

Supplementary information (ESI) for Chemical Communications

1. Setup

The focal point of the setup is a specially adapted quartz reactor tube (6 mm o.d. and 1 mm i.d.), which has been ground down on three sides to approximately 200 μm to ensure sufficient X-ray transmission (see Supplementary Figure 1). This is then mounted in a square stainless steel furnace, (heated using 4 x 200 W cartridge heaters with a maximum usable temperature of 650°C) housed in a porous alumina insulating block (Supplementary Figure 2). The furnace and insulating block have been designed to allow measurements to be performed using the three techniques simultaneously. Since the ED-EXAFS measurements are performed in transmission it is necessary to obtain Raman and UV-Vis information orthogonal to it and opposite to each other.

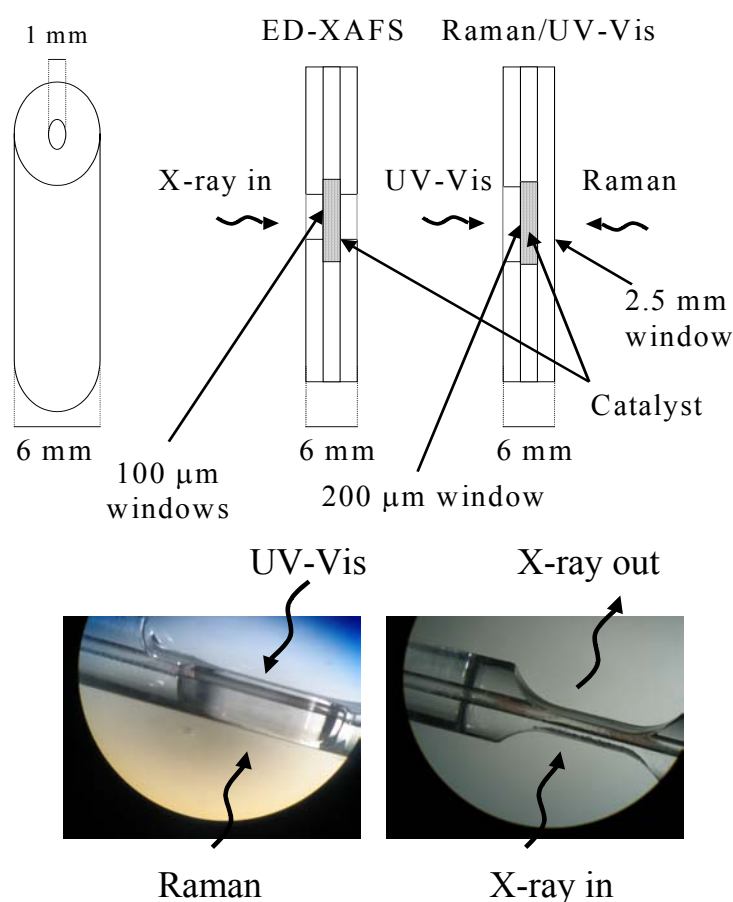


Figure S1. Design drawing (above) and photographs (below) of the specially adapted quartz reactor tube detailing the positions at which measurements were made.

ED-XAFS data were collected on ID24 at the ESRF, Grenoble. The data were collected in transmission mode using X-rays focused to a spot size of 300 μm using a Si[311] polychromator mounted in a Laue configuration and a Peltier cooled, phosphor masked, CCD camera (Princeton) for detection. The resultant ED-XANES data were processed (pre-edge removal and normalisation) using software developed in-house. Raman data were collected using a Kaiser Optical Systems RXN spectrometer with a diode laser operating at 532 nm and output power of 70 mW. A

5.5" objective lense was used to focus a laser beam to a spot size of 200 μm and to collect the scattered radiation. A CCD camera was used to record the data. All Raman spectra were offset-corrected using Thermo Galactic Grams AI v. 7.0 software. UV-Vis spectra were recorded in diffuse reflectance mode from 280 – 900 nm using an AVASPEC fibre optical AVS-SD2000 spectrometer (Avantes) and a 400 μm fibre optical cable. Since the data collected were noisy in order to aid interpretation Fourier smoothing was employed. Downstream analysis of the behaviour of specific mass spectrum fragments from 2–44 Daltons was performed using a Pfeiffer mass spectrometer. A deconvolution procedure using the known fragmentation patterns of the reactants and possible products was employed in order to determine the relative quantities of these with time.

