Molybdenum oxide on Fe_2O_3 core-shell catalysts; probing the nature of the structural motifs responsible for methanol oxidation catalysis.

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Supporting information:

1. **XPS**

   XPS data are shown below in figure 1 for the Mo3d states for three calcination temperatures and show no change in peak position, with the binding energy indicative of Mo^{6+}. There may be some broadening to lower binding energy at the higher temperatures, which could be due to environmental changes.

   The only significant change seen is that there is a decrease in the Mo:Fe ratio as temperature increases (figure 2), suggesting some loss of Mo from the surface to the bulk, probably due to the incorporation of Fe into the top layers as ferric molybdate, as proposed in the main text (see figure 11 there).
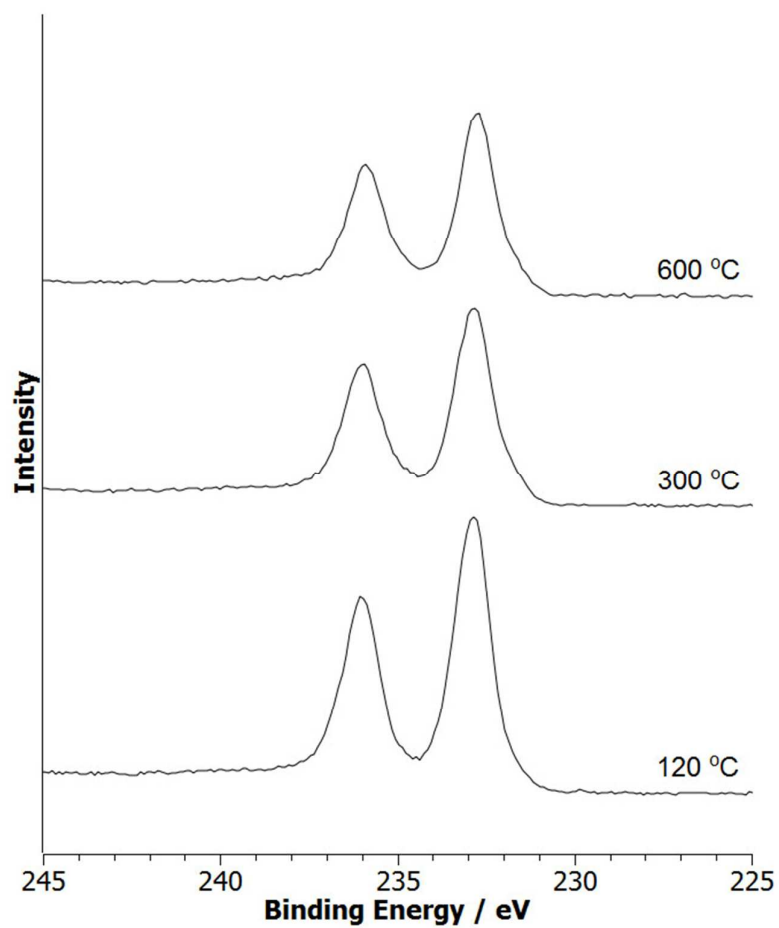
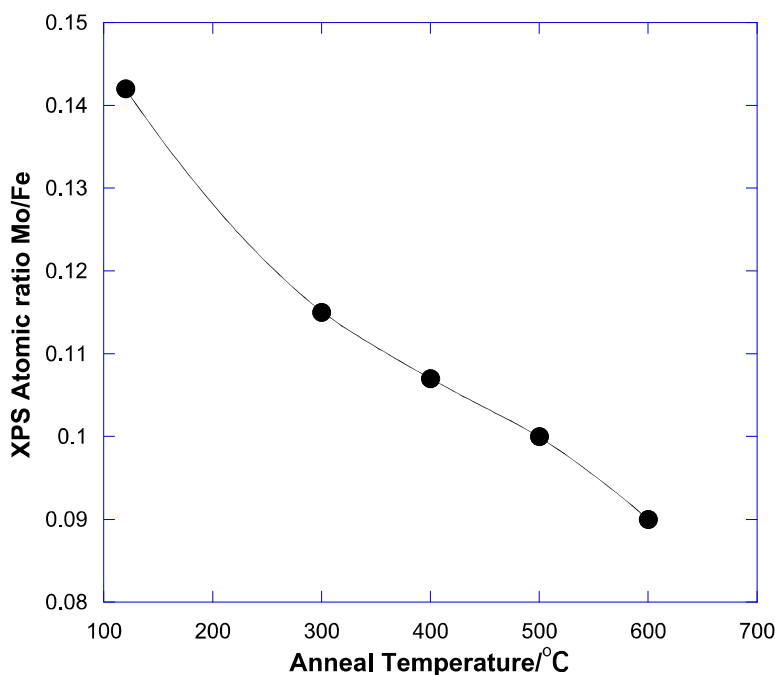**Figure S1.** Mo 3d XPS spectra for three calcination temperatures.

Figure S2. The change in Mo:Fe ratio with annealing from the XPS data.

