Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

The effect of ZnO on acid-base properties and catalytic performance of ZnO/ZrO_2-SiO_2 catalysts in 1,3-butadiene production from ethanol-water mixture

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Experimental Section

1. Acid-base properties measurements

Desorption of NH_3 and CO_2 from the samples were studied by one-pass temperature-programmed desorption (TPD) with mass-spectrometry control (a chamber pressure of 10-7 Pa, a sample weight of 20 mg, a heating rate of 0.5 K/sec, a short distance (0.5 cm) between the sample and a MS detector). Time-of-flight mass-spectrometer MSX-3PC (Electron, Ukraine) with sensitivity 2.2×10^{-5} A $Torr^{-1}$ (an accelerating voltage of 0.5 kV, a pulse frequency of 3 kHz) was used. Application of this TPD-technique was described in detail in the ref.[1]

Before adsorption of NH_3 and CO_2, the samples were heated in a constant Ar flow (30 ml/min) at 773 K for 2 hours, then cooled in the Ar flow to room temperature. Adsorption of NH_3 and CO_2 was carried out using a gaseous solution of NH_3 and CO_2 in Ar (at flow rate of 30 ml/min) for 1 hour.

Analysis of acid-base properties of ZnO/ZrO_2-SiO_2 catalysts samples was also performed by adsorption of pyridine and deuterated chloroform ($CDCl_3$) followed by infrared spectroscopy. Fourier Transform Infrared (FTIR) measurements were performed on a Spectrum One FTIR spectrometer (Perkin Elmer, USA). Typically, 24 scans with a resolution of 1 cm^{-1} were codded to give one spectrum. The catalyst sample was pressed at ~ 2 $ton\cdot cm^{-2}$ into thin wafers of ca. 12 $mg\cdot cm^{-2}$ and placed inside the IR cell.

Before adsorption of pyridine, the cell was connected to a vacuum-adsorption apparatus allowing a residual pressure below 10^{-3} Pa. The samples were outgassed (10^{-3} Pa) at 693 K for 1 h. Then, pyridine was adsorbed at 423 K for 15 minutes. The spectra were recorded under ambient conditions after pyridine desorption at 423 K and 523 K.

Before adsorption of $CDCl_3$, the catalyst-containing IR cell was heated in a constant Ar flow (~60 $mL\cdot min^{-1}$). Once 773 K was reached, the treatment lasted 1 h. Then, the sample was cooled to 373 K, and a baseline was recorded. To carry the probe molecule to the IR cell, Ar was sent through the $CDCl_3$-containing gas bubbler for 30 min. After that, the mixture passed through the IR cell for 30 min to avoid physical adsorption of $CDCl_3$, and the spectra of adsorbed $CDCl_3$ were recorded. All measured spectra were recalculated to a “normalized” wafer weight.

2. Catalytic properties measurements and calculations

Catalytic activity tests were carried out in a fixed-bed flow quartz reactor with inner diameter of 4 mm at 598-673 K and atmospheric pressure. Samples with grains of 0.25–0.5 mm were loaded into the reactor. Ethanol-water mixture feed (96% EtOH – 4% H_2O; 80% EtOH – 20% H_2O; 50% EtOH – 50% H_2O) was introduced to the evaporator via a syringe infusion pump and the argon with flow of 7 $mL \cdot min^{-1}$ carried the feed into the reactor. Reaction was carried out at WHSV of 0.65–2.6 $g_{EtOH} \cdot g_{cat}^{-1} \cdot h^{-1}$. Before the reaction, the catalysts were annealed at 773 K under flowing argon for 1 h. The reagents and reaction products were analyzed on a gas chromatograph (KristalLyuks 4000M, MetaChrome) equipped with a TCD detector and a packed column (10 % $NiSO_4$ on coal, 3 m × 3 mm) for CO and CO_2, and a FID detector and a capillary column (HP-FFAP, 50 m × 0.32 mm) for organic compounds.

Catalytic properties of the catalysts were characterized by EtOH conversion (X), selectivity to products (S_i), BD yield (Y_{BD}), BD productivity (P_{BD}) and initial reaction rate of BD formation (r_{BD}). These indices were calculated using following formulas:

$$X = \frac{n^0_{EtOH} - n_{EtOH}}{n^0_{EtOH}} \cdot 100\%,$$

$$S_i = \frac{n_i}{(n^0_{EtOH} - n_{EtOH})} \cdot 100\%,$$

$$Y_i = \frac{X \cdot S_i}{100\%},$$

$$Pi = \frac{Y_i \cdot WHSV \cdot k}{100\%},$$

$$r_{BD} = \frac{Y^{15}_{BD} \cdot WHSV \cdot k}{54 \cdot 100\%} * 10^3,$$

where $\mathbf{n^0_{EtOH}}$ is the initial amount of C moles of EtOH; $\mathbf{n_{EtOH}}$ and $\mathbf{n_i}$ are the amount of C moles of unreacted EtOH and product **i** in the stream of the reaction products, respectively; ***k*** is the maximum possible amount of the same product (g) that can be produced from 1 g of EtOH, for BD ***k***=0.587. Y_{BD}^{15} – BD yield calculated at 15 % EtOH conversion.

