

## Supplementary Information

Selectively Direct Conversion of Aqueous Ethanol into Butadiene via Rational

Design of Multifunctional Catalysts

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## 1. Catalyst preparation

### 1.1. Materials

Triblock copolymer Pluronic 123 (P123, Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol); EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was purchased from the Sigma-Aldrich Co., LLC. Tetraethyl orthosilicate (TEOS, 98 %) was obtained from the Kanto Chemical Co., Inc. Hydrochloric acid (HCl, 35 %), cyclohexane (99.0 %), n-butanol (99.0 %), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0 %), and zirconyl nitrate dihydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, 97.0 %) were purchased from the Wako Pure Chemical Corporation.

### 1.2. Supports synthesis

MCF was synthesized according to a literature method.<sup>[1]</sup> Typically, Triblock copolymer Pluronic P123 of 2 g was dissolved in HCl solution (2.0 mol·L<sup>-1</sup>) of 70 mL under stirring for 2 h. After the P123 was completely dissolved under stirring, the cyclohexane of 2.4 g was added into mixture stirring 1 h, and then TEOS of 4.2 g was added to the homogeneous solution. This gel mixture was continuously stirred at 35 °C for 24 h and finally crystallized in a Teflon-lined autoclave at 100 °C for 24 h. After crystallization the solid product was centrifuged, washed with deionized water, dried at 60 °C overnight, and calcined at 550 °C in the air for 24 h to remove the organic template to obtain MCF support.

SBA-15 was prepared by hydrothermal synthesis, as reported by Choi et al.<sup>[2]</sup> Typically, P123 of 2 g, deionized water of 15 g, and HCl solution (2 mol·L<sup>-1</sup>) of 60 g were mixed in a beaker under stirring until the P123 completely dissolved. Then, TEOS of 4.25 g was added into the mixture. The mixture was kept stirring at 500 rpm for 24 h and transferred into a Teflon-lined autoclave for hydrothermal synthesis at 100 °C for 24 h. Then, the solid product in the autoclave was centrifuged at 2500 rpm, washed with deionized water, and dried at 60 °C for 12 h. Finally, the SBA-15 support was obtained after calcination in air at 550 °C for 24 h.

KIT-6 was synthesized by referring to the previously reported method.<sup>[3]</sup> In brief, Triblock copolymer Pluronic P123 of 2.0 g was dissolved in H<sub>2</sub>O of 72 g and 36 % HCl solution of 3.84 g under stirring at 35 °C for 1 h, and then n-butanol of 2 g was added and stirred for 1 h. Subsequently, TEOS of 4.3 g was added to the solution. The resulting mixture was stirred vigorously for 24 h at 35 °C, and this solution was placed in a Teflon-lined stainless steel autoclave and hydrothermally treated at 100 °C for 24 h. After crystallization the solid product was centrifuged, filtered, washed with deionized water, and dried in air at 60 °C, and calcined in static air at 550 °C for 24 h to decompose the template and obtained a powder KIT-6 support.

### 1.3. Catalyst preparation

The various catalysts were synthesized by incipient impregnation. In a typical process, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O of 0.15 g and ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O of 0.33 g were dissolved into water of 20mL under stirring to obtain a solution. The above-mentioned supports of MCF, SBA-15, KIT-6, or Si-beta of 1.50 g were added into this solution under stirring for 6 h and then heated at 100 °C to remove the water. After the resultant solid was calcined at 500 °C in static air for 5 h with a temperature ramp of 2 °·min<sup>-1</sup>, the as-prepared samples were denoted as Zn<sub>0.02</sub>Zr<sub>0.05</sub>/MCF, Zn<sub>0.02</sub>Zr<sub>0.05</sub>/SBA-15, and Zn<sub>0.02</sub>Zr<sub>0.05</sub>/KIT-6 catalysts.

Zn<sub>0.02</sub>Zr<sub>0.05</sub>/Si-beta-di was prepared by the dry impregnation method. Si-beta powder of 1.0 g was finely ground with an appropriate amount of decomposable Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O and calcined at 500 °C in the air for 6 h. The final product was labeled as Zn<sub>0.02</sub>Zr<sub>0.05</sub>/Si-beta-di.

To investigate impregnation sequences, we reversed the order for impregnation of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O during the synthesis. Zn<sub>0.02</sub>/Zr<sub>0.05</sub>/Si-beta was prepared by two-step incipient impregnation. In brief, ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O of 0.13 g was dissolved into water of 20 mL under stirring to obtain a solution. The Si-beta of 1.50 g was added into this

solution under stirring for 6 h and then heated at 100 °C to remove the water. After the resultant solid was calcined at 500 °C in air for 5 h and obtained  $Zr_{0.05}/Si$ -beta sample. Then,  $Zn(NO_3)_2 \cdot 6H_2O$  of 0.15 g was dissolved into water of 20 mL under stirring to obtain a solution. The above-mentioned  $Zr_{0.05}/Si$ -beta was added into this solution under stirring and then heated at 100 °C to remove the water. After the resultant solid was calcined at 500 °C in the air for 5 h, and the resulting sample was denoted as  $Zn_{0.02}/Zr_{0.05}/Si$ -beta.

