

Supporting Information

Unveiling the Role of Oxygen Species in Surface Promoted Fe-Mn Oxides for Chemical Looping Oxidative Dehydrogenation of Ethane

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DSC Measurements

The heat of reduction was calculated by integrating the heat flow signal (in mW) from the onset of reduction until both the first and second derivatives of the heat flow returned to zero. The cumulative heat release was also determined for each redox cycle, leading to a cumulative value in J for the total amount of samples measured (by timing the sample weight and integration with time).

This heat flow value was then normalized using a factor based on the ratio of (a) the expected heat release, i.e. H_2 lower heating value times the mole of lattice oxygen release (i.e. the amount of hydrogen combustion), to (b) the cumulative heat release within an entire redox cycle, as shown in Equation S1:

Normalized Heat Flow

$$= \frac{-242 \frac{\text{kJ}}{\text{mol}} \times \text{mol of reversible [O] release}}{\text{Cumulative Heat Flow for the entire redox cycle}} \times \frac{\text{measured heat flow}}{\text{mol of [O] release/uptake}}$$

Equation S 1

The initial heat flow value (before reactive gas introduction) was set to zero to generate a “zeroed” heat flow curve. A linear baseline was calculated from the reduction start and end, and then subtracted from this to calculate the final heat flow used for integration.

The final heat flow was integrated using the trapezoid rule to obtain a cumulative heat release in kilojoules. The sum of the integrated heat flow was calculated for each time point and divided by the total mol of O released at that time point to attain the cumulative heat release per mol O released. The average heat of reduction was calculated from the cumulative heat release of the entire reduction step divided by the total mol of O released. The moles of O released were calculated via the sample weight change divided by atomic mass of O.

Table S1. Volume, density, and flow rates for each catalyst fixed bed, using 500 mg of catalyst, GHSV = 4500 h⁻¹.

Sample	Volume (cm ³)	Density (g cm ⁻³)	C ₂ H ₆ /Ar rates (sccm)	flow C ₂ H ₆ /7.5	Ar purge flow rate (sccm)	O ₂ /Arflow rates (sccm)
NaW-Mn _x O _y	0.50	1.00	29.9 Ar	C ₂ H ₆ /7.5	29.9 Ar	6.4 O ₂ /29.9 Ar
NaMgW-Mn _x O _y	0.43	1.16	25.9 Ar	C ₂ H ₆ /6.5	25.9 Ar	5.5 O ₂ /25.9 Ar
NaW- (Fe _{0.1} Mn _{0.9}) _x O _y	0.58	0.86	34.8 Ar	C ₂ H ₆ /8.7	34.8 Ar	7.4 O ₂ /34.8 Ar
NaMgW- (Fe _{0.1} Mn _{0.9}) _x O _y	0.44	1.14	26.4 Ar	C ₂ H ₆ /6.6	26.4 Ar	5.6 O ₂ /26.4 Ar
NaW- (Fe _{0.2} Mn _{0.8}) _x O _y	0.38	1.33	22.6 Ar	C ₂ H ₆ /5.7	22.6 Ar	4.8 O ₂ /22.6 Ar
NaMgW- (Fe _{0.2} Mn _{0.8}) _x O _y	0.45	1.10	27.1 Ar	C ₂ H ₆ /6.8	27.1 Ar	5.8 O ₂ /27.1 Ar
NaW- (Fe _{0.4} Mn _{0.6}) _x O _y	0.52	0.95	31.5 Ar	C ₂ H ₆ /7.9	31.5 Ar	6.7 O ₂ /31.5 Ar
NaMgW- (Fe _{0.4} Mn _{0.6}) _x O _y	0.45	1.12	26.7 Ar	C ₂ H ₆ /6.7	26.7 Ar	5.7 O ₂ /26.7 Ar
NaMgW- (Fe _{0.1} Mn _{0.9}) _x O _y (10.8% O ₂)	0.44	1.14	26.4 Ar	C ₂ H ₆ /6.6	26.4 Ar	3.3 O ₂ /26.4 Ar
NaMgW- (Fe _{0.1} Mn _{0.9}) _x O _y (4.3% O ₂)	0.44	1.14	26.4 Ar	C ₂ H ₆ /6.6	26.4 Ar	1.3 O ₂ /26.4 Ar