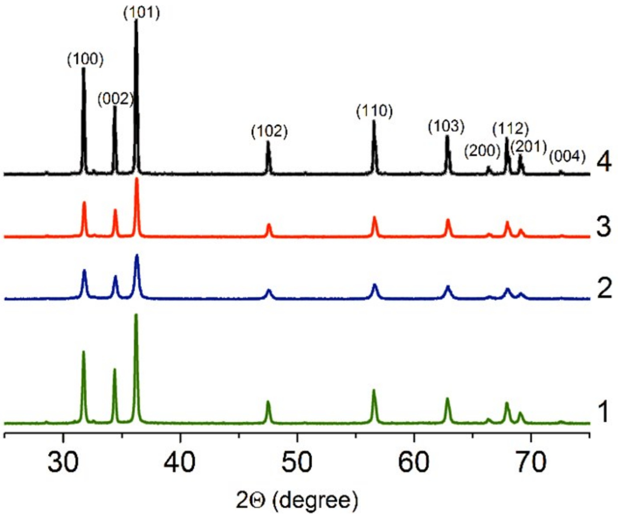
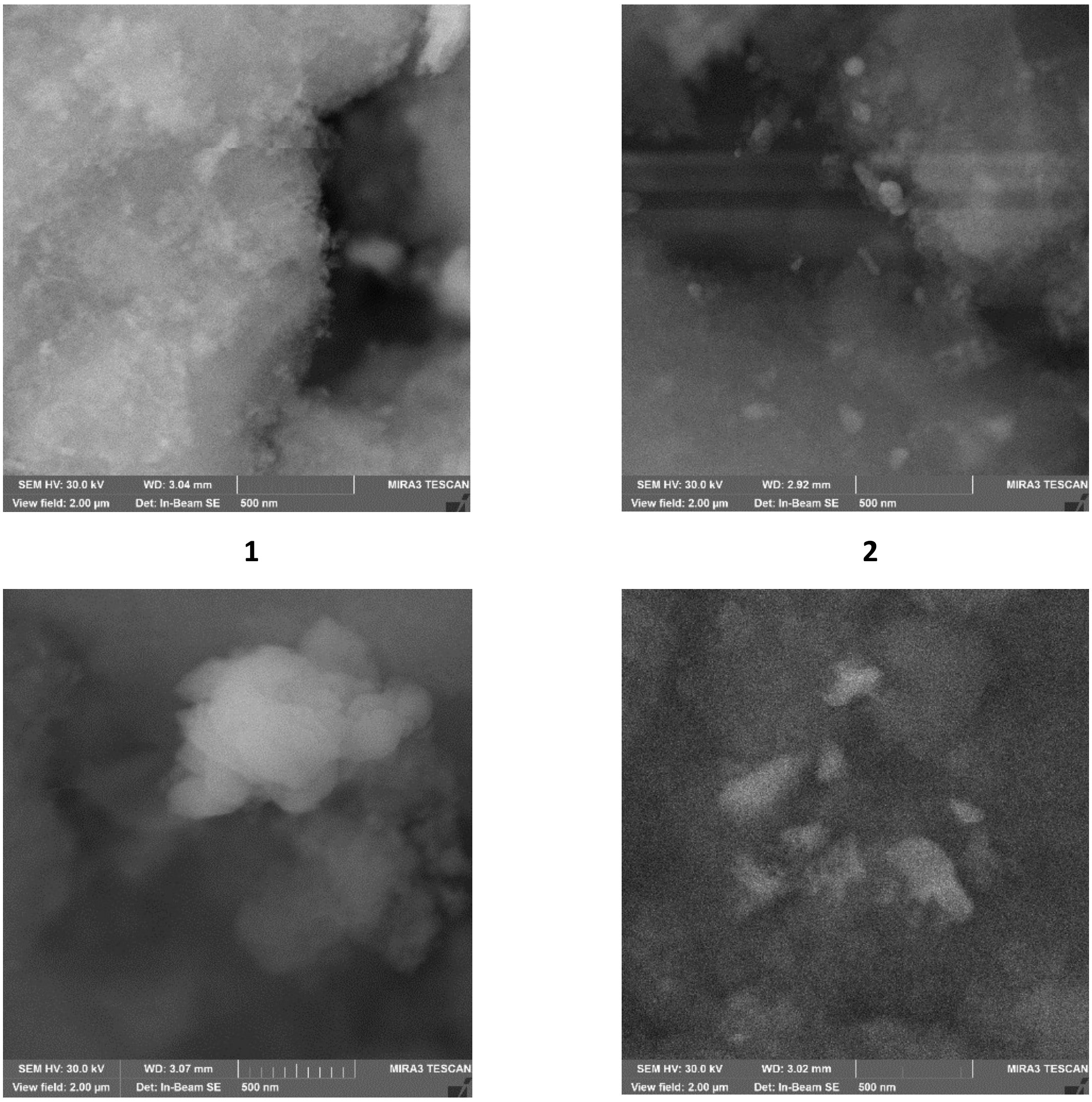


Fig. S1. XRD patterns of zinc oxide samples: 1 – ZnO-I, 2 – ZnO-N, 3 – ZnO-M, 4 – ZnO-C.



1 **2**

3 **4**

Fig. S2. FESEM images of the samples: 1 – ZnO-I/ZrO_2-SiO_2, 2 – ZnO-N/ZrO_2-SiO_2, 3 – ZnO-M/ZrO_2-SiO_2, 4 – ZnO-C/ZrO_2-SiO_2.

