Electronic Supplementary Information for:

Evolution of Mo species and ZSM-5 microstructure with temperature and its impact on methane dehydroaromatisation activity

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Catalyst Characterization

Table S1. Chemical analysis and textural properties of Mo zeolite materials.

Catalyst	Mo Loading (wt. %)	Measured Mo Loading (EDX) (wt. %)	Micropore Volume (cc/g)	Micropore Area (m^2/g)	External Surface Area (m^2/g)
H-ZSM-5	-	-	0.17	380	46
Mo2-Z5	2	1.9	0.15	330	41
Mo4-Z5	4	3.8	0.14	310	41

Table S1 summarizes the results from SEM/EDX chemical analysis and N_2 physisorption. A 0.2 wt. % loss in Mo loading is observed for the Mo4-Z5, possibly due to sublimation of MoO_3 but the value is well within the error range of the technique.

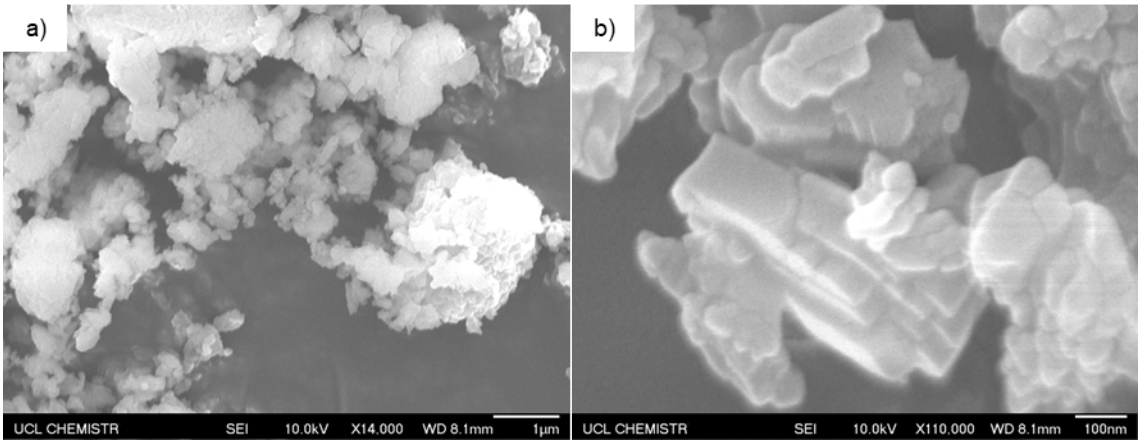

Figure S1. Overview (a) and zoomed in (b) SEM micrographs of zeolite precursors H-ZSM-5.

