Supplementary information for: Understanding methanol dissociative adsorption and oxidation on amorphous oxide films

Sri Krishna Murthy Padavala,[1] Kateryna Artyushkova,[2] Shannon W. Boettcher,[3] Slavomir Nemsak,[4] Kelsey A. Stoerzinger[1,5,*]

[1]School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, Oregon 97331, USA

[2]Physical Electronics Inc. Chanhassen MN, 55317 USA

[3]Department of Chemistry & Biochemistry and the Materials Science Institute, University of Oregon, Eugene, Oregon 97403, USA

[4]Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

[5]Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

*kelsey.stoerzinger@oregonstate.edu

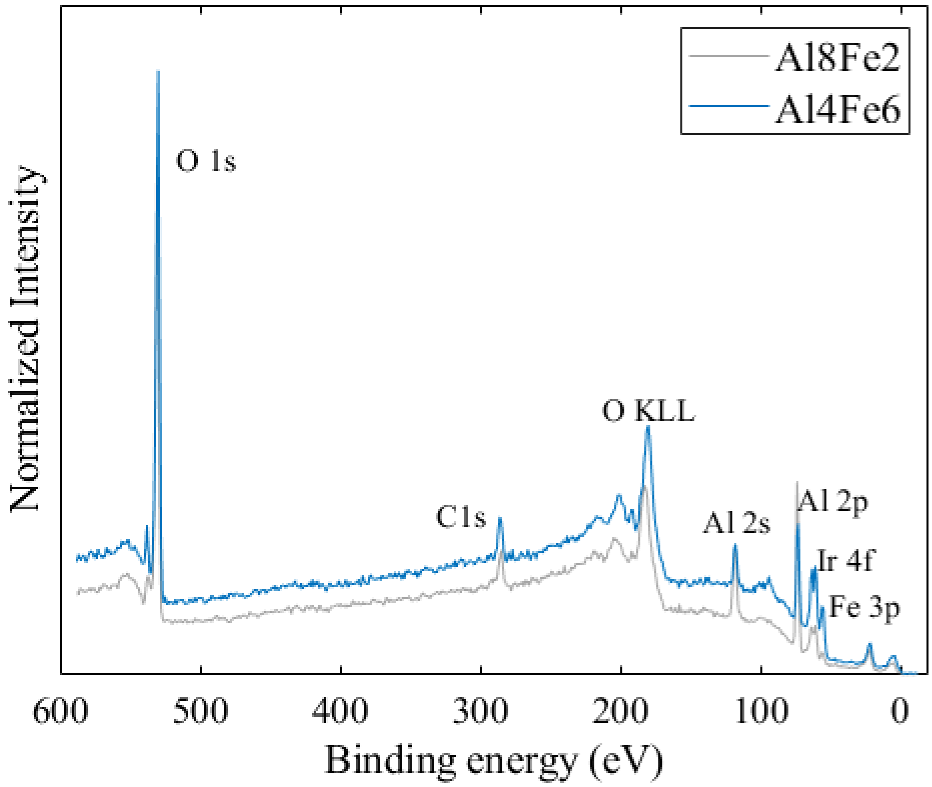
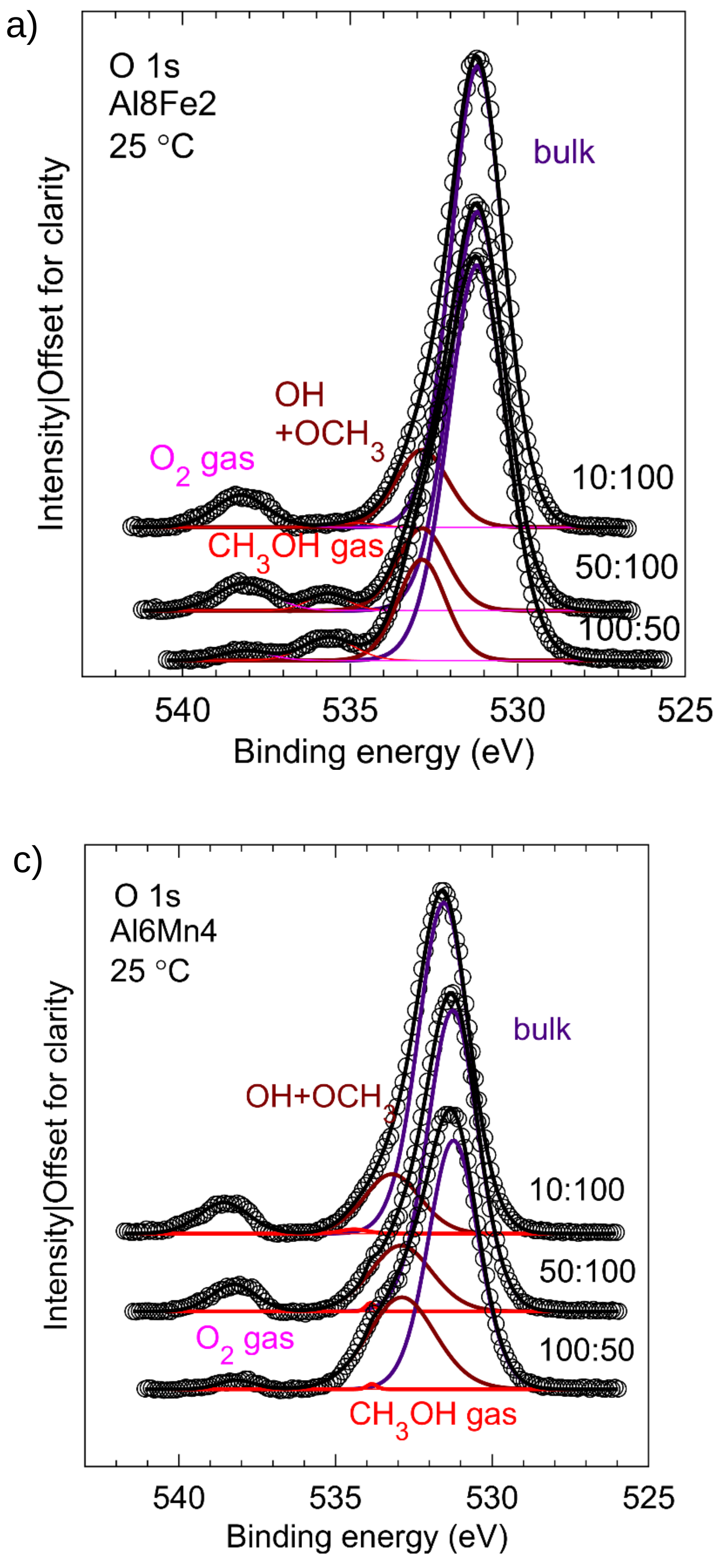