$Zr_{0.05}/Zn_{0.02}/Si$ -beta was also prepared by two-step incipient impregnation with the similar procedure and load amounts mentioned above in  $Zn_{0.02}/Zr_{0.05}/Si$ -beta catalyst, except for different impregnation sequences. The resulting sample was denoted as  $Zr_{0.05}/Zn_{0.02}/Si$ -beta.

## 2. Supplementary Figures and Tables

**Table S1.** Catalytic performance of various support catalysts in the direct AETB conversion.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /MCF	80.8	37.3	37.8	12.0	8.1	4.8	30.1
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /SBA-15	71.6	37.9	30.7	16.4	9.2	5.8	27.1
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /KIT-6	77.1	37.1	35.5	13.2	8.6	5.6	28.6
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /Si-beta	75.8	45.6	11.9	21.6	5.9	15.0	34.6

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.

**Table S2.** Effect of ethanol concentration on the catalytic performance of direct AETB conversion over  $Zn_{0.02}Zr_{0.05}/KIT-6$  catalyst.

Ethanol concentration	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	$C_2^=$	AcH	DEE	Others	
95 %	91.2	53.5	15.5	6.4	13.2	11.4	48.8
80 %	77.1	37.1	35.5	13.2	8.6	5.6	28.6

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD,  $C_2^=$ , AcH, and DEE, respectively.

**Table S3.** Catalytic performance of various synthesis methods in the direct AETB conversion.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /Si-beta	75.8	45.6	11.9	21.6	5.9	15.0	34.6
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /Si-beta-di	61.6	37.7	15.2	30.2	6.8	10.1	23.2
Zn <sub>0.02</sub> /Zr <sub>0.05</sub> /Si-beta	68.1	40.3	11.6	31.1	6.8	10.2	27.4
Zr <sub>0.05</sub> /Zn <sub>0.02</sub> /Si-beta	63.7	38.9	10.3	33.2	6.2	11.4	24.8

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.

**Table S4.** Catalytic performance of various Zn/Si molar ratio catalysts in the direct AETB reaction.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> <sup>=</sup>	AcH	DEE	Others	
Zn <sub>0.005</sub> Zr <sub>0.05</sub> /Si-beta	61.8	40.0	18.1	18.6	18.6	4.7	24.7
Zn <sub>0.01</sub> Zr <sub>0.05</sub> /Si-beta	72.8	42.3	15.4	20.1	11.7	10.5	30.8
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /Si-beta	75.8	45.6	11.9	21.6	5.9	15.0	34.6
Zn <sub>0.03</sub> Zr <sub>0.05</sub> /Si-beta	79.8	43.8	9.0	24.3	4.3	18.6	35.0
Zn <sub>0.04</sub> Zr <sub>0.05</sub> /Si-beta	82.6	40.7	7.5	26.2	3.2	22.4	33.6

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub><sup>=</sup>, AcH, and DEE, respectively.



**Table S5.** Catalytic performance of various Zr/Si molar ratio catalysts in the direct AETB reaction.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
Zn <sub>0.02</sub> Zr <sub>0.005</sub> /Si-beta	65.5	35.4	7.3	35.1	1.7	20.5	23.2
Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	70.7	48.1	9.8	23.2	2.1	16.8	34.0
Zn <sub>0.02</sub> Zr <sub>0.05</sub> /Si-beta	75.8	45.6	11.9	21.6	5.9	15.0	34.6
Zn <sub>0.02</sub> Zr <sub>0.08</sub> /Si-beta	77.4	37.8	18.2	20.1	9.1	14.8	29.3

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.

**Table S6.** Effect of various promoters on catalytic performance in the direct AETB reaction.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
Ga-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	98.1	5.5	65.6	9.4	0.0	19.5	5.4
Mg-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	49.2	35.4	17.8	26.0	15.4	5.4	17.5
In-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	53.3	38.2	6.2	41.6	7.6	6.4	20.4
Ce-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	79.6	52.9	8.1	20.0	2.6	16.4	42.1
La-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	76.1	58.3	6.6	18.2	2.7	14.2	44.4
Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	80.2	60.4	7.7	13.1	2.4	16.4	48.4

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.

**Table S7.** Comparison the catalytic performance of the catalyst with the same mole of Y and La promoter.

Catalysts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> <sup>=</sup>	AcH	DEE	Others	
3%La-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	76.1	58.3	6.6	18.2	2.7	14.2	44.4
1.9%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	78.1	59.2	7.8	14.5	2.4	16.1	46.2

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub><sup>=</sup>, AcH, and DEE, respectively.