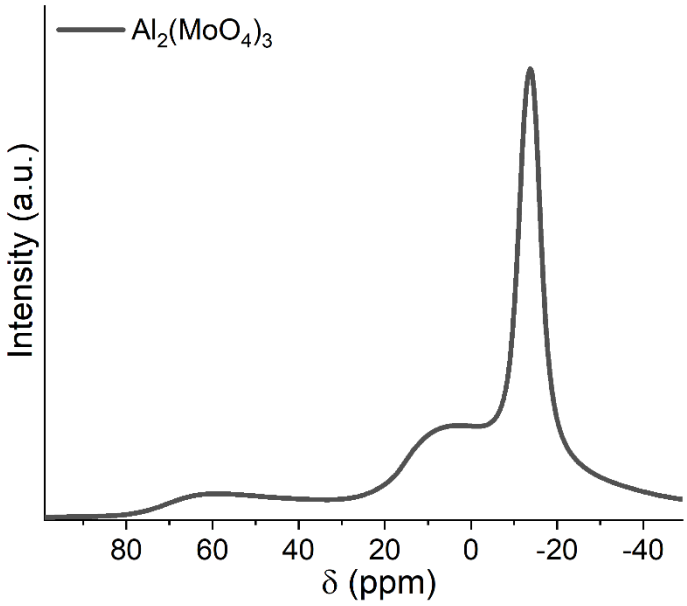

Figure S2. 27Al MAS NMR spectra of Aluminum molybdate

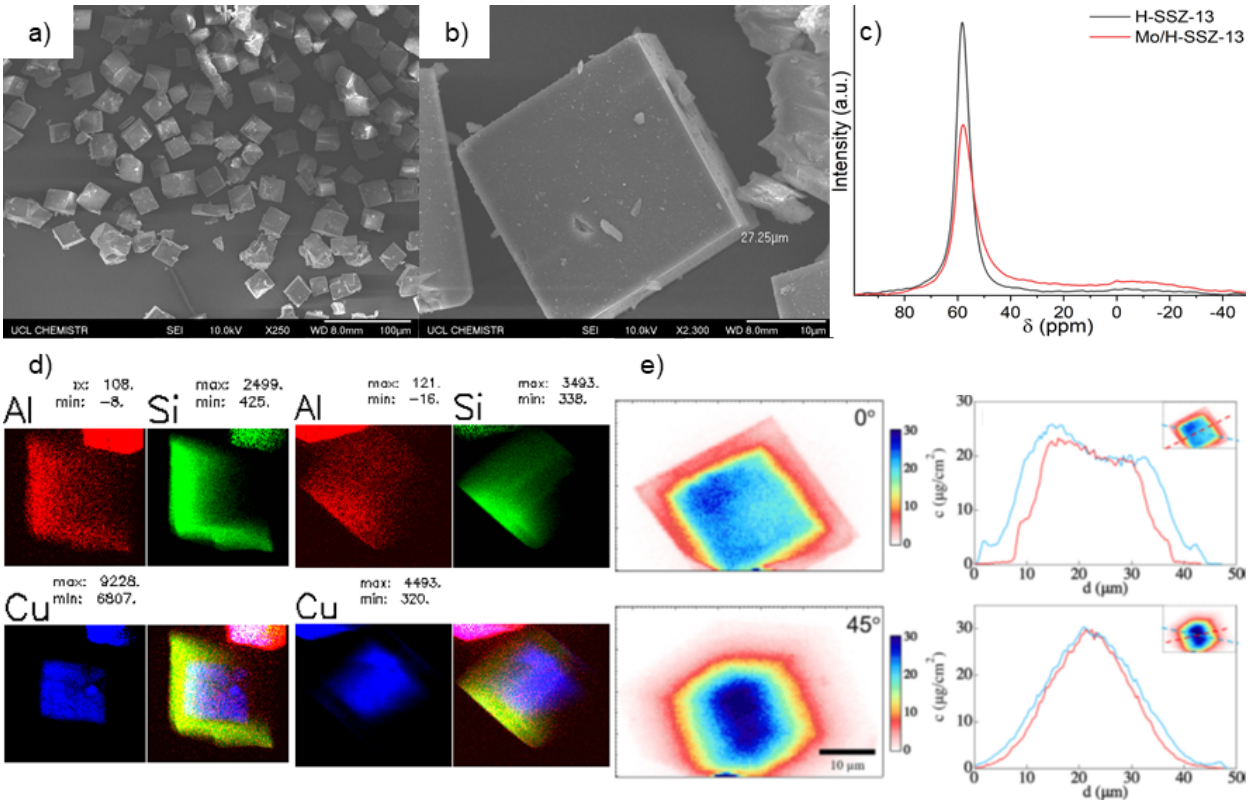

Figure S3. a), and b) SEM micrographs of the as prepared H-SSZ-13. c) ^{27}Al MAS NMR spectra of the H-SSZ-13 (black line) and 4 wt. % Mo/H-SSZ-13 (red line). d) Al, Si, Cu and overlayed XRF 2D scans from two 30 μm Cu-SSZ-13 crystals. e) Projected Cu maps and line profiles at 0° and 45 °of XRF tomography on another 30 μm Cu-SSZ-13 crystal.

Model CHA zeolite SSZ-13 with a very large crystallite size (and with a Si/Al ratio of 15) is synthesised using a method described previously (Figure S4a and b).[64] Trimethyl-adamantammonium hydroxide was used as the structure-directing agent (SDA), and the synthesis was carried out in fluoride media. Since the SDA used has a large molecular weight and the large average crystallite size of the SSZ-13, a carefully designed calcination program is employed for H-form conversion to ensure the removal of the SDA and to minimise damage to the zeolite framework. The sample was calcined in air at 1 °C min^{-1} to 120 °C and held for 2.5 h, then at 2 °C min^{-1} to 350 °C, and held for another 3 h; and finally, at 1 °C to 630 °C, and held for 10 h.