Figure S1: Survey spectra collected at 690 eV for 50 mTorr methanol and 100 mTorr oxygen at 25 °C for the Al8Fe2 and Al4Fe6 films. The spectra are normalized to the intensity of the bulk oxygen at 690 eV. The Ir 4f is from the underlying conductive layer on the substrate, but remains beneath the surface from depth profiling by changing the incident photon energy (Figure S4).


a)
O 1s
Al8Fe2
25 °C
bulk
OH
+OCH3
O2 gas
10:100
CH3OH gas
50:100
100:50
Intensity|Offset for clarity
540
535
530
525
Binding energy (eV)
b)
C 1s
Al8Fe2
25 °C
OCH3
adventitious
10:100
CH3OH
gas
50:100
100:50
CO3
Intensity|Offset for clarity
295
290
285
280
Binding energy (eV)
c)
O 1s
Al6Mn4
25 °C
bulk
OH+OCH3
10:100
50:100
O2 gas
100:50
CH3OH gas
Intensity|Offset for clarity
540
535
530
525
Binding energy (eV)
d)
C 1s
Al6Mn4
25 °C
adventitious
OCH3
10:100
50:100
100:50
CH3OH
gas
CO3
Intensity|Offset for clarity
295
290
285
280
Binding energy (eV)

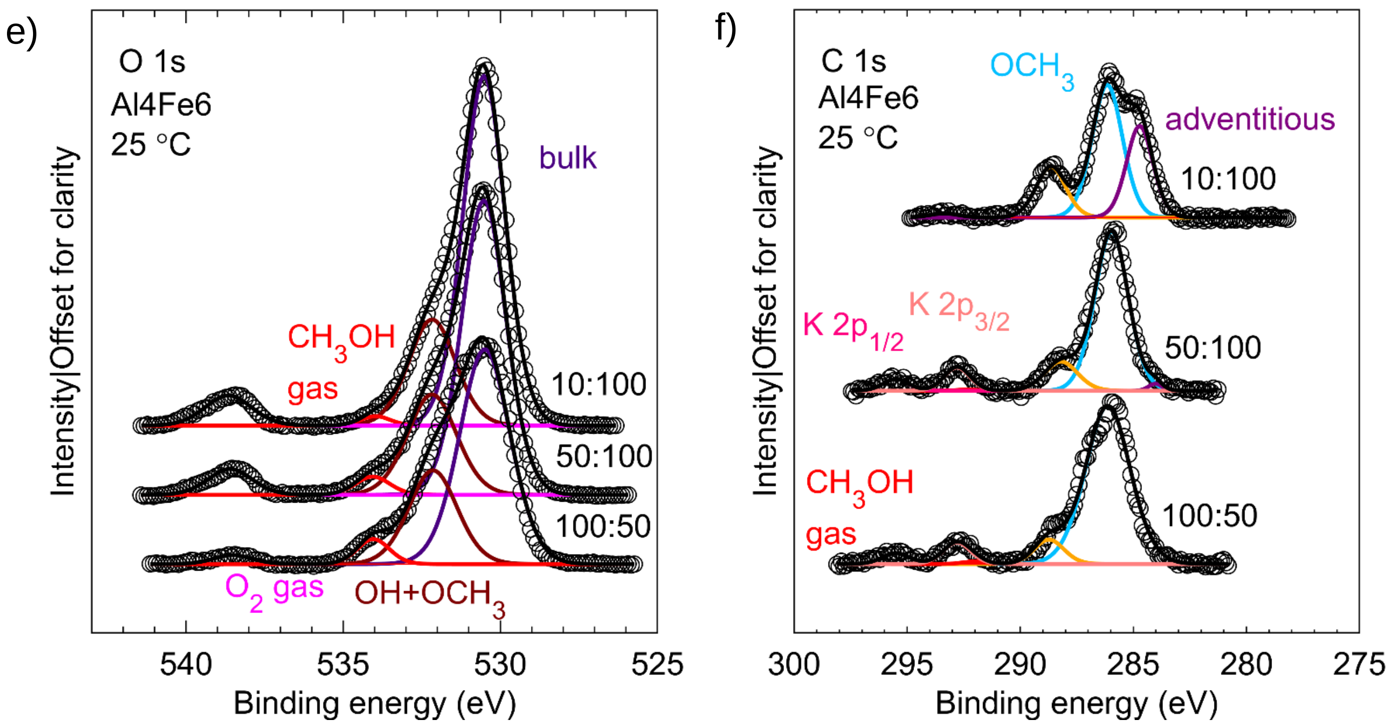


Figure S2: Oxygen and carbon core levels for Al8Fe2 and Al6Mn4 at 25 °C for different methanol: oxygen gas pressures: a) O 1s probed at 690 eV for Al8Fe2, b) C 1s probed at 490 eV for Al8Fe2 c) O 1s probed at 690 eV for Al6Mn4 d) C 1s probed at 490 eV for Al6Mn4 e) O 1s probed at 690 eV for Al4Fe6 and