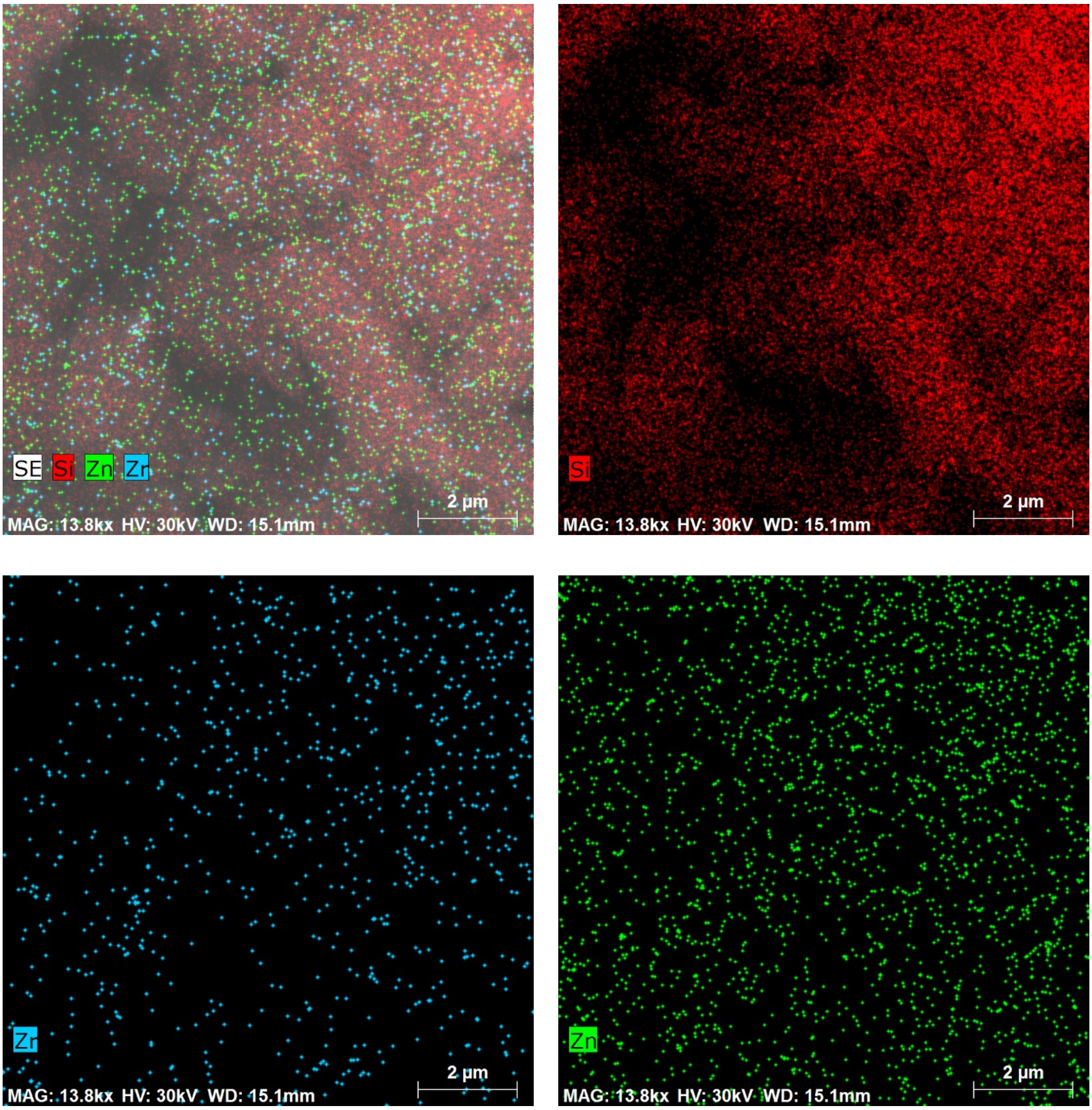


Fig. S3-A. EDX mapping for Si, Zr and Zn atoms of ZnO-I/ZrO_2-SiO_2 sample.

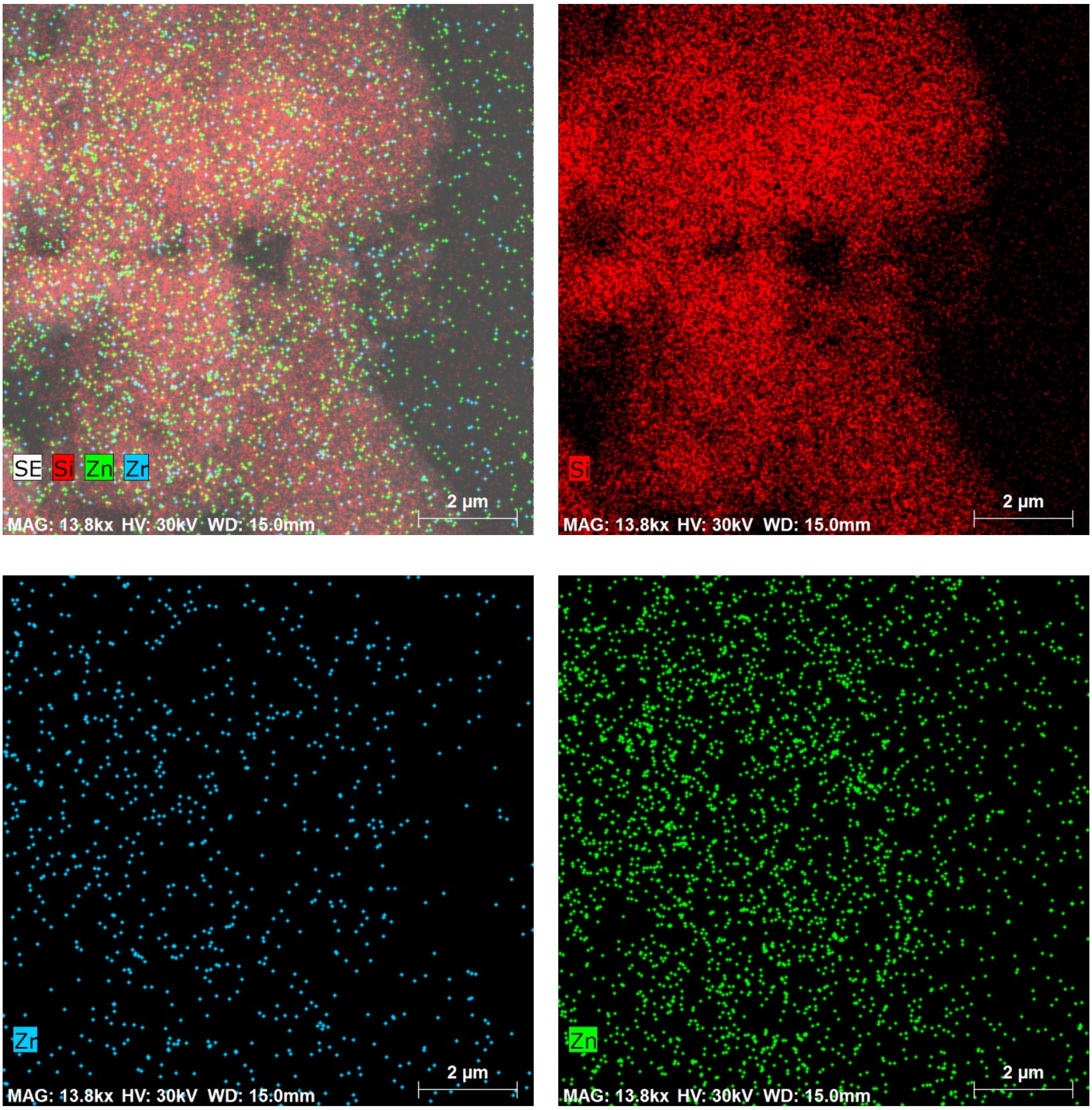


Figure S3-B. EDX mapping for Si, Zr and Zn atoms of ZnO-N/ZrO_2-SiO_2 sample.