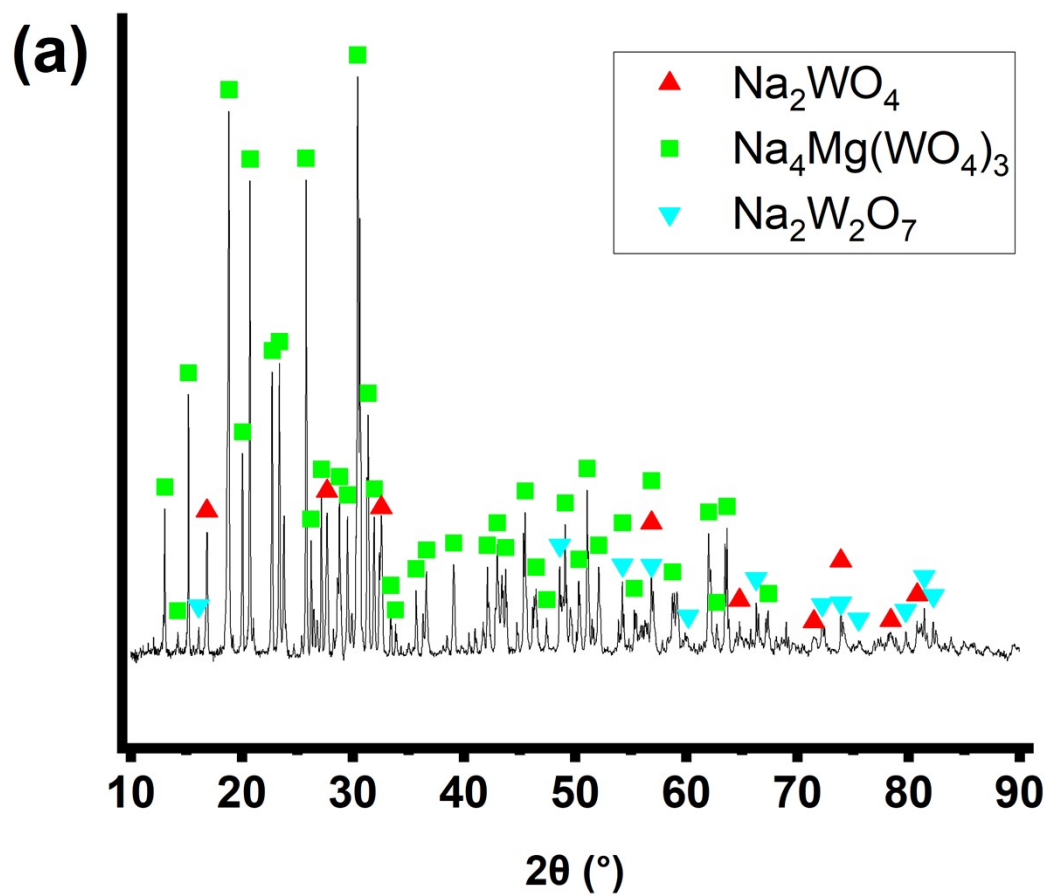


Figure S1. *Ex situ* XRD of as-synthesized $\text{Na}_4\text{Mg}(\text{WO}_4)_3$.¹

Table S2. CL-ODH detailed performance results for promoted Fe-Mn oxide catalysts, GHSV=4500 h⁻¹, T = 800-850°C.

NaMgW-Mn _x O _y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%*
800	20.49%	61.56%	92.44%	2.28%	0.89%	2.02%	2.27%	0.11%	0.00%	7.06%
825	34.30%	61.68%	91.40%	2.99%	1.17%	1.90%	2.30%	0.23%	0.00%	11.67%
850	45.28%	54.98%	90.19%	4.09%	1.42%	2.41%	1.51%	0.39%	0.00%	16.24%
NaW-Mn _x O _y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	25.99%	77.98%	90.55%	1.98%	1.19%	1.95%	4.26%	0.07%	0.00%	5.58%
825	45.74%	80.07%	81.41%	2.79%	6.76%	5.20%	3.67%	0.17%	0.00%	8.17%
850	61.06%	79.61%	80.00%	3.48%	2.09%	3.45%	4.07%	0.36%	6.55%	10.82%
NaMgW-(Fe _{0.1} Mn _{0.9}) _x O _y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	45.00%	84.27%	87.88%	2.86%	1.39%	2.96%	4.78%	0.13%	0.00%	6.74%
825	65.19%	89.94%	81.80%	3.82%	1.96%	4.68%	7.38%	0.36%	0.00%	6.39%
850	81.94%	93.65%	72.89%	5.12%	2.38%	7.34%	11.56%	0.71%	0.00%	5.30%
NaW-(Fe _{0.1} Mn _{0.9}) _x O _y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	34.12%	70.34%	92.93%	2.45%	1.30%	2.28%	1.03%	0.02%	0.00%	8.94%
825	53.98%	80.54%	89.06%	3.29%	1.67%	3.79%	1.84%	0.35%	0.00%	9.30%
850	73.53%	88.06%	82.04%	4.52%	2.19%	6.02%	4.51%	0.72%	0.00%	8.09%
NaMgW-(Fe _{0.2} Mn _{0.8}) _x O _y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	25.17%	67.34%	93.86%	2.35%	0.99%	1.91%	0.81%	0.08%	0.00%	7.35%
825	46.14%	78.48%	90.57%	3.14%	1.51%	3.25%	1.36%	0.16%	0.00%	8.74%