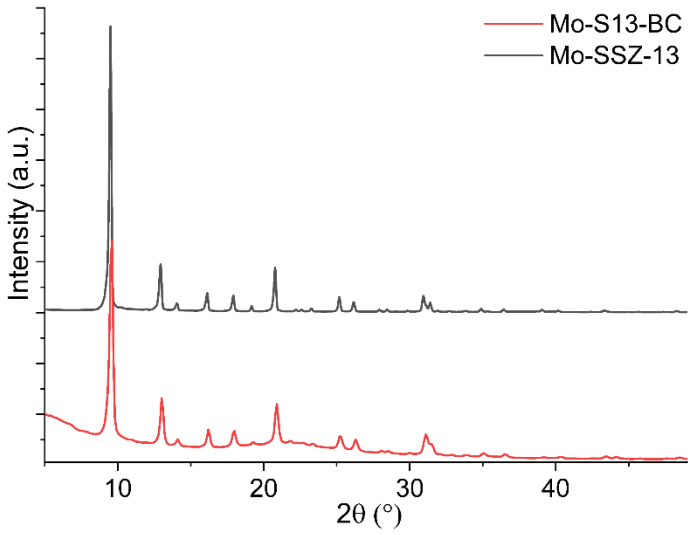

Figure S4. PXRD patterns of the as prepared 4 wt.% Mo–SSZ–13 (black line) is shown against Mo–S13–BC (red line).

PXRD measurement shown the diffuse scatter peak centred at 22° is observed, indicating the presence of an amorphous component, the peak intensities corresponding to the crystalline CHA structure are maintained to a large extent.