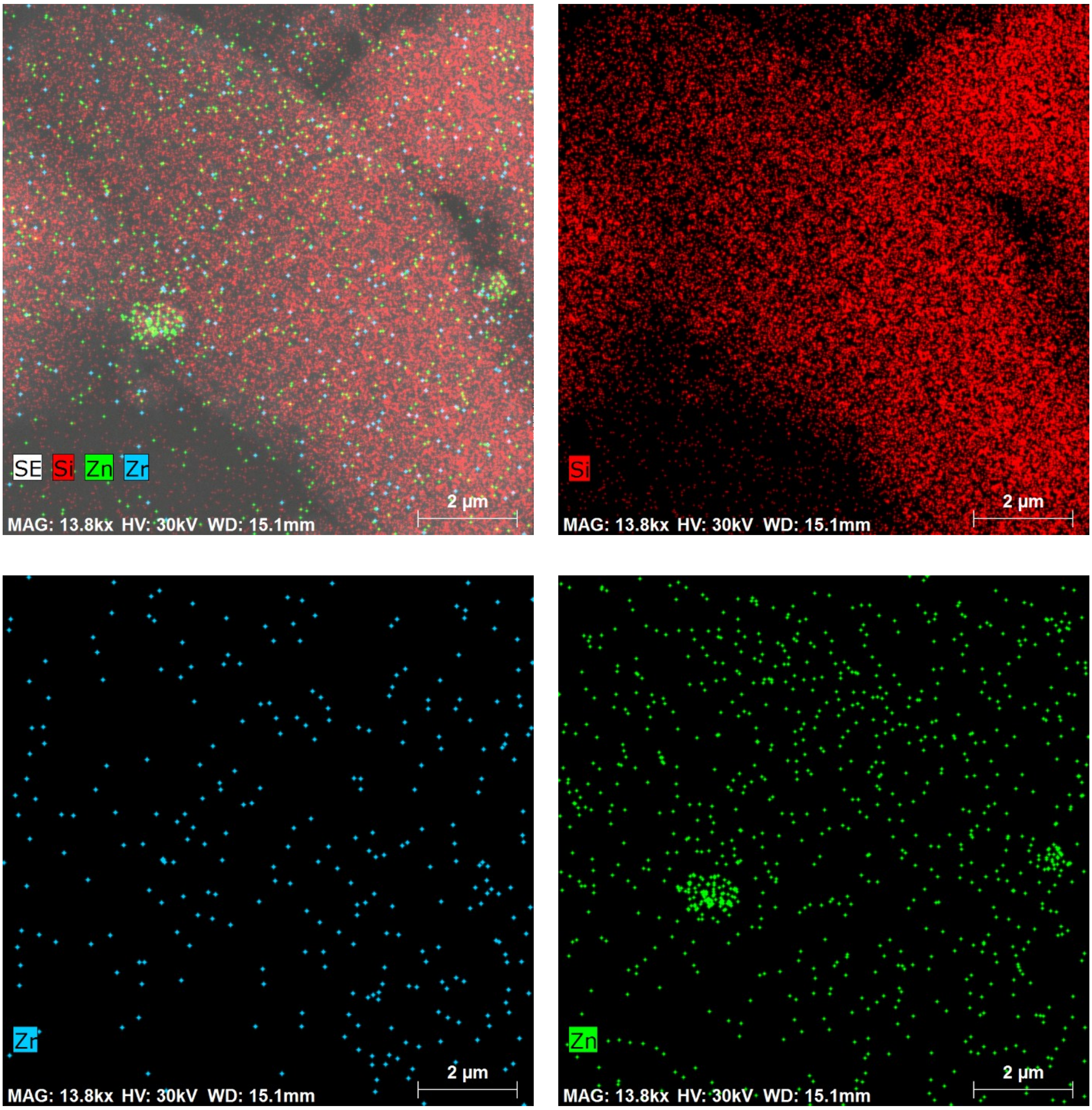


Figure S3-C. EDX mapping for Si, Zr and Zn atoms of ZnO-M/ZrO_2-SiO_2 sample.

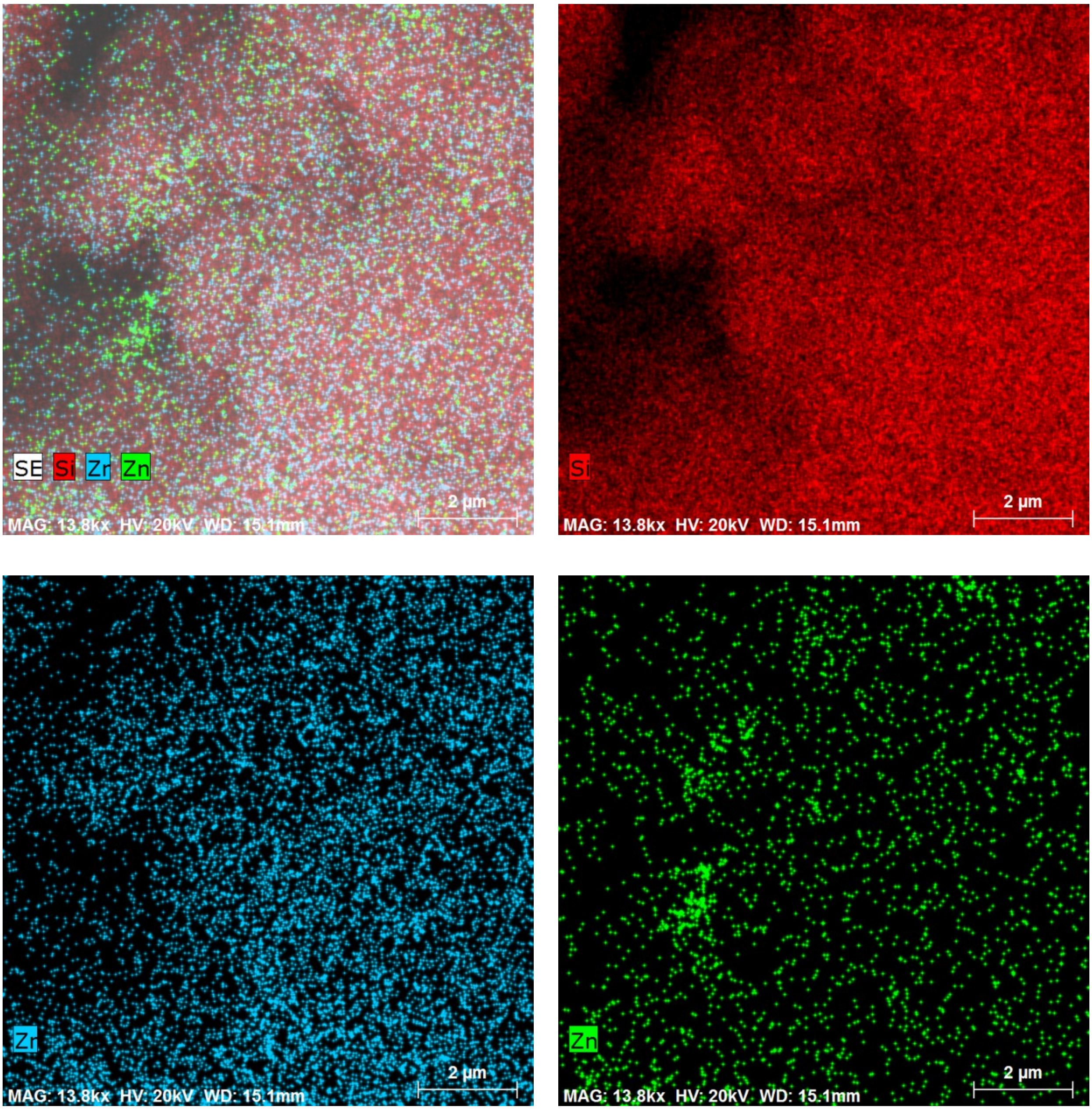


Figure S3-D. EDX mapping for Si, Zr and Zn atoms of ZnO-C/ZrO_2-SiO_2 sample.