850	81.20%	89.94%	77.30%	5.92%	4.01%	7.40%	5.37%	0.00%	0.00%	7.52%
NaW-(Fe_{0.2}Mn_{0.8})_xO_y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	53.69%	82.24%	89.64%	3.19%	1.67%	3.61%	1.62%	0.27%	0.00%	8.48%
825	73.42%	90.18%	82.71%	4.54%	2.23%	5.89%	4.11%	0.52%	0.00%	6.69%
850	88.06%	93.91%	71.40%	6.28%	2.54%	8.18%	10.27%	0.91%	0.41%	5.29%
NaMgW-(Fe_{0.6}Mn_{0.4})_xO_y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	35.37%	64.88%	93.00%	2.91%	1.05%	1.78%	1.08%	0.18%	0.00%	10.64%
825	55.56%	77.29%	89.22%	3.87%	1.62%	3.08%	1.81%	0.41%	0.00%	10.75%
850	73.21%	85.75%	82.95%	5.30%	2.02%	4.07%	3.85%	0.81%	0.99%	9.04%
NaW-(Fe_{0.6}Mn_{0.4})_xO_y										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	35.63%	73.83%	92.62%	2.64%	1.07%	2.20%	1.33%	0.15%	0.00%	8.28%
825	53.14%	84.32%	89.35%	3.50%	1.63%	3.43%	1.78%	0.31%	0.00%	7.45%
850	70.30%	87.34%	84.05%	4.86%	2.08%	5.16%	3.25%	0.60%	0.00%	7.93%

*Volume percent is calculated on an inert-free basis.

The yield of each carbonaceous species during CL-ODH is defined as follows:

$$\text{Yield (\%)} = \frac{\text{Mol C from Species}}{\text{Mol C reacted from Ethane}} \quad \text{Equation S 2}$$

The total H₂ combusted by the catalysts during CL-ODH is defined as follows:

$$\text{H}_2 \text{ Combusted (\%)} = \frac{H_{2,\text{generated}} - H_{2,\text{out}}}{H_{2,\text{generated}}} \quad \text{Equation S 3}$$

Table S3. CL-ODH detailed performance results for NaMgW-(Fe_{0.1}Mn_{0.9})_xO_y under varying reoxidation conditions, GHSV=4500 h⁻¹, T = 800-850°C.

17% O ₂ /Ar reoxidation, 180s duration, 5 min. post oxidation purge										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	45.00%	84.27%	87.88%	2.86%	1.39%	2.96%	4.78%	0.13%	0.00%	6.74%
825	65.19%	89.94%	81.80%	3.82%	1.96%	4.68%	7.38%	0.36%	0.00%	6.39%
850	81.94%	93.65%	72.89%	5.12%	2.38%	7.34%	11.56%	0.71%	0.00%	5.30%
17% O ₂ /Ar reoxidation, 180s duration, 20 min. post oxidation purge										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	47.52%	81.13%	90.33%	3.10%	1.52%	2.80%	2.04%	0.21%	0.00%	8.03%
825	66.60%	87.69%	85.50%	4.38%	2.06%	3.74%	3.82%	0.48%	0.00%	7.38%
850	82.12%	90.87%	78.25%	6.15%	2.40%	4.88%	7.46%	0.86%	0.00%	6.81%
17% O ₂ /Ar reoxidation, 90s duration, 5 min. post oxidation purge										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	42.77%	74.47%	91.88%	3.02%	1.34%	2.38%	1.19%	0.19%	0.00%	9.48%
825	62.75%	82.90%	87.70%	4.32%	1.93%	3.31%	2.31%	0.42%	0.00%	9.25%
850	79.88%	90.71%	79.20%	6.05%	2.47%	4.52%	6.96%	0.82%	0.00%	6.72%
10% O ₂ /Ar reoxidation, 180s duration, 5 min. post oxidation purge										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	43.24%	74.85%	91.77%	2.99%	1.38%	2.40%	1.27%	0.19%	0.00%	9.46%
825	63.06%	83.08%	87.43%	4.30%	1.93%	3.50%	2.43%	0.41%	0.00%	9.24%
850	79.22%	88.99%	80.47%	6.07%	2.38%	4.26%	5.34%	0.78%	0.71%	7.65%
4% O ₂ /Ar reoxidation, 180s duration, 5 min. post oxidation purge										
T (°C)	Ethane Conv.	H ₂ Conv.	C ₂ H ₄ Sel.	CH ₄ Sel.	C ₃ Sel.	C ₄₊ Sel.	CO _x Sel.	C ₂ H ₂ Sel.	Coking Sel.	H ₂ Vol.%
800	43.15%	74.36%	91.82%	3.01%	1.37%	2.18%	1.42%	0.19%	0.00%	9.62%
825	60.60%	80.50%	88.37%	4.32%	1.82%	3.16%	1.93%	0.40%	0.00%	10.04%

