



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: In situ studies of formation of iron molybdate and cobalt Molybdate catalysts by using	Experiment number: 26-01-844
Beamline: BM26A	Date of experiment: from: 15/05/09 to: 18/05/09	Date of report: 01/07/09
Shifts: 4	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Wim Bras, DUBBLE CRG, ESRF, Grenoble, France Vladimir Martis* DUBBLE, CRG, ESRF, Grenoble France, (UCL) Prof G. Sankar*, University College London, Dep. of Chemistry, London, UK Martin Martis* University College London, Dep. of Chemistry, London, UK		

Report:

The EXAFS spectra were collected at Mo K-edge (20 000 eV) and Co K-edge edge (7 709 eV) in transmission mode. The X-ray beam was monochromatized using Si(111) double crystal monochromator. The acquisition time for EXAFS spectra was 40 min. The XRD data were collected using a wavelength of 1.64 Å. The acquisition time for diffraction pattern was 2 min. The EXAFS spectra and XRD data were collected sequentially. The typical cycle of collection EXAFS/XRD data lasted between 42-44 min.

The measured samples were in the form of powder pressed into 13 mm pellets. The pellets were mounted on the holder placed inside the furnace. During experiments samples were heated in the furnace using kanthal wire from room temperature to 400 °C at rate of 5 °C/min and then up to 550 °C at rate of 2.5 °C/min. The Pt-Rh thermocouple was used to measure temperature on the samples.

The preliminary results

In Figure 1a) are shown XRD patterns of as-synthesised cobalt molybdate collected during heating from room temperature to 550 °C. Diffraction pattern obtained at room temperature contains only two reflections. These reflections do not undergo any changes up to temperature of 250 °C. Increasing the temperature to 360 °C, the β -isomorph peak appears at 28°. This peak remains at the same position during heating up to 550 °C. Diffraction pattern of CoMoO₄ acquired at 550 °C corresponds to β -phase of CoMoO₄.

Normalized EXAFS spectra collected at Co K-edge are shown in Figure 1b) obtained from combined XAS/XRD measurements. Considering the XANES region of the XAS spectra, we can extract information about geometric characteristics of cobalt molybdate. The Co²⁺ ions in CoMoO₄ occupy sites with octahedral coordination, since we don't observe changes during transformation to β -phase. Moreover, we also followed phase transformation of as-prepared CoMoO₄ to β -phase at Mo K-edge in order to find out coordination of Mo⁶⁺ ions in this catalyst. More detailed data analysis are in progress to quantitatively determine the state of

cobalt and molybdenum sites. The EXAFS spectra of CoMoO_4 collected at Mo K-edge is displayed in Figure 2a.

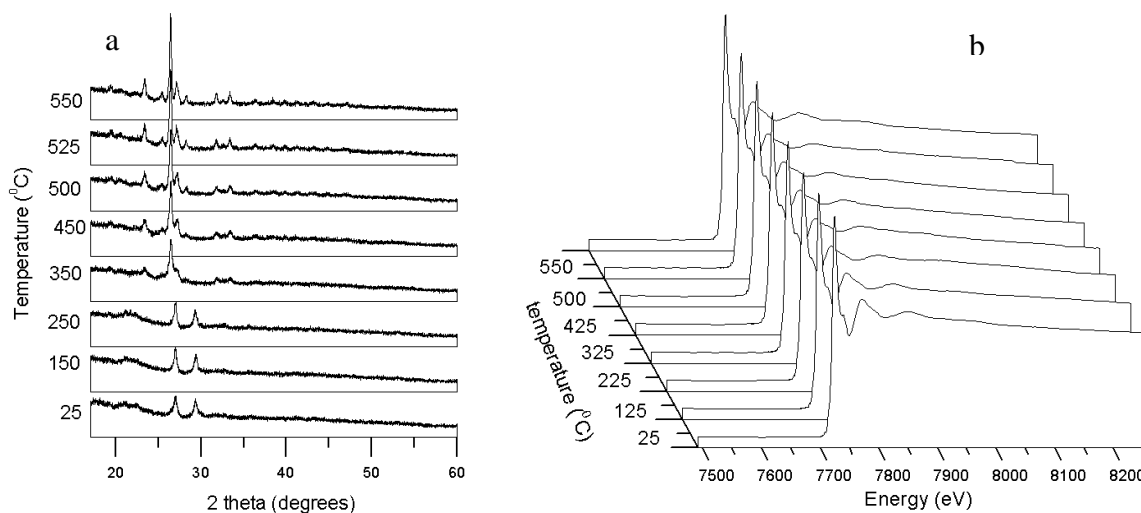


Figure 1 a) Stacked XRD pattern showing formation of $\beta\text{-CoMoO}_4$ from CoMoO_4 during heating from room temperature up to 550 °C in the air. Sample was heated to 400 °C at rate of 5 °C/min and then 2.5 °C/min up to 550 °C. b) Normalised EXAFS spectra of CoMoO_4 . Data were collected at Co K-edge during heating to 550 °C in the air at rate of 5 °C/min up to 400 °C and then at rate of 2.5 °C/min up to 550 °C.

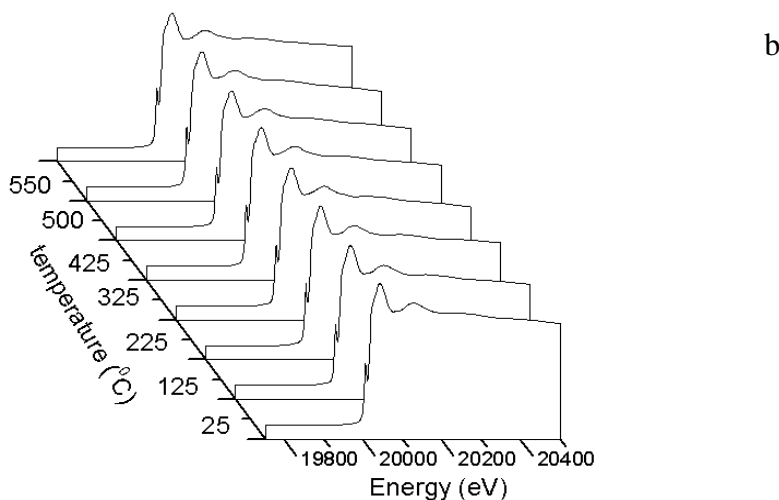


Figure 2 Normalized EXAFS spectra of CoMoO_4 (a) collected at Mo K-edge during heating from room temperature up to 550 °C in the air. Sample was heated to 400 °C at rate of 5 °C/min and then 2.5 °C/min up to 550 °C

Conclusion

Employing combined in situ XAS/XRD measurements enabled us to follow structural transformation in the model system CoMoO_4 and $\text{CoMoO}_4 - \text{H}_2\text{O}$ which took place during heating at elevated temperatures. Collecting data at Co K-edge and Mo K-edge allowed us to obtain information on changes in coordination around Co^{2+} and Mo^{6+} in these catalysts during transformation. The XRD was used to identify phases present during heat treatment process.