SUPPORTING INFORMATION

High accessibility to active sites of hierarchical nanocrystalline Zr-β zeolite in ethanol-acetaldehyde conversion to 1,3-butadiene

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Supplemental Data and Figures

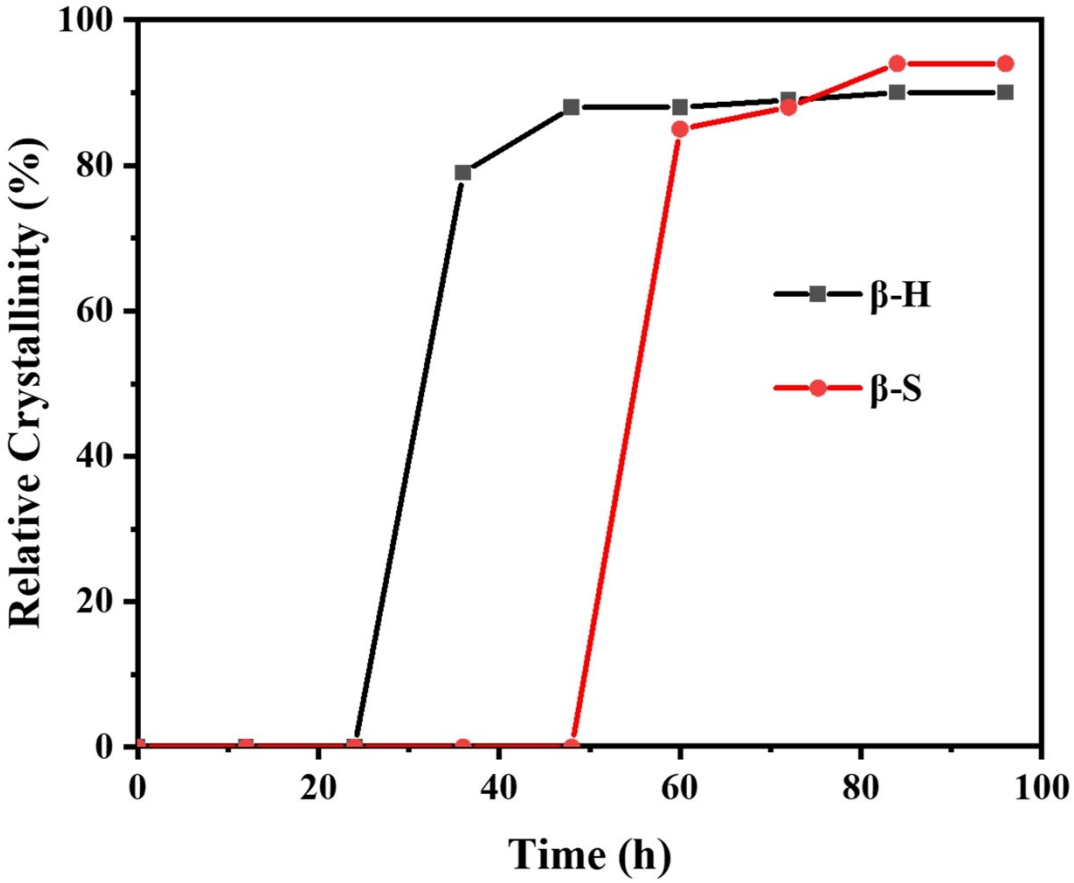

Fig. S1. The crystallization curves of β-S and β-H zeolites. Relative crystallinity is determined by (302) plane diffraction peak in XRD.