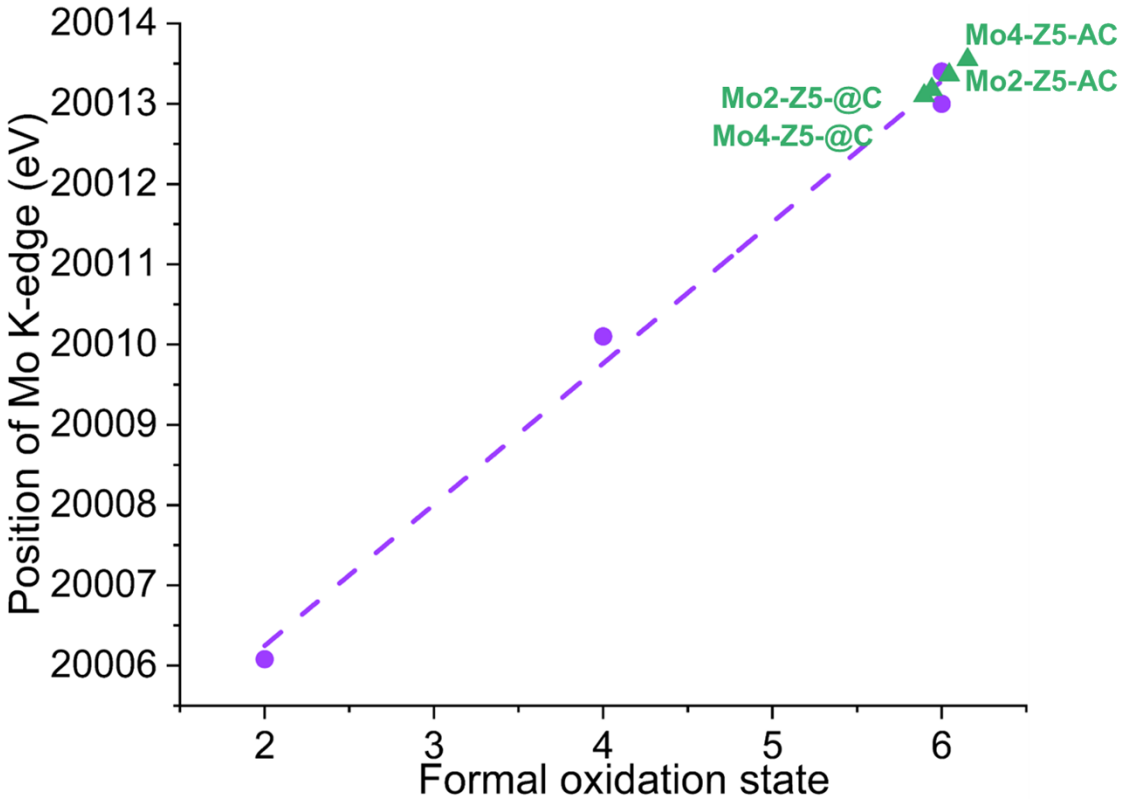

Figure S5. Linear regression fitting showing correlation between the Mo K–edge energies and Mo formal oxidation state. References indicated by purple dots; sample indicated by green triangles.

To estimate the oxidation state of Mo ions present in each sample, a least-square linear regression model was constructed to correlate the formal oxidation state with Mo K-edge energies of various Mo reference compounds (Mo_2C, MoO_2, and MoO_3). The K-edge energy is

determined as the energy position at half the height of the normalised edge step. The fitted regression line is plotted in Figure S6 along with all the references used. The fitted regression model has a satisfactory R-square value of 0.993. Using the fitted model, the Mo K-edge energies of the four collapsed samples are estimated.

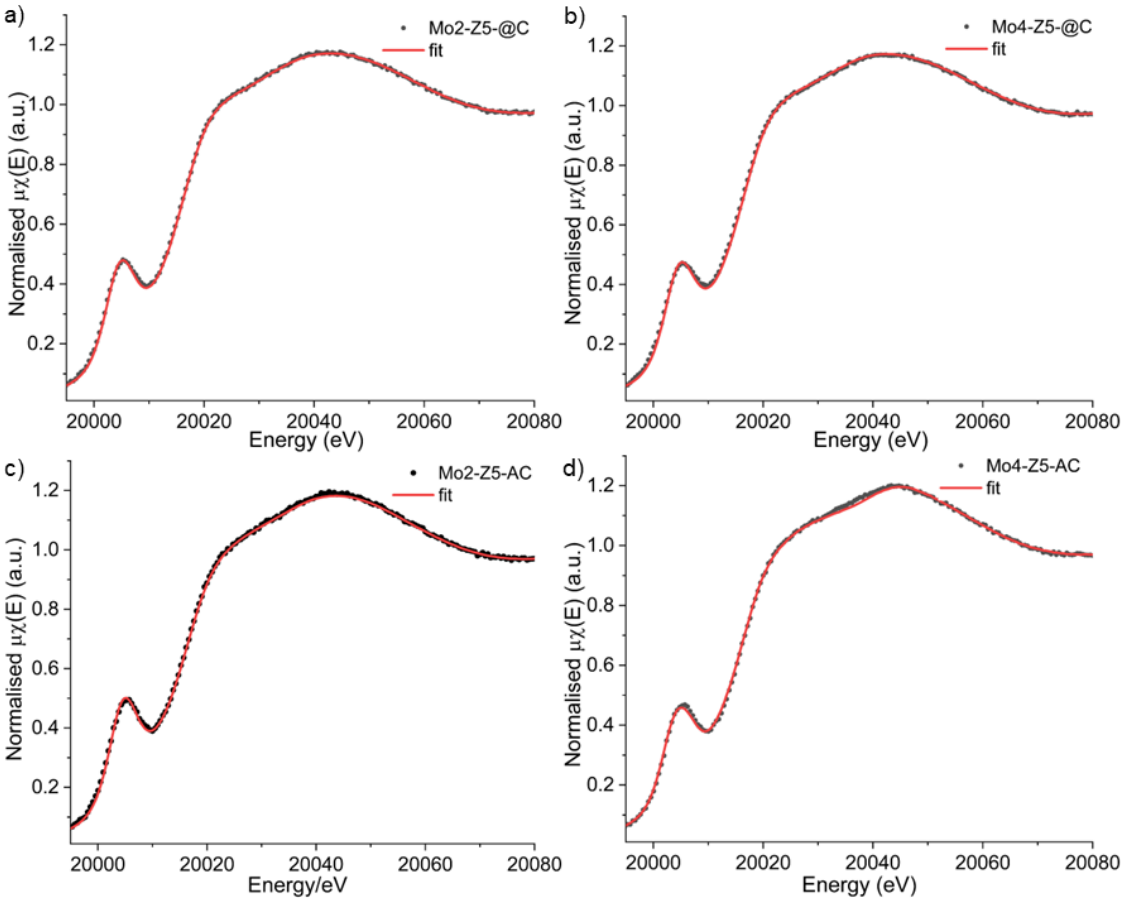

Figure S6. LCF fits (red lines) of the Mo K-edge XANES spectra of a) Mo2-Z5-@C, b) Mo4-Z5-@C, c) Mo2-Z5-AC, and d) Mo4-Z5-AC, using MoZ-700 and MoZ-RT as the reference spectra.