**Table S8.** Comparison of the catalytic performance obtained in this work with reported literatures.<sup>a</sup>

Catalysts	WHSV (h <sup>-1</sup> )	Temp. (°C)	EtOH conv. (%)	BD sel. (%)	BD yield (%)	Ref.
ZnO-N/ZrO <sub>2</sub> -SiO <sub>2</sub>	2.6	375	50.4	56.9	28.7	4
ZnLa-ZrSiBEA	2.8	380	31.1	61.7	19.2	5
ZnO/MgO-SiO <sub>2</sub>	1.0	425	44.8	56.2	25.2	6
Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	1.0	350	80.2	60.4	48.4	This work

<sup>a</sup>80 % aqueous ethanol.

**Table S9.** Effect of the reaction temperature on catalytic performance for the direct AETB conversion over Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalyst.

Temperature (°C)	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> <sup>=</sup>	AcH	DEE	Others	
300	25.6	54.9	5.1	17.2	13.2	9.6	14.1
325	59.9	57.3	7.4	14.8	8.8	11.7	34.3
350	80.2	60.4	7.7	13.1	2.4	16.4	48.4
375	97.9	44.9	9.4	8.8	1.6	35.3	44.0
400	98.7	38.4	9.9	8.1	1.0	42.6	37.9

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub><sup>=</sup>, AcH, and DEE, respectively.

**Table S10.** Effect of the WHSV on catalytic performance for the direct AETB conversion over Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalyst.

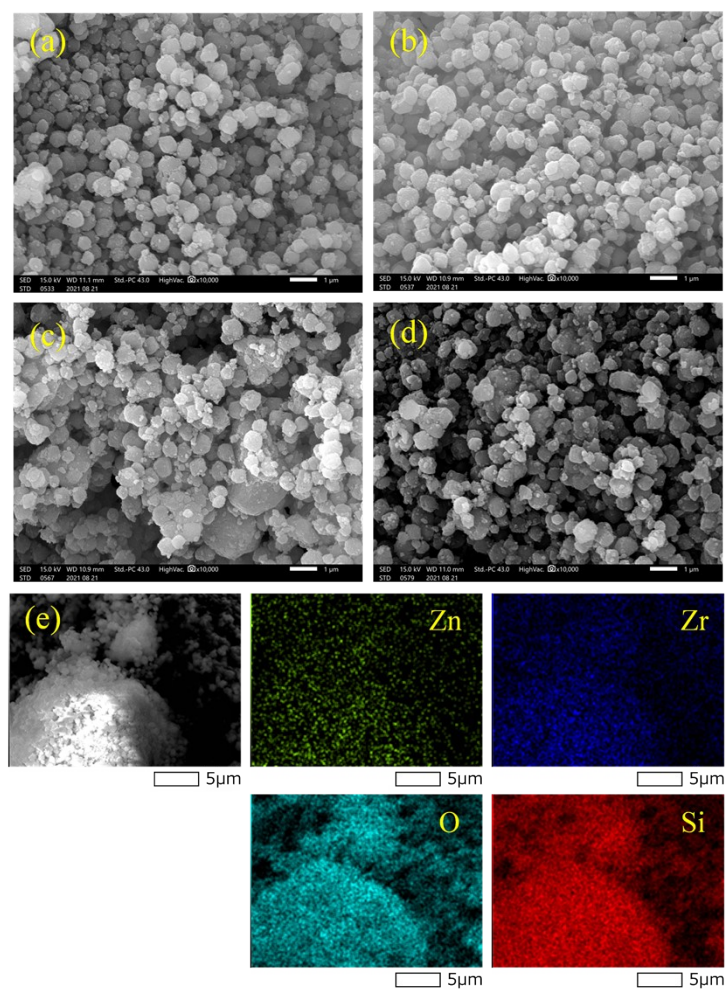
WHSV (h <sup>-1</sup> )	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
0.5	95.8	41.3	10.8	5.1	1.2	41.6	39.6
0.7	89.7	48.5	9.2	9.1	1.4	31.8	43.5
1.0	80.2	60.4	7.7	13.1	2.4	16.4	48.4
1.2	76.7	53.6	7.9	19.4	3.9	15.2	41.1
1.4	72.5	50.8	6.1	23.2	5.2	14.7	36.8
2.4	63.8	46.3	5.1	28.9	7.3	12.4	29.5

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, T = 350 °C, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.