2. EXAFS analysis

The data generated from fitting the extracted EXAFS data are in general agreement with the inference made from the XANES analysis. The data and experimental fitting parameters for 3ML MoO_x/Fe_2O_3 calcined to 120 and 300 °C (figure 1a and b) are almost identical and both show Mo in a distorted O_h geometry, with limited dimensionality. The disorder with respect to the oxygen distances is represented by including two oxygen shells, one at 1.71 Å and another at ~ 2.2 Å. The shorter distance is reasonably well defined with only a small level of disorder, as seen by a relatively small Debye Waller factor. However, the longer shell at 2.2 Å has a much larger Debye Waller factor (0.03 in comparison to 0.004) and therefore represents a more disordered environment. We assume this is because there is a greater range of O distances comprised within this shell. The model for these two samples also includes a small Mo contribution (at a distance expected for MoO_3) indicating the lack of long range order in the samples. The fitting parameters for the 3ML MoO_x/Fe_2O_3 400 °C (figure 1c) sample are similar to those calcined at lower temperature except for a much larger Mo contribution. This has been discussed in the main body of text and is indicative of formation of MoO_3. The EXAFS data for the 3ML MoO_x/Fe_2O_3 samples

calcined to 500 and 600 °C (figure 1 d and e) can be modelled by one Mo – O contribution at 1.75 Å (coordination number ~ 4) as expected and closely resembles what would be expected for iron molybdate. The additional overlayer predicted by the XANES studies would have limited Mo – Mo interactions, so we would not expect this to have a significant contribution further out in R space. Moreover, the structure of the overlayer would also have a large Mo – O contribution similar to that found in iron molybdate. However, what we would expect to see is a slight dampening of the Mo – O shell as a result of the distorted octahedral environment of the overlayer as is evidenced in the comparison of the Fourier transform data with an iron molybdate reference spectrum (figure 2).

Table S1. EXAFS fitting parameters for 3ML MoOx/Fe_2O_3 calcined at different temperatures.

Calcination temperature	Abs. Sc.	N	R / Å	$2\sigma^2$ / Å^2	E_f /eV	R_{factor}
120 °C	Mo – O	3 (fixed)	1.71 (1)	0.005 (1)	-1 (3)	0.02
	Mo – O	3 (fixed)	2.24 (5)	0.03 (2)		
	Mo - Mo	1.6 (7)	3.68 (3)	0.006 (3)		
300 °C	Mo – O	3 (fixed)	1.71 (1)	0.005 (1)	-1 (4)	0.02
	Mo – O	3 (fixed)	2.23 (5)	0.03 (2)		
	Mo - Mo	1.6 (6)	3.68 (3)	0.007 (3)		
400 °C	Mo – O	3 (fixed)	1.67 (3)	0.006 (1)	-7 (3)	0.02
	Mo – O	3 (fixed)	2.24 (3)	0.013 (4)		
	Mo - Mo	3 (1)	3.66 (2)	0.006 (2)		
500 °C	Mo – O	4.5 (3)	1.75 (1)	0.004 (1)	8 (2)	0.01
600 °C	Mo – O	4.5 (3)	1.75 (1)	0.003 (1)	7 (2)	0.01

Fitting parameters: S_0^2 = 0.82; Fit range 3<k<12, 1<R<4 (1-3 for the 500 and 600 °C samples, with 11 independent points); # of independent points = 16.

(a)

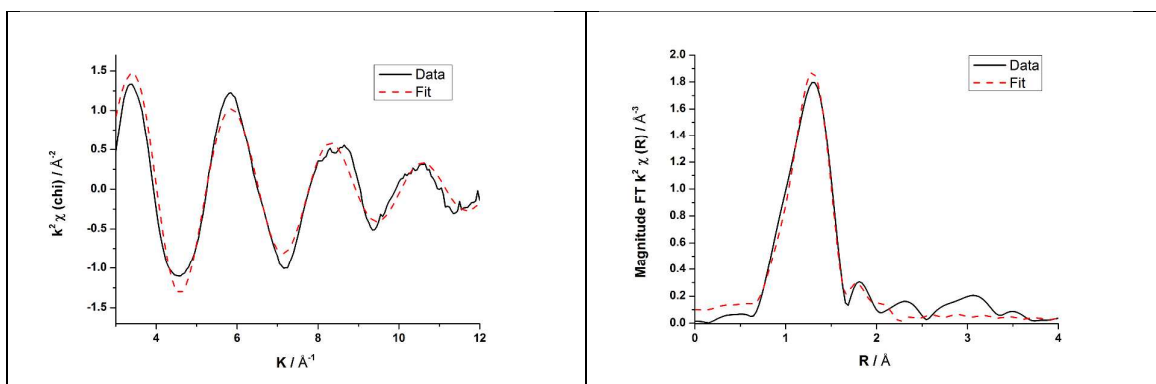**(b)**

(c)

(d)

