



**Experiment title:**

XAFS studies of hybrid organic-inorganic mesoporous materials

**Experiment number:**

CH1603

**Beamline:**

BM29

**Date of experiment:**

from: 16/11/03 to: 18/11/03

**Date of report:**

31/7/04

**Shifts:**

6

**Local contact(s):**

Dr. Pier Lorenzo Solari

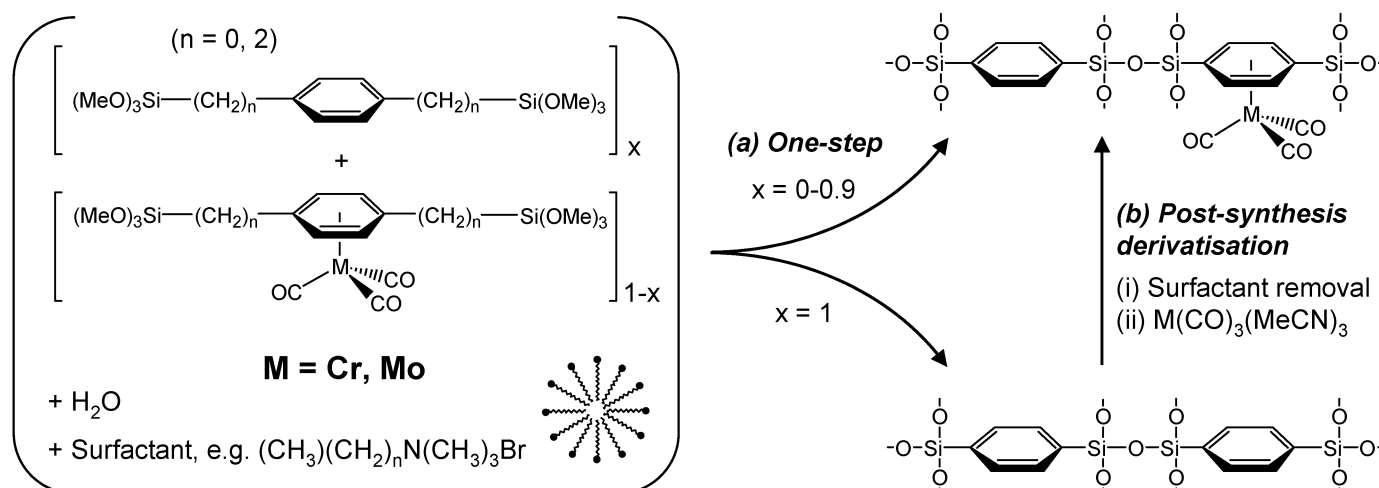
*Received at ESRF:*

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**Aims.** In this experiment, X-ray absorption fine structure (XAFS) measurements were carried out in the solid-state for a series of periodic mesoporous organosilicas (PMOs). The materials were synthesised in advance with the aim of engineering functionalised derivatives containing organometallic groups as an integral part of the structure. Scheme 1 summarises the approaches taken. Basically, the metal species were introduced either by one-step surfactant-templated hydrolytic polycondensation of  $(R'O)_3Si-R-Si(OR')_3$  precursors (a) or by post-synthesis derivatisation (b). The objective of experiment CH1603 was to characterise the average local structural environments of the different metals in the synthesised materials using XAFS spectroscopy.

