



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:
Spatial mapping of the metal phases present inside an extrudate during catalyst preparation

Experiment number:
CH-2535

Beamline: ID15B	Date of experiment: from: 23 April 2008 to: 28 April 2008	Date of report: 25-8-2008 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Dr Marco Di Michiel	

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Report:

During this experimental time we have continued our previous work (July 2007) and further modified and refined the multi-technique setup for collection of 1-dimensional tomographic data over a catalyst bed in operando conditions. We have also collected high quality WAXS data on the reduction of MoO_3 directly to MoO_2 and performed Rietveld analysis allowing us to study this conversion in substantial detail.

From our previous work we had already successfully collected a series of data on the reduction and oxidation of both iron molybdate and its component oxide MoO_3 . The 'open' nature of the catalytic cell allowed us to probe the catalyst bed along its length and combine a series of techniques (WAXS, Raman, UV-Vis, fluoresce and online mass spectrometry) congruently on the sample. However, the low vapor pressure of water (compared to the methanol) made it difficult to supply sufficient vapor to the catalyst to compare the effect of leaching (which is believed to be a key factor in the deactivation iron molybdate) under these two environments. In this current work we have developed a new pipe heating system which largely overcomes this problem and have now successfully recorded the flow of water vapor over the catalyst bed for 12 hours which will now allow for a direct comparison. Due to the number of techniques and the quantity of the data recorded in these experiments, the analysis of this work is still ongoing; however we believe that these measurements will result in an increased understanding into the effect of reactants and products on molybdenum containing catalysts.

In the second part of our work we collected high quality WAXS diffraction images from a single point within the catalyst using the high resolution 2D PIXIUM4700 detector. The specific conditions utilized in this reaction inhibit the formation of complex sub-oxides during reduction of MoO_3 and this, in combination with the quality of the WAXS data, allowed us to follow the direct reduction of MoO_3 to MoO_2 in very high detail by performing Rietveld analysis on each of the datasets recorded. In combination with UV-Vis, Raman and mass spec we can then detail the reaction occurring at the surface of the catalyst (Uv-Vis and mass spec) and within the bulk (Raman and WAXS). We believe the most important result of this work will be the fact that towards the end of the experiment, when bulk MoO_2 is observed forming, the Rietveld analysis of MoO_3

indicates an increase in both the bond length and thermal activity of one of the three unique oxygen environments (specifically O1) (figure 1).

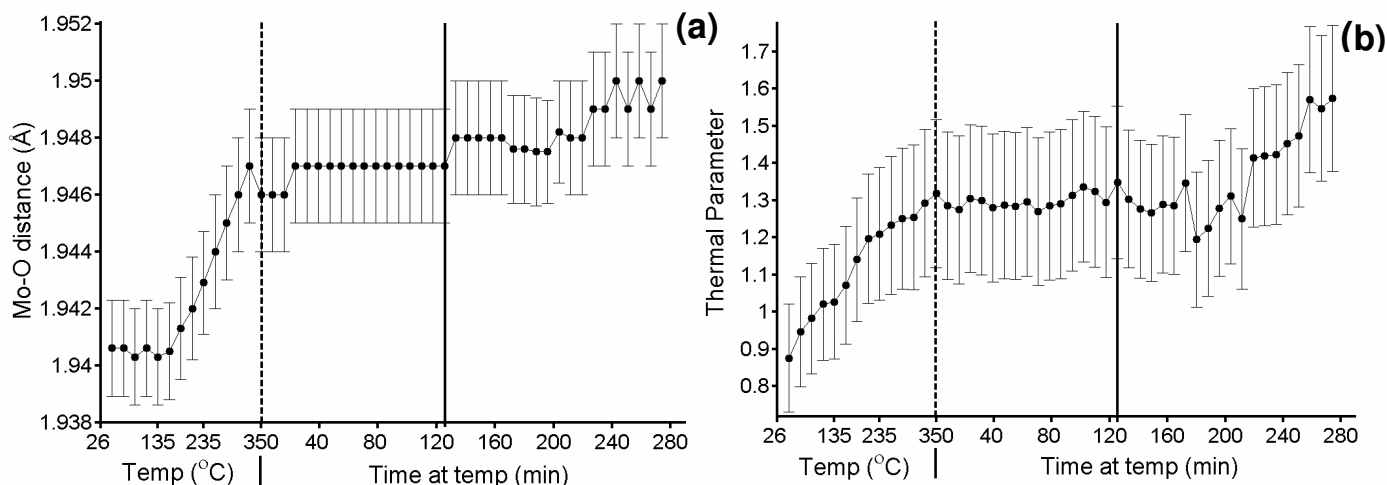


Figure 1: Variation in the bond length Mo-O1b (a) and the thermal parameter of O1 (b) during the reduction of MoO₃. Changes during the initial heating period (dashed line) and upon formation of bulk MoO₂ (solid line) are observed

This appears to indicate this is the most labile oxygen within the catalyst bulk during oxygen transfer *via* the Mars van Krevelin mechanism to regenerate the surface active sites. Indeed, this is supported by complementary changes in the Raman peak intensities, which indicate that the Mo-O1 bond is broken at a considerably faster rate than the others in the system (figure 2).

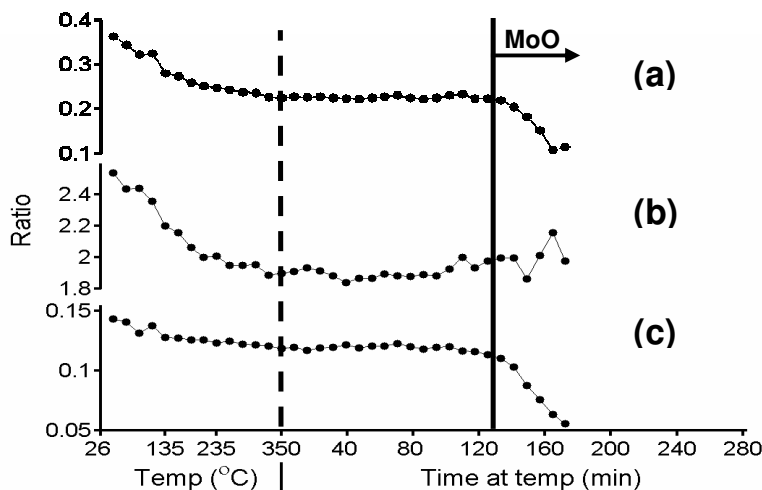


Figure 2: Variation in the ratio of the peak intensities at 667:994 (a), 820:994 (b) and 667:820 (c) in the Raman spectrum reveal that the intensity of the 664 band decreases far more rapidly than the other bands indicating a more rapid breaking of the Mo-O1 bond.

Although work continues on this analysis and how the changes relate to both the UV-Vis and mass spectrum data, it is clear that an understanding of the oxygen involved in the anaerobic reduction of this catalyst would be of considerable importance as it is this oxygen which maintains the reactivity at the catalyst's surface.

In addition to this we were also able to obtain some data regarding the mapping of crystalline phases during the preparation of catalyst extrudates. These data will serve as a good foundation/preliminary studies for obtaining further information on these types of preformed objects during catalyst preparation.