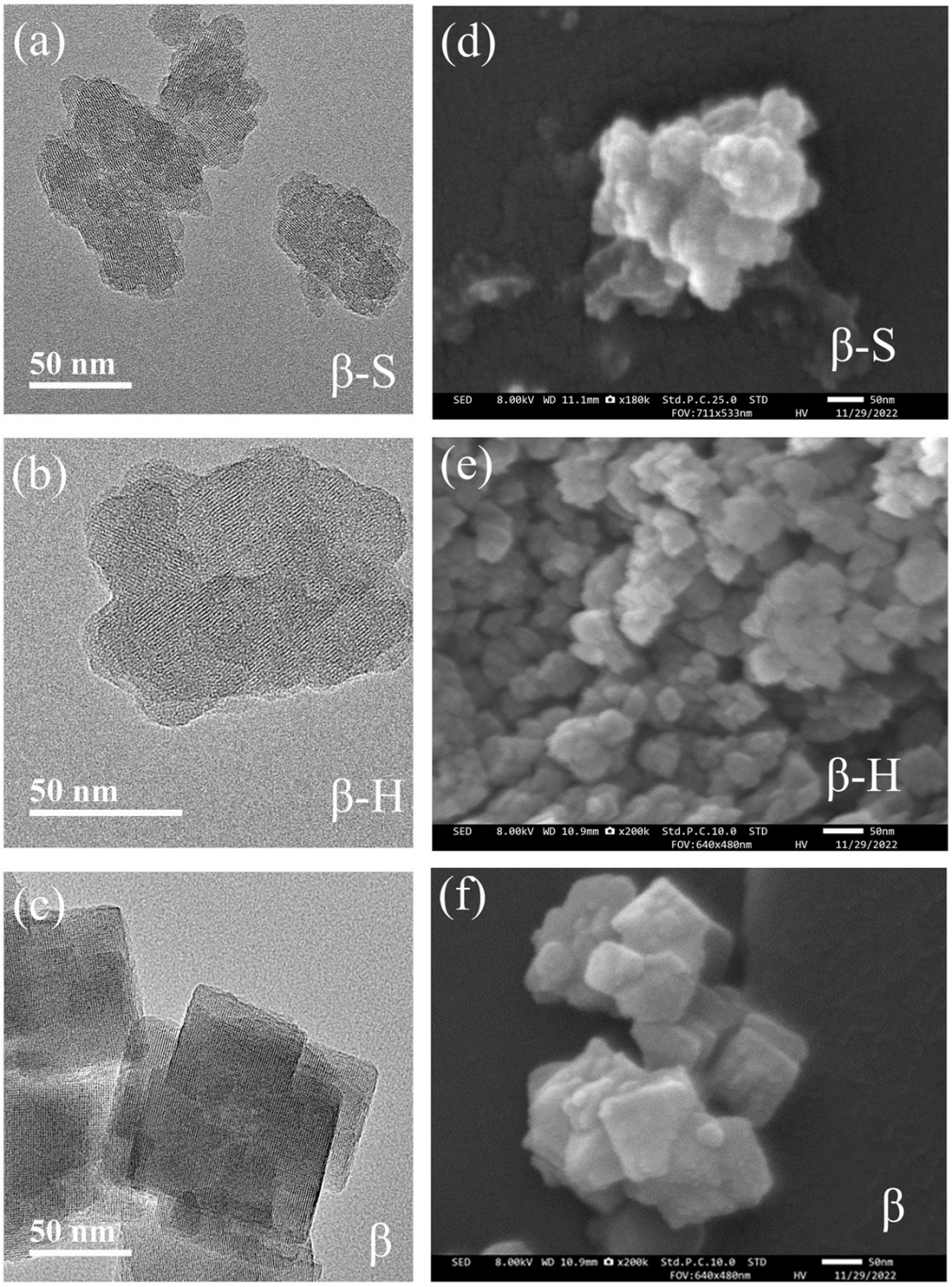

Fig. S2. TEM (a-c) and SEM (d-f) images of β-S, β-H and β zeolites.

