

Zinc Oxide-Modified Mordenite as an Effective Catalyst for the Dehydrogenation of (bio)Ethanol to Acetaldehyde.

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Supplementary Information:

$$\text{Conversion} = 100 \times \left(\frac{\text{Quantity of Ethanol Detected (C mmol min}^{-1}\text{)}}{\text{Quantity of Ethanol Fed (C mmol min}^{-1}\text{)}} \right)$$

$$\text{Carbon Balance} = 100 \times \left(\frac{\text{Quantity of Carbon Detected (C mmol min}^{-1}\text{)}}{\text{Quantity of Carbon Fed (C mmol min}^{-1}\text{)}} \right)$$

$$\text{Yield} = 100 \times \left(\frac{\text{Quantity of Species Detected (C mmol min}^{-1}\text{)}}{\text{Quantity of Carbon Fed (C mmol min}^{-1}\text{)}} \right)$$

$$\text{Selectivity} = 100 \times \left(\frac{\text{Quantity of Species Detected (C mmol min}^{-1}\text{)}}{\text{Total Product Carbon Detected (C mmol min}^{-1}\text{)}} \right)$$

$$\text{Effluent Composition} = 100 \times \left(\frac{\text{Quantity of Species Detected (C mmol min}^{-1}\text{)}}{\text{Total Carbon Detected (C mmol min}^{-1}\text{)}} \right)$$

GC-MS Analysis Conditions

Product analysis was performed using on-line tandem GC-MS-BID analysis. The reactor effluent line was plumbed into a Shimadzu GC-2010 Plus gas chromatograph *via* trace heated lines maintained at 170 °C. The reactor effluent passed through two 6 port Vici valves kept in a heated box (180 °C) through which two samples were automatically taken from the reactor effluent *via* a 0.5 mL sample loop on each Vici valve. The two samples were independently flushed to and injected through two separate split valves with the injection ports maintained at 220 °C (Sample 1) and 200 °C (Sample 2). Sample 1 was injected with a 250:1 He split ratio and chromatography performed over either a SGE Analytical BPX90 capillary column with a 90% cyanopropyl polysilphenylene-siloxane stationary phase (length 30 m, I.D. 0.25 mm, film

thickness 0.25 μm) or a Thames Restek RTX-VMS fused silica capillary column (Length 30 m, I.D. 0.25 mm, film thickness 0.25 μm). Sample 2 was injected with a 10:1 He split ratio and chromatography performed over a Restek ShinCarbon ST packed column with a high surface area ($\sim 1,500 \text{ m}^2 \text{ g}^{-1}$) carbon molecular sieve stationary phase (length 2 m, I.D. 1.00 mm, O.D. 1/16", packed 100/120 mesh). Both columns were mounted in the same oven and hence underwent the same heating profile throughout the chromatography stage. A typical GC oven program used for analysis of ethanol conversion products involved injection onto the column at 80 $^{\circ}\text{C}$ at which it was held for 7.0 min before being ramped at 30 $^{\circ}\text{C min}^{-1}$ to 250 $^{\circ}\text{C}$ at which it was held for 8.0 min to give a total run time of approximately 20 min. For longer GC programs the time at which the column oven was held at 250 $^{\circ}\text{C}$ was extended. Sample 1 was analysed using a Shimadzu GC-MS-QP2010 SE mass spectrometer maintaining interface and ion source temperatures at 220 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ respectively. Mass spectrometry was performed over the entirety of the GC program with the first event occurring at 0.1 min and further events occurring every 0.3 s. Ions were detected in an m/z range of 10–200 with a scan speed of 666 ms. Sample 2 was analysed using a Shimadzu BID-2010 Plus detector maintaining the He plasma at 300 $^{\circ}\text{C}$. Analysis was performed over the entirety of the GC program with a sampling rate of 40 ms.

Note on GCMS analysis

Low carbon balances were observed when using the BPX-90 GC column, which was used in our initial studies. The method using the BPX-90 column was only calibrated for ethanol, acetaldehyde and ethylene (given below) due to the poor separation of other components, resulting in low carbon balance values.

Unfortunately, small oscillations may be observed for some data points, particularly in reference to carbon balance. We believe that the oscillatory behaviour of the carbon balance is resultant from a physical issue pertaining to our flow reactor set-up, likely from dewing within the pipework or similar. We have tried to overcome this to the best of our ability by trace-heating all reactor lines and minimising cold-spots and condensation points. To confirm this, we have included an example MS and BID detector trace from a typical reaction (Figure S.1) alongside tables stating the expected peak positions of both calibrated and non-calibrated products for each detection column. We believe that these traces demonstrate a lack of significant amounts of non-calibrated carbon containing products within our reactor effluent, and therefore confirm that our reported selectivities are relatively unaffected by the oscillating carbon balances.

Calibrated Compounds

The following compounds were sufficiently resolved and quantitatively calibrated for each GC column:

BPX-90: Ethanol, acetaldehyde, diethyl ether.

Species	Retention Time /min	Calibrated Ion / m/z
Ethylene	1.61	28.00
Acetaldehyde	1.73	44.00
Ethanol	1.84	31.00
Toluene	2.19	91.00

RTX-VMS: Ethanol, diethyl ether, ethyl acetate, isopropyl alcohol, acetone, butanol, acetaldehyde, butadiene, isobutene, linear butenes, isobutene.

Species	Retention Time /min	Calibrated Ion / m/z
Isobutene	1.97	43.05
Linear Butenes	2.02	56.05
Butadiene	2.05	54.05
Isobutane	2.08	56.05
Acetaldehyde	2.13	44.05
Ethanol	2.33	46.05
Diethyl Ether	2.34	74.05
Isopropyl Alcohol	2.53	59.05
Acetone	2.65	58.05
Ethyl Acetate	3.39	88.05
Butanol	4.38	74.05

ShincarbonST: Ethylene, ethane, propylene, propane.