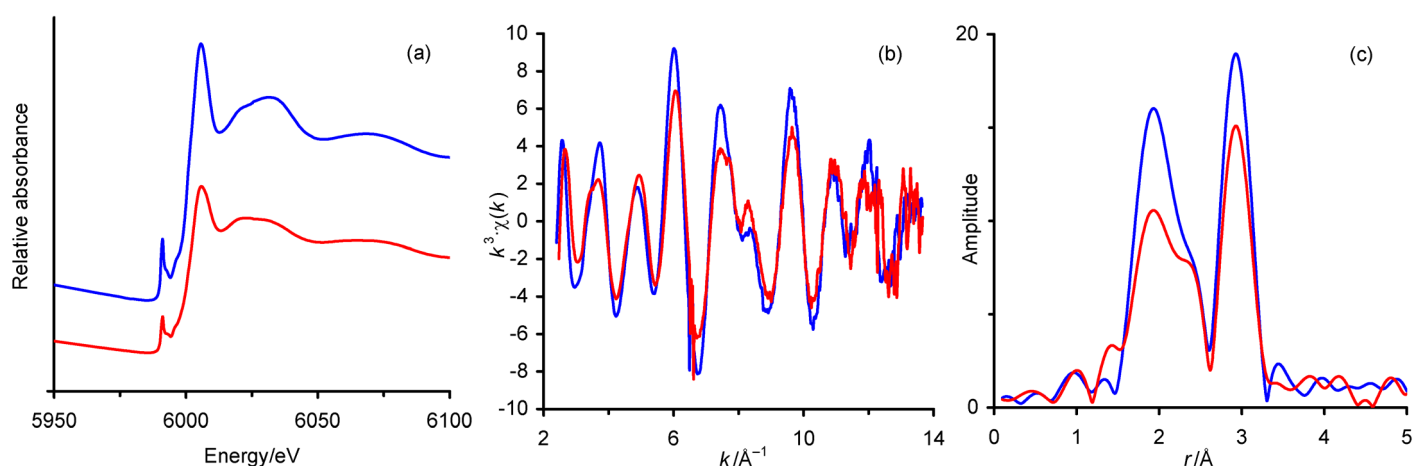


**Scheme 1.** Summary of synthetic routes to PMOs functionalised with organometallic groups.

**Experimental details.** Cr K- (5.99 keV) and Mo K-edge (20.00 keV) X-ray absorption spectra were collected for samples in the solid state at 300 K and also at *ca.* 40 K (using an 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 uniform fill mode with typical currents of 170–200 mA. The order-sorting double Si(311) crystal monochromator was detuned by 40-50% 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 50 spectra were recorded over the two days. Materials prepared by method (a) ( $x = 0-0.9$ ) or method (b) (with various metal loadings), with  $M = \text{Cr}$  or  $\text{Mo}$ , were analysed. The metal carbonyls  $\text{M}(\text{CO})_6$ ,  $\text{M}(\text{CO})_3(\text{MeCN})_3$  and  $(\text{C}_6\text{H}_3\text{Me}_3)\text{M}(\text{CO})_3$  were also measured as model compounds.

**Results.** Analysis of the results is proceeding, using the programs EXCALIB, EXBACK and EXCURVE (EXCURV98, Daresbury Laboratory, UK). Some preliminary results are reported here for a material prepared by method (a) with  $M = \text{Cr}$  and  $x = 0$ . Fig. 1(a) shows the room-temperature Cr K-edge X-ray absorption near-edge (XANES) data for  $(\text{C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3$  and the PMO material (before surfactant removal). The similarity between the two spectra was an initial indication that a material functionalised with benzene tricarbonyl chromium species had successfully been prepared. This was subsequently confirmed by comparing the EXAFS data [Fig. 1(b)]. EXAFS curve-fitting analyses (using fast curved waved theory with multiple scattering) have revealed the expected shells for the model complex: 3 C at 1.83 Å, 6 C at 2.23 Å and 3 O at 2.96 Å. A similar structural model was obtained in the fit to the EXAFS of the PMO material, confirming that the average local environment of Cr centers is consistent with the presence of  $(\text{C}_6\text{H}_4\text{R}_2)\text{Cr}(\text{CO})_3$  species. XAFS analysis of this material (and other examples with  $x > 0$ ) after surfactant removal show that the structural integrity of the organometallic groups was disturbed. These results have prompted us to devise more benign methods for the surfactant removal. Method (b) circumvents this problem by preparing a metal-free PMO, removing the surfactant, and then derivatising via surface organometallic chemistry. Work is ongoing to analyse the XAFS results for these materials.



**Fig. 1.** Room temperature Cr K-edge XANES (a),  $k^3$ -weighted EXAFS (b) and Fourier transform (c) of  $(\text{C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3$  (—) and as-synthesised PMO (—) prepared by method (a) with  $x = 0$ .

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