Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Zr-incorporated SBA-15 for conversion of ethanol-acetaldehyde mixture to butadiene

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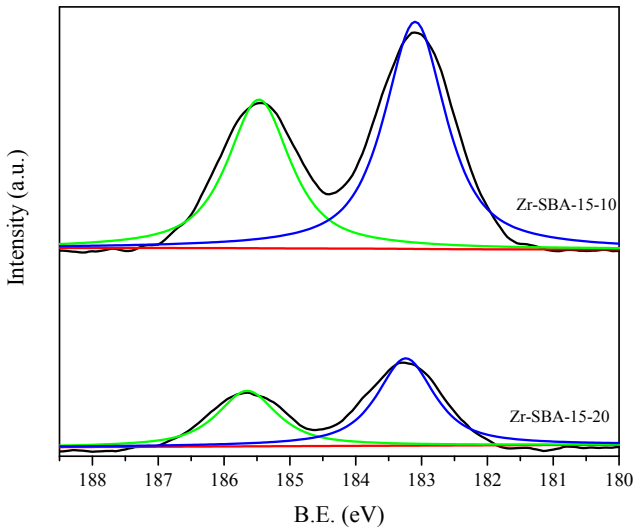

Figure S1. Zr 3d XPS spectra of Zr-SBA-15-10 and Zr-SBA-15-20.

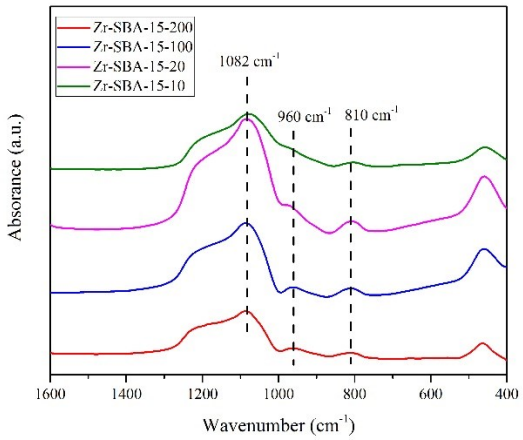

Figure S2. FT-IR spectra in the skeletal region of Zr-SBA-15 with different Si/Zr ratio .

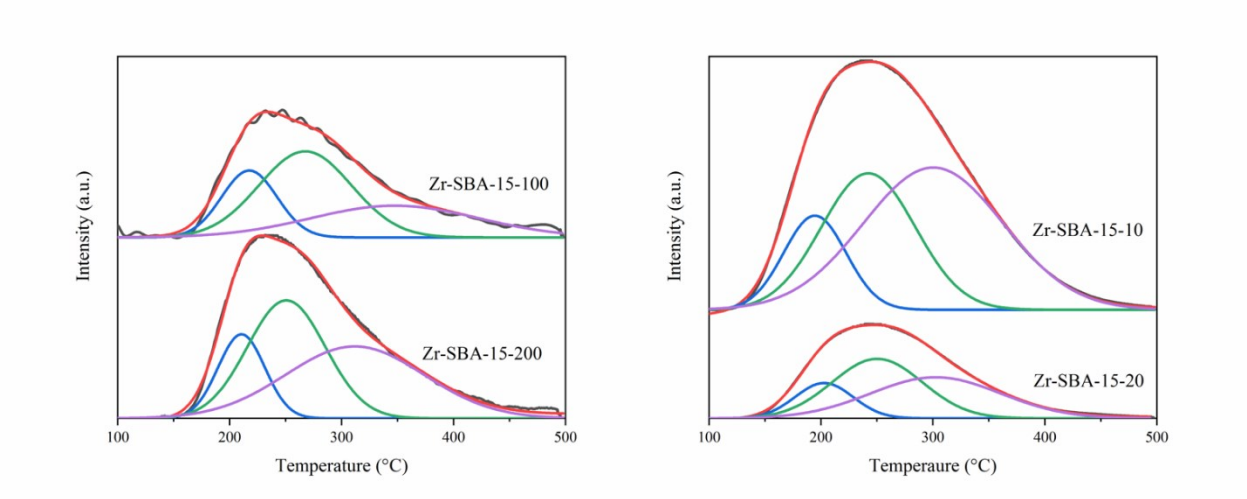

Figure S3. Deconvoluted NH_3-TPD profiles of Zr-SBA-15.

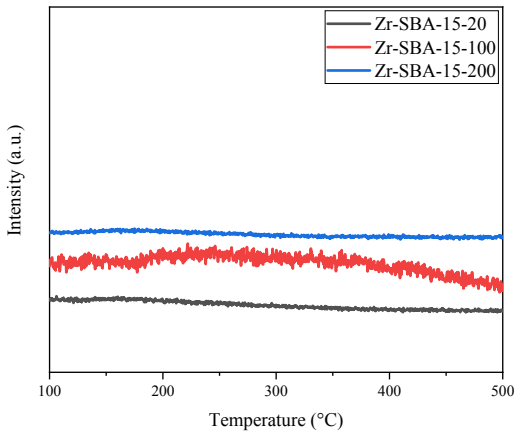

Figure S4. CO_2-TPD profiles of Zr-SBA-15.