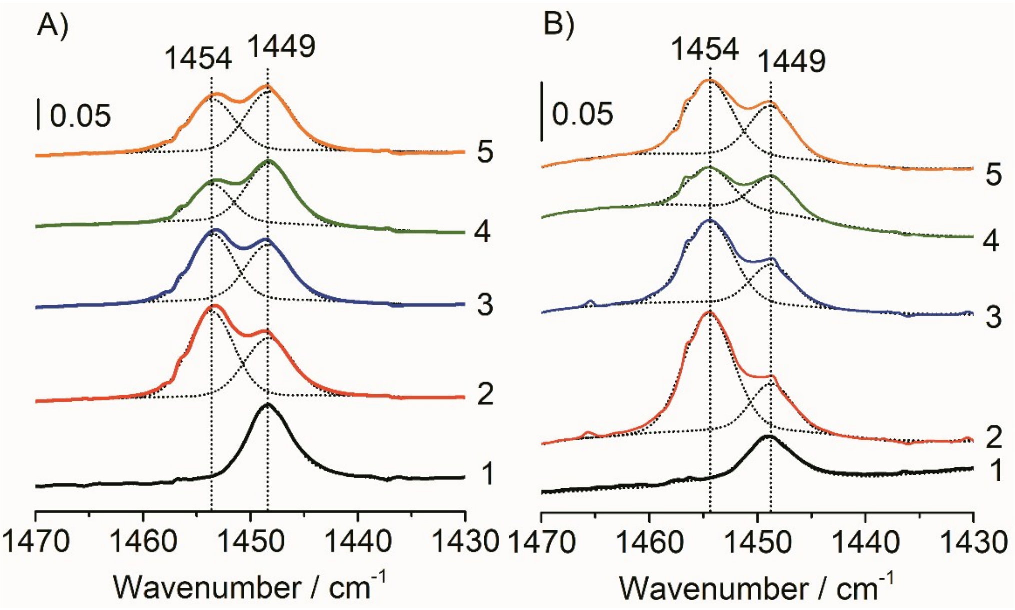


Fig. S4. Deconvoluted FTIR spectra of adsorbed pyridine on as-prepared catalyst samples after desorption at 423 K (A) and 523 K (B): 1 – ZrO_2-SiO_2, 2 – ZnO-I/ZrO_2-SiO_2, 3 – ZnO-N/ZrO_2-SiO_2, 4 – ZnO-M/ZrO_2-SiO_2, 5 – ZnO-C/ZrO_2-SiO_2.

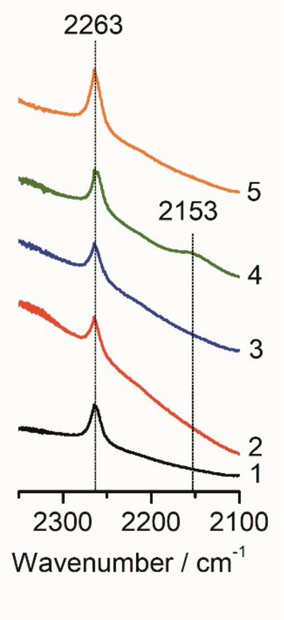


Fig. S5. *In situ* FTIR spectra of adsorbed $CDCl_3$ over the catalysts: 1 – ZrO_2-SiO_2, 2 – ZnO-I/ZrO_2-SiO_2, 3 – ZnO-N/ZrO_2-SiO_2, 4 – ZnO-M/ZrO_2-SiO_2, 5 – ZnO-C/ZrO_2-SiO_2.

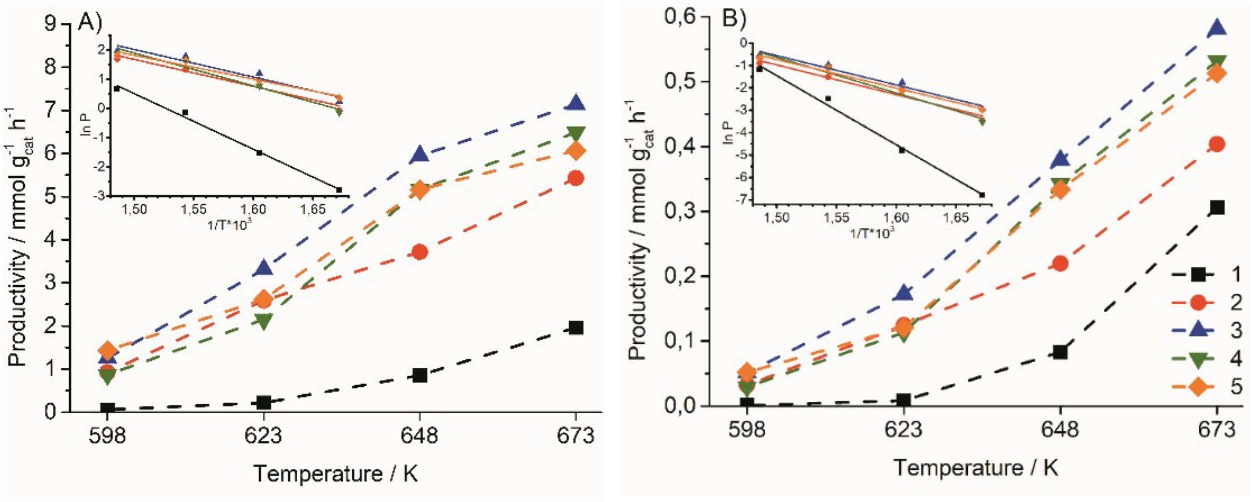


Fig. S6. Temperature dependencies of the catalysts productivities to 1,3-butadiene (A) and butene (B) and their formation rates (insert) in ETB process: 1 – ZrO2-SiO2, 2 – ZnO-I/ZrO2-SiO2, 3 – ZnO-N/ZrO2-SiO2, 4 – ZnO-M/ZrO2-SiO2, 5 – ZnO-C/ZrO2-SiO2 (WHSV = 1.3 gEtOH·gcat-1·h-1, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source).