Species	Retention Time /min	Calibrated
Hydrogen	0.57	No
Carbon Monoxide	1.57	No
Methane	3.03	No
Carbon Dioxide	6.99	No
Ethylene	12.89	Yes
Ethane	13.87	Yes
Propylene	21.10	Yes
Propane	22.00	Yes

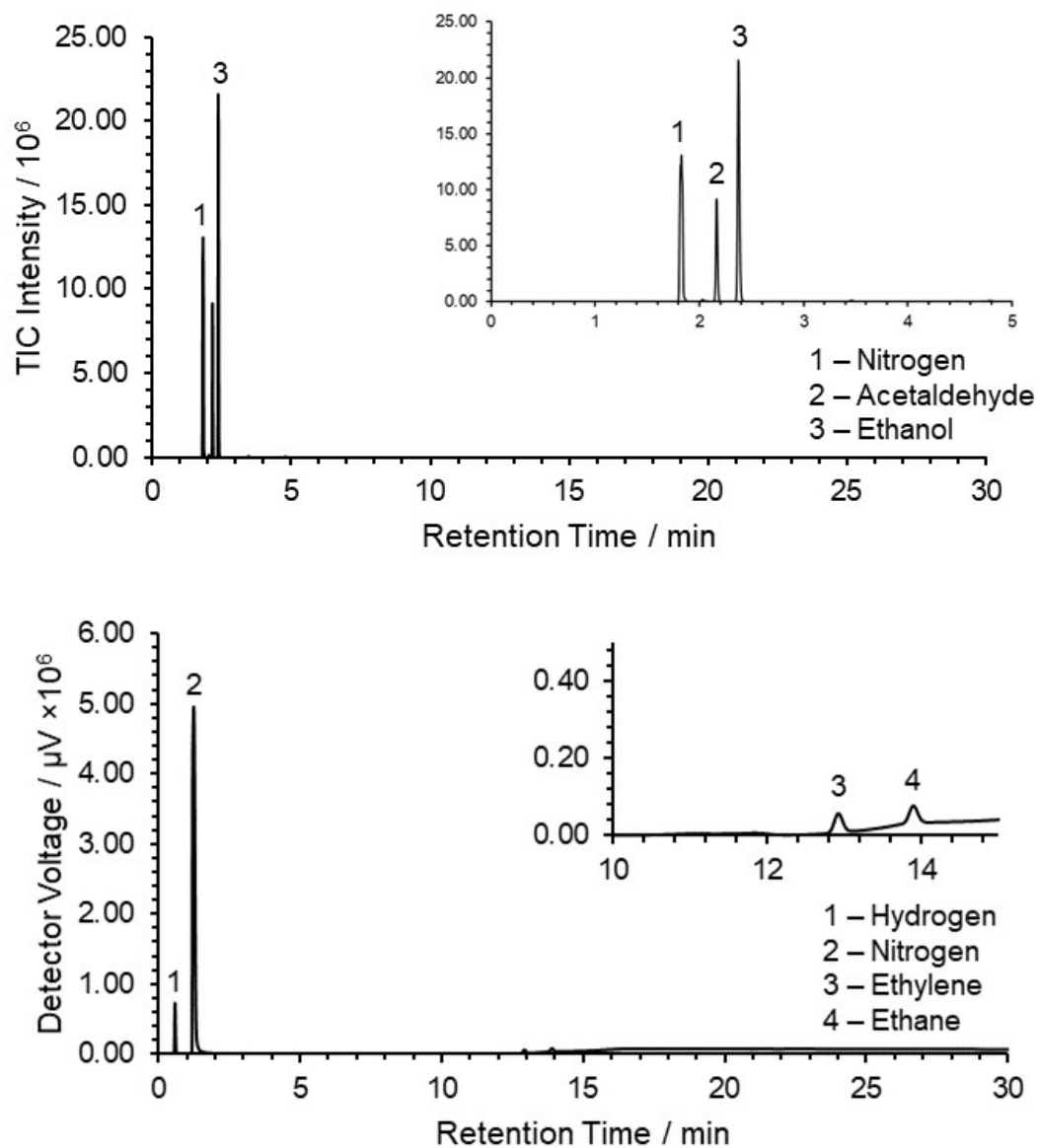


Figure S.1: Example MS (top) and BID (bottom) traces resulting from an ethanol to acetaldehyde reaction over ZnO/Rb-MOR-(7) at 400 °C highlighting retention times of products of interest. Detection columns: RTX-VMS (MS), ShinCarbon ST (BID). TOS = 2.5 h.

Table S.1: Elemental compositions of $M_xO_y/Na-MOR-(7)$ materials obtained by ICP-OES where $M = Ag, Cr, Co, Cu, Fe, Ga, Mg, Mn, Ni, Pd, Ru$ and Zn . Target M wt% = 3.00. Values are averaged over multiple wavelengths where possible and appropriate. *These values were measured by ED-XRF as complete dissolution in HF in preparation for ICP-OES analysis could not be achieved.

Material	Al Wt%	Na Wt%	M Wt%
Na-MOR-(7)	4.32	3.72	N/A
Ag/Na-MOR-(7)	4.88	4.21	2.92
Cr ₂ O ₃ /Na-MOR-(7)	4.80	4.15	2.69
Co ₃ O ₄ /Na-MOR-(7)	4.79	4.21	3.07
CuO/Na-MOR-(7)	5.27	4.22	4.12
Fe ₂ O ₃ /Na-MOR-(7)	5.17	4.09	3.64
Ga ₂ O ₃ /Na-MOR-(7)	4.77	4.16	1.81
MgO/Na-MOR-(7)	5.19	3.97	2.97
Mn ₃ O ₄ /Na-MOR-(7)	5.21	4.02	3.21
NiO/Na-MOR-(7)	4.81	4.27	2.91
PdO/Na-MOR-(7)	4.78	4.11	3.13*
Ru ₂ O ₃ /Na-MOR-(7)	4.77	4.14	3.64*
ZnO/Na-MOR-(7)	4.90	3.77	3.22

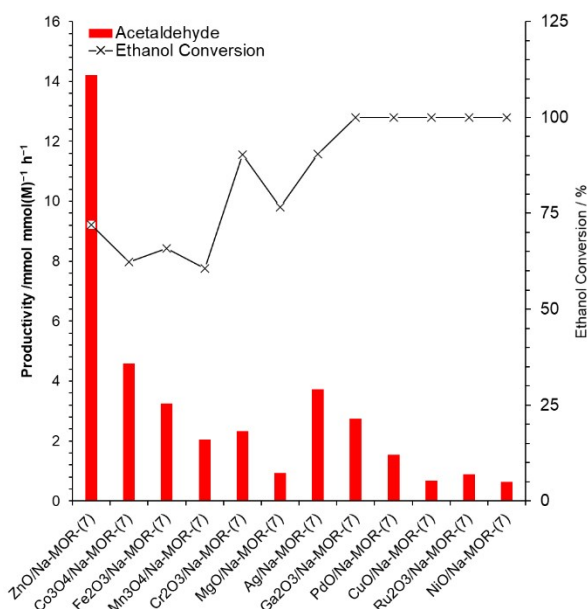


Figure S.2: Acetaldehyde productivities normalized to metal content alongside ethanol conversion values resulting from reaction of ethanol over ZnO/Na-MOR-(7), Co₃O₄/Na-MOR-(7), Fe₂O₃/Na-MOR-(7), Mn₃O₄/Na-MOR-(7), Cr₂O₃/Na-MOR-(7), Ag/Na-MOR-(7), MgO/Na-MOR-(7), Ga₂O₃/Na-MOR-(7), Ru₂O₃/Na-MOR-(7), CuO/Na-MOR-(7), PdO/Na-MOR-(7) and NiO/Na-MOR-(7) at 400 °C. Ethanol feed rate = 0.171 mmol min⁻¹, catalyst mass = 0.300 g. Detection column: BPX90. TOS = 1.75 h.