(e)
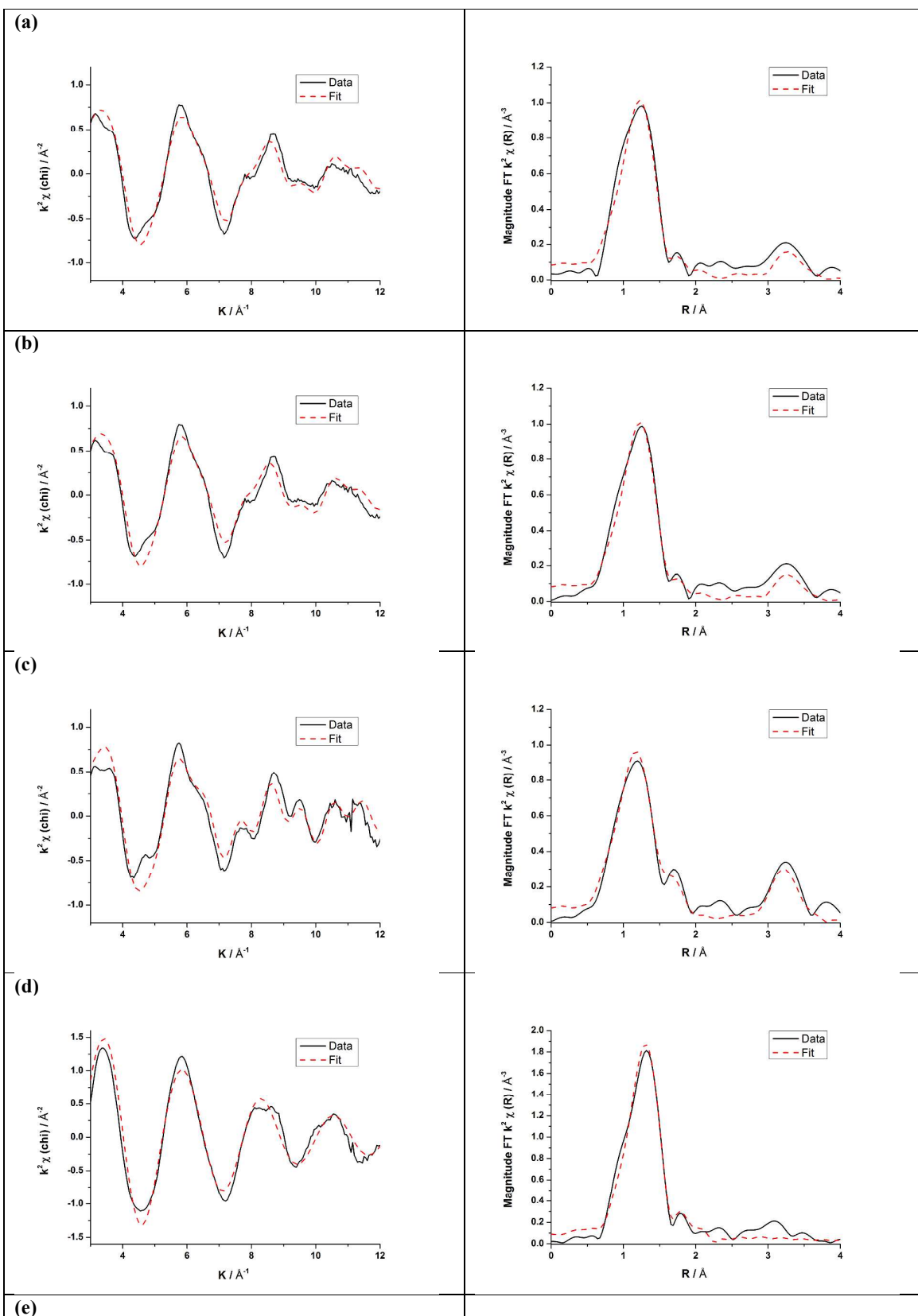
Figure S3. Experimental chi data and fourier transform with associated fit (generated from paraemters in table 1) for 3ML MoO_x/Fe_2O_3 calcined to (a) 120 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, and (e) 600 °C

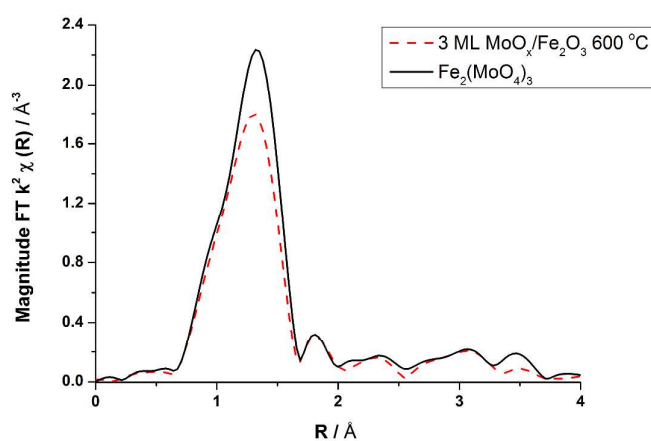**Figure S4.** Fourier transform of the EXAFS chi data of iron molybdate and 3ML MoO_x/Fe_2O_3 calcined to 600 °C