



	<b>Experiment title:</b> XAFS studies of tailored oxomolybdenum catalysts	<b>Experiment number:</b> CH1294
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 26/2/02 to: 28/2/02	<b>Date of report:</b> 16/7/02
<b>Shifts:</b> 6	<b>Local contact(s):</b> Silvia Ramos	<i>Received at ESRF:</i>
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In this experiment, XAFS measurements were carried out at several absorption edges for a series of tailored oxomolybdenum catalysts:

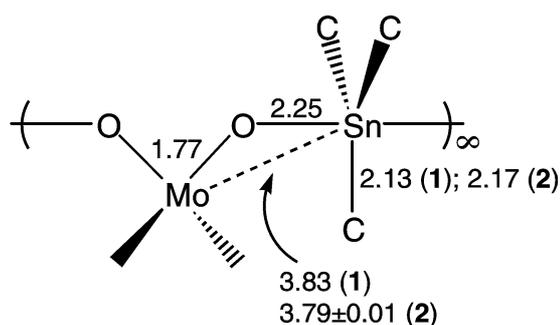
**1. Micelle-templated silicas** MCM-41 (hexagonal symmetry) and MCM-48 (cubic symmetry) functionalised with Lewis base adducts of the type  $\text{MoO}_2\text{X}_2\text{L}$ , where L is the bidentate N,N-ligand 1,3-diazabutadiene  $\text{RN}=(\text{CPh})(\text{PhC})=\text{NR}$  [ $\text{R} = -(\text{CH}_2)_3\text{Si}(\text{OEt})_n$ ]. This study is related to previous XAFS measurements of oxomolybdenum and oxorhenium catalysts supported on MCM-41 functionalised with bipyridyl groups (CH1082).<sup>1,2</sup> The precursor complex  $\text{MoO}_2\text{X}_2\text{L}$  ( $n = 3$ ) and also a second complex with  $\text{L} = [\text{Me}(\text{C}_6\text{H}_4)\text{N}=\text{CMe}]_2$  were measured as reference compounds. Early indications from the EXAFS data are that the local coordination environment of Mo in the complex is not disrupted during grafting to the silica surface.

**2. Organotin-oxomolybdate coordination polymers** formulated as  $[(\text{Me}_3\text{Sn})_2\text{MoO}_4]$  and  $[(\text{Me}_2\text{R}^*\text{Sn})_2\text{MoO}_4]$  ( $\text{R}^*$  is a chiral (-)-menthyl group). This work was undertaken following the useful results obtained previously on BM29 (at the Mo *K*- and Sn *K*-edges) for analogous derivatives of the type  $[(\text{R}_3\text{Sn})_2\text{MoO}_4]$  ( $\text{R} = n\text{Bu}, \text{C}_6\text{H}_5, \text{C}_7\text{H}_7, \text{C}_6\text{H}_{10}$ ) (CH1082).<sup>3</sup> The trimethyltin derivative is a good model compound since its structure is known from single crystal X-ray diffraction (while the other derivatives are not amenable to such studies).