Table S2. LCA fitting results of the Mo K-edge XANES.

Percentage	MoZ-700	MoZ-RT	Reduced χ^2
Mo2-Z5-@C	75.5 (3.3)	24.5 (0.7)	$3.3x10^{-5}$
Mo4-Z5-@C	73.2 (3.5)	26.8 (0.8)	$3.7x10^{-5}$
Mo2-Z5-AC	90.5 (5.8)	9.5 (0.7)	$3.4x10^{-5}$
Mo4-Z5-AC	83.4 (5.1)	16.6 (1.2)	$8.7x10^{-5}$

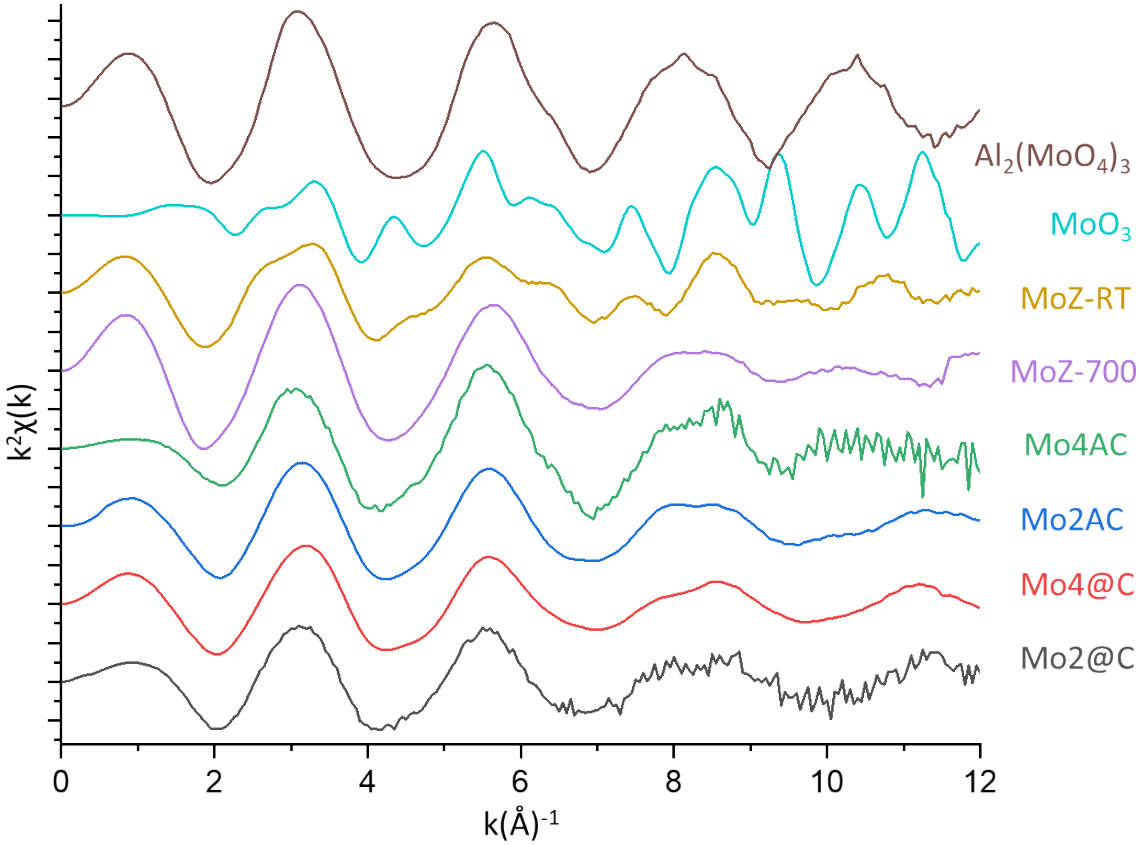

Figure S7. k^2 weighted Mo K-edge EXAFS spectra of the thermally collapsed Mo/H-ZSM-5 compared against reference compounds.