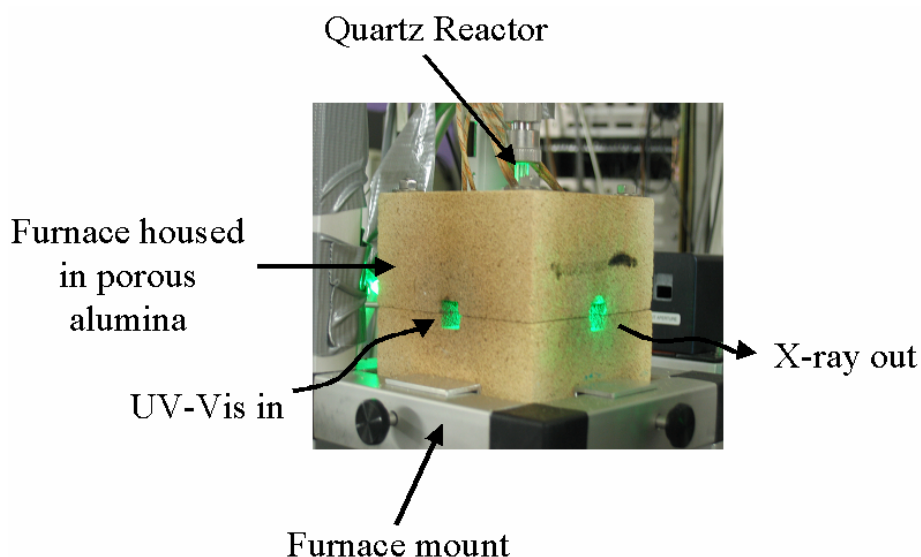


Figure S2. Insulated furnace used to heat the quartz reactor for combined UV-Vis/Raman and ED-XAFS measurements. The green glow is from the Raman Laser hidden to the right hand side.

Acquisition times for the three techniques ranged from 50-2000 ms for 1 scan although in order to improve the signal-to-noise ratio multiple spectra were recorded and summed. Typically for these experiments the acquisition times employed were 400 ms for EDXAFS data, 1 s for Raman, 2 s for the UV-Vis and 10 s for the mass spectrometer.

2. Catalyst preparation and reaction conditions

The 13 wt% molybdenum catalysts were prepared by incipient wetness impregnation of 1 g SiO_2 (Davisil) and Al_2O_3 (Sasol) using a 1.6 M ammonium heptamolybdate tetrahydrate (Acros) solution. In a typical experiment approximately 15 mg of crushed and sieved catalyst particles (170 – 250 μm) were loaded into the quartz reactor. An activation step was then employed during which the catalyst was heated at $5^\circ\text{C}/\text{min}$ to 550°C and held for 30 min in 5% O_2 in He gas mixture (20 ml/min flow rate). Subsequent propane dehydrogenation/oxidative regeneration experiments were carried out at the same temperature and using a similar flow rate. For the 13 wt% Mo/SiO_2 catalyst the cycle times employed were 30 min for dehydrogenation and 25 min. for regeneration. For 13 wt% $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts 30 min was used for both.

3. Effect of UV-Vis correction to obtain true Raman intensities

Raman spectroscopy is normally applied in a qualitative manner. However, it is possible to obtain quantitative information regarding the behaviour of Raman active species providing that the absorption/scattering properties of the material do not change during reaction and that variations in the instrumental performance and sample positioning are avoided. In order to overcome this problem a standard (such as BN) of known concentration can be added to the catalyst. More recently we have demonstrated¹ that it is possible to use changes in the diffuse reflectance signal measured by UV-Vis, in order to obtain this quantitative information therefore avoiding the need to add an internal standard and thereby demonstrating an additional advantage of combining these particular spectroscopic techniques.

By using equations (1) and (2) it is possible to show that changes in the diffuse reflectance signal $G(R_\infty)$ at 573.2 nm can be used to obtain a true Raman intensity (ρI_o) from the observed intensity.

$$\psi_\infty = \frac{\rho I_o}{s} \cdot G(R_\infty) \quad (1)$$

$$G(R_\infty) = \frac{R_\infty(1+R_\infty)}{(1-R_\infty)} \quad (2)$$

As can be seen in Figure S3 for the 13 wt% Mo/SiO₂ catalyst the true Raman intensity for the band at 820 cm⁻¹ corresponding to the Mo-O-Mo band^{2,3} in MoO₃ during both regeneration cycles, tends to be lower than the observed intensity. Furthermore the difference in true intensity between the cycles was also much smaller suggesting that the MoO₃ clusters had grown to reach a critical size at the end of the first cycle (OR1) and that these were maintained during the subsequent propane and regeneration steps (PC2 and OR2).

