EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

ESRF	**Experiment title:** **Determination of the deactivation conditions of an iron molybdate catalyst and the identification of unknown phases using combined diffraction and Raman techniques**	**Experiment number**: CH-2693
Beamline: BM1B	**Date of experiment**: from: 28-1-2009 to: 3-2-2009	**Date of report**: 14-11-2009
Shifts: 15	**Local contact(s)**: Olga Safonova	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. M. G. O'Brien*, Dr Andrew Beale*

Department of Inorganic Chemistry and Catalysis, Utrecht University, Debye Institute, The Netherlands

Report:

Iron molybdates are essential materials for the industrial production of formaldehyde from methanol. (1) As such understanding their deactivation and the conditions under which this occurs is of considerable interest as it will allow for a more efficient catalyst with an extended lifetime. In a recent paper we have identified 2 previously un-observed structures in the iron molybdate material formed under highly anaerobic conditions (2). The first