Supplementary Information

Al-doped Fe2O3 as a support for molybdenum oxide methanol oxidation catalysts

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1. Catalyst preparation. In addition to the preparation description in the main text, the following shows the relationship between wt% loading of Al and the atomic fraction present in the sample

For example for the 5 wt% Al_2O_3 sample, there are 0.05g./102 g.mol = 5 x 10-4 mol, whereas the Fe_2O_3 is 0.95g/160 g. mol^{-1} = 5.9 x 10^{-3} mol. And so the cation % Al = 5 $x10^{-4}/64x10^{-4}$ = 7.8%. Similar calculations for the other samples yield the graph in figure S1

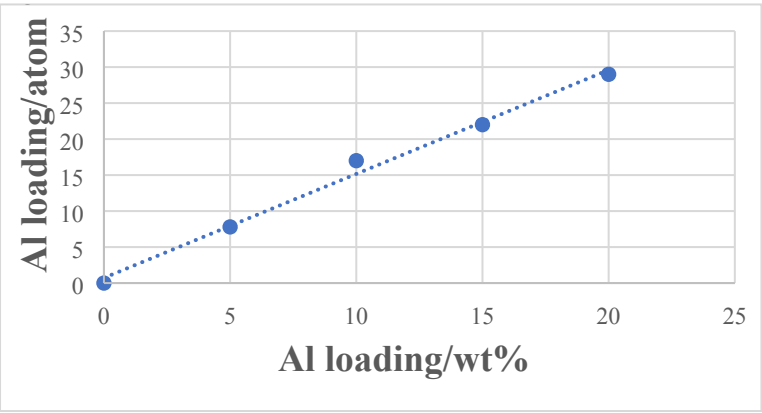


Figure S1. *Dependence of atomic fraction of Al upon wt% loading.*

2. XRD. Figure S2 shows the XRD patterns for the various Al doped samples and undoped haematite

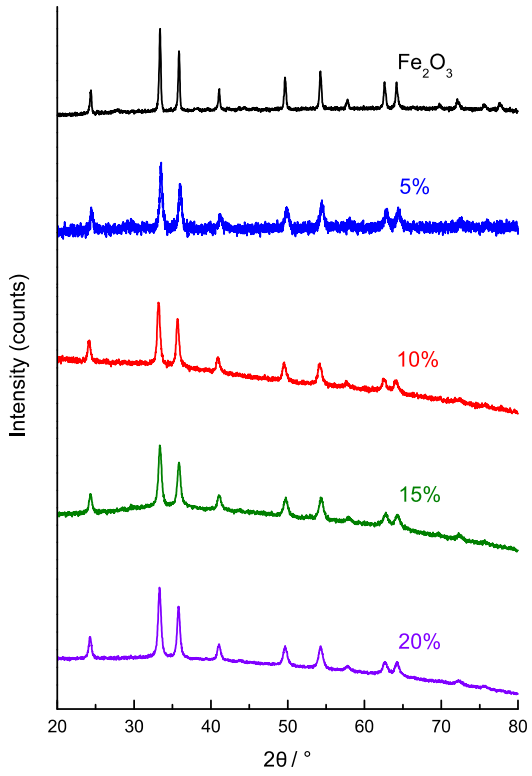
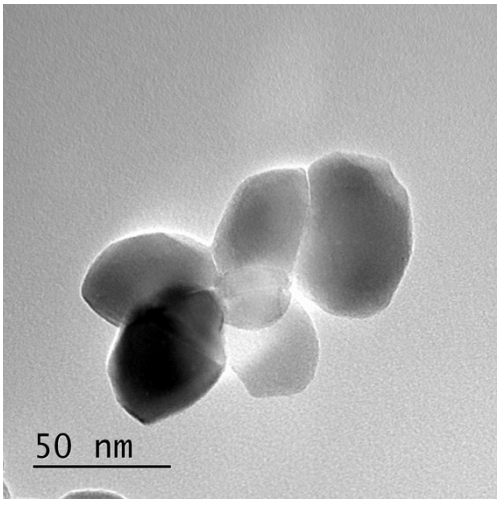
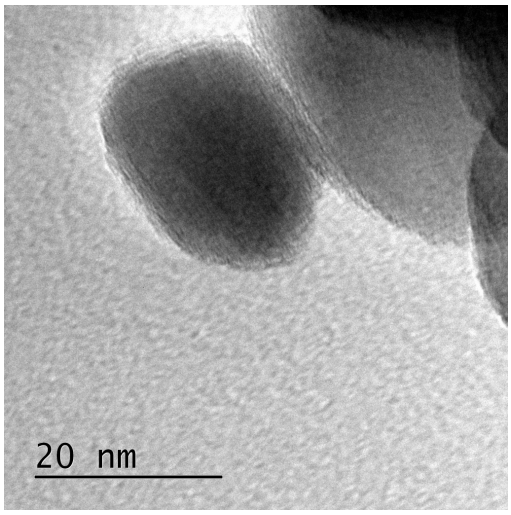