f) C 1s probed at 490 eV for Al4Fe6. In the above figure, 10:100, 50:100 and 100:50 denote the pressure of methanol:oxygen in mTorr. We note that the intensity scale for the O 1s and C 1s shown are independent and chosen to highlight changes in surface speciation. The intensity of the gas phase feature relative to the bulk depends on the proximity of the sample to the nose cone, and the O:C ratio of gas phase methanol is consistent with the experimentally measured RSF.

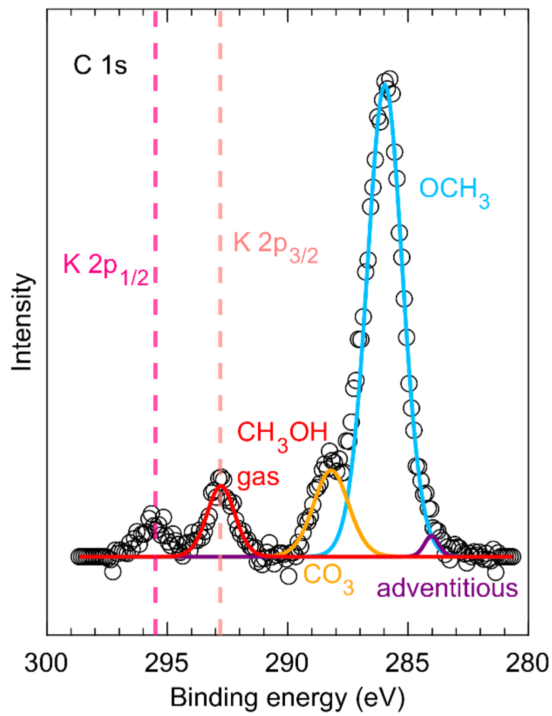


Figure S3: C 1s spectrum probed at 490 eV for 50 mTorr of methanol and 100 mTorr oxygen at 25 °C for the Al4Fe6 film. The above spectrum depicts the K 2p features characteristic of potassium contamination; based on tabulated cross sections, the abundance of K is ~10x lower than its intensity ratio with C at 490 eV. Dashed lines show the K $2p_{1/2}$ and K $2p_{3/2}$ features which overlap with the gas phase methanol peak. These features are removed from the adsorbates and do not affect the intensity of the adsorbates observed.

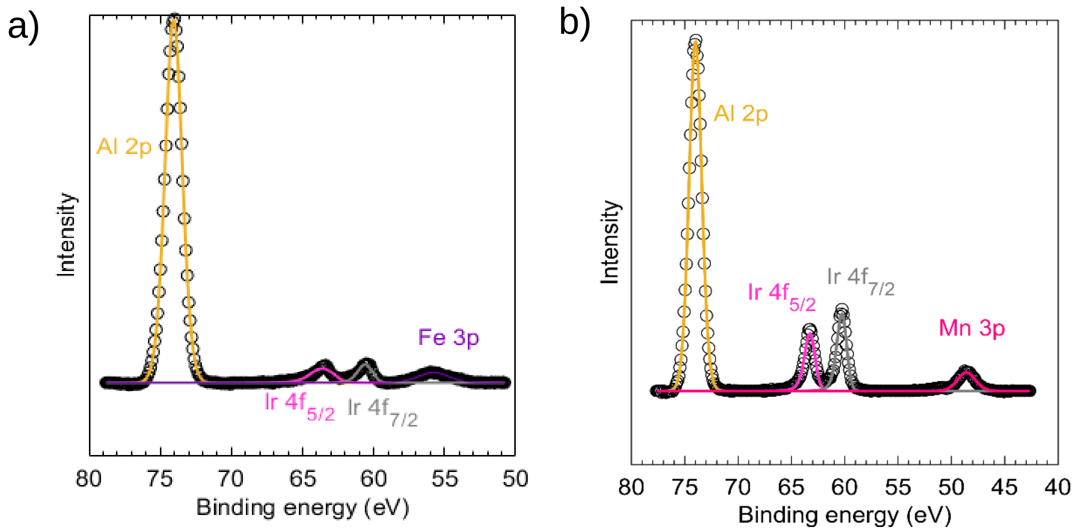


Figure S4: Metallic core levels probed at 490 eV for 100 mTorr of methanol and 50 mTorr of oxygen at room temperature depicting different features observed for a) Al8Fe2 and b) Al6Mn4