**Table S11.** The elemental composition of the synthesized catalysts.

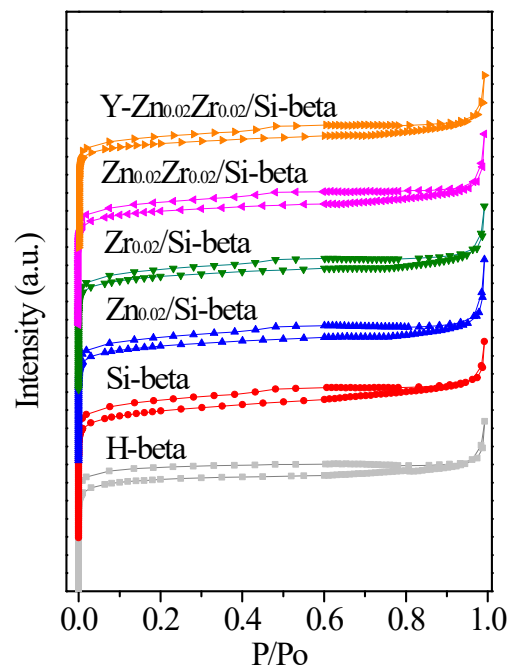
Sample	Experimental value (wt%) <sup>a</sup>				Theoretical value (wt%) <sup>b</sup>			
	Zn	Zr	Si	Y	Zn	Zr	Si	Y
Zn <sub>0.02</sub> /Si-beta	4.4	/	95.6	/	4.5	/	95.4	/
Zr <sub>0.02</sub> /Si-beta	/	6.0	94.0	/	/	6.3	93.7	/
Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	4.2	5.8	90.0	/	4.3	6.0	89.7	/
Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	4.1	5.7	87.2	3.0	4.0	5.5	87.1	3.4

<sup>a</sup>The elemental composition of these catalysts was obtained by EDX analysis; <sup>b</sup>The dosages of the elements were calculated according to the amount of raw materials in the catalyst preparation.

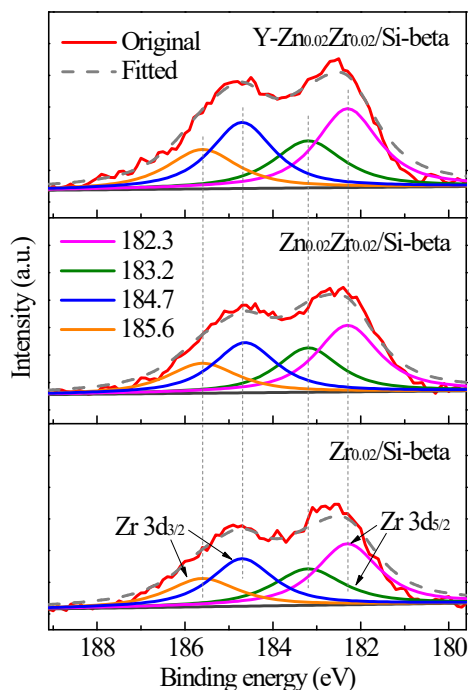


**Fig. S1.** SEM and EDX elemental mapping images of the synthesized catalysts. (a)  $Zn_{0.02}/Si$ -beta, (b)  $Zr_{0.02}/Si$ -beta, (c)  $Zn_{0.02}Zr_{0.02}/Si$ -beta, (d)  $Y-Zn_{0.02}Zr_{0.02}/Si$ -beta, and (e) EDX elemental mapping images of the  $Zn_{0.02}Zr_{0.02}/Si$ -beta catalyst.