Figure S2. *A comparison of XRD patterns for 0, 5, 10, 15, 20% HSA Fe2O3 with an Fe2O3 reference.*

3. TEM





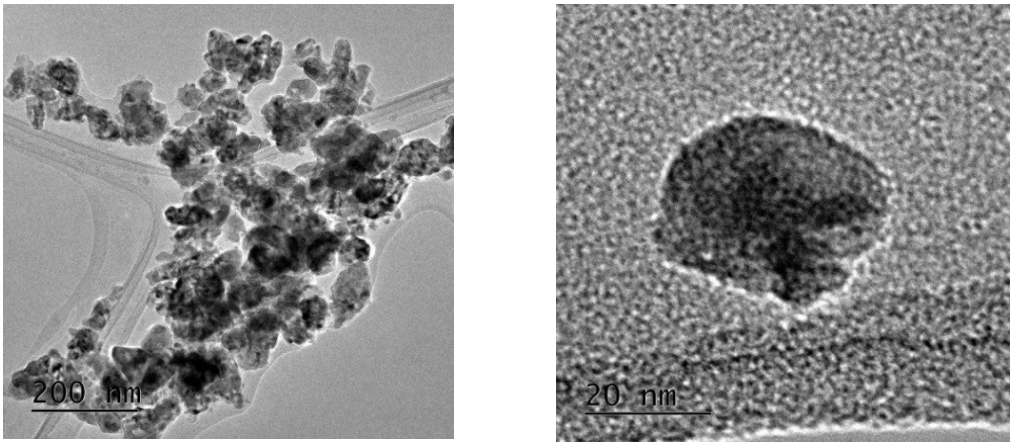
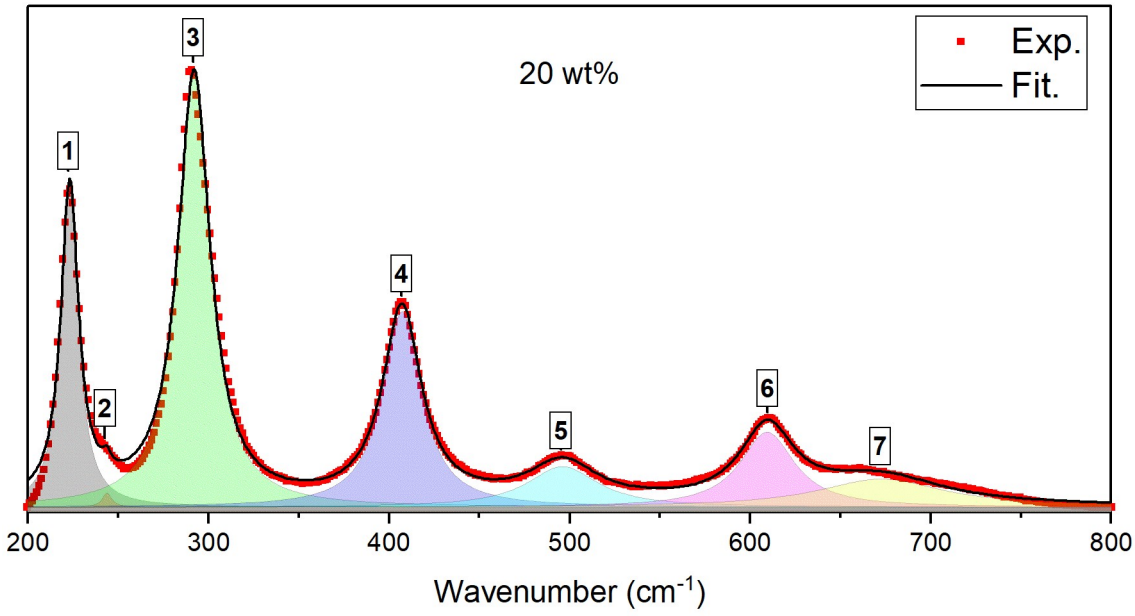


Figure S3. *Some TEM images of the haematite samples. Top left panel: An example TEM image of 10% HSA Fe_2O_3: average particle diameter is approximately 45 nm. Top right panel: An example TEM image of 15% HSA Fe_2O_3: the diameter of the individual particle is 25 nm, while the average particle diameter including particles to the right of the image is approximately 35 nm. Images of 5% samples are in the lower figures.*