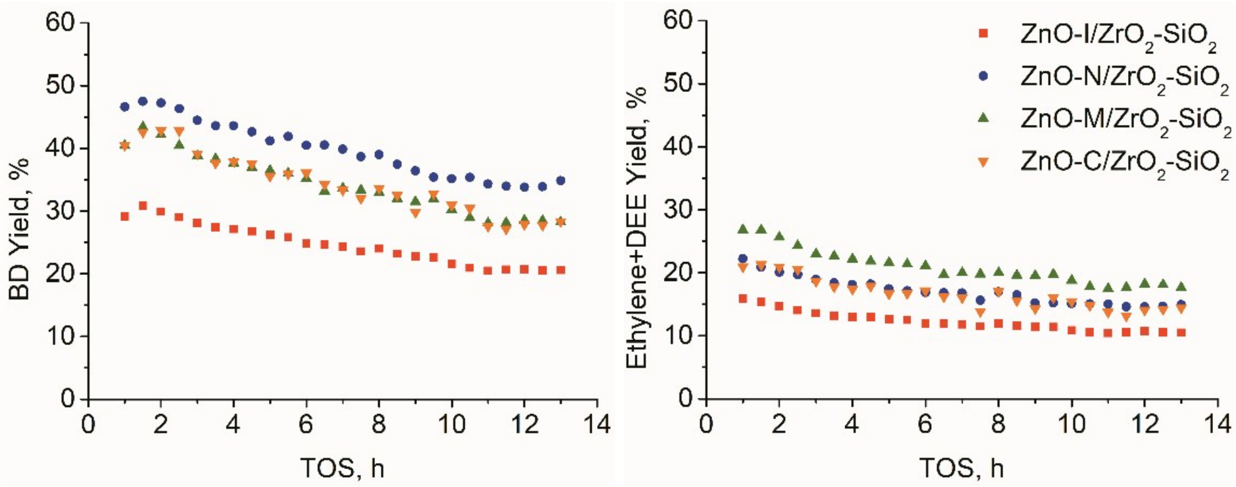


Fig. S7. BD and ethylene+DEE yields over ZnO/ZrO_2-SiO_2 catalysts as a function of time-on-stream (WHSV = 1.3 $g_{EtOH}·g_{cat}^{-1}·h^{-1}$, T = 648 K).

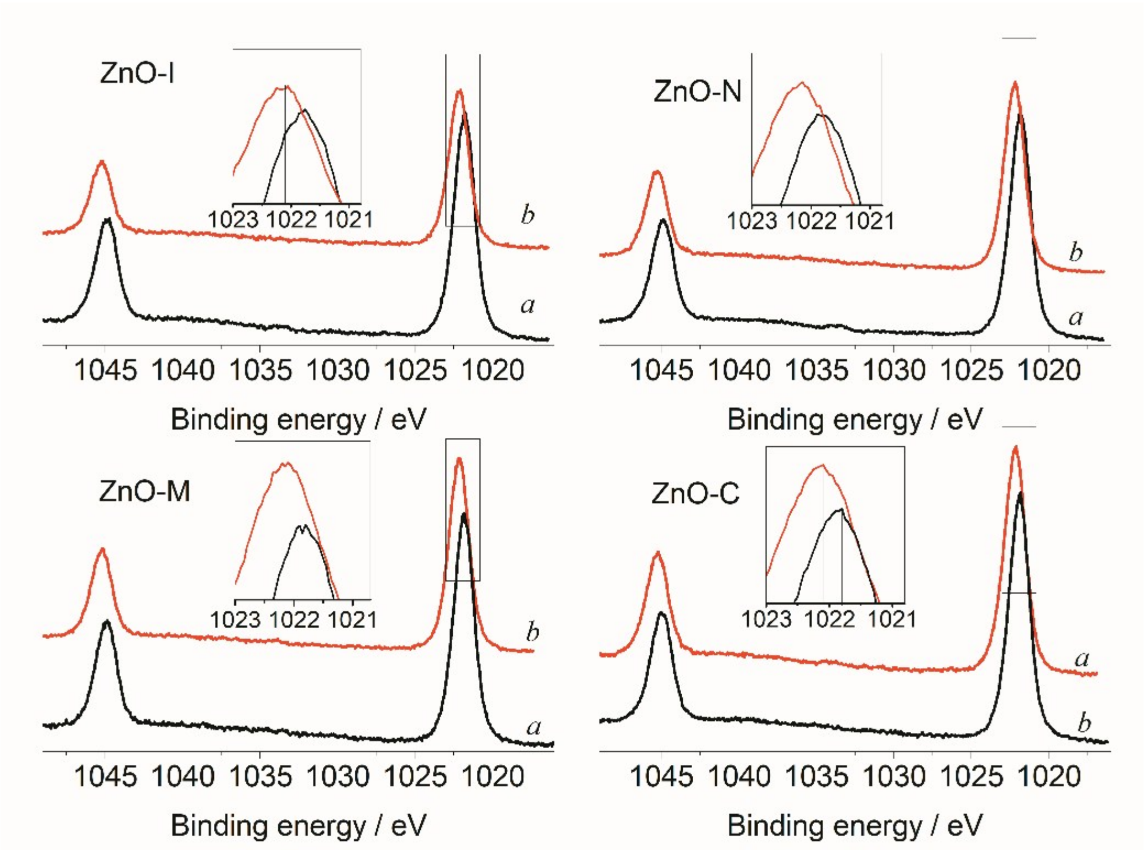


Fig. S8. Zn $2p_{3/2}$ NAP-XPS spectra of zinc oxide samples under O_2 (a) and EtOH+H_2O (b) flows: 1 – ZnO-I, 2 – ZnO-N, 3 – ZnO-M, 4 – ZnO-C.

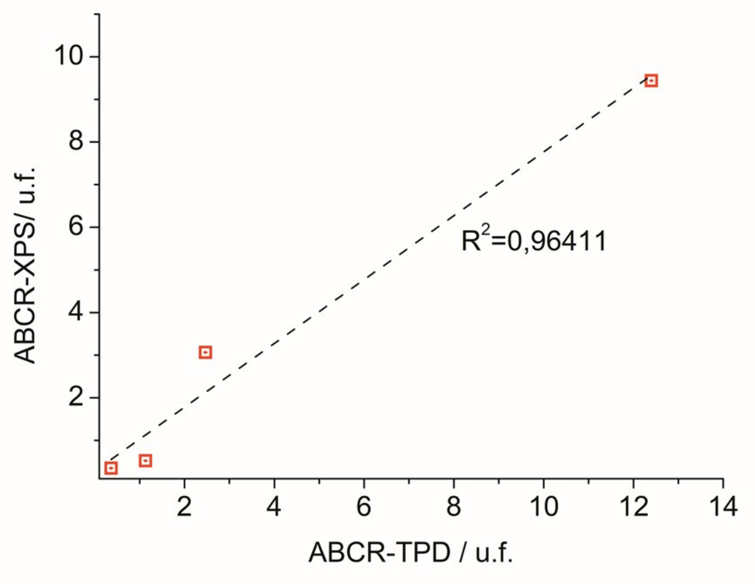


Fig. S9. The interrelationship between acid/base capacity ratios for the zinc oxide samples calculated according to NH_3/CO_2-TPD data (marked as ABCR-TPD) and the data of O 1s NAP-XPS spectra under O_2 flow (marked as ABCR-XPS).