850	71.37%	83.24%	85.27%	6.27%	2.04%	3.53%	2.24%	0.64%	0.00%	9.74%
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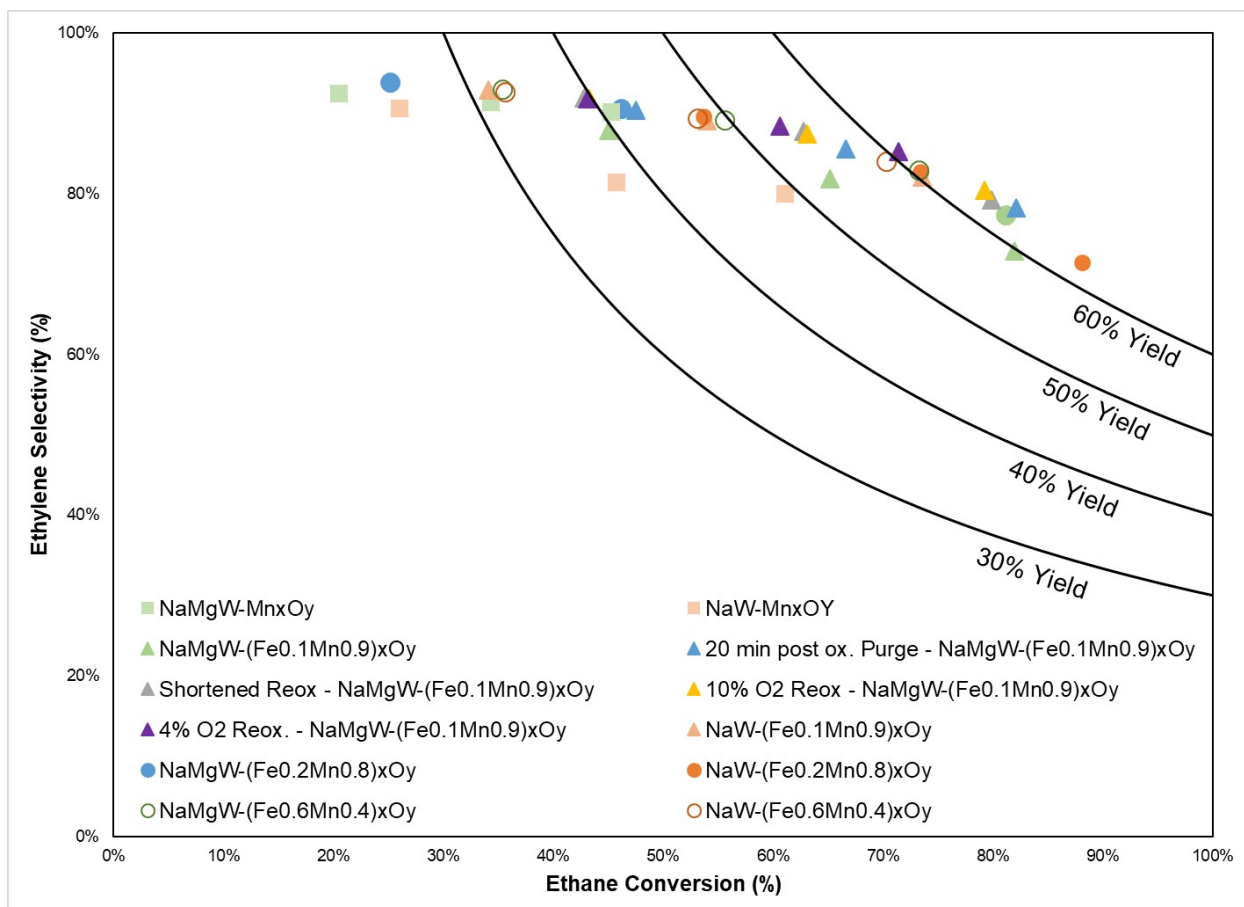


Figure S2. CL-ODH ethylene selectivity vs. ethane conversion for all Fe-Mn catalysts, including varied reoxidation experiments.

Table S4-9. XPS fitting parameters for unpromoted, NaW-promoted, and NaMgW-promoted ($\text{Fe}_{0.1}\text{Mn}_{0.9}$) $_x\text{O}_y$ catalysts.

(Fe_{0.1}Mn_{0.9})_xO_y						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						37.25%
<u>C 1s</u>	284.79	1.84	1	3533.09	33.92%	
<u>C 1s</u>	287.81	2	1	346.49	3.33%	
O						45.88%
<u>O 1s</u>	529.51	1.46	2.93	2870.73	27.56%	
<u>O 1s</u>	530.92	2.92	2.93	1907.73	18.32%	
Mn						15.49%
<u>Mn(I) 2p_{3/2}</u>	641.09	2.5	9.17	1036.19	9.97%	
Mn(I) 2p _{1/2}	652.55	2.5	4.74	1002.31		
<u>Mn(II) 2p_{3/2}</u>	643.22	3	9.17	574.07	5.52%	
Mn(II) 2p _{1/2}	654.48	3	4.74	555.27		
Mn 3s	83.28	2.2	0.674	779.82		
Mn 3s	88.77	2.2	0.674	457.91		
Fe						1.21%
<u>Fe 2p_{3/2}</u>	711.22	3.5	10.82	126.08	1.21%	
Fe 2p _{1/2}	724.29	3.5	5.6	121.80		

