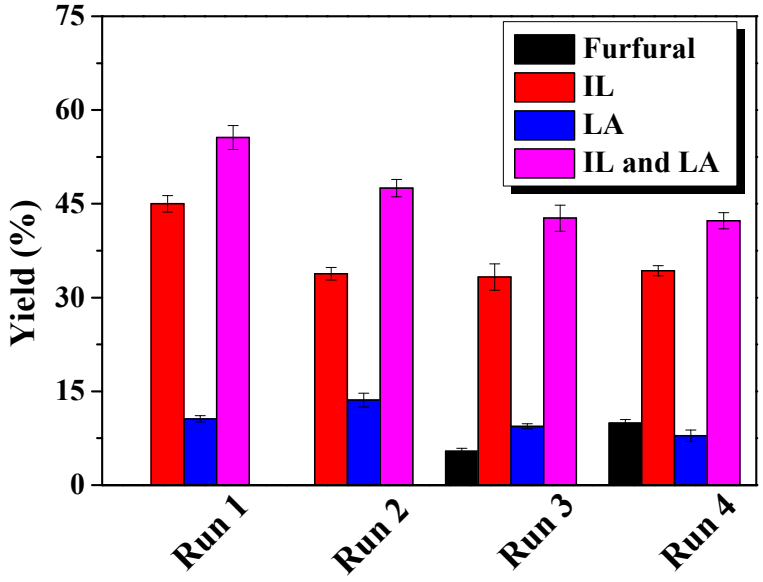

Fig. S4 Recycle tests of conversion of xylose to LA and IL. Reaction conditions: T = 190°C; t = 2 h; P_{N2} = 3 MPa (at room temperature); stirring speed = 400 rpm; catalyst loading: 5 wt%; reactant loading: 0.1 g; isopropanol: 9.9 g.

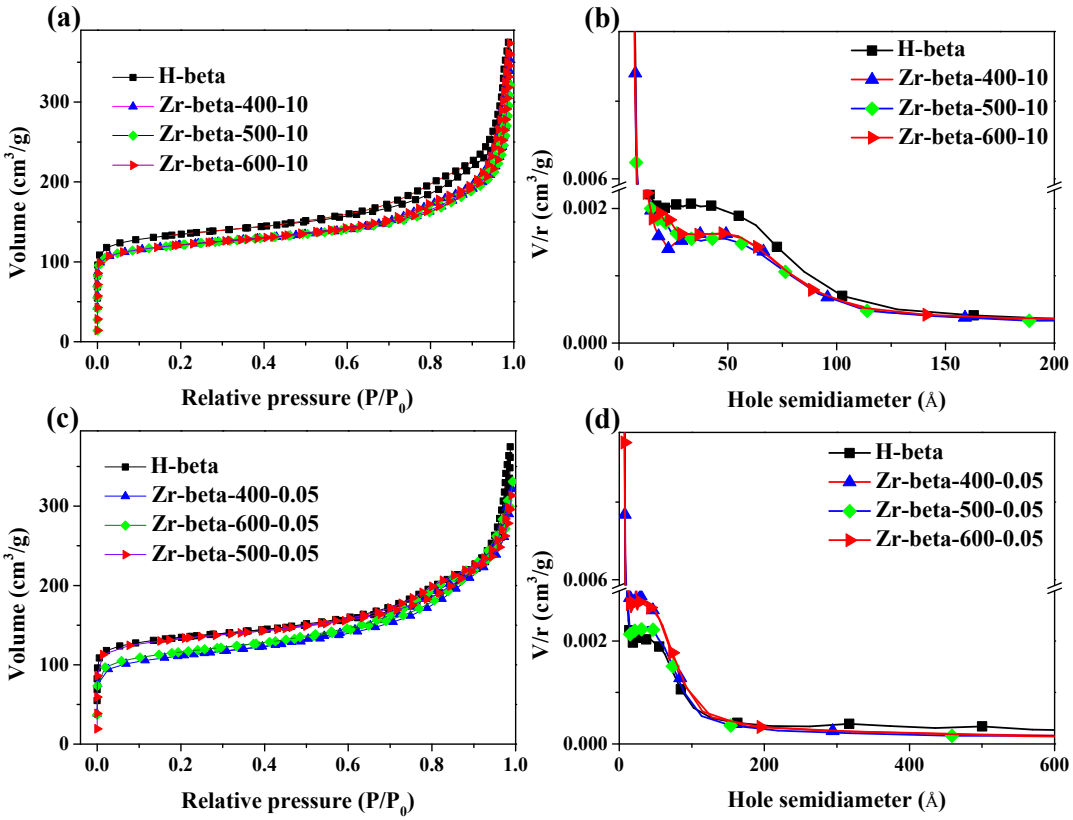

Fig. S5 N_2 adsorption–desorption isotherm of H-beta and Zr-beta zeolite catalysts.