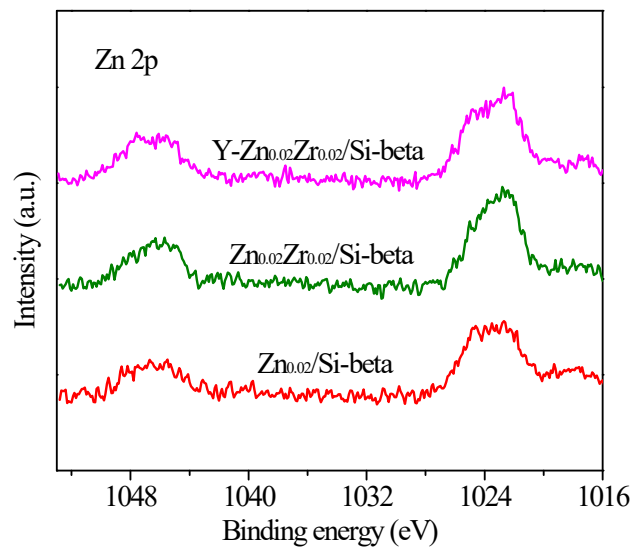




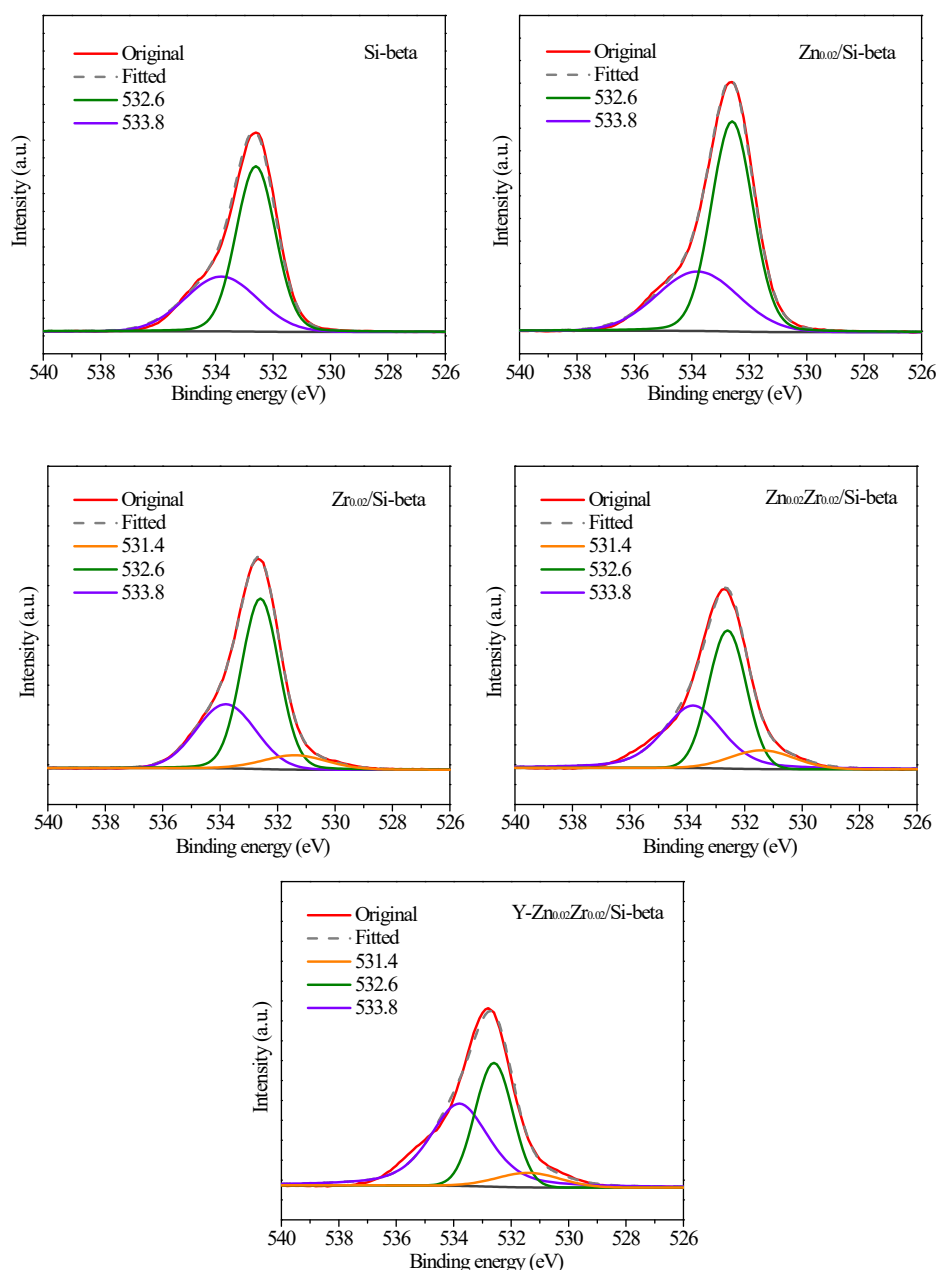
**Fig. S2.** Nitrogen adsorption and desorption isotherms of the H-beta, Si-beta, and synthesized catalysts.



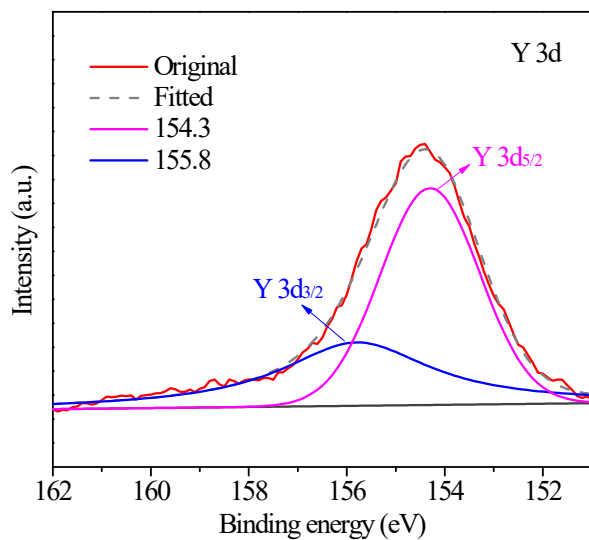
**Fig. S3.** Deconvolution of Zr 3d region for the  $\text{Zr}_{0.02}/\text{Si-beta}$ ,  $\text{Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$ , and  $\text{Y-Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$  catalysts. The peaks are fitted to two contributions from  $\text{ZrO}_2$  and  $\text{Zr-OH}$ . The Zr 3d doublet peaks from  $\text{ZrO}_2$  has binding energy at 184.7 and 182.3 eV with an energy separation of 2.4 eV, corresponding to contributions from Zr  $3d_{3/2}$  and Zr  $3d_{5/2}$ , respectively. Meanwhile, the area ratio of the two spin orbit peaks ( $\text{Zr}d_{3/2}$ -to- $\text{Zr}d_{5/2}$ ) is 2:3. The full width at half maximum (FWHM) is 1.7 eV for both peaks. The Zr 3d doublet peaks from  $\text{Zr-OH}$  has binding energy at 185.6 and 183.2 eV, which are assigned to contributions from Zr  $3d_{3/2}$  and Zr  $3d_{5/2}$ , respectively. Two spin orbit peaks are separated by an energy separation of 2.4 eV and the  $\text{Zr}d_{3/2}$ -to- $\text{Zr}d_{5/2}$  area ratio of 2:3. The FWHM is 1.9 eV for both peaks. These results are in agreement with the reported value in literatures.<sup>[7-9]</sup>