NaW-(Fe_{0.1}Mn_{0.9})_xO_y						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						42.00%
<u>C 1s</u>	284.89	2.06	1	4308.27	42.00%	
O						40.48%
<u>O 1s</u>	529.54	1.67	2.93	2389.19	23.29%	
<u>O 1s</u>	530.78	2.1	2.93	1162.87	11.34%	
<u>O 1s</u>	532.67	3	2.93	600.13	5.85%	
Mn						10.52%
<u>Mn(I) 2p_{3/2}</u>	641.04	2.5	9.17	721.59	7.04%	
Mn(I) 2p _{1/2}	652.5	2.5	4.74	705.55		
<u>Mn(II) 2p_{3/2}</u>	642.9	2.96	9.17	356.37	3.48%	
Mn(II) 2p _{1/2}	654.26	2.96	4.74	348.40		
Mn 3s	83.31	2.2	0.674	522.76		
Mn 3s	88.85	2.2	0.674	288.38		
Fe						0.69%
<u>Fe 2p_{3/2}</u>	711.27	3.5	10.82	71.06	0.69%	
Fe 2p _{1/2}	724.52	3.5	5.6	68.65		
W						3.39%
<u>W 4f_{7/2}</u>	35.16	1.55	5.48	347.65	3.39%	
W 4f _{5/2}	37.17	1.55	4.32	330.75		
W 5p _{3/2}	38.11	1.21	0.811	243.77		
Na						2.86%
<u>Na 1s</u>	1069.1	2.47	8.52	293.37	2.86%	

NaMgW-(Fe _{0.1} Mn _{0.9}) _x O _y (fresh)						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						42.10%
<u>C 1s</u>	284.81	1.98	1	4416.02	39.22%	
<u>C 1s</u>	287.98	2	1	324.56	2.88%	
O						39.47%
<u>O 1s</u>	529.49	1.67	2.93	2814.14	24.99%	
<u>O 1s</u>	530.87	2.02	2.93	1091.28	9.69%	
<u>O 1s</u>	532.91	3	2.93	538.97	4.79%	
Mg						0.00%
<u>Mg 1s</u>	1301.3	3	5.15*	0	0.00%	
Mn						11.00%
<u>Mn(I) 2p_{3/2}</u>	640.93	2.5	9.17	801.58	7.12%	
Mn(I) 2p _{1/2}	652.41	2.5	4.74	783.78		
<u>Mn(II) 2p_{3/2}</u>	642.75	3	9.17	436.65	3.88%	
Mn(II) 2p _{1/2}	654.13	3	4.74	426.90		
Mn 3s	83.25	2.2	0.674	499.63		
Mn 3s	88.74	2.2	0.674	391.26		
Fe						0.63%
<u>Fe 2p_{3/2}</u>	710.96	3.5	10.82	71.04	0.63%	
Fe 2p _{1/2}	724.03	2.5	5.6	129.39		
W						3.15%
<u>W 4f_{7/2}</u>	35.05	1.6	5.48	355.10	3.15%	
W 4f _{5/2}	37.13	1.6	4.32	337.84		
W 5p _{3/2}	38.61	3	0.811	503.95		
Na						3.63%
<u>Na 1s</u>	1068.98	2.41	8.52	408.62	3.63%	

NaMgW-(Fe _{0.1} Mn _{0.9}) _x O _y (Cycled, 17% O ₂ /Ar)						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						33.09%
<u>C 1s</u>	284.9	2.46	1	2160.8	33.09%	
O						46.11%
<u>O 1s</u>	529.46	1.94	2.93	1322.60	20.25%	
<u>O 1s</u>	531.04	2.22	2.93	819.13	12.54%	
<u>O 1s</u>	533.05	3	2.93	869.43	13.31%	
Mg						0.79%
<u>Mg 1s</u>	1301.3	3	5.15	51.29	0.79%	
Mn						8.89%
<u>Mn(I) 2p_{3/2}</u>	640.76	2.5	9.17	393.10	6.03%	
Mn(I) 2p _{1/2}	652.22	2.5	4.74	384.37		
<u>Mn(II) 2p_{3/2}</u>	642.79	2.71	9.17	186.73	2.86%	
Mn(II) 2p _{1/2}	654.27	2.71	4.74	182.58		
Mn 3s	82.9	1.47	0.674	111.10		
Mn 3s	88.4	1.51	0.674	61.20		
Fe						0.64%
<u>Fe 2p_{3/2}</u>	711	3.5	10.82	42.07	0.64%	
Fe 2p _{1/2}	724.03	2.5	5.6	40.64		
W						4.01%
<u>W 4f_{7/2}</u>	35.11	1.77	5.48	261.78	4.01%	
W 4f _{5/2}	37.01	1.77	4.32	249.05		
W 5p _{3/2}	38.17	1.84	0.811	474.76		
Na						6.35%
<u>Na 1s</u>	1069	2.82	8.52	414.70	6.35%	