4. Raman spectra and deconvolution



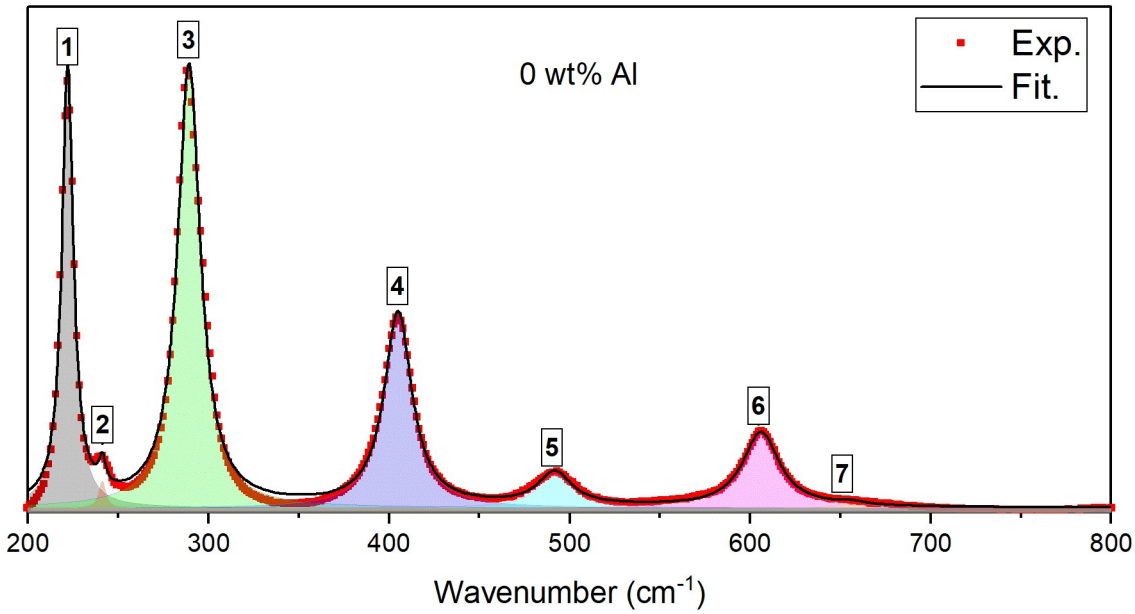


Figure S4. *Examples of Raman spectra fitting obtained for 0 and 20 wt% Al-doped-haematite samples and their fits, particularly showing the band at ~ 670 cm^{-1}.*

4. TPD

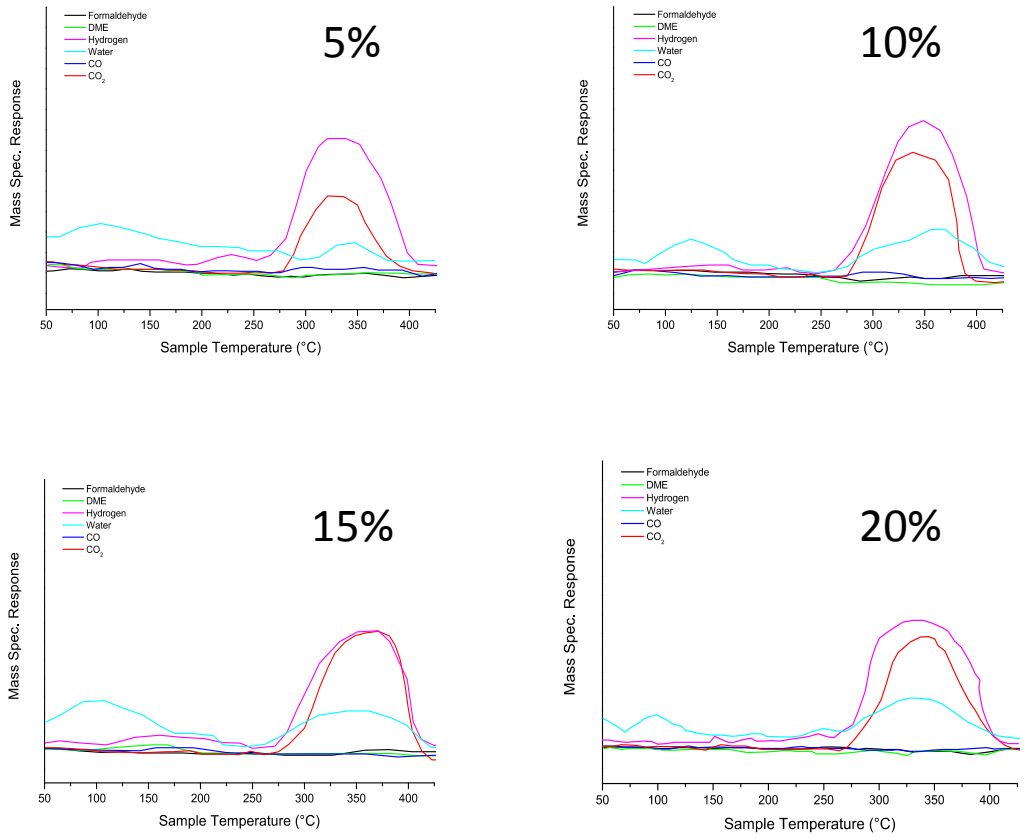


Fig S5. *TPD from four loading of Al in Fe_2O_3*

Table S1. Estimated parameters (peak position and FWHM) of Raman spectra for Al-doped-haematite samples (Al wt% reported); the error evaluated as standard deviation is reported in parentheses.