Table S.2: Acetaldehyde and ethylene productivities normalized to catalyst mass resulting from ethanol conversion over metal impregnated Na-MOR-(7) at 400 °C. Ethanol feed rate = 0.171 mmol min⁻¹, catalyst mass = 0.300 g. Detection column: BPX90.

Time on stream /h	0.5		1.0		1.5		2.0	
	Acetaldehyde	Ethylene	Acetaldehyde	Ethylene	Acetaldehyde	Ethylene	Acetaldehyde	Ethylene
Na-MOR-(7)	0.00	2.65	1.71	3.02	1.42	3.86	1.41	4.91
Ag/Na-MOR-(7)	0.85	23.73	0.95	23.63	0.98	22.19	1.01	21.26
Cr ₂ O ₃ /Na-MOR-(7)	1.02	6.09	1.12	7.39	1.10	5.65	1.20	5.32
Co ₃ O ₄ /Na-MOR-(7)	0.58	17.78	2.25	8.32	2.48	7.05	2.40	6.21
CuO/Na-MOR-(7)	0.95	0.15	0.41	8.17	0.43	8.17	0.43	7.07
Fe ₂ O ₃ /Na-MOR-(7)	0.85	19.69	2.35	9.88	2.27	8.80	2.12	8.35
Ga ₂ O ₃ /Na-MOR-(7)	0.39	7.22	0.59	11.05	0.61	7.33	0.71	7.75
MgO/Na-MOR-(7)	0.33	4.91	1.07	3.56	1.20	3.67	1.14	3.28
Mn ₃ O ₄ /Na-MOR-(7)	1.17	13.57	1.26	10.20	1.24	9.01	1.20	8.51
NiO/Na-MOR-(7)	0.45	4.36	0.55	7.17	0.28	7.22	0.32	6.80
PdO/Na-MOR-(7)	0.26	9.58	0.39	9.56	0.36	11.17	0.45	10.24
Ru ₂ O ₃ /Na-MOR-(7)	0.63	8.81	0.65	8.81	0.67	9.24	0.32	0.53
ZnO/Na-MOR-(7)	2.63	9.80	6.87	3.96	6.93	3.30	7.00	3.05

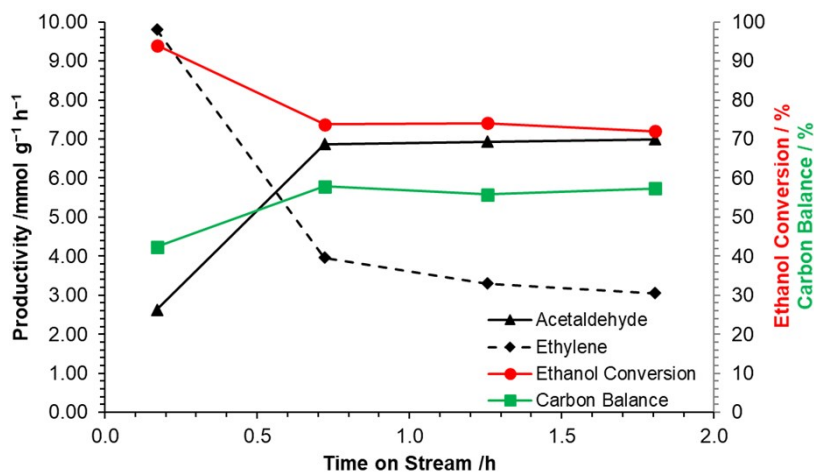


Figure S.3: Acetaldehyde (▲) and ethylene (◆) productivities, ethanol conversion (●) and carbon balance (■, ethanol, acetaldehyde, ethylene only) resulting from reaction of ethanol over ZnO/Na-MOR-(7) for 2 hours TOS. Ethanol feed rate = 0.171 mmol min⁻¹, catalyst mass = 0.300 g. Detection column: BPX90.

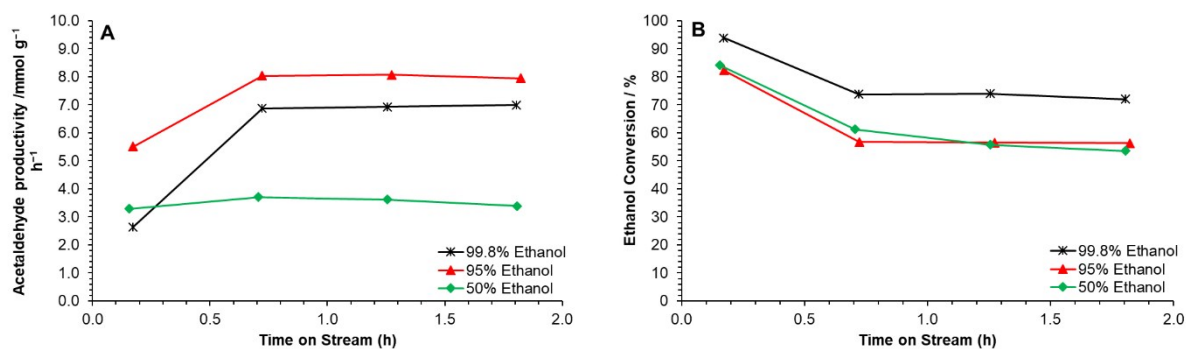


Figure S.4: Acetaldehyde productivities (A) and ethanol conversion (B) resulting from reaction of ethanol over ZnO/Na-MOR-(7) for 2 hours TOS feeding 99.8% ethanol (x, 0.171 mmol min⁻¹), 95% ethanol (▲, 0.162 mmol min⁻¹), 50% ethanol (◆, 0.086 mmol min⁻¹). Liquid flow rate = 0.01 mL min⁻¹ Catalyst mass = 0.300 g. Detection column: BPX90.