NaMgW-(Fe _{0.1} Mn _{0.9}) _x O _y (Cycled, 10% O ₂ /Ar)						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						67.68%
<u>C 1s</u>	284.82	2.2	1	7410.93	58.16%	
<u>C 1s</u>	287.68	3.89	1	1212.7	9.52%	
O						25.05%
<u>O 1s</u>	529.5	1.64	2.93	832.74	6.54%	
<u>O 1s</u>	530.97	2.01	2.93	943.82	7.41%	
<u>O 1s</u>	533.02	2.63	2.93	1415.44	11.11%	
Mg						0.00%
<u>Mg 1s</u>	1301.3	3	5.15	0	0.00%	
Mn						2.90%
<u>Mn(I) 2p_{3/2}</u>	640.96	2.49	9.17	230.93	1.81%	
Mn(I) 2p _{1/2}	652.45	2.49	4.74	223.38		
<u>Mn(II) 2p_{3/2}</u>	642.84	2.96	9.17	137.97	1.08%	
Mn(II) 2p _{1/2}	654.3	2.96	4.74	133.45		
Mn 3s	83.01	3.44	0.674	412.24		
Mn 3s	88.61	3.43	0.674	244.97		
Fe						0.28%
<u>Fe 2p_{3/2}</u>	711.22	3.5	10.82	35.82	0.28%	
Fe 2p _{1/2}	724.28	3.5	5.6	34.61		
W						1.87%
<u>W 4f_{7/2}</u>	35.57	1.82	5.48	238.24	1.87%	
W 4f _{5/2}	37.644	1.82	4.32	226.66		
W 5p _{3/2}	38.49	1.44	0.811	58.06		
Na						2.23%
<u>Na 1s</u>	1069.3	2.94	8.52	283.81	2.23%	

NaMgW-(Fe _{0.1} Mn _{0.9}) _x O _y (Cycled, 17% O ₂ /Ar, 20 min. post oxidation purge)						
Species	Position (eV)	FWHM	RSF	Corrected Area	At%	Surface At%
C						54.10%
<u>C 1s</u>	284.78	2.28	1	5259.98	54.10%	
O						31.68%
<u>O 1s</u>	529.45	1.81	2.93	1104.88	11.36%	
<u>O 1s</u>	530.9	2.05	2.93	1262.90	12.99%	
<u>O 1s</u>	533.01	3	2.93	713.01	7.33%	
Mg						0.00%
<u>Mg 1s</u>	1301.3	3	5.15	0	0.00%	
Mn						4.94%
<u>Mn(I) 2p_{3/2}</u>	640.91	2.5	9.17	352.58	3.64%	
Mn(I) 2p _{1/2}	652.4	2.5	4.74	344.76		
<u>Mn(II) 2p_{3/2}</u>	642.91	2.53	9.17	125.24	1.29%	
Mn(II) 2p _{1/2}	654.26	2.53	4.74	122.44		
Mn 3s	82.68	2.2	0.674	343.66		
Mn 3s	88.67	2.2	0.674	180.52		
Fe						0.65%
<u>Fe 2p_{3/2}</u>	711.04	3.5	10.82	63.15	0.65%	
Fe 2p _{1/2}	723.64	3.5	5.6	61.01		
W						3.86%
<u>W 4f_{7/2}</u>	35.31	1.74	5.48	375.20	3.86%	
W 4f _{5/2}	37.33	1.74	4.32	356.97		
W 5p _{3/2}	38.2	1.22	0.811	185.88		
Na						4.33%
<u>Na 1s</u>	1069.12	2.86	8.52	420.65	4.33%	