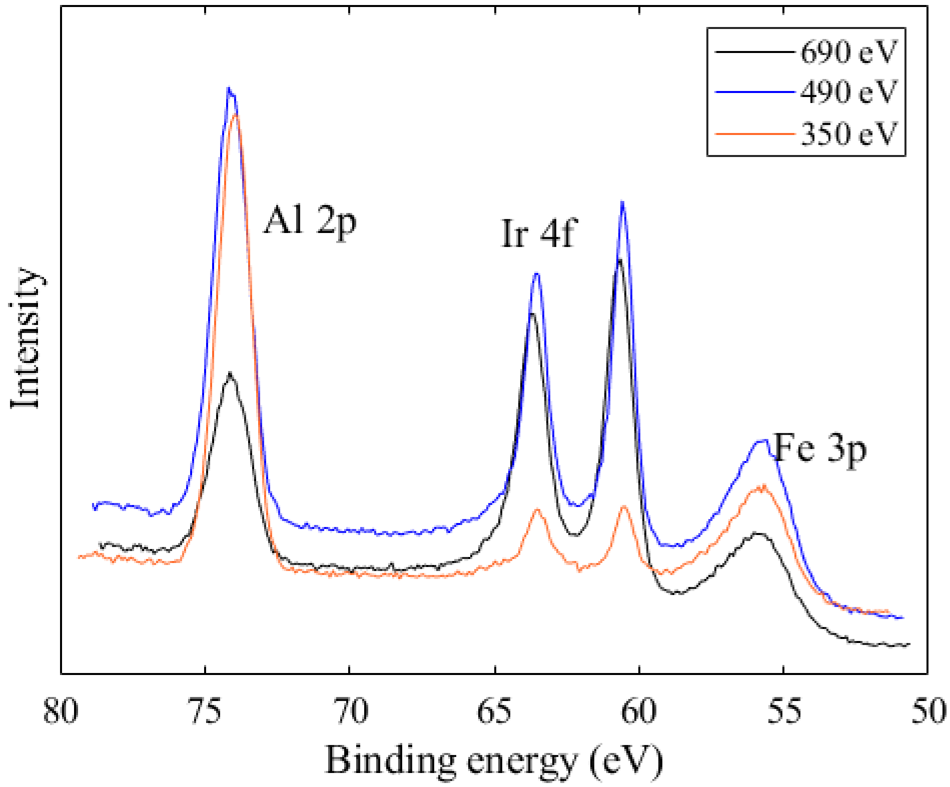


Figure S5: Al 2p, Ir 4f and Fe 3p core levels for Al4Fe6 film for 100 mTorr of methanol and 50 mTorr of oxygen at room temperature for IPEs of 690 eV, 490 eV and 350 eV respectively. The visibility of Ir 4f is more for 690 eV compared to 490 eV and 350 eV due to the greater IMFP at 690 eV but exhibits no change in either intensity or binding energy (BE) (indicative of oxidation state), demonstrating the robustness of the film. A similar trend was observed for the other films, temperatures, and atmospheres as well.

Feature	Parameter	Al8Fe2	Al4Fe6	Al6Mn4
Bulk	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.95 ± 0.05	1.78 ± 0.12	1.91 ± 0.03
	BE (eV)	531.09 ± 0.1	530.46 ± 0.07	531.32 ± 0.08
OH	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.61 ± 0.09	1.64 ± 0.08	2.22 ± 0.13
	BE (eV)	Bulk + 1.65	Bulk + 1.65	Bulk + 1.65
CH_3OH_{gas}	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.32 ± 0.23	1.09 ± 0.09	0.76 ± 0.34
	BE (eV)	535.05 ± 0.37	533.87 ± 0.1	534.02 ± 0.29
O_{2gas}	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.67 ± 0.13	1.57 ± 0.11	1.6 ± 0.16
	BE (eV)	537.82 ± 0.23	538.3 ± 0.14	538.18 ± 0.13

Table S1: Average fitted parameters for the features across different methanol:oxygen gas ratios at different temperatures observed in O 1s at 690 eV for the three samples in terms of average plus or minus standard deviation.

Feature	Parameter	Al8Fe2	Al4Fe6	Al6Mn4
Methoxy	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.62 ± 0.11	2.02 ± 0.28	1.82 ± 0.07
	BE (eV)	286.08 ± 0.18	285.96 ± 0.12	286.2 ± 0.09
Carbonate	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	2.24 ± 0.22	1.62 ± 0.53	1.76 ± 0.21
	BE (eV)	288.61 ± 0.16	288.57 ± 0.12	288.69 ± 0.08
Adventitious carbon	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.43 ± 0.05	1.29 ± 0.35*	1.39 ± 0.05
	BE (eV)	284.48 ± 0.14	284.37 ± 0.3*	284.54 ± 0.06
CH_3OH_{gas}	Lineshape	GL(30)	GL(30)	GL(30)
	FWHM (eV)	1.46 ± 0.45	1.56 ± 0.87	1.67 ± 0.54
	BE (eV)	291.74 ± 0.22	292.3 ± 0.96	293.62 ± 0.45

Table S2: Average fitted parameters for the features observed across different methanol:oxygen gas ratios at different temperatures observed in C1s probed at 490 eV for the three samples in terms of average plus or minus standard deviation. *The adventitious carbon feature was not observed for 100 mTorr of methanol and 50 mTorr of oxygen.