Table S.3: Elemental compositions of ZnO/M-MOR-(7) materials at varying Zn loadings obtained by ICP-OES. Values are averaged over multiple wavelengths where possible and appropriate.

Material	Al Wt%	Zn Wt%	Na Wt%
Na-MOR-(7)	4.32	0.00	3.72
ZnO/Na-MOR-(7)-1.0%	5.23	0.98	3.99
ZnO/Na-MOR-(7)-3.5%	4.90	3.77	3.22
ZnO/Na-MOR-(7)-5.0%	5.13	4.80	3.85
ZnO/Na-MOR-(7)-10%	4.85	9.79	3.76

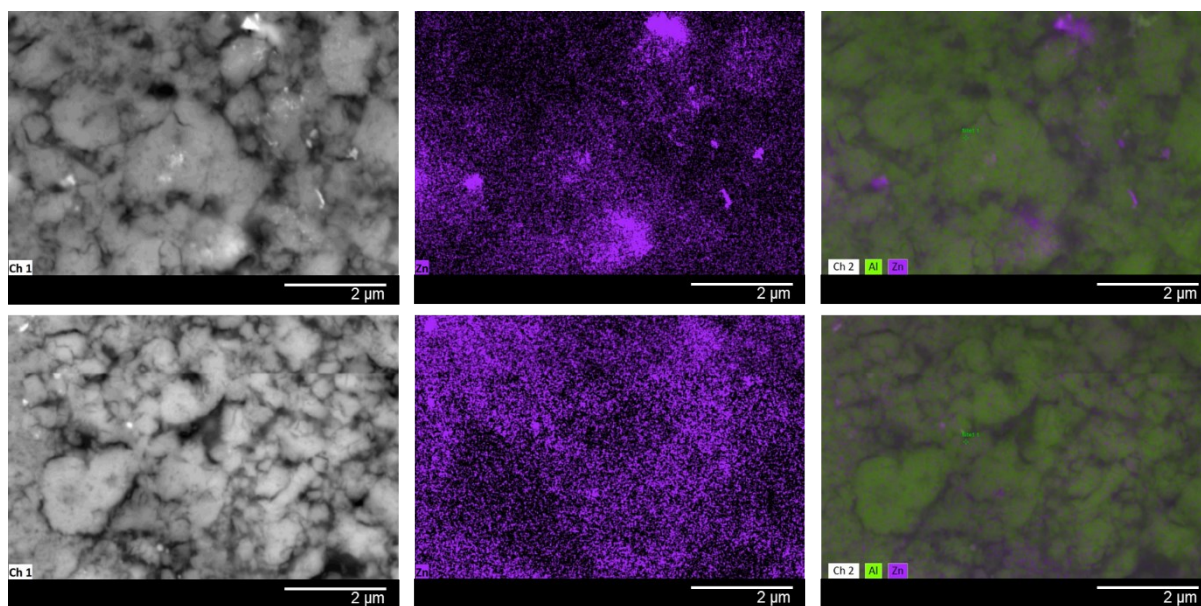


Figure S.5: SEM image (left), Zn elemental map (centre) and Zn, Al elemental overlays (right) of ZnO/Na-MOR-(7)-10% following grinding and polishing at two different locations.

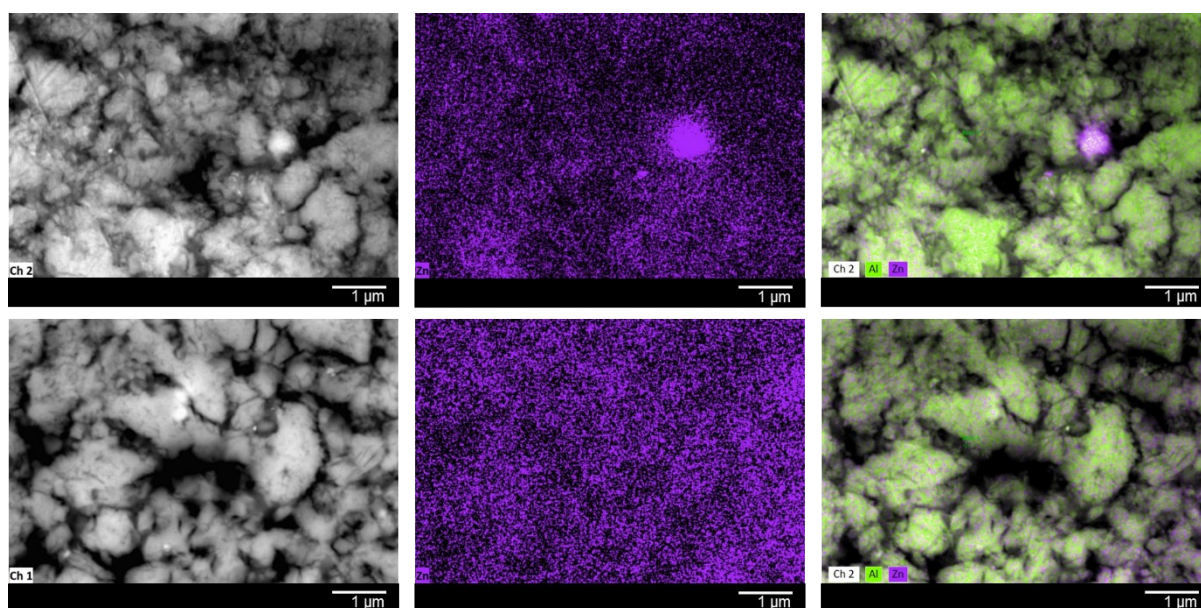


Figure S.6: SEM image (left), Zn elemental map (centre) and Zn, Al elemental overlays (right) of ZnO/Na-MOR-(7)-5.0% following grinding and polishing at two different locations.