**Mg 1s RSF was determined from a MgO standard.*

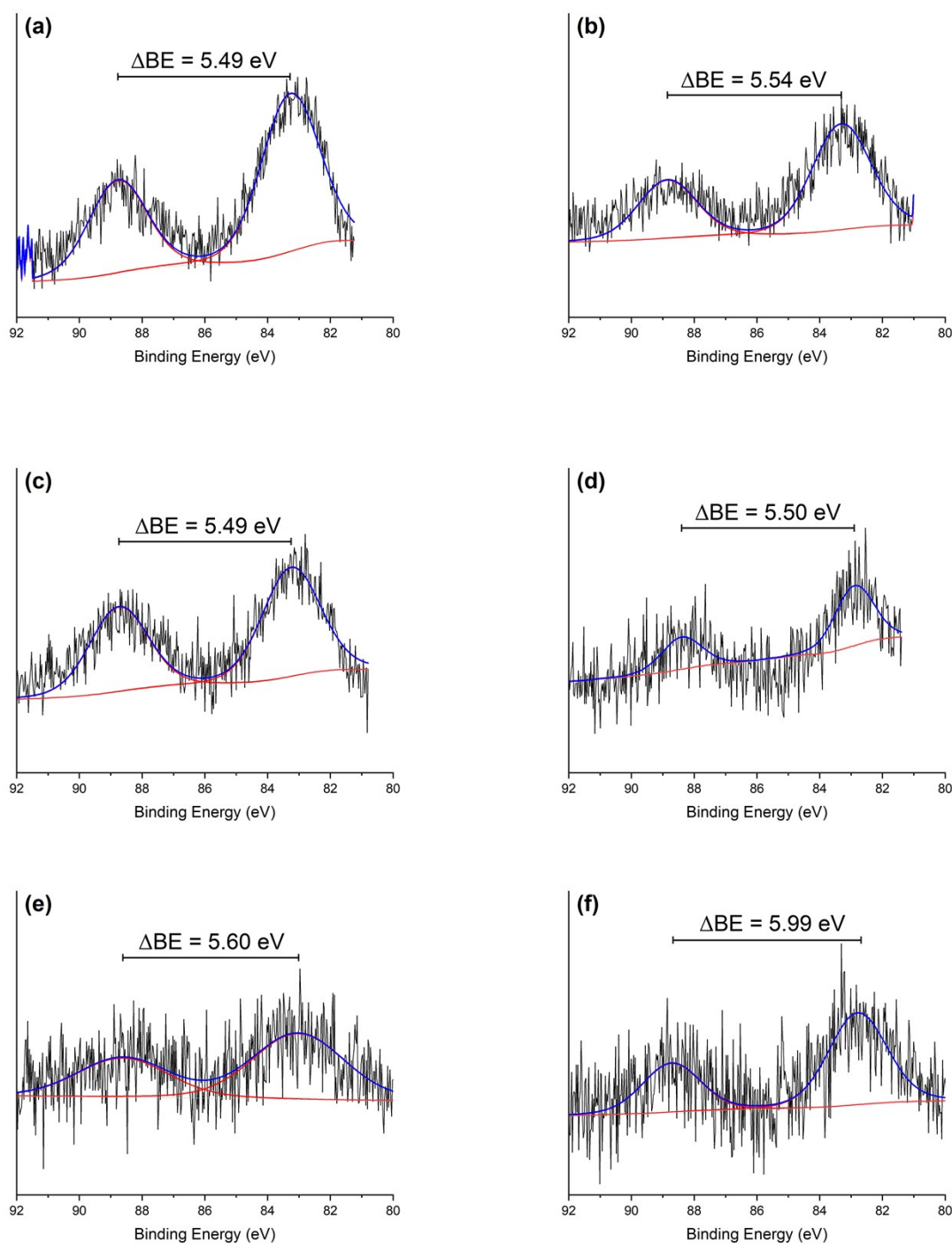


Figure S3. Mn 3s XPS spectra for (a) fresh $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$, (b) fresh NaW- $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$, (c) fresh NaMgW- $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$, (d) cycled NaMgW- $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$, (e) NaMgW- $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$ cycled with 10% O_2/Ar , and (f) NaMgW- $(\text{Fe}_{0.1}\text{Mn}_{0.9})_x\text{O}_y$ cycled with 20-minute post-oxidation purge.

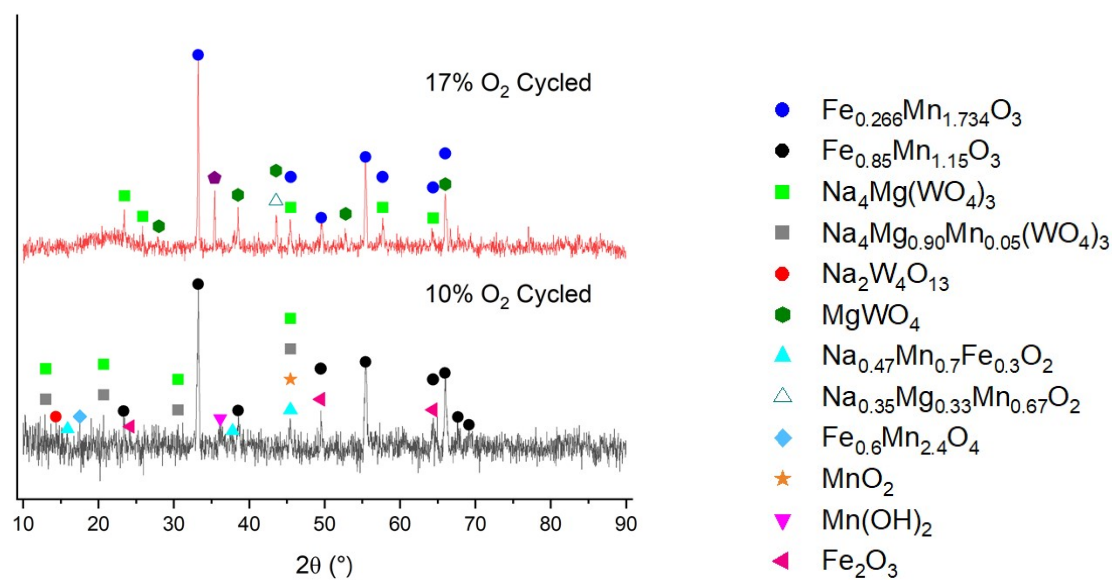


Figure S4. XRD of NaMgW-(Fe_{0.1}Mn_{0.9})_xO_y after cycling with 10% O₂ and 17% O₂ reoxidation and quenching.