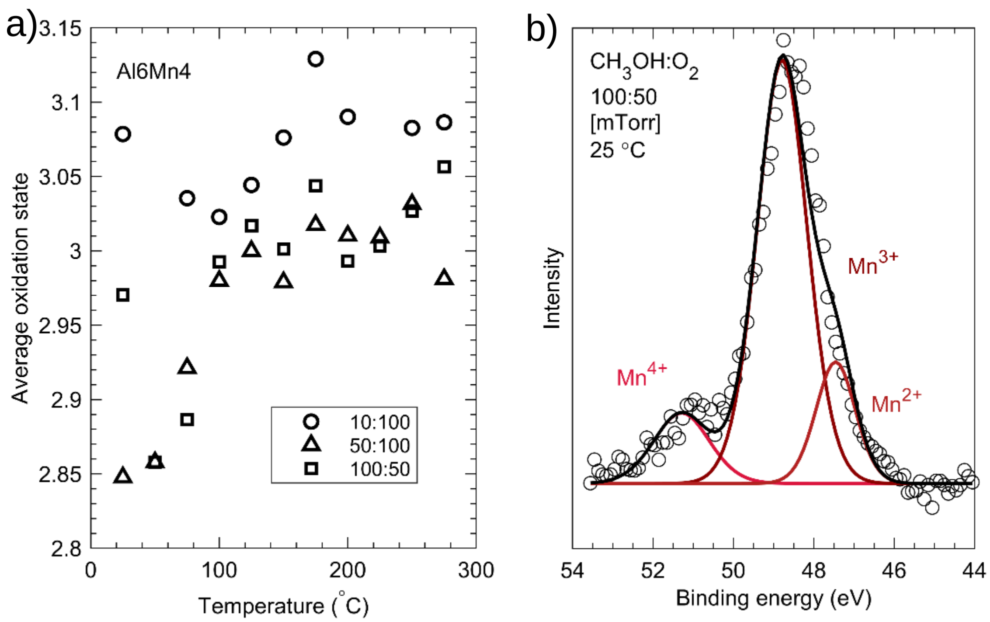


Figure S6: a) Average oxidation state of Mn with increase in temperature for Mn 3p spectra collected at 490 eV. b) Spectrum for 100 mTorr of methanol and 50 mTorr of oxygen at 25 ℃ for Al6Mn4 depicting the intensities of the different Mn oxidation states. In the above figure, 1-10 denotes 10 mTorr methanol and 100 mTorr oxygen, 5-10 denotes 50 mTorr methanol and 100 mTorr oxygen and 10-5 denotes 10 mTorr methanol and 100 mTorr oxygen. The BE of the different oxidation states are taken from Ilton *et al*[1].

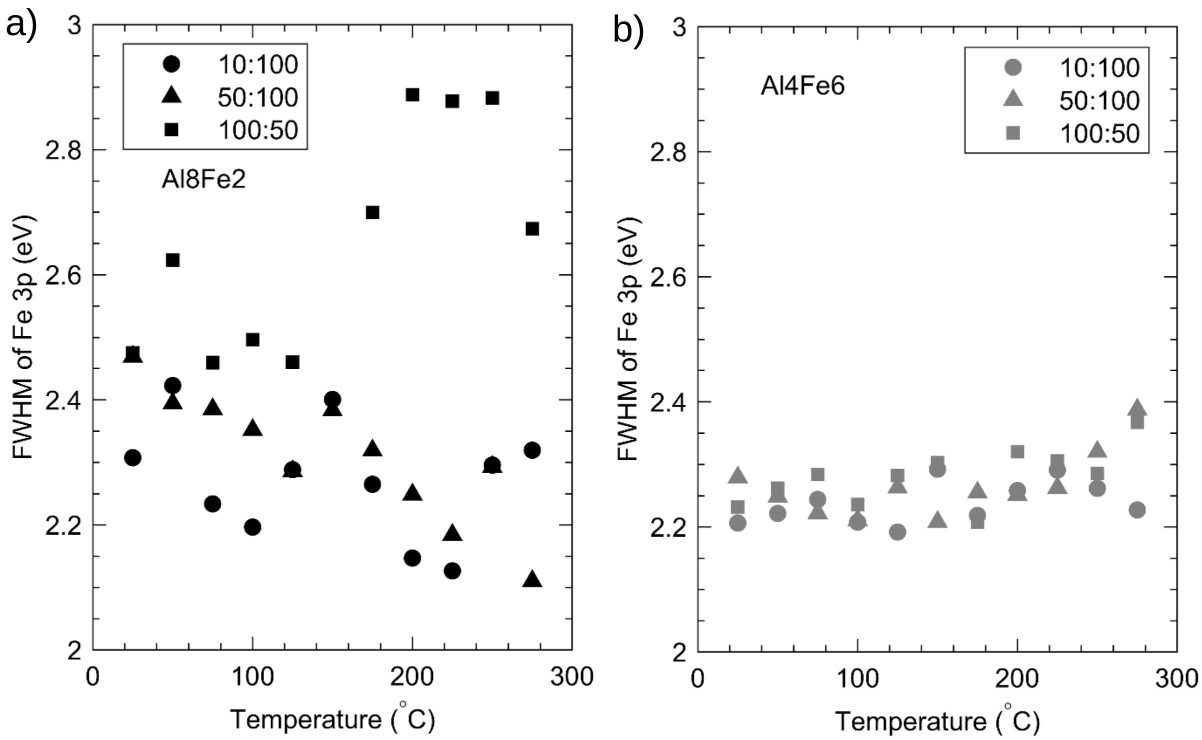


Figure S7: Full width half maximum of Fe 3p for a) Al8Fe2 and b) Al4Fe6 for the different methanol:oxygen gas ratios. In the above figure, 10:100, 50:100 and 100:50 denote the pressures of methanol:oxygen in mTorr.