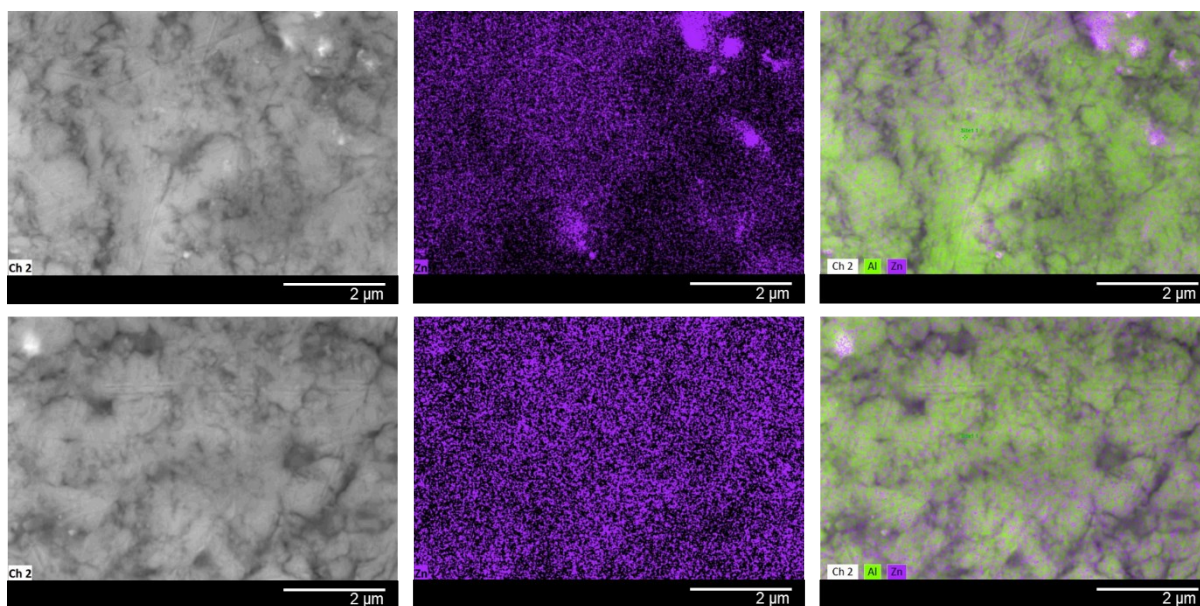


Figure S.7: SEM image (left), Zn elemental map (centre) and Zn, Al elemental overlays (right) of ZnO/Na-MOR-(7)-3.5% following grinding and polishing at two different locations.

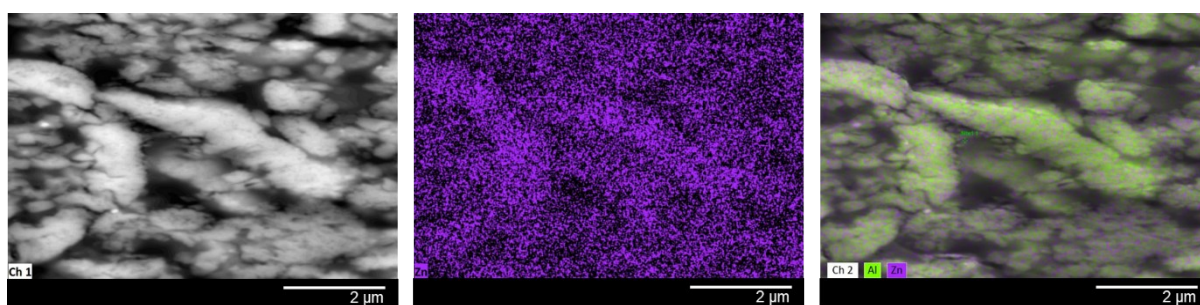


Figure S.8: SEM image (left), Zn elemental map (centre) and Zn, Al elemental overlays (right) of ZnO/Na-MOR-(7)-1.0% following grinding and polishing.

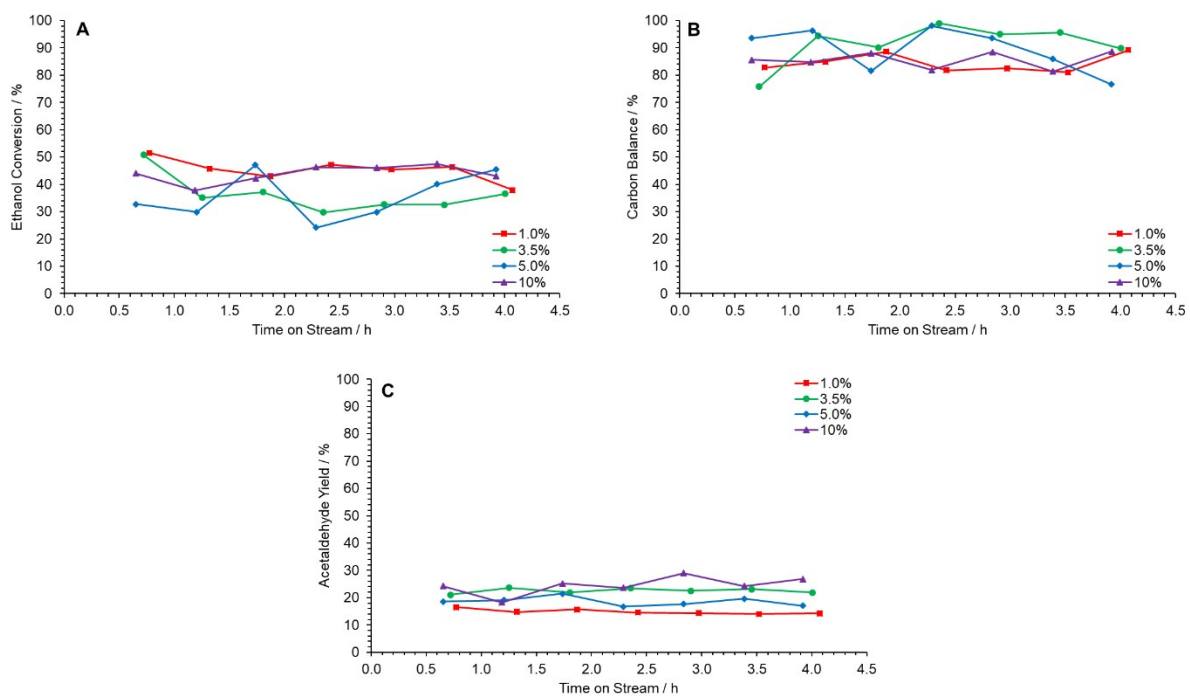


Figure S.9: Ethanol conversion (A) and carbon balance (B) and acetaldehyde yield (C) following reaction of ethanol over ZnO/Na-MOR materials at 400 °C for 4 h TOS at nominal Zn loadings of = 1.0 wt% (■), 3.5 wt% (●), 5.0 wt% (◆) and 10 wt% (▲). Ethanol feed rate = 0.330 mmol min⁻¹, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST.

Table S.4: Catalyst coking (C wt%) of variously loaded ZnO/Na-MOR-(7.0) catalysts following ethanol dehydrogenation at 400 °C as determined by CHN microanalysis.