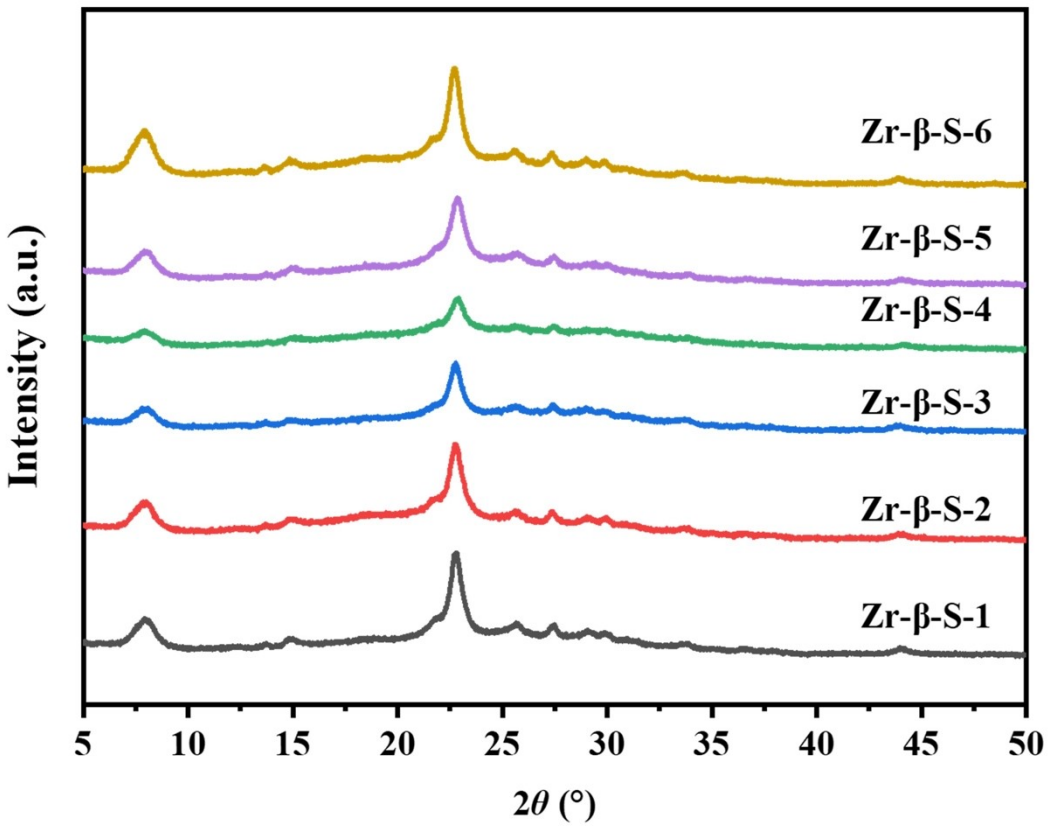

Fig. S3. XRD patterns of series catalysts Zr-β-S-1 to Zr-β-S-6. The diffraction peaks at 2θ = ~8.0° and 22.4° represent (101) and (302) crystal planes of β zeolite, respectively.

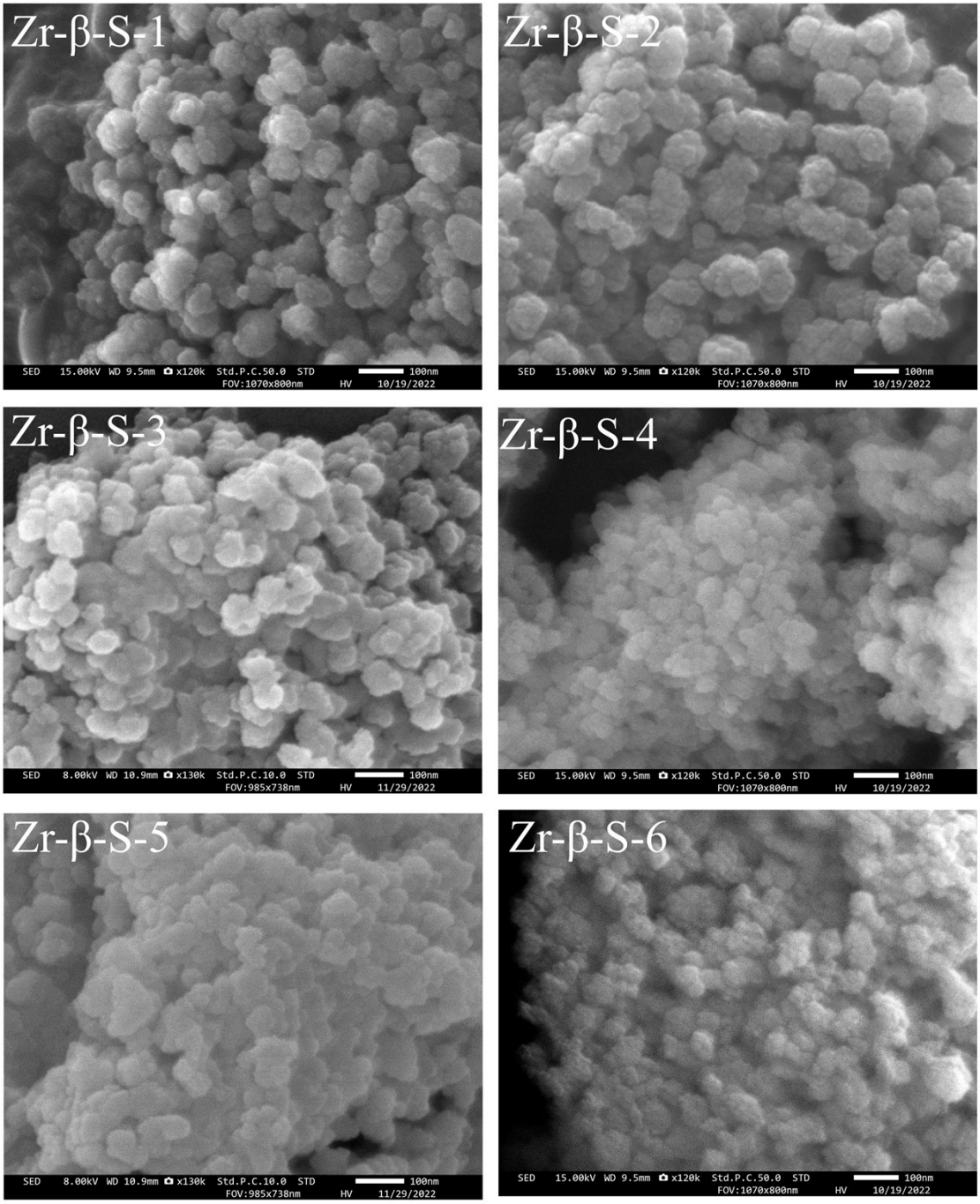

Fig. S4. SEM images of series catalysts β-S-1 to β-S-6.