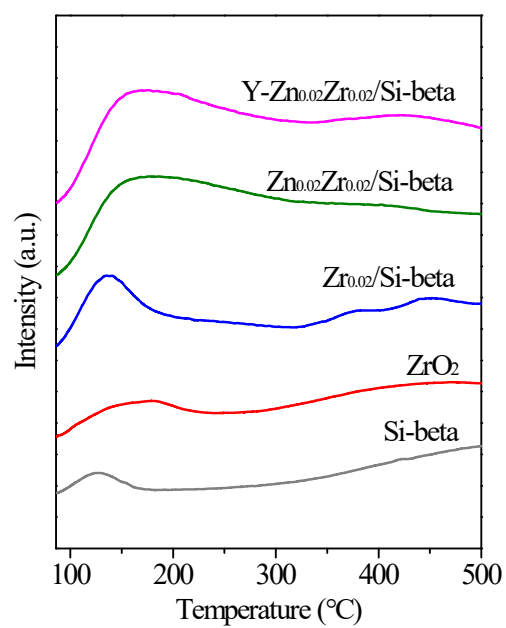
**Fig. S4.** Zn 2p region for the Zn<sub>0.02</sub>/Si-beta, Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, and Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalysts.



**Fig. S5.** Deconvolution of O 1s region for the Si-beta,  $\text{Zn}_{0.02}/\text{Si-beta}$ ,  $\text{Zr}_{0.02}/\text{Si-beta}$ ,  $\text{Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$ , and  $\text{Y-Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$  catalysts. Over Si-beta, Si-OH is located at 533.8 eV with FWHM of 3.0 eV, and Si-O-Si is centered at 532.6 eV with FWHM of 1.6 eV. Over  $\text{Zn}_{0.02}/\text{Si-beta}$ , the FWHM of the O 1s peaks at 533.8 and 532.6 eV are 3.3 and 1.7 eV, respectively. Meanwhile, the O 1s peaks at 533.8 and 532.6 eV in  $\text{Zr}_{0.02}/\text{Si-beta}$ ,  $\text{Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$ , and  $\text{Y-Zn}_{0.02}\text{Zr}_{0.02}/\text{Si-beta}$  catalysts have FWHM of 1.5 and 2.2 eV, and Zr-OH is found at 531.4 eV with FWHM of 2.6 eV. These are in agreement with the data reported in the literature.<sup>[9,10]</sup>



**Fig. S6.** Y 3d XPS region for the Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalysts. The Y 3d doublet peaks at 155.8 and 154.3 eV with an energy separation of 1.5 eV, which are attributed to the Y 3d<sub>3/2</sub> and Y 3d<sub>5/2</sub>, respectively. The spin-orbit doublet peaks were fitted with a fixed Yd<sub>3/2</sub>-to-Yd<sub>5/2</sub> area ratio of 2:3 and the FWHM of 3.5 and 2.4 eV, respectively. The results are consistent with the reported value in the literature.<sup>[11]</sup>

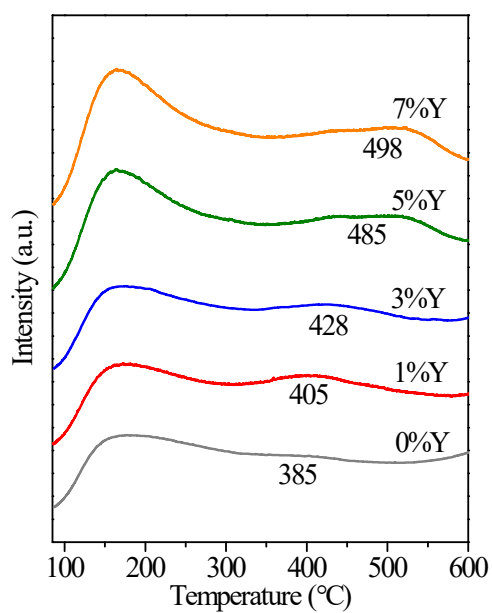


**Fig. S7.** NH<sub>3</sub>-TPD profiles of the Si-beta, ZrO<sub>2</sub>, Zr<sub>0.02</sub>/Si-beta, Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, and Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalysts.

**Table S12.** The catalytic performance of the direct AETB conversion over Y-supported Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalyst with different Y loading amounts.