Sample	Catalyst Coking (C Wt%)	Proportion of feed carbon deposited as coke /%
ZnO/Na-MOR-(7.0)-1.0%	5.12	0.81
ZnO/Na-MOR-(7.0)-3.5%	4.03	0.63
ZnO/Na-MOR-(7.0)-5.0%	4.20	0.66
ZnO/Na-MOR-(7.0)-10%	3.02	0.48

Table S.5: Elemental compositions of ZnO/M–MOR–(7) materials obtained by ICP-OES where M = Na, K, Rb, or Cs. Target ZnO loading = 3.5 wt% by Zn. n.d. = Not detected.

Material	Al Wt%	Zn Wt%	Na Wt%	K Wt%	Rb Wt%	Cs Wt%
ZnO/Na–MOR–(7)	4.80	3.71	4.43	n.d.	n.d.	n.d.
ZnO/K–MOR–(7)	4.87	2.62	0.00	6.83	0.00	0.00
ZnO/Rb–MOR–(7)	4.56	3.12	0.00	0.00	14.43	0.00
ZnO/Cs–MOR–(7)	4.23	3.09	0.01	0.00	0.00	16.52

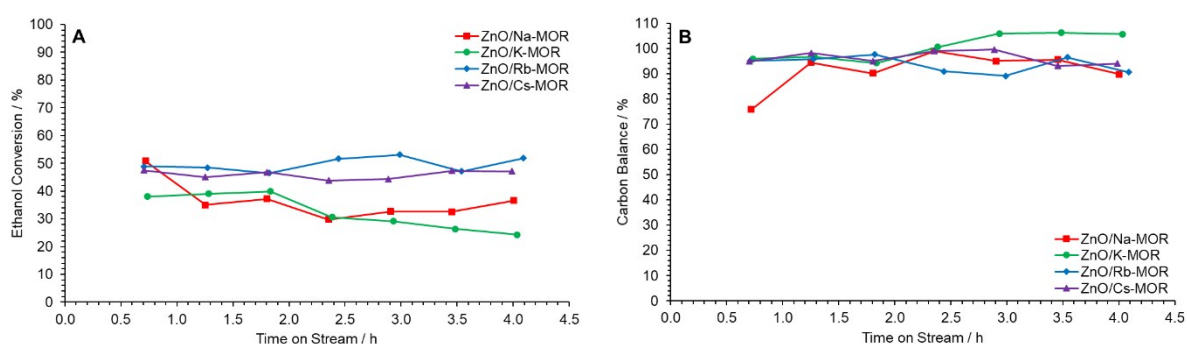


Figure S.10: Ethanol conversion (A) and carbon balance (B) following reaction of ethanol over ZnO/M–MOR materials at 400 °C for 4 h TOS where M = Na (■), K (●), Rb (◆) and Cs (▲). Ethanol feed rate = 0.330 mmol min⁻¹, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST.

Table S.6: Catalyst coking (C wt%) of ZnO/M–MOR–(7.0) catalysts following ethanol dehydrogenation at 400 °C as determined by CHN microanalysis.

Sample	Catalyst Coking (C Wt%)	Proportion of feed carbon deposited as coke /%
ZnO/Na–MOR–(7.0)	4.35	0.69
ZnO/K–MOR–(7.0)	4.00	0.63
ZnO/Rb–MOR–(7.0)	3.52	0.56
ZnO/Cs–MOR–(7.0)	2.34	0.37