Al loadings	Bands	1	2	3	4	5	6	7	R-square
0 wt%	position	221.9(0.04)	241.2(0.4)	289.2(0.05)	404.9(0.1)	491.9(0.8)	606.0(0.4)	655.6(7.2)	0.9937
	FWHM	7.7(0.1)	4.7(1.3)	15.3(0.1)	18.6(0.3)	23.3(2.2)	24.7(1.1)	18.2(22.2)	
5 wt%	position	223.4(0.05)	241.2(0.9)	291.5(0.06)	407.7(0.2)	497.0(0.9)	609.8(0.6)	672.9(0.7)	0.9917
	FWHM	9.9(0.2)	7.0(2.9)	18.4(0.2)	23.7(0.6)	37.9(2.8)	31.1(2.1)	73.7(20.2)	
10 wt%	position	225.2(0.06)	243.6(0.9)	293.2(0.06)	410.9(0.2)	499.7(0.9)	613.4(0.5)	669.6(5.7)	0.9882
	FWHM	9.2(0.2)	6.4(2.9)	16.2(0.2)	19.0(0.5)	31.7(2.7)	26.1(1.9)	57.7(17.6)	
15 wt%	position	225.1(0.06	245.1(0.9)	293.3(0.06)	410.7(0.2)	499.9(0.9)	613.5(0.6)	671.4(5.7)	0.9902
	FWHM	10.6(0.2)	5.7(2.8)	18.1(0.2)	21.3(0.5)	31.2(2.6)	29.9(1.9)	46.8(18.2)	
20 wt%	position	223.1(0.07)	243.8(1.1)	292(0.06)	407.1(0.2)	496.2(1.0)	609.5(0.5)	672.6(3.1)	0.9927
	FWHM	11.8(0.2)	6.4(3.3)	21.7(0.2)	26.1(0.5)	47.9(3.3)	36.8(2.1)	85.7(8.6)	