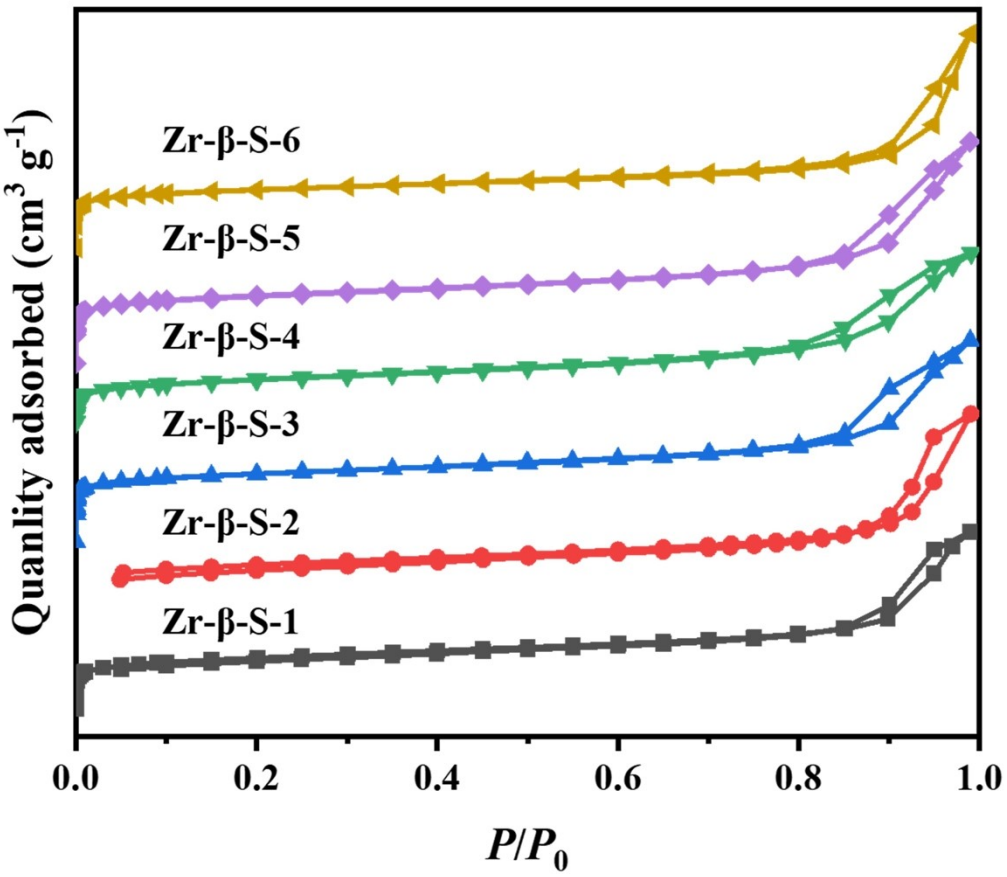

Fig. S5. N_2 absorption-desorption isotherms of series catalysts β-S-1 to β-S-6.