Y amounts	EtOH conv. (%)	Selectivity (%)					BD yield (%)
		BD	C <sub>2</sub> =	AcH	DEE	Others	
0%	70.7	48.1	9.8	23.2	2.1	16.8	34.0
1%	73.6	52.1	8.1	20.0	2.4	17.4	38.3
3%	80.2	60.4	7.7	13.1	2.4	16.4	48.4
5%	86.3	53.3	7.5	10.4	2.5	26.3	46.0
7%	88.5	48.9	7.2	9.5	2.1	32.3	43.3

Reaction conditions: aqueous ethanol, catalyst = 0.2 g, WHSV = 1.0 h<sup>-1</sup>, and TOS = 5 h. The ethanol, butadiene, ethylene, acetaldehyde, and diethyl ether were abbreviated as EtOH, BD, C<sub>2</sub>=, AcH, and DEE, respectively.



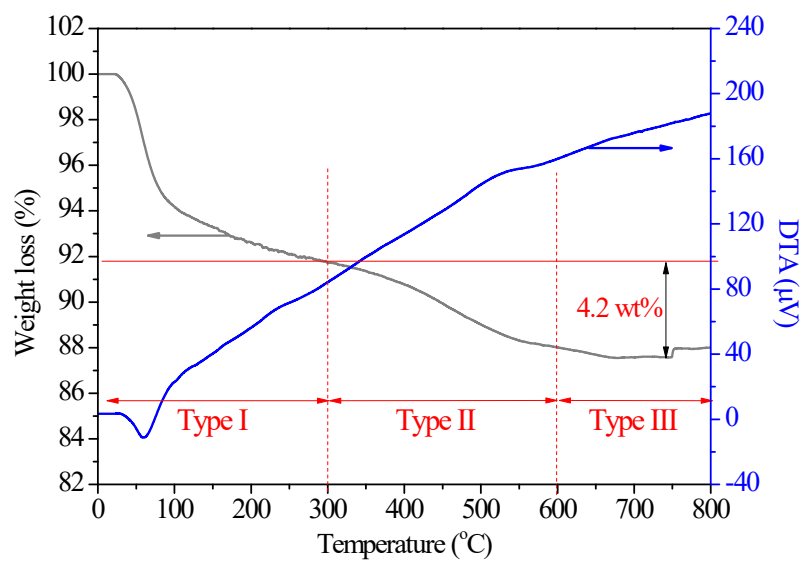
**Fig. S8.** NH<sub>3</sub>-TPD profiles of the Y-supported Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalysts with different Y loading amounts. (0%Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, 1%Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, 3%Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, 5%Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta, and 7%Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta).



**Table S13.** The acid amounts of the catalysts with different Y loading amounts.

Catalysts	Acid amounts (mmol·g <sup>-1</sup> ) <sup>a</sup>				
	Weak	Strong	Total	Strong /Total	Weak /Total
0%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	0.11	0.01	0.12	0.08	0.91
1%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	0.11	0.02	0.13	0.15	0.87
3%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	0.13	0.02	0.15	0.13	0.85
5%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	0.17	0.09	0.26	0.34	0.65
7%Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	0.19	0.13	0.32	0.40	0.59

<sup>a</sup>Acid amount was obtained via NH<sub>3</sub>-TPD.

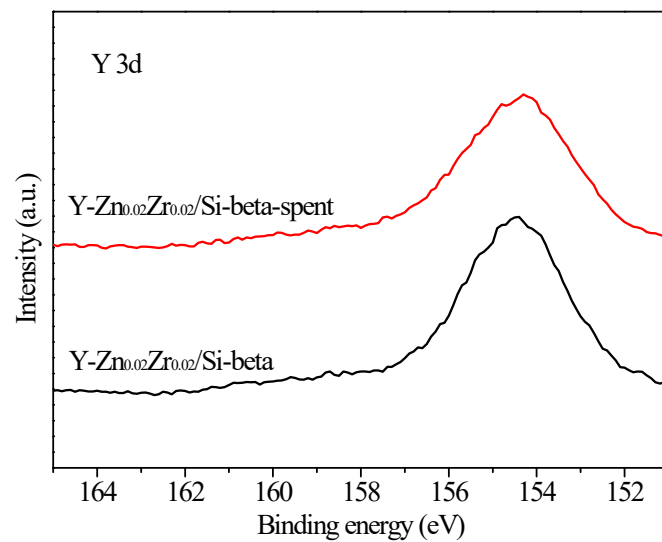


**Fig. S9.** TG analysis of the spent Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalyst.

**Table S14.** Textural properties of fresh and spent catalysts of Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta and Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta.