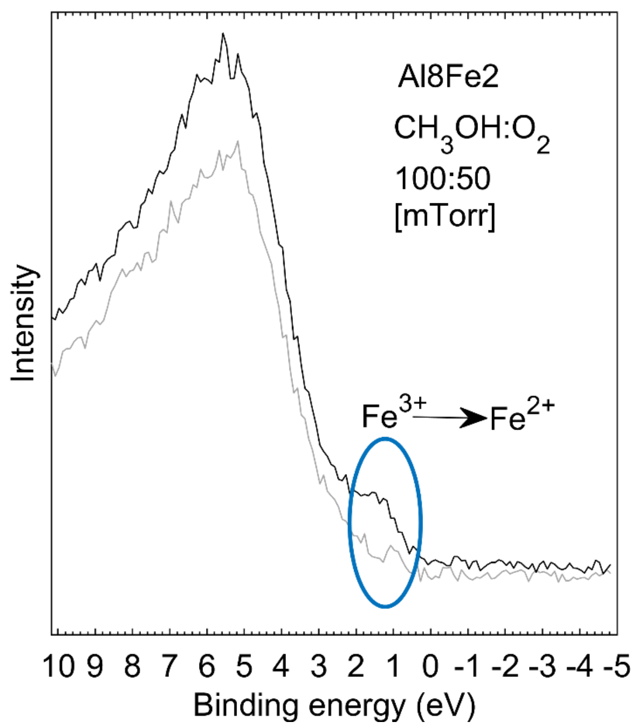


Figure S8: VB spectra for Al8Fe2 for 100:50 methanol:oxygen gas ratio at 25 ℃ (grey trace) and 275 ℃ (black trace). The increase in the intensity of the peak at ~1 eV indicates the formation of Fe^{2+} resulting from (partial) reduction in Fe oxidation state with increasing temperature.

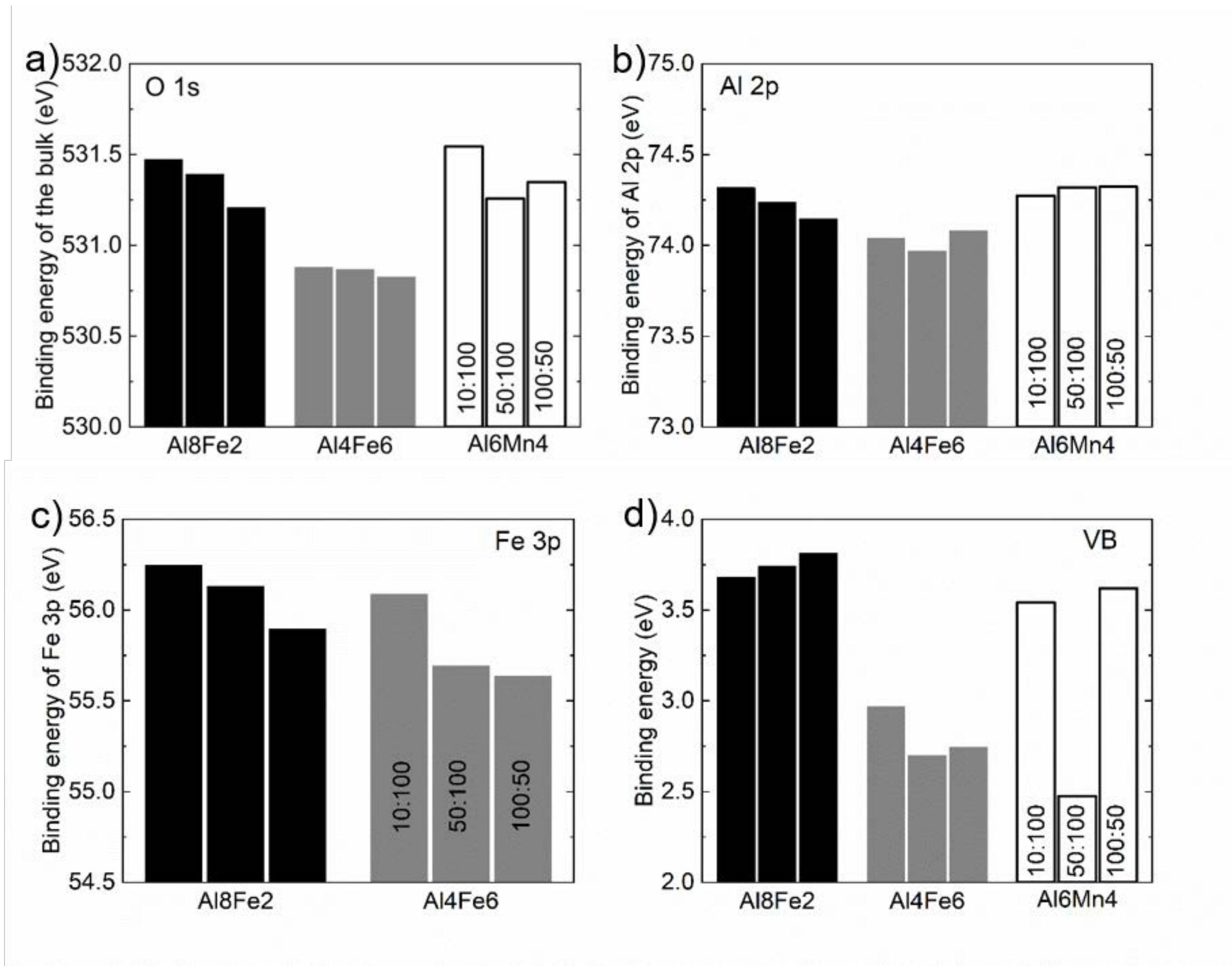


Figure S9: BE of the different core levels for Al8Fe2, Al4Fe6 and Al6Mn4 films at 25 °C for different methanol:oxygen gas pressures: a) Bulk O probed at 690 eV, b) Al 2p probed at 490 eV c) Fe 3p probed at 490 eV and d) Valence band edge probed at 350 eV. In the above figure, 10:100, 50:100 and 100:50 denote the pressure of methanol:oxygen in mTorr.