ABCR-TPD values were obtained by dividing the area under curve of NH_3-TPD by the area under curve of CO_2-TPD presented in Fig. 2, main text of the manuscript. *ABCR-XPS values* were obtained by dividing the area under curve of the peak at 532.6 eV by the area under curve of the peak at 531.6 eV presented in Fig. 8, main text of the manuscript.

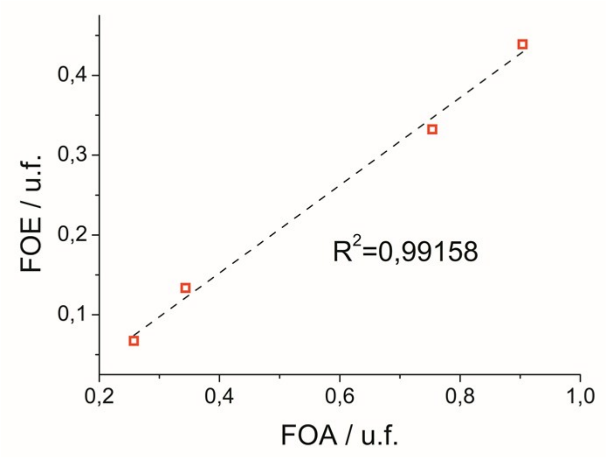


Fig. S10. The interrelationship between unit fraction of surface oxygen including oxygen corresponding to acidic sites (marked as FOA) and unit fraction of surface oxygen including oxygen corresponding to chemosorbed ethoxy/carboxy species (marked as FOE).

The unit fraction of surface oxygen including oxygen corresponding to acidic sites (marked as FOA) was calculated from O 1s NAP-XPS data for zinc oxide samples under O_2 flow using following formula:

$$\mathrm{FOA} = \frac{\text{area of O 1s NAP-XPS peak at 532.6 eV}}{\text{area of O 1s NAP-XPS peak at 531.6 eV} + \text{area of O 1s NAP-XPS peak at 531.6 eV}} \cdot \text{(u.f.)}$$

The unit fraction of surface oxygen including oxygen corresponding to chemosorbed ethoxy/carboxy species (marked as FOE) was calculated from O 1s NAP-XPS data for zinc oxide samples under EtOH+H_2O flow using following formula:

$$\mathrm{FOE} = \frac{\text{area of O 1s NAP-XPS peak at 532.6 eV}}{\text{area of O 1s NAP-XPS peak at 531.6 eV} + \text{area of O 1s NAP-XPS peak at 531.6 eV}} \cdot \text{(u.f.)}$$

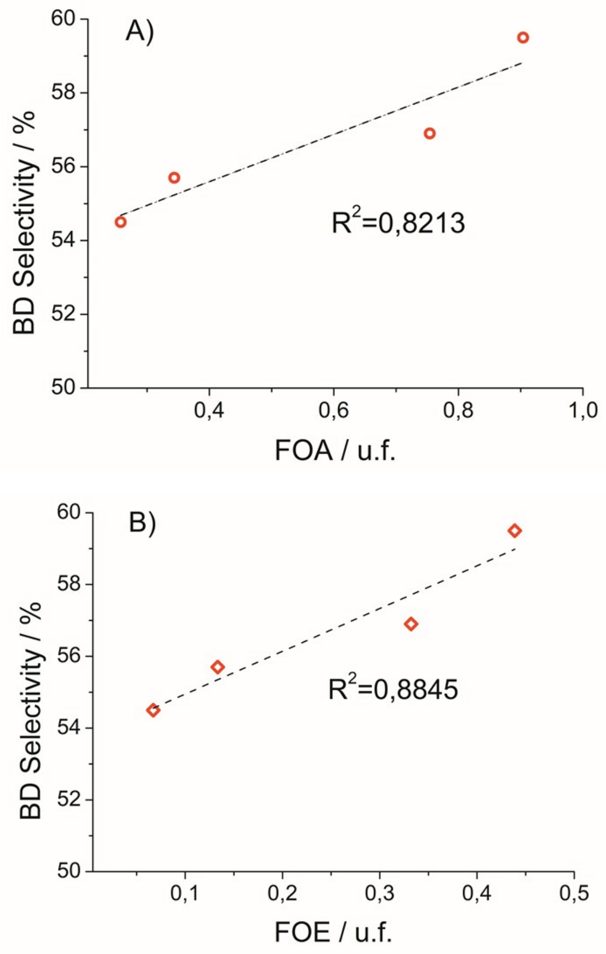


Fig. S11. BD selectivity of ETB process over ZnO/ZrO_2-SiO_2 at □50% ethanol conversion as functions of FOA (unit fraction of surface oxygen including oxygen corresponding to acidic sites, calculated from O 1s NAP-XPS data for zinc oxide samples under O_2 flow, A) and FOE (unit fraction of surface oxygen including oxygen corresponding to chemosorbed ethoxy/carboxy species, calculated from O 1s NAP-XPS data for zinc oxide samples under EtOH+H_2O flow, B).