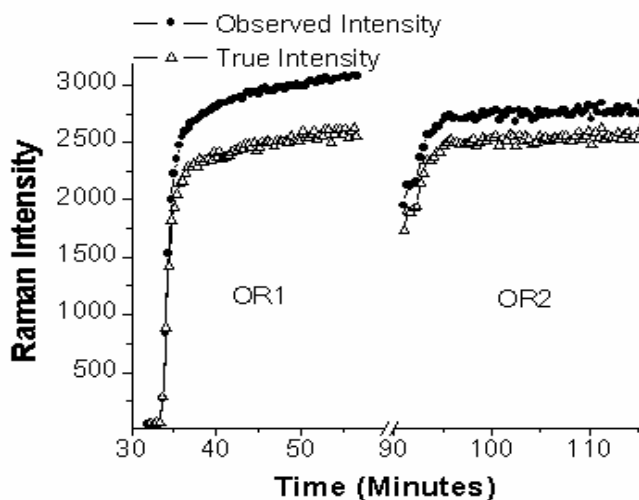


Figure S3. Demonstration of the effect of the UV-Vis correction to obtain the true Raman intensity of the band at 820 cm⁻¹.

However, since the overall true intensity observed in OR2 is lower in intensity than in OR1 it is possible that MoO_3 spreading over the catalyst surface had occurred resulting in a reduction in MoO_3 cluster size. Although this could also be inferred from a comparison of the observed intensity the changes in the true intensity are much smaller and are more consistent with only a very small reduction in MoO_3 cluster size occurring. This observation is given further support by the small increase in the 1s-4d transition intensity observed in the ED-XANES data (Fig. 3) since such a change would be expected if the dispersion would yield isolated tetrahedral molybdenum species on the catalyst surface.

4. Raw data for 13 wt% $\text{Mo}/\text{Al}_2\text{O}_3$

Shown in Figure S4 are the raw data collected during PC1 for the 13 wt% $\text{Mo}/\text{Al}_2\text{O}_3$ sample. Unlike the 13 wt% Mo/SiO_2 material the changes that occurred during these studies were much less obvious. This was mainly due to the absence of any strong bands in the Raman data corresponding to MoO_3 , which would suggest a better dispersion of molybdenum oxide on the catalyst surface. The reduction in the Raman baseline fluorescence and the increase in UV-Vis absorption in the early stages suggested that coking of the catalyst was occurring.

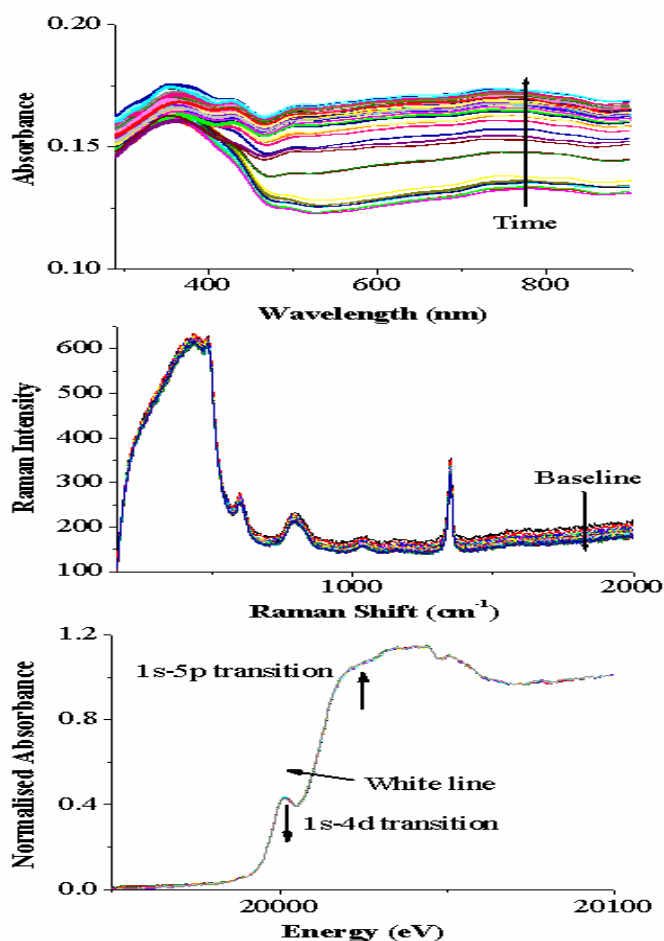


Figure S4. UV-Vis (top), Raman (middle) and ED-XANES (bottom) data acquired during PC1 for the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst. The observed increase in UV-Vis absorption coincided with a decrease in the intensity of the Raman bands corresponding to the background fluorescence. The appearance of bands

at 420, 470, 680 and 780 nm in the UV-Vis data and the broad signal around 500 cm⁻¹ in the Raman data are from the quartz reactor.

5. References

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- ² C. C. Williams, J. G. Ekerdt, J. M. Jehng, F. D. Hardcastle, A. M. Turek, and I. E. Wachs, *J. Phys. Chem.*, 1991, **95**, 8781.
- ³ M. Delarco, S. R. G. Carrazan, C. Martin, V. Rives, J. V. Garciamamos, and P. Carmona, *Spectrochim. Acta A*, 1994, **50**, 2215.