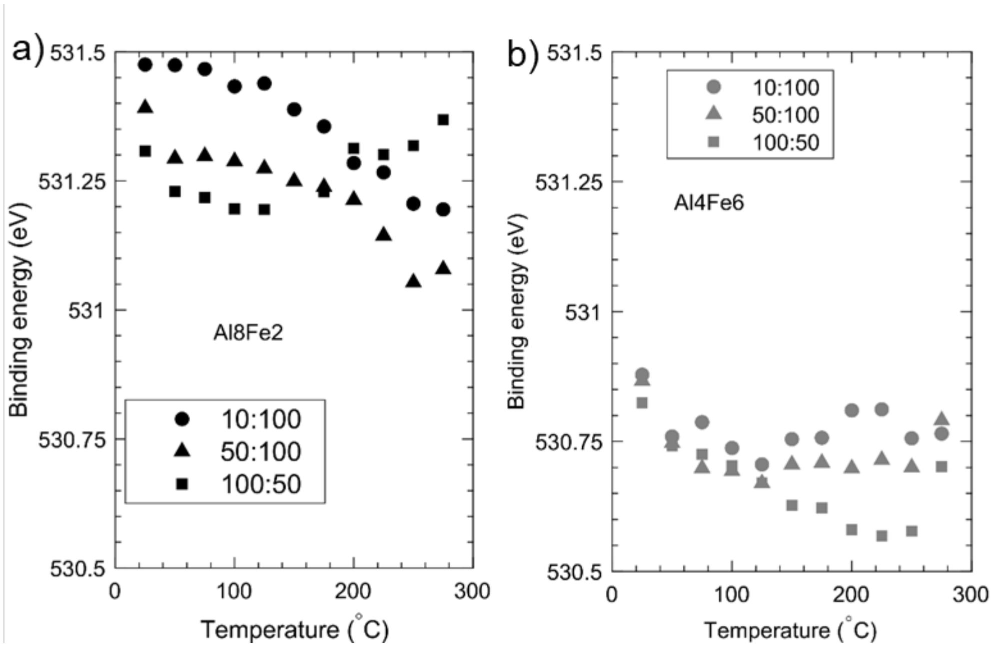


Figure S10: BE of bulk oxygen with temperature for different methanol:oxygen gas ratios for a) Al8Fe2 and b) Al4Fe6. In the above figure, 10:100, 50:100 and 100:50 denote the pressures of methanol:oxygen in mTorr.