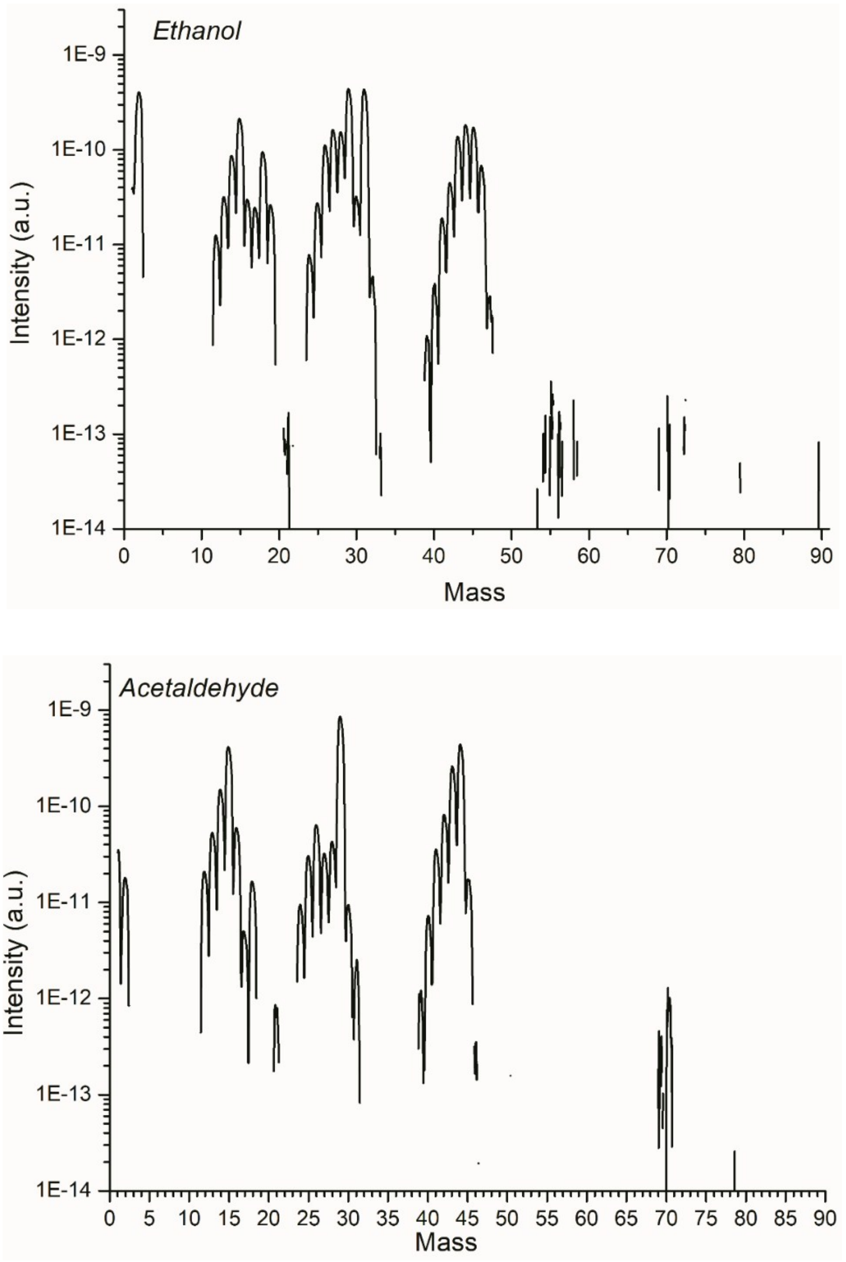


Fig. S12. QMS spectra of the reaction mixture over ZnO-SiO$_2$ (1:1) during the XPS measurements in the EtOH and AA flow.

Table S1. Catalytic performance of ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
598	8.5	5.3	6.4	54.8	31.9	0.1	0.1	1.4	0.4	0.003
623	23.4	6.8	4.0	66.8	21.1	0.3	0.1	0.9	1.6	0.012
648	51.2	12.3	3.0	69.7	13.2	1.2	0.1	1.7	6.3	0.048
673	85.7	16.8	2.1	69.9	8.2	2.5	0.0	0.5	14.4	0.110

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source.

Table S2. Catalytic performance of ZnO-I/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
598	14.9	45.4	19.7	23.0	9.8	1.4	0.6	0.1	6.8	0.052
623	34.2	55.6	12.6	22.8	5.4	2.6	0.5	0.5	19.0	0.145
648	49.0	55.7	12.9	23.3	3.6	3.2	0.6	0.7	27.3	0.208
673	70.7	56.4	11.2	24.8	2.0	4.0	0.4	1.2	39.9	0.304

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source.

Table S3. Catalytic performance of ZnO-N/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH con version (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}*g_{cat}^{-1}*h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
598	18.3	50.3	13.7	22.8	10.6	2.0	0.4	0.2	9.2	0.070
623	42.6	57.0	8.9	24.0	6.1	2.9	0.4	0.7	24.3	0.185
648	72.9	60.0	9.5	22.1	3.2	3.7	0.5	1.1	43.6	0.333
673	88.0	59.5	9.2	22.9	1.8	4.7	0.3	1.6	52.4	0.400

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source.

Table S4. Catalytic performance of ZnO-M/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
598	14.6	43.6	13.7	28.2	12.5	1.4	0.3	0.3	6.4	0.049
623	31.1	47.6	11.9	28.4	8.6	2.4	0.7	0.4	15.8	0.121
648	67.9	55.8	6.8	28.8	4.1	3.6	0.3	0.6	37.9	0.289
673	85.5	55.7	7.7	28.7	2.2	4.4	0.2	1.1	47.6	0.363

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source.

Table S5. Catalytic performance of ZnO-C/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
598	18.1	58.0	14.6	15.9	7.5	2.0	0.9	1.1	10.5	0.080
623	32.5	59.3	11.2	20.1	6.1	2.6	0.6	0.1	19.2	0.147
648	64.3	59.0	9.0	23.5	3.5	3.7	0.4	0.1	38.0	0.290
673	79.4	56.1	9.4	26.2	2.3	4.6	0.4	1.0	44.6	0.340

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 80% EtOH in water as an ethanol source.

Table S6. Catalytic performance of ZnO-N/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
648	76.1	59.2	7.8	23.0	3.9	4.5	0.3	1,3	45.0	0.343
673	97.1	60.1	5.3	24.9	2.0	6.0	0.2	1,5	58.3	0.445

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 96% EtOH in water as an ethanol source.

Table S7. Catalytic performance of ZnO-N/ZrO_2-SiO_2 compositions in EtOH conversion[a]

Temperature (K)	EtOH conversion (%)	Product selectivity (C mol%)							BD yield (C mol%)	BD productivity, $g_{BD}\cdot g_{cat}^{-1}\cdot h^{-1}$
		BD	AA	ethylene	DEE	butenes	ethyl acetate	others		
648	38.4	44.1	19.6	29.5	3.6	2.0	0.5	0.7	16.9	0.129
673	59.1	47.4	14.6	31.8	1.9	2.7	0.5	0.8	28.0	0.214

[a] WHSV = 1.3 $g_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$, time-on-stream = 2-5 h, 50% EtOH in water as an ethanol source.

References

1 V. M. Gun'ko, V. I. Zarko, B. A. Chuikov, V. V. Dudnik, Y. G. Ptushinskii, E. F. Voronin, E. M. Pakhlov and A. A. Chuiko, Temperature-programmed desorption of water from fumed silica, titania, silica/titania, and silica/alumina, *Int. J. Mass Spectrom. Ion Process.*, 1998, **172**, 161–179.