5. Reactor data.

Figure S6a

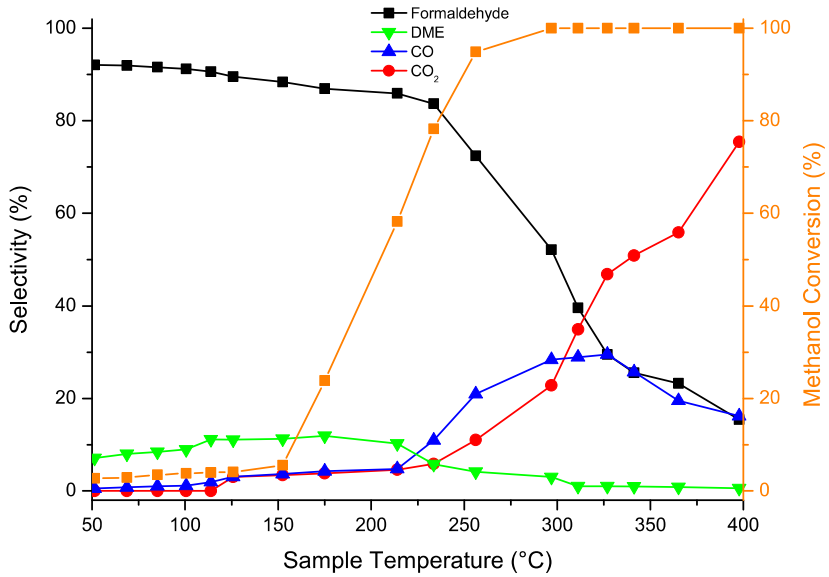


Figure S6b

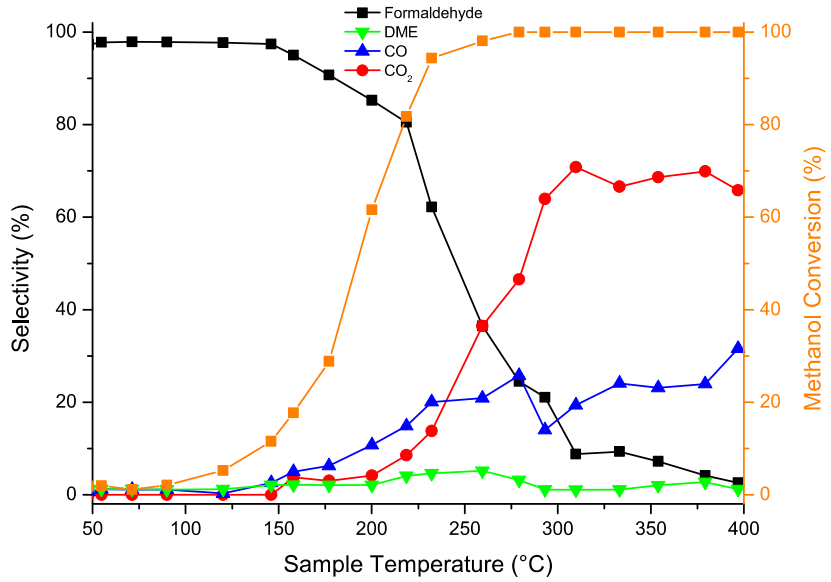


Figure S6c

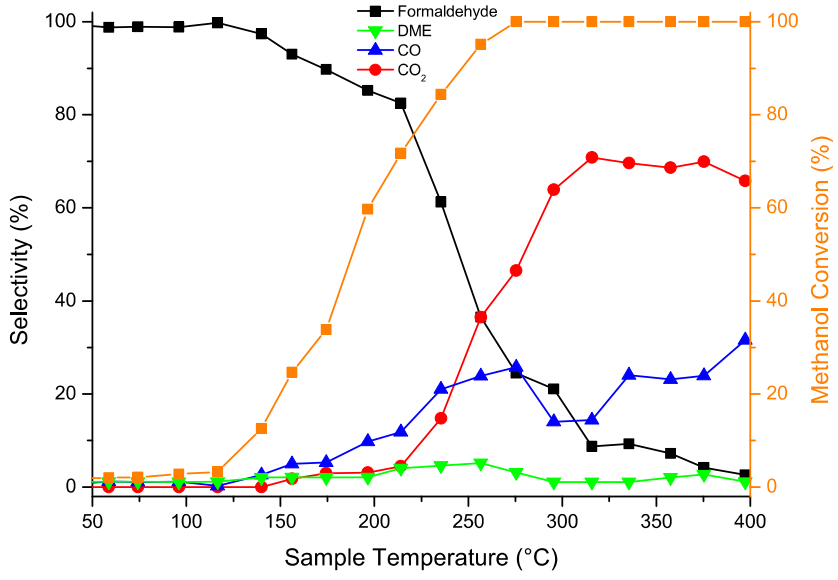


Figure S6d

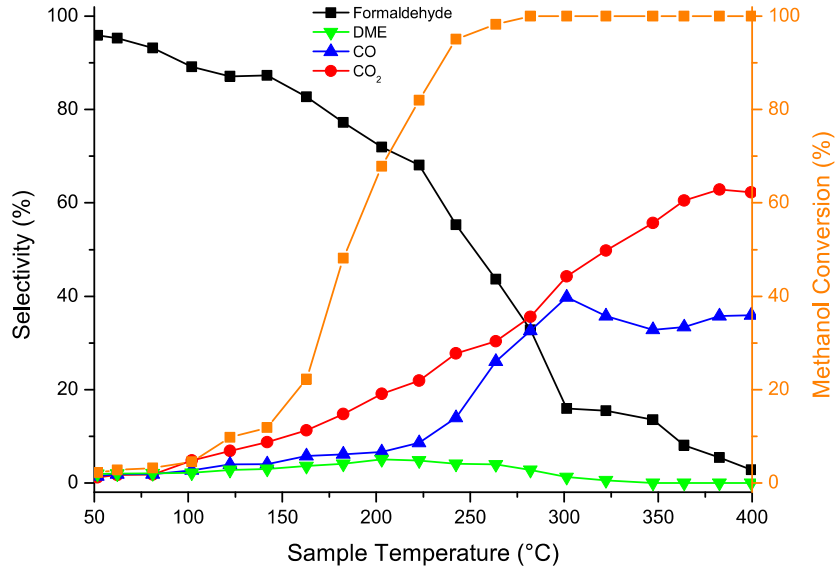


Figure S6e

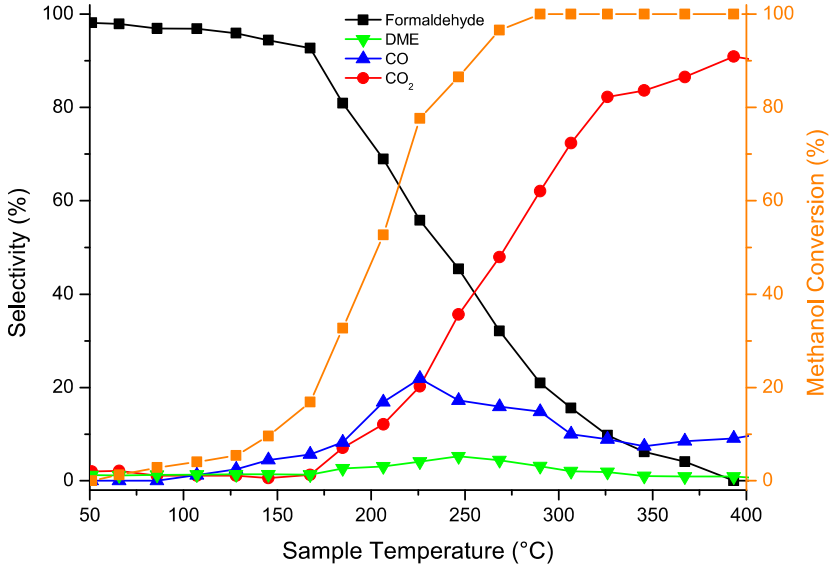


Figure S6. *Pulsed flow reactor data from 3ML of Mo on a) Fe_2O_3, and on b) 5% HSA, c) 10% HSA, d) 15% HSA, and e) 20% HSA.*