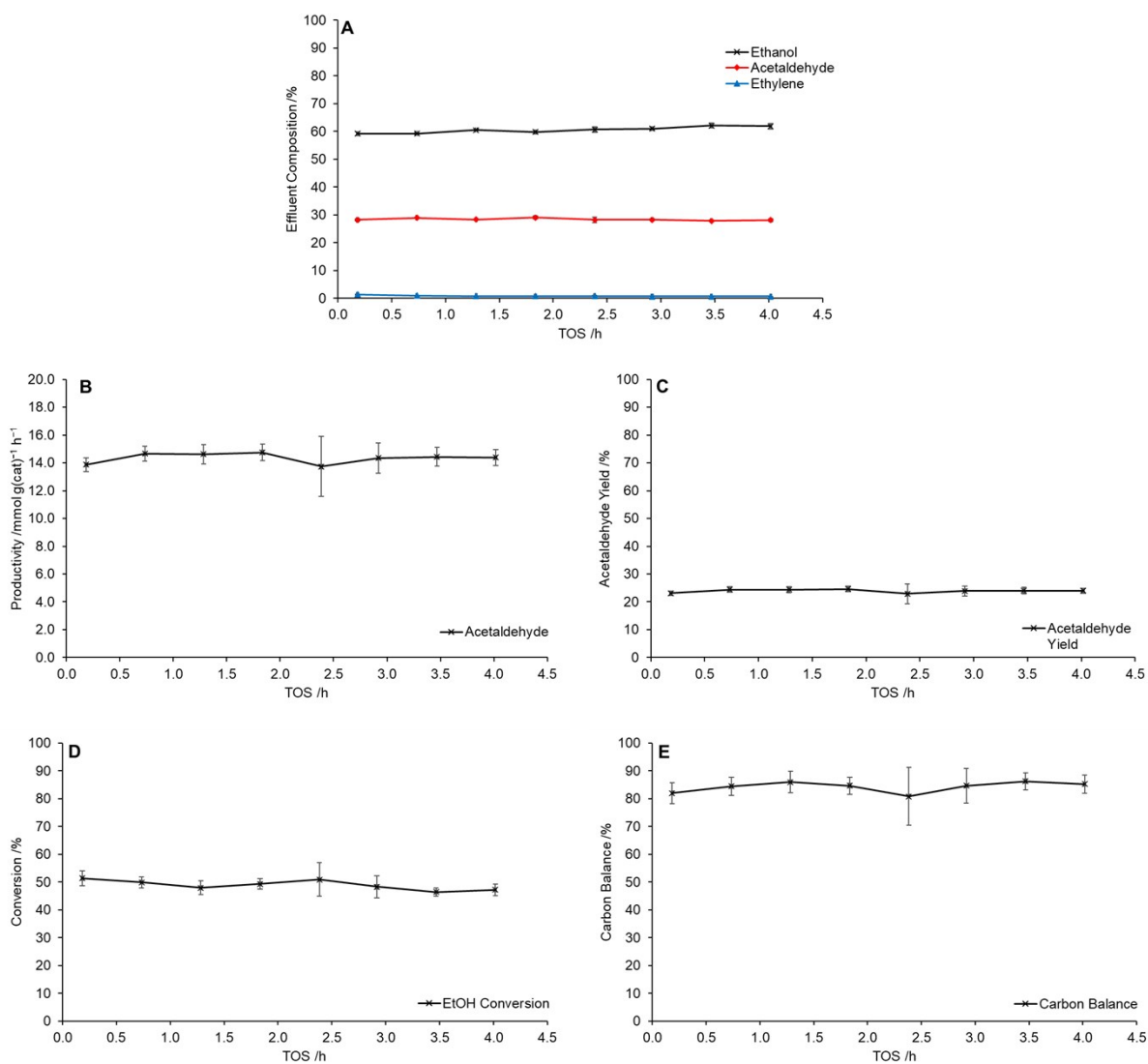


Figure S.11: Effluent composition (A), acetaldehyde productivity (B), acetaldehyde yield (C), ethanol conversion (D) and carbon balance (E) following reaction of ethanol over ZnO/Rb-MOR-(7) at 400 °C for 4 h TOS. Error bars are plotted as one standard deviation calculated from three experimental repeats. Effluent composition (A) depicts only major contributions from ethanol, acetaldehyde and ethylene. Ethanol feed rate = 0.300 mmol min⁻¹, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST.

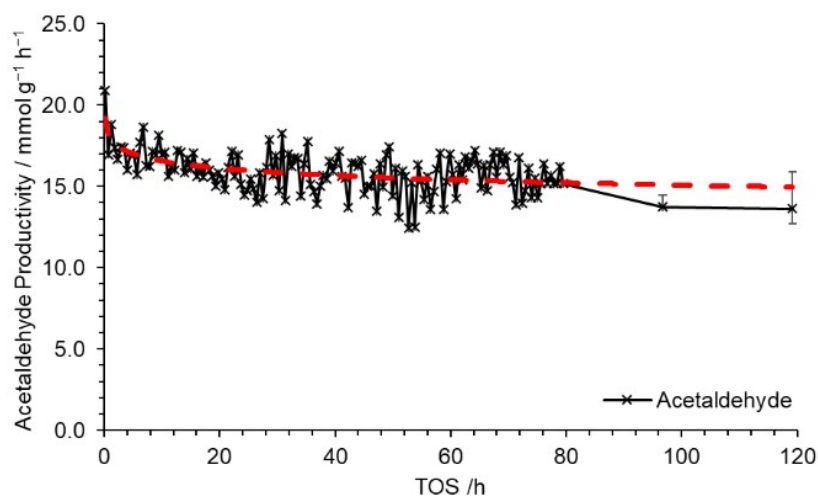


Figure S.12: Mass-resolved acetaldehyde productivity following reaction of ethanol over ZnO/Rb-MOR-(7) at 400 °C for 120 h TOS. Error bars dictate outliers from five subsequent averaged measurements. Ethanol feed rate = 0.330 mmol min⁻¹, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST. Red dashed lines have been added to help guide the readers' eye only.

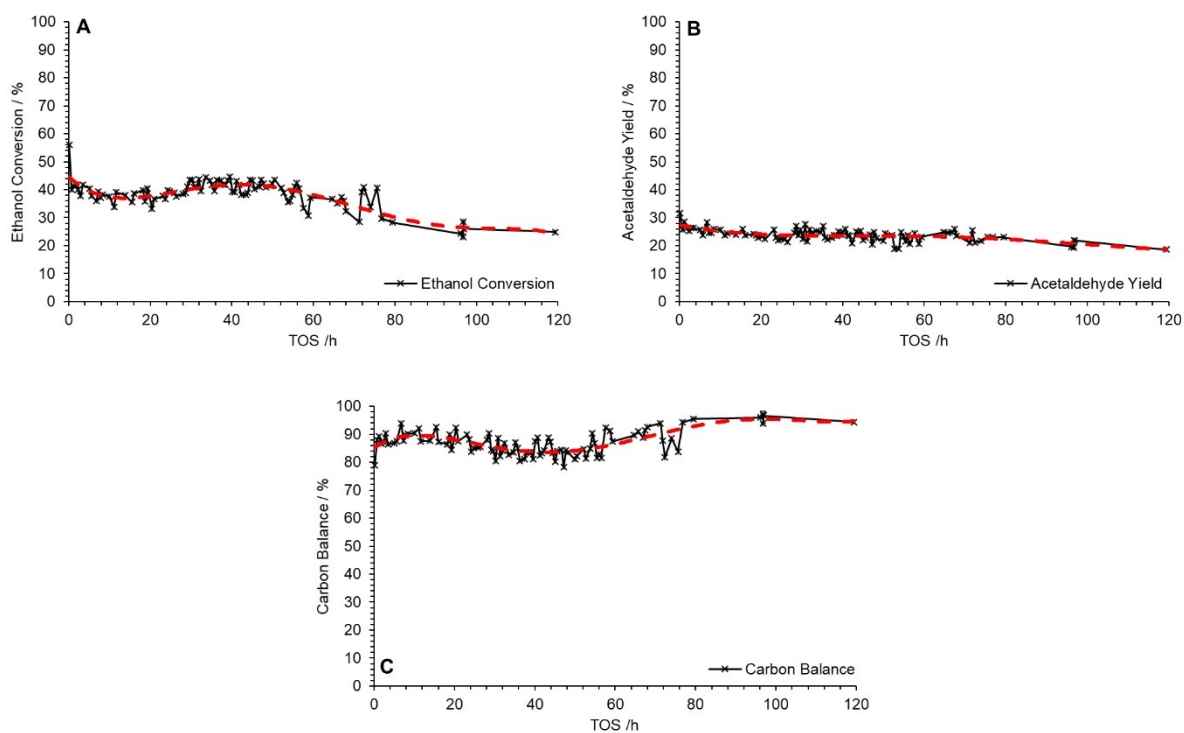


Figure S.13: Ethanol conversion (A), acetaldehyde yield (B) and carbon balance (C) following reaction of ethanol over ZnO/Rb-MOR-(7) at 400 °C for 120 h TOS. Ethanol feed rate = 0.330 mmol min⁻¹, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST. Red dashed lines have been added to help guide the readers' eye only.