Samples	A <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> ) <sup>a</sup>	V <sub>micro</sub> (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>b</sup>	V <sub>meso</sub> (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>c</sup>	V <sub>total</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	D <sub>micro</sub> (nm) <sup>d</sup>	D <sub>meso</sub> (nm) <sup>e</sup>
Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta-fresh	479	0.19	0.38	0.57	0.65	3.16
Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta-spent	404	0.15	0.32	0.47	0.66	3.19
Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta-fresh	465	0.18	0.36	0.54	0.65	3.05
Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta-spent	353	0.12	0.29	0.41	0.66	3.15

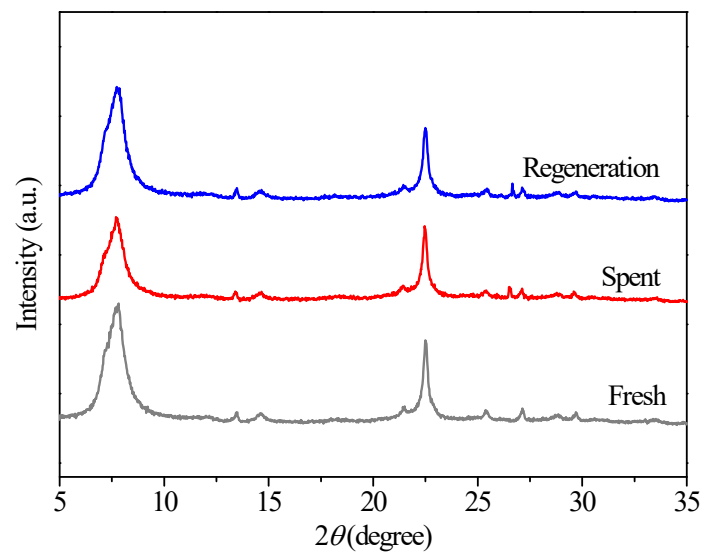
<sup>a</sup>BET surface area; <sup>b</sup>micropore volume calculated by t-plot method; <sup>c</sup>mesopore volume calculated by BJH method; <sup>d</sup>average diameter for micropores evaluated by HK method; <sup>e</sup>average diameter of mesopores evaluated by the BJH method.



**Fig. S10.** Y 3d region for the Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta and Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta-spent catalysts.



**Fig. S11.** Appearance images of the spent and regenerated Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta catalyst.



**Fig. S12.** XRD pattern of the fresh, spent, and regeneration catalysts of Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta.

**Table S15.** Textural properties of fresh, spent, and regeneration catalysts of Y-Zn<sub>0.02</sub>Zr<sub>0.02</sub>/Si-beta.

Y-Zn <sub>0.02</sub> Zr <sub>0.02</sub> /Si-beta	A <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> ) <sup>a</sup>	V <sub>micro</sub> (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>b</sup>	V <sub>meso</sub> (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>c</sup>	V <sub>total</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )
Fresh	465	0.18	0.36	0.54
Spent	353	0.12	0.29	0.41
Regeneration	461	0.16	0.35	0.51

<sup>a</sup>BET surface area; <sup>b</sup>micropore volume calculated by t-plot method; <sup>c</sup>mesopore volume calculated by BJH method.

## References

- [1] Y. Han, S. S. Lee and J. Y. Ying, *Chem. Mater.* 2007, **19**, 2292-2298.
- [2] M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chem. Commun.* 2003, 1340-1341.
- [3] K. Soni, B. S. Rana, A. K. Sinha, A. Bhaumik, M. Nandi, M. Kumar and G. M. Dhar, *Appl. Catal. B: Environ.* 2009, **90**, 55-63.
- [4] O. V. Larina, P. I. Kyriienko, D. Y. Balakin, M. Vorokhta, I. Khalakhan, Y. M. Nychiporuk, V. Matolín, S. O. Solovieva and S. M. Orlyk, *Catal. Sci. Technol.* 2019, **9**, 3964-3978.
- [5] O. V. Larina, N. D. Shcherban, P. I. Kyriienko, I. M. Remezovskyi, P. S. Yaremov, I. Khalakhan, G. Mali, S. O. Solviev, S. M. Orlyk and S. Dzwigaj, *ACS Sustainable Chem. Eng.* 2020, **8**, 16600-16611.
- [6] P. I. Kyriienko, O. V. Larina, D. Y. Balakin, A. O. Stetsuk, Y. M. Nychiporuk, S. O. Soloviev and S. M. Orlyk, *Appl. Catal. A: Gen.* 2021, **616**, 118081.
- [7] V. Maurice, M. Salmeron and G. A. Somojai, *Surf. Sci.* 1990, **237**, 116.
- [8] Y. M. Wang, Y. S. Li, P. C. Wong and K. A. R. Michell, *Appl. Surf. Sci.* 1993, **72**, 237.
- [9] M. A. Gondal, T. A. Fasasi, Umair Baig and A. Mekki, *J. Nanosci. Nanotechnol.* 2018, **18**, 4030-4039.
- [10] S. Z. Khan, Y. D. Yuan, A. Abdolvand, M. Schmidt, P. Crouse and L. Li, *Journal of Nanopart. Res.* 2008, **11**, 1421.
- [11] P. A. W. van der Heide, *J. Electron Spectrosc.* 2006, **151**, 79-91.