Table S1. Catalytic performance of Zr-SBA-15. Reaction temperature 350 °C, WHSV 1.6 h^{-1}, EtOH/AcH molar ratio 3.0.

Sample	EtOH/AcH Conversion(%)	EtOH Conversion	AcH Conversion	Carbon Selectivity(mol %)								BD Yield(%)
				Butadiene	ethylene	Diethyl ether	Propylene	Butylene isomers	Ethyl acetate	crotonal-dehyde	Others	
Zr-SBA-15-200	13.4	16.0	5.9	51.6	22.2	7.9	1.9	3.5	2.0	4.3	6.6	6.9
Zr-SBA-15-100	15.4	18.3	7.9	47.3	23.6	16.0	1.6	3.3	1.6	2.9	3.7	7.3
Zr-SBA-15-20	61.9	65.3	56.2	44.0	31.9	7.6	2.2	7.1	1.0	0.8	5.4	27.2
Zr-SBA-15-10	69.0	70.8	63.6	29.7	31.7	9.7	2.3	10.4	3.7	0.3	12.2	20.5

Table S2a. Effect of temperature on the catalytic performance of Zr-SBA-15-20. WHSV 1.6 h^{-1}, EtOH/AcH molar molar ratio 3.0.

Reaction Temp. (℃)	EtOH/AcH Conversion	EtOH Conversion	AcH Conversion	Carbon Selectivity(mol %)							
				Butadiene	ethylene	Diethyl ether	Propylene	Butylene isomers	Ethyl acetate	crotonal-dehyde	Others
350	61.9	65.3	56.2	44.0	31.9	7.6	2.2	7.1	1.0	0.8	5.4
325	39.1	39.9	36.6	51.6	24.5	8	2	6.7	1.8	0.6	4.8

300	31.3	30.4	33.7	58.4	16.1	11.6	1.6	5.4	2.5	0.8	3.6
275	19.2	18.7	20.9	68.9	6.5	9.3	1.1	3.6	3.5	2.3	4.8

Table S2b. Effect of EtOH/AcH ratio on the catalytic performance of Zr-SBA-15-20. Reaction temperature 275 °C, WHSV 1.6 h^{-1}.

EtOH/AcH Molar Ratio	EtOH/AcH Conversion	EtOH Conversion	AcH Conversion	Carbon Selectivity(mol %)							
				Butadiene	ethylene	Diethyl ether	Propylene	Butylene isomers	Ethyl acetate	crotonal-dehyde	Others
1.2	20.3	17.7	23.4	69.2	2.8	2.8	1.2	2.5	3.9	13.0	3.4
2	16.5	17.3	14.7	71.3	3.9	4.0	1.2	2.8	3.9	6.6	5.4
3	19.2	18.7	20.9	68.9	6.5	9.3	1.1	3.6	3.5	4.8	4.4

Table S2c. Effect of WHSV on the catalytic performance of Zr-SBA-15-20. Reaction temperature 275 °C, EtOH/AcH molar ratio 2.0.

WHSV (h^{-1})	EtOH/AcH Conversion	EtOH Conversion	AcH Conversion	Carbon Selectivity(mol %)							
				Butadiene	ethylene	Diethyl ether	Propylene	Butylene isomers	Ethyl acetate	crotonal-dehyde	Others
0.32	42.8	37.8	52.7	70.6	9.9	4.1	1.8	4.5	1.7	1.1	6.4
0.64	33.4	28.4	43.6	70.7	9.1	4	1.6	4.2	2.8	1.7	5.9
0.96	28.3	25.5	33.9	74.0	6.4	3.8	1.5	3.2	2.9	2.6	5.6
1.28	24	21.1	30.0	73.8	5.4	3.4	1.4	2.3	3.1	3.9	6.7
1.6	18.3	15.6	23.7	72.0	4.7	3.4	1.3	1.7	3.6	5.8	7.5

Table S3. Effect of catalyst preparation method on the catalytic performance. Reaction temperature 275 °C, EtOH/AcH molar ratio 2.0, WHSV 0.96 h^{-1}.

Catalyst	EtOH/AcH Conversion	Carbon Selectivity(mol %)							
		Butadiene	ethylene	Diethyl ether	Propylene	Butylene isomers	Ethyl acetate	crotonal-dehyde	Others

Zr-SBA-15-20	28.3	74.0	6.4	3.8	1.5	3.2	2.9	2.6	5.6
ZrO_2/SBA-15-M	9.0	46.2	5.3	14.8	0.6	0.7	4.5	14.8	13.1