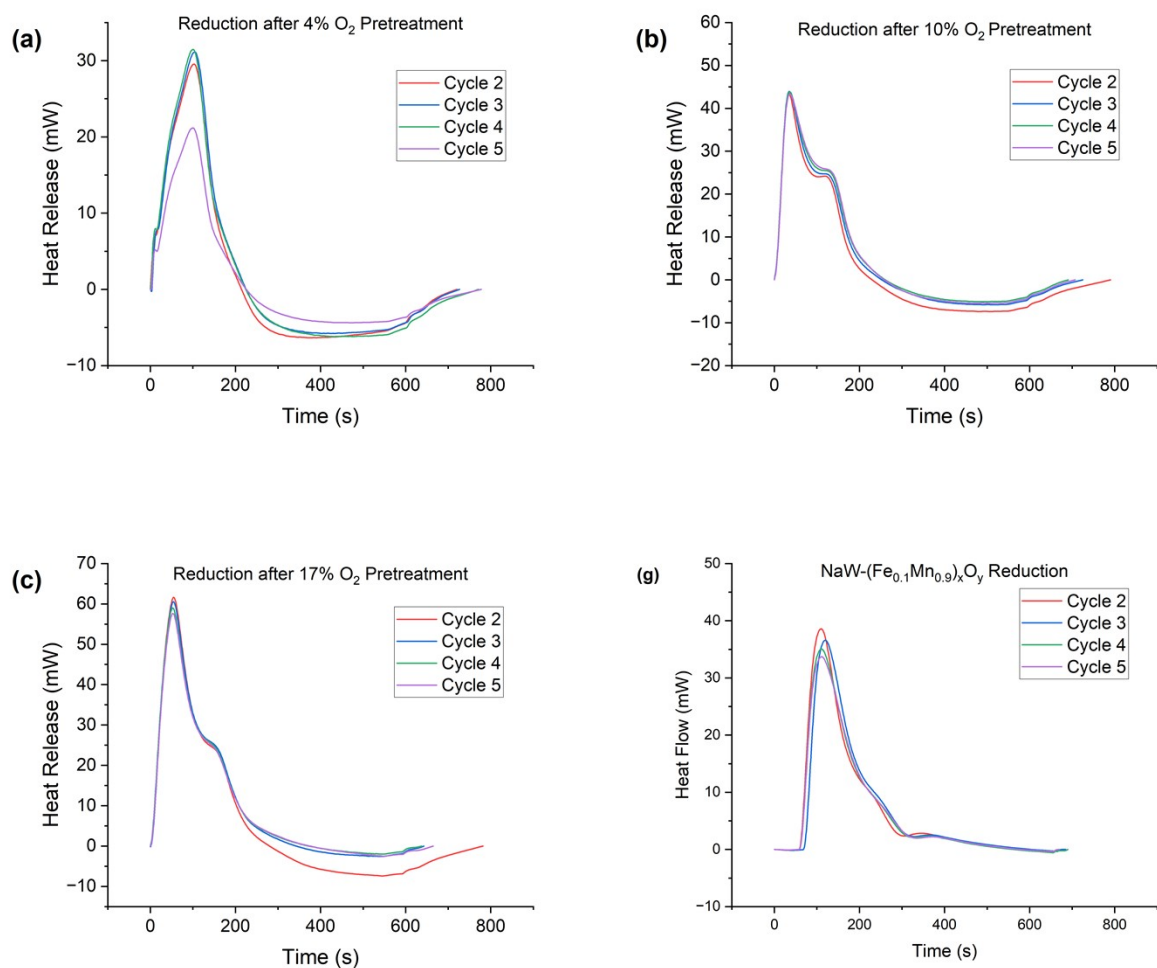


Figure S 5. Heat release over time during reduction cycles for (a) NaMgW-(Fe_{0.1}Mn_{0.9})_xO_y cycled with 4% O₂, (b) cycled with 10% O₂, (c) cycled with 17% O₂, and (d) NaW-(Fe_{0.1}Mn_{0.9})_xO_y cycled with 17% O₂.

References

- (1) Chacko, D.; Neal, L. M.; Lis, B. M.; Liu, J.; Pedersen, A.; Wachs, I. E.; Li, F. Effective CO_x Suppression by a Na₄Mg(WO₄)₃ Promoter in Chemical Looping Oxidative Dehydrogenation of Ethane. *ACS Catal.* **2025**, *15* (5), 3992–4006. <https://doi.org/10.1021/acscatal.4c07851>.