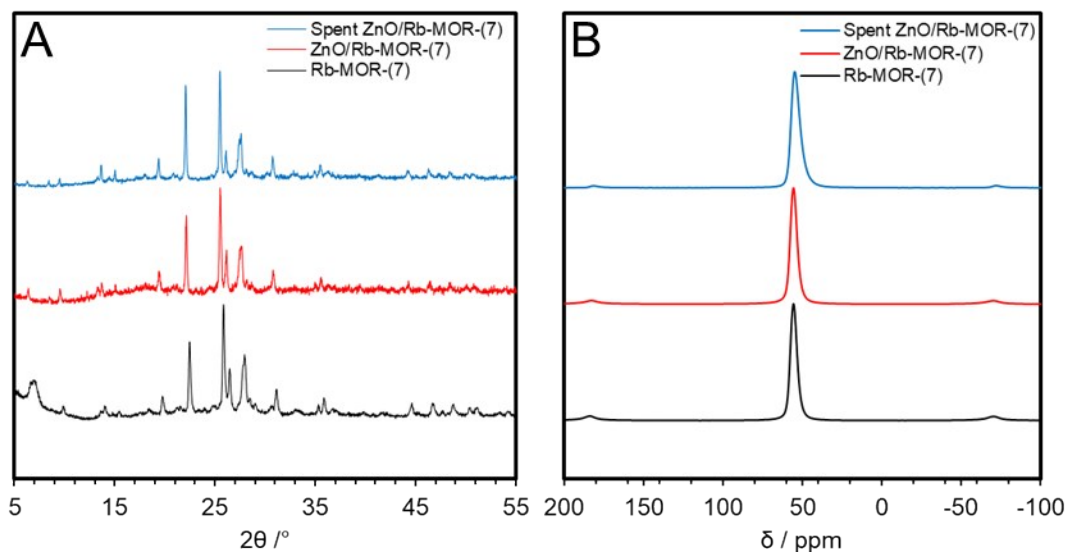


Figure S.14: A) pXRD patterns within the $2\theta = 5\text{--}55^\circ$ range and B) Solid-state ^{27}Al NMR spectra for Rb-MOR-(7), ZnO(3.5)/Rb-MOR-(7) and the same material following ethanol conversion at 400°C for 120+ h TOS.

Table S.7: Catalyst coking (C wt%) of ZnO/Rb-MOR-(7.0) catalysts following ethanol dehydrogenation at 400°C at 4 and 120 h TOS as determined by CHN microanalysis.

Sample	Time on Stream / h	Catalyst Coking (C Wt%)	Proportion of feed carbon deposited as coke /%
ZnO/Rb-MOR-(7.0)	4.0	3.52	0.56
ZnO/Rb-MOR-(7.0)	120	4.67	0.02

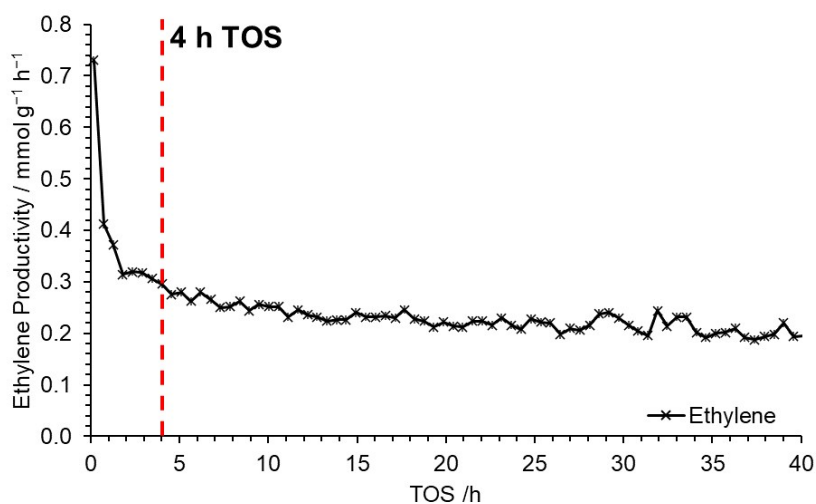


Figure S.15: Ethylene productivity following reaction of ethanol over ZnO/Rb-MOR-(7) at 400°C for 120 h TOS. The x-axis has been cut at 40 h TOS and a marker added at 4 h TOS to improve clarity. Ethanol feed rate = $0.330 \text{ mmol min}^{-1}$, catalyst mass = 0.300 g. Detection Columns: RTX-VMS + ShinCarbon ST.

Table S.8: Reaction conditions, conversion values and selectivities for literature ZnO materials utilized for ethanol conversion to acetaldehyde.

Entry	Catalyst	Reaction Conditions		Conversion / %	Selectivities / %		Reference
		Temperature / °C	TOS /h		Acetaldehyde	Ethylene	
1	ZnO (commercial, Sigma)	400	—	38-62	80	20	S1
2	ZnO (various syntheses plus 1 commercial)	350	6	15-20	84-94	<8	S2
3	ZnO (various syntheses)	400	—	20	80	20	S3
4	ZnO/SiO ₂ 0.5 wt% Zn From Zn(NO ₃) ₂	360	0.5	66	57	10	S4
			10	67	62	7.5	
5	ZnO (1 commercial and 1 prepared)	350	—	21-32	62-72	38-28	S5
6	ZnO(3.5)/Rb-MOR-(7)	400	4	52	94	0.9	This paper
			120	25	96	1.5	

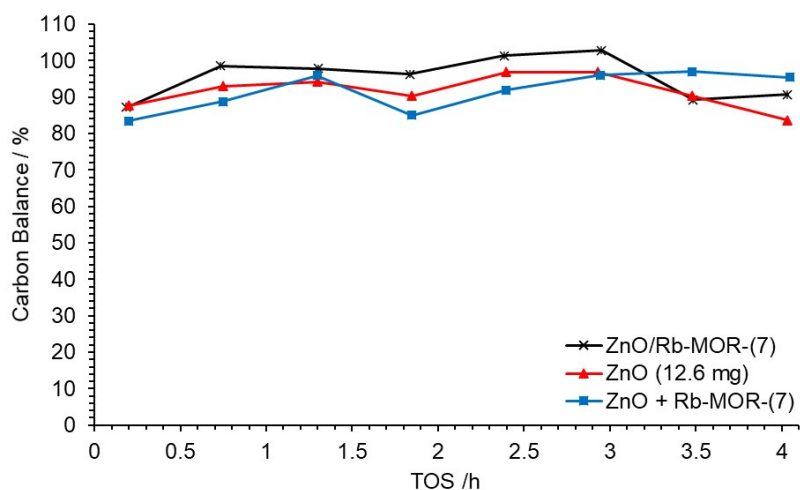


Figure S.16: Carbon balance for ZnO/Rb-MOR-(7) (×, 300 mg), ZnO (▲, 12.6 mg) and a physical mixture of ZnO and Rb-MOR-(7) (■, 12.6 mg + 300 mg) at 400 °C over 4 h TOS. Ethanol feed rate = 0.399 mmol min⁻¹. Detection Columns: RTX-VMS + ShinCarbon ST.

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