



	Experiment title: EXAFS studies of mesoporous silica-grafted dioxomolybdenum(VI) catalysts	Experiment number: CH1082
Beamline: BM29	Date of experiment: from: 2/4/01 to: 5/4/01	Date of report: 1/7/01
Shifts: 6	Local contact(s): Stuart Ansell	<i>Received at ESRF:</i>
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Report:

Aims. In this experiment, XAFS measurements were carried out for a series of tailored oxomolybdenum catalysts. The first group examined comprised micelle-templated silicas (MCM-41) derivatised with the complexes $\text{MoO}_2\text{X}_2(\text{THF})_2$ ($\text{X} = \text{Cl}, \text{Br}$), by either primary or secondary grafting methods. In the case of primary grafting, the complexes were introduced into pristine pure silica MCM-41 by pore volume impregnation of a solution of each complex in CH_2Cl_2 , with or without the concomitant addition of triethylamine (TEA). In the case of secondary grafting, the complexes were reacted with MCM-41 previously modified with pendant bipyridyl groups (to give immobilised species of the type $\text{MoO}_2\text{X}_2(\text{N-N})$). The aim of the Mo K-edge XAFS experiments was to elucidate the exact nature of the active, surface-modified metal entities. The second group of oxomolybdenum catalysts examined comprised organometallic oxides with formulas $[\text{MoO}_2(\text{OSnR}_3)_2]_\infty$ ($\text{R} = \text{nBu}, \text{C}_6\text{H}_5, \text{C}_7\text{H}_7, \text{C}_6\text{H}_{10}$) and $[\text{MoO}_2(\text{OSiPh}_3)_2]$. The complex $[\text{MoO}_2(\text{OSiPh}_3)_2]$ may be used as a molecular species for modelling the active sites of the primary MoO_2 -grafted mesoporous silicas.

Experimental details. Mo K-edge and Sn K-edge X-ray absorption spectra were collected for samples in the solid state at room temperature and also at 20 K in transmission mode with ion chamber detectors on BM29, with the ESRF operating at 6 GeV in 2/3 filling mode with typical currents of 170–200 mA. Typically, scans were set up to record the pre-edge at 5 eV steps and the post-edge region in 0.025–0.05 \AA^{-1} steps (2s per step), giving a total acquisition time of *ca.* 40 min per scan. The order-sorting double Si(311) crystal monochromator was detuned to give 40%

harmonic rejection. Most samples were air-sensitive and pellet preparation (BN matrix) was carried out using the glove box on BM29. The programs EXCALIB, EXBACK and EXCURVE (EXCURV98, Daresbury Laboratory, UK) have been used for background subtraction and EXAFS curve-fitting analyses.

Results. Most samples gave good quality EXAFS data up to $16\text{--}20 \text{ \AA}^{-1}$ and analysis of the results is progressing. Preliminary findings are reported here for the primary MoO_2 -grafted MCM-41 materials. The room temperature Mo K-edge EXAFS of *cis*- $\text{MoO}_2\text{Cl}_2(\text{THF})_2$ has been fitted by a model comprising 2 oxygens at 1.69 \AA ($\text{Mo}=\text{O}$) and 2 chlorines at 2.35 \AA ($\text{Mo}-\text{Cl}$). In the case of *cis*- $\text{MoO}_2\text{Br}_2(\text{THF})_2$, 2 oxygens were found at 1.70 \AA , 2 oxygens at 2.28 \AA ($\text{Mo}-\text{O}_{\text{THF}}$) and 2 bromines at 2.51 \AA ($\text{Mo}-\text{Br}$). Immobilisation of these complexes in MCM-41, in the absence of TEA, gave materials with *ca.* 1 mass% Mo. The EXAFS data indicates that the Cl or Br neighbours are replaced by oxygen neighbours at 1.92 \AA , consistent with surface-fixed monomeric species of the type $[\text{MoO}_2(\text{OSi}\equiv)_2(\text{THF})_n]$ or $[\text{MoO}_2\text{X}(\text{OSi}\equiv)(\text{THF})_n]$. The inclusion of TEA in the grafting reactions activates the surface silanols and materials with much higher metal loadings are obtained (6-8%). The EXAFS data reveals that immobilisation of the dichloro complex in the presence of TEA gives almost exclusively surface-fixed mono-oxo-bridged $[\text{Mo}_2\text{O}_5]^{2+}$ entities (Fig. 1). By contrast, the surface chemistry of the dibromo complex under the same conditions is different: mainly monomeric species of the type $[\text{MoO}_2(\text{OSi}\equiv)_2(\text{THF})_n]$ are present on the surface, even at these high loadings. These results have important implications concerning the catalytic activity of the derivatised materials.

Acknowledgements. We are grateful to the director of the ESRF for the provision of facilities and to the staff involved with BM29 for their help.

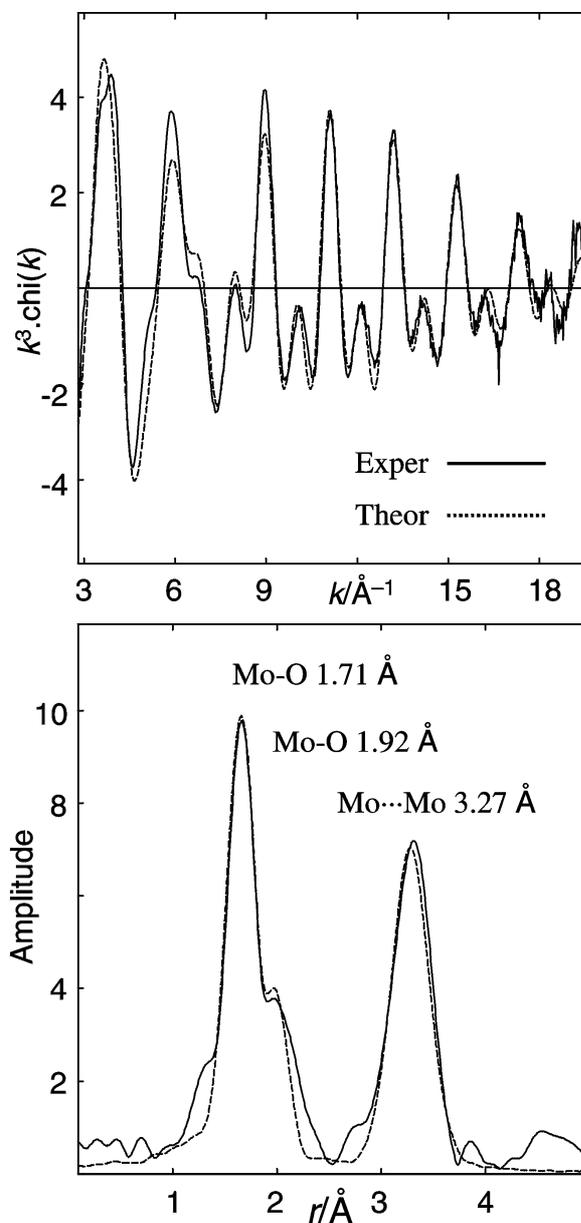


Fig. 1 Mo K-edge EXAFS and FT (r.t.) of MCM-41/ $\text{MoO}_2\text{Cl}_2(\text{THF})_2/\text{TEA}$