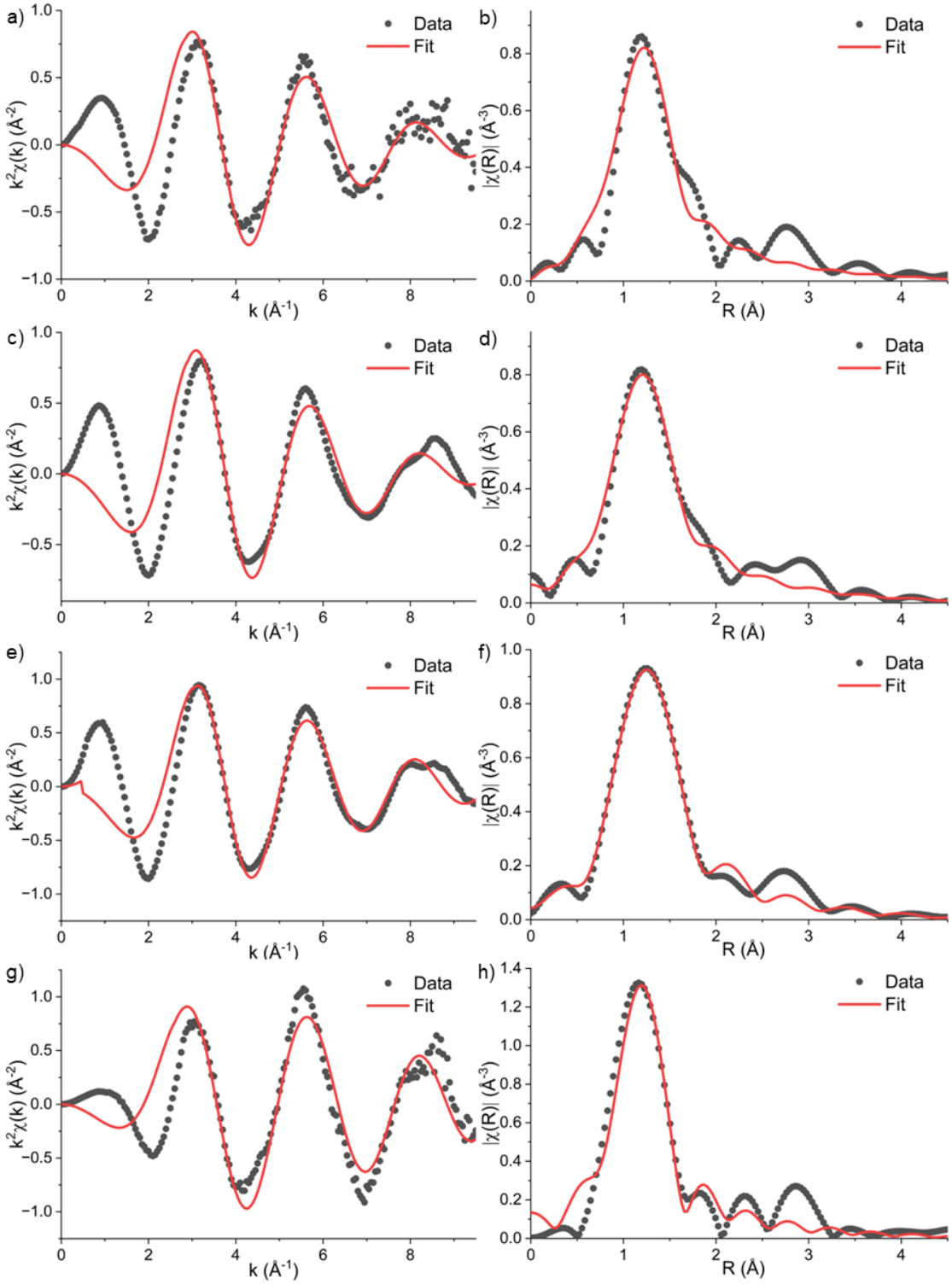

Figure S8. k^2 weighted Mo K-edge χ(k) EXAFS spectra and FT-EXAFS moduli along with the fitted spectra (red line) from the best fit for samples: a) b) Mo2-Z-@C, c) d) Mo4-Z-@C, e) f) Mo2-Z-AC, and g) h) Mo-Z-4AC.