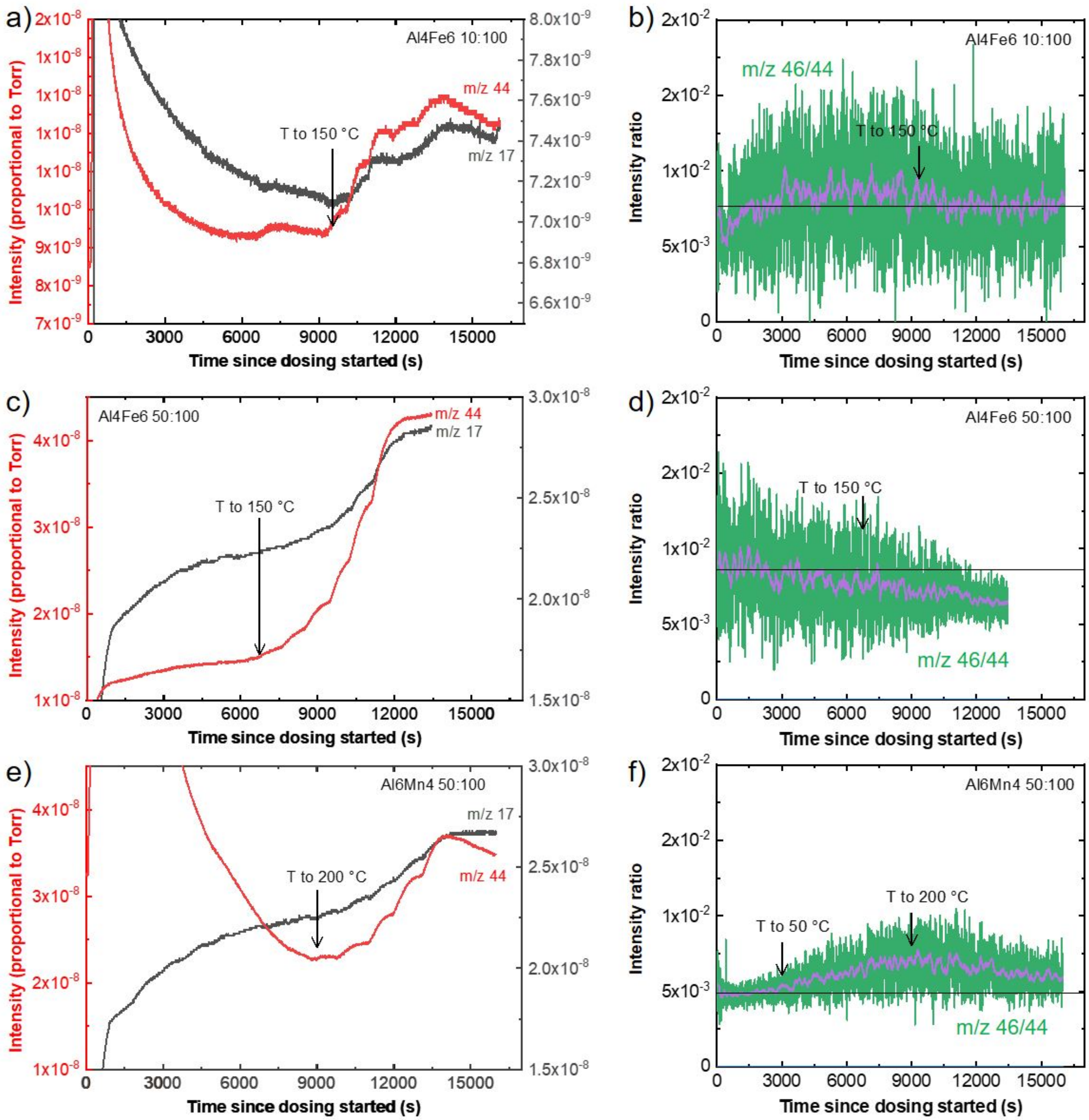


Figure S11: Evolution of noted m/z feature (a,c,e) or feature ratio (b,d,f) with time for the Al4Fe6 films for 10:100 (a-b) and 50:100 (c-d) methanol:oxygen gas ratio and Al6Mn4 in 50:100 methanol:oxygen (e-f). m/z 44 corresponds to carbon dioxide (CO_2), m/z 17 corresponds to water (selected to avoid overlap with methanol fragments), and an m/z 46/44 ratio corresponds to dimethyl ether (where the ratio accounts for overlap with a CO_2 fragment), where the purple line average is to guide the eye in comparing against the baseline (black) at room temperature. For Al6Mn4 in 10:100 methanol:oxygen and Al8Fe2 in all gas environments, the residual CO_2 background in the chamber was too high for product assessment. Mass spectra were not collected at elevated temperatures in the 100:50 methanol:oxygen gas ratio for any films.

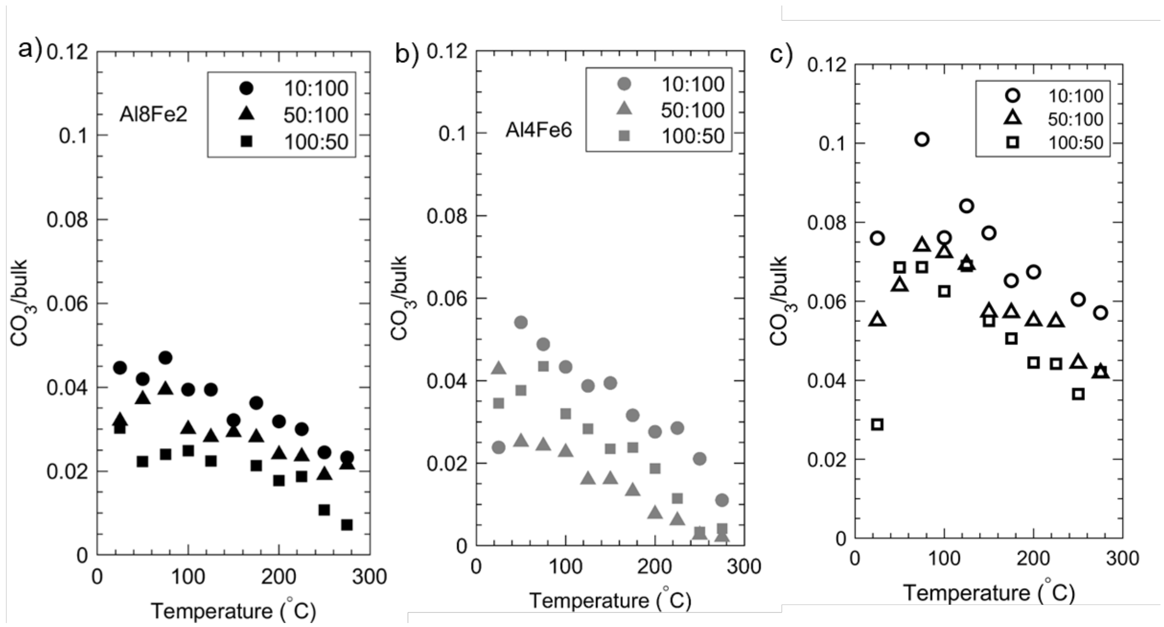


Figure S12: Ratio of the carbonate (C 1s) and bulk (O 1s) with temperature for different methanol:oxygen gas pressures for the a) Al8Fe2, b) Al4Fe6 and c) Al6Mn4 films. In the above figure, 50:100 and 100:50 denote the pressure of methanol:oxygen in mTorr.

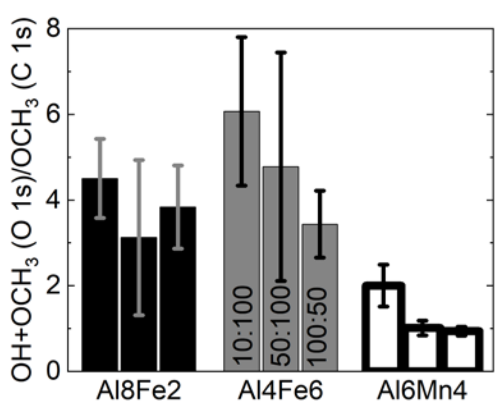


Figure S13: Average across temperatures for the ratio of $OH+OCH_3$ feature (O 1s) to OCH_3 feature (C 1s) for different methanol:oxygen gas pressures for the Al8Fe2, Al4Fe6 and Al6Mn4 films when the BE constrain for the $OH+OCH_3$ feature is relaxed in the O 1s. In the above figure, 10:100, 50:100 and 100:50 denote the pressure of methanol:oxygen in mTorr.

References

1. E. S. Ilton, J. E. Post, P. J. Heaney, F. T. Ling and S. N. Kerisit, *Applied Surface Science*, 2016, **366**, 475-485.