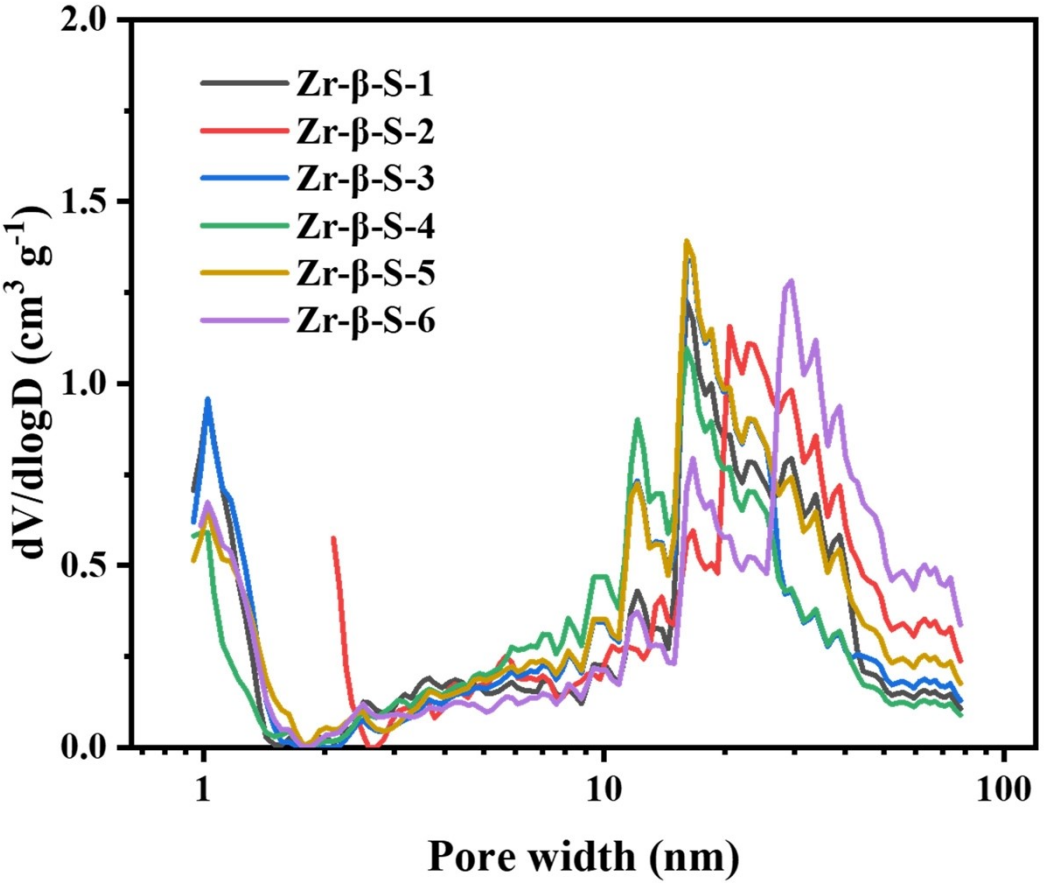

Fig. S6. Pore size distributions of series catalysts Zr-β-S-1 to Zr-β-S-6 according to the DFT method on the adsorption branch.

Table S1. The textural properties and catalytic activities for ethanol to butadiene of series Zr-β-S catalysts.

Porosity	Sample	S_{BET} [a] ($m^2 g^{-1}$)	V_{Total} [b] ($cm^3 g^{-1}$)	V_{Micro} [c] ($cm^3 g^{-1}$)	V_{Meso} [d] ($cm^3 g^{-1}$)	V_{Micro}/V_{Total}	Con. [e] (%)	Sel. [e] (%)							
								Butadiene	Ethylene	Ether	Propylene	Butene	Ethyl acetate	Croton-aldehyde	Others
Micropores	Zr-β	643	0.729	0.196	0.533	0.306	26.1	62.8	2.4	1.3	1.3	1.4	4.9	12.3	13.7
	Zr-β-S-1	654	0.753	0.211	0.542	0.280	48.6	65.1	1.5	0.7	1.8	2.0	4.6	9.8	14.6
	Zr-β-S-2	593	0.867	0.221	0.646	0.255	49.6	66.3	1.8	1.2	1.8	2.7	3.4	6.4	16.3
	Zr-β-S-3	631	0.771	0.190	0.581	0.246	53.0	69.3	2.0	1.1	2.0	2.2	5.6	6.6	11.2
Hierarchies	Zr-β-S-4	586	0.730	0.168	0.562	0.230	48.1	70.3	2.2	1.0	2.2	1.7	4.5	7.3	10.8
	Zr-β-S	712	0.979	0.216	0.763	0.221	55.1	73.5	2.1	1.3	2.2	2.2	3.0	5.5	10.2
	Zr-β-S-5	621	0.848	0.182	0.666	0.215	46.3	69.5	3.1	1.9	2.1	2.6	5.4	5.1	10.3
	Zr-β-S-6	537	0.819	0.171	0.648	0.209	50.6	67.2	2.4	1.0	1.9	2.4	4.5	7.4	13.2

[a] Specific BET surface areas obtained from N_2 adsorption branch.

[b] Total pore volume calculated from the N_2 quality adsorbed at $P/P_0 = 0.97$.

[c] Micropore volume calculated by t-plot method.

[d] Mesopore volume calculated from the difference between V_{Total} and V_{Micro}.

[e] Reaction conditions: 598 K, WHSV = 1.04 h^{-1}, TOS = 6 h.