Fitting of EXAFS spectra of the thermally collapsed Mo/H-ZSM-5 samples were carried out in R space. Only the first shell single scattering paths were considered in the fitting metrics. Based on observation from the XANES analysis, $Al_2(MoO_4)_3$, which contains tetrahedrally coordinated $[MoO_4]^{2-}$ is used as the reference compound and single scattering contributions are constructed from the crystallographic data. The amplitude reduction factor S_0^2 was obtained by fitting the EXAFS spectra of $Al_2(MoO_4)_3$ with 4 Mo-O bonds, and this value (0.79) was then fixed throughout the subsequent fit.

Table S3. SEM/EDX chemical analysis of the collapsed 4 wt.% Mo/H-ZSM-5 catalysts.

Catalyst	Measured Mo Loading (EDX) (wt. %)
Mo4-Z5-@C	1.1
Mo4-Z5-AC	1.1

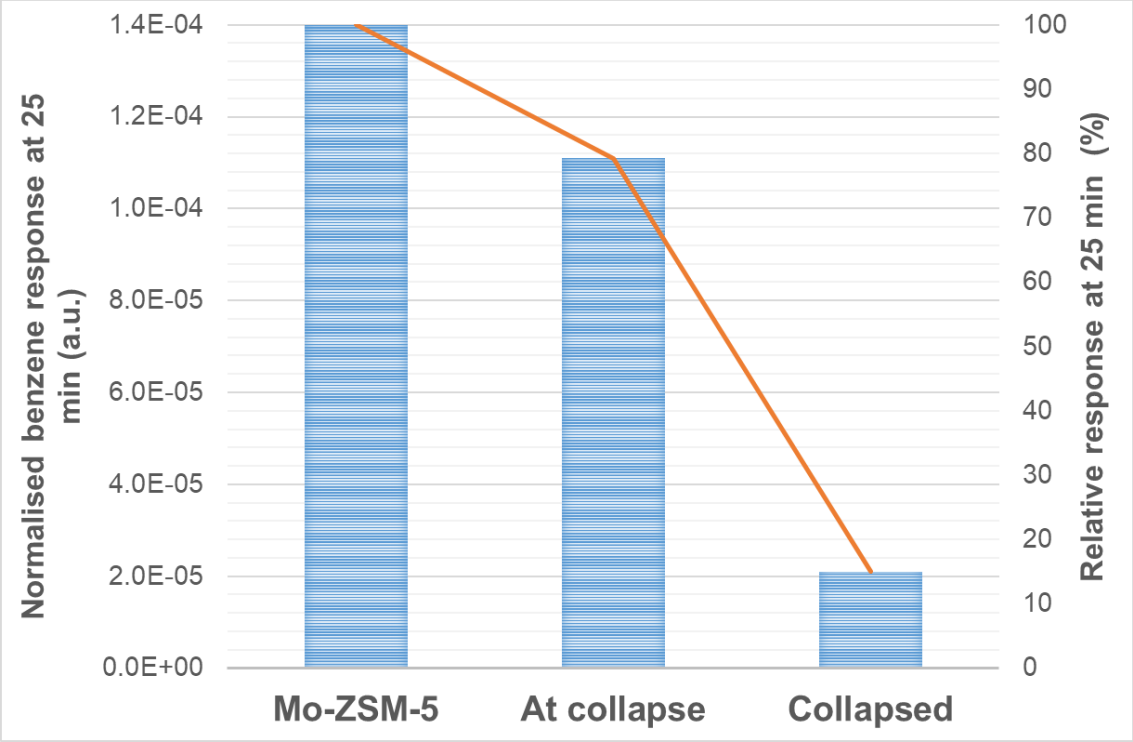

Figure S9. Normalised benzene at 25 mins during the MDA reaction at 700 °C for Mo4-Z5-@C (at collapse) and Mo4-Z5-AC (collapsed).