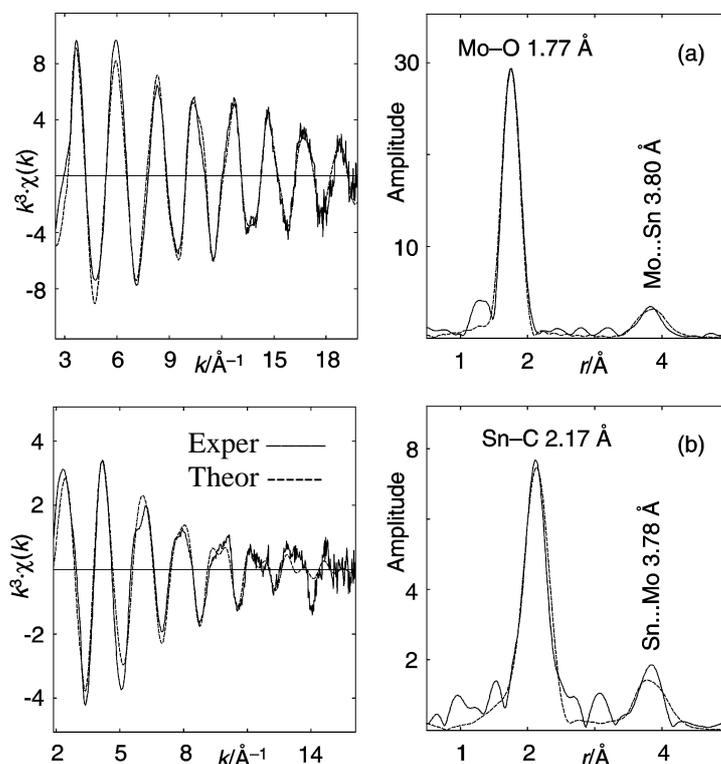
**3. Heterobimetallic complexes.** The cation in  $[\text{Ru}([\text{14}]\text{aneS}_4)(\text{bpym})](\text{BF}_4)_2$  ( $\text{bpym} = \text{bipyrimidine}$ ) has been used as a “metalloligand” to bind oxometal fragments  $[\text{MoO}_2\text{Cl}_2$  and  $\text{MeReO}_3$  (methyltrioxorhenium)] at the free coordination site. The resulting adducts are too unstable to obtain crystals suitable for X-ray diffraction, and therefore XAFS spectroscopy was used to characterise the Ru–bpym–M bridge. The mononuclear complexes  $[\text{Ru}([\text{14}]\text{aneS}_4)(\text{bpym})](\text{BF}_4)_2$ ,  $[\text{Ru}([\text{14}]\text{aneS}_4)(\text{MeCN})_2](\text{BF}_4)_2$ ,  $\text{MoO}_2\text{Cl}_2(\text{bpym})$ ,  $\text{MeReO}_3$ ,  $\text{MeReO}_3(\text{bpym})$  and  $(\text{Me}_2\text{Et}_2\text{N})\text{ReO}_4$  were also measured as reference compounds.

**Experimental details.** Mo *K*- (20.0 keV), Ru *K*- (22.1 keV), Sn *K*- (29.2 keV) and Re *L*<sub>III</sub>-edge (12.5, 10.5 keV) X-ray absorption spectra were collected for samples in the solid state at 300 K and also at *ca.* 30 K (Oxford Instruments cryostat filled with He exchange gas) 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. The order-sorting double Si(311) crystal monochromator was detuned by 40% to guarantee harmonic rejection. Usually, scans were set up to record the pre-edge at 5 eV steps and the post-edge region in 0.025–0.05 Å<sup>-1</sup> steps (2s per step), giving a total acquisition time of *ca.* 45 min per scan. A total of about 40 spectra were recorded over the two days. For the MCM samples, four scans were recorded at 300 K for each sample in order to improve the signal-to-noise. Analysis of the results is ongoing, using the programs EXCALIB, EXBACK and EXCURVE (EXCURV98, Daresbury Laboratory, UK). Some preliminary findings are reported here for the organotin-oxomolybdate coordination polymers.

**Organotin-oxomolybdates.** Analysis of the low temperature (30 K) Mo *K*-edge and Sn *K*-edge EXAFS of the compounds [(Me<sub>3</sub>Sn)<sub>2</sub>MoO<sub>4</sub>] (**1**) and [(Me<sub>2</sub>R\*Sn)<sub>2</sub>MoO<sub>4</sub>] (**2**) confirms that the structures arise from the self-assembly of tetrahedral [MoO<sub>4</sub>]<sup>2-</sup> anionic sub-units and [R<sub>3</sub>Sn]<sup>+</sup> cationic spacers (Fig. 1). The EXAFS-derived Mo...Sn separation in the trimethyltin derivative is a uniform 3.83 Å, while that in the chiral derivative is 3.79±0.01 Å (Fig. 2). In general, recording the spectra at low temperature was essential to adequately observe these more distant M...M shells.



**Fig. 1.** Summary of the EXAFS-derived structural information for **1** and **2**. The Sn–O distance could only be determined for **1**.



**Fig. 2.** Mo *K*-edge (a) and Sn *K*-edge (b) *k*<sup>3</sup>-weighted EXAFS and Fourier transforms of **2**.

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[3] M. Abrantes, A. Valente, M. Pillinger, I. S. Gonçalves, J. Rocha, C. C. Romão, *J. Catal.*, 2002, **209**, 237.