6. XAS data. Data for the 1 ML sample are shown below

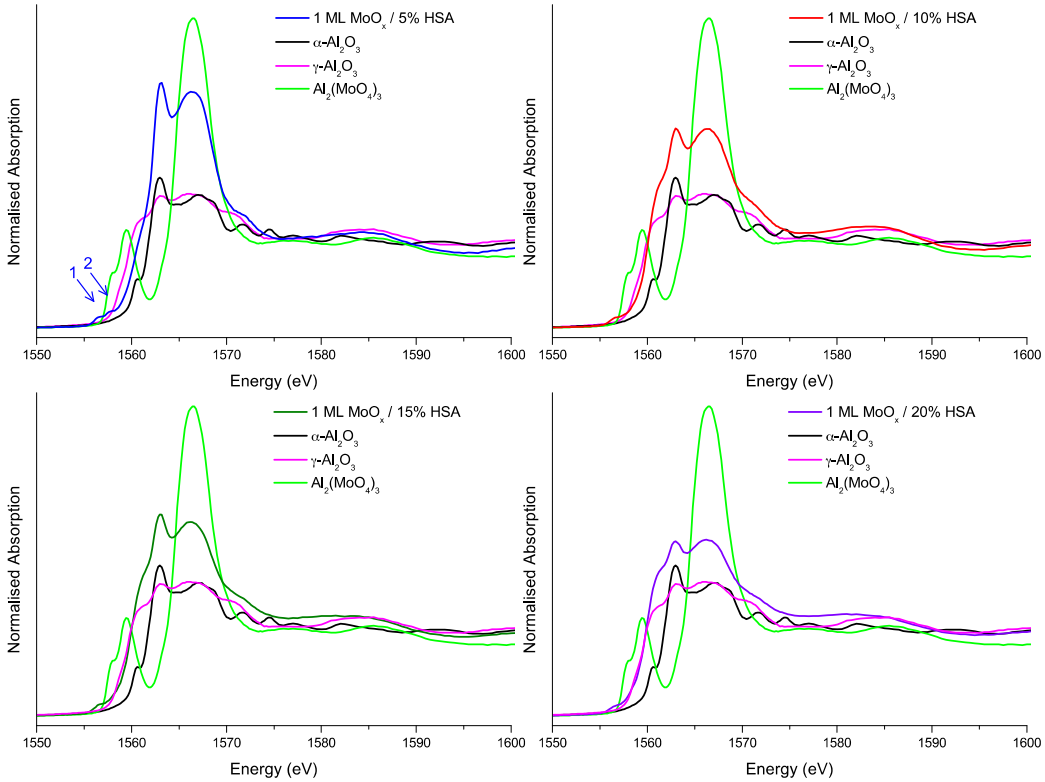


Fig S7a. *A comparison of fluorescence XANES features for 1ML MoOx/HSA catalysts against reference compounds. Peaks 1 and 2 correspond with Fe3d excitations.*

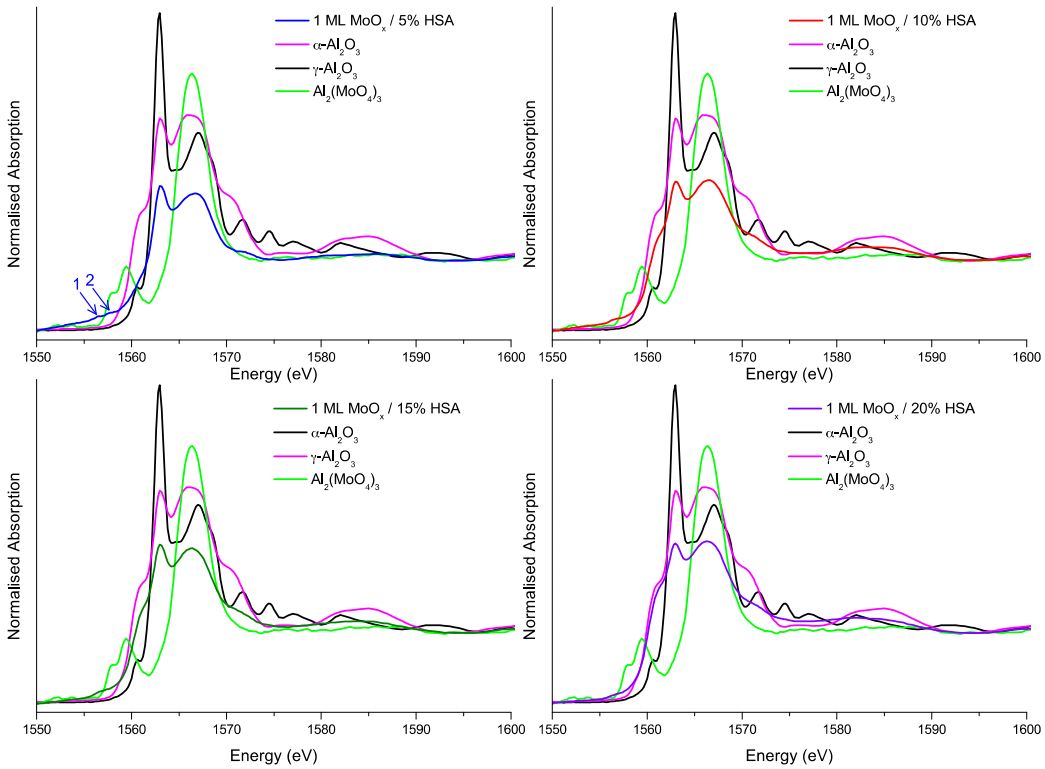


Figure S7b. *A comparison of TEY XANES features for 1 ML MoOx/HSA Fe2O3 catalysts against reference compounds. Peaks 1 and 2 correspond to Fe 3d excitations.*

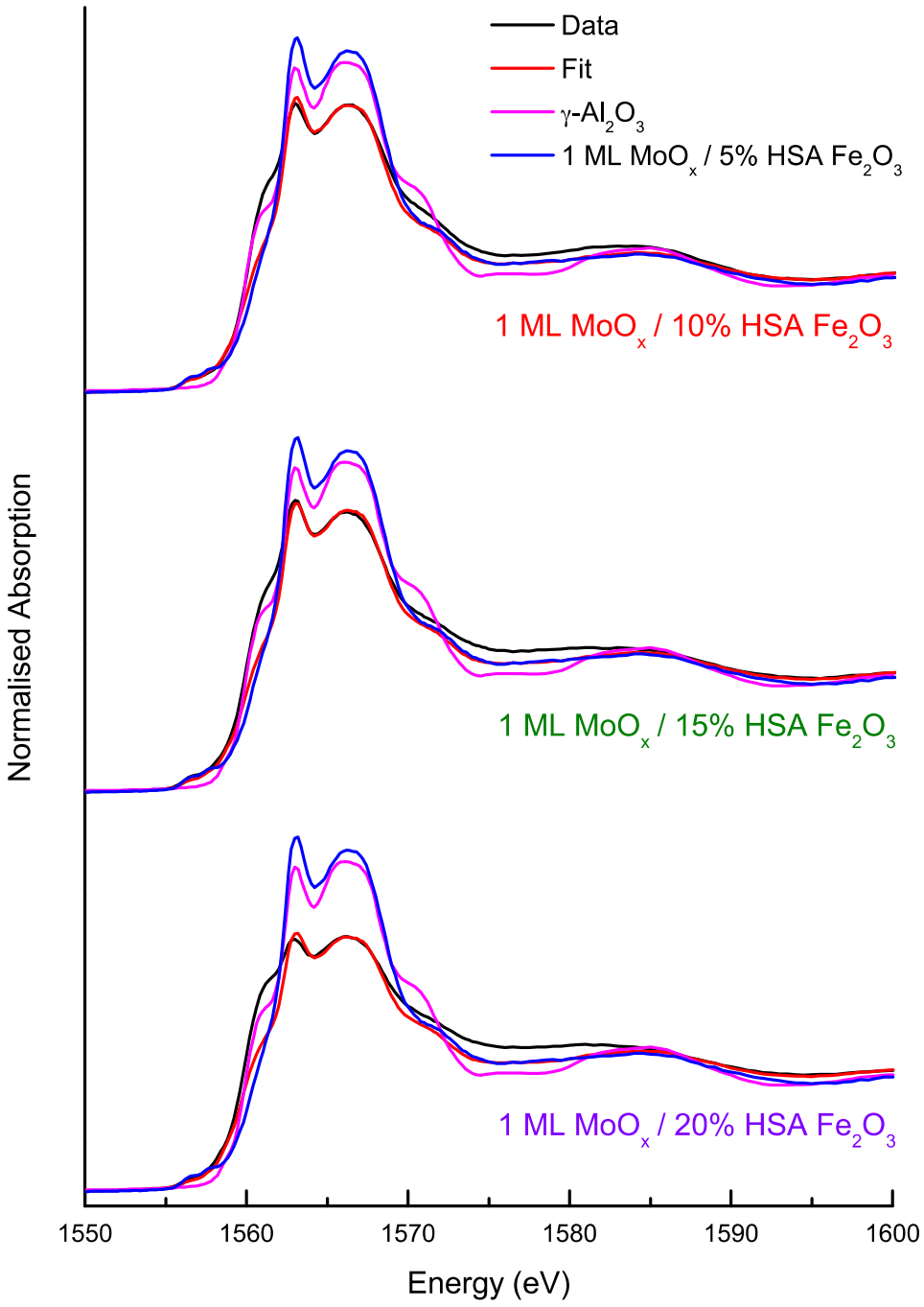


Figure S7c: *A comparison of LCF results for 1 ML MoOx/10%, 15% and 20% HSA Fe2O3 catalysts using γ-Al2O3 and 1 ML MoOx /5% HSA Fe2O3 as standards.*

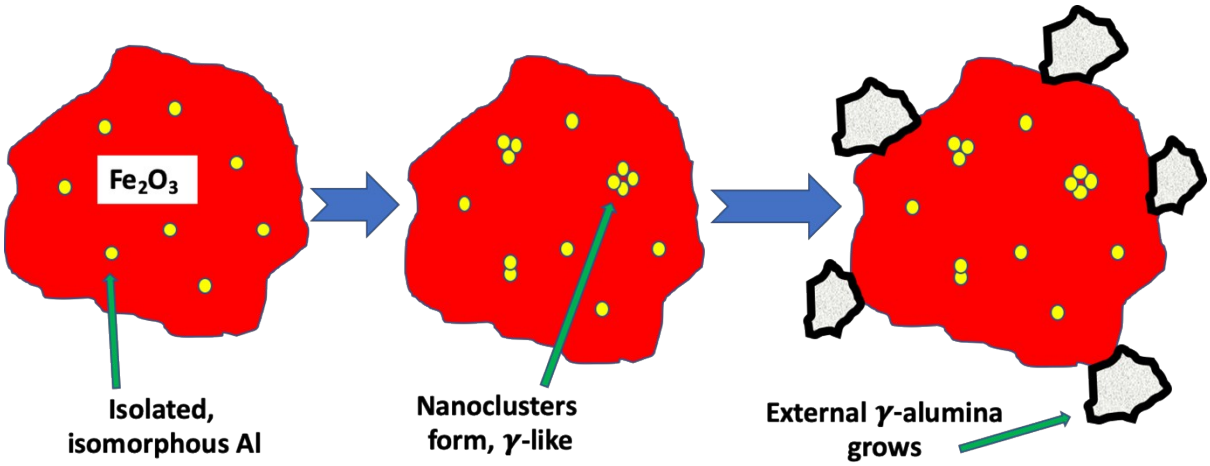


Figure S8. Showing the evolution of the structure when doping Al into haematite. First the Al is substituted in the lattice with the same corundum structure as the iron oxide. Then small nanoclusters begin to form within the haematite nanoparticles. Finally separated alumina nanocrystals begin to form.

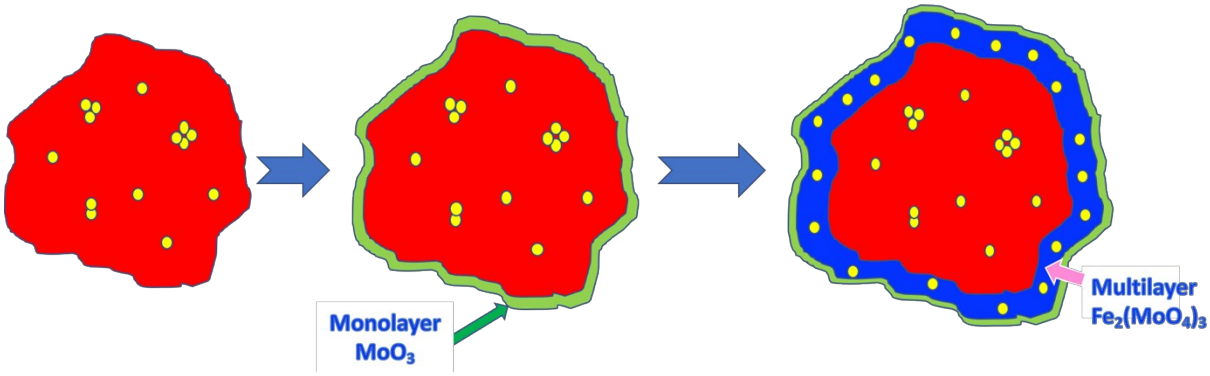


Figure S9. Showing the evolution of structure as Mo is dosed onto the surface of an intermediately Al-doped haematite. First with 1 monolayer equivalent deposited (middle panel), a single layer of MoO_3-like material covers the surface. When 3 monolayers of Mo are deposited (right panel), after annealing, the surface monolayer remains, but sublayers of iron molybdate are formed above the core of doped haematite. Al edge XAS indicates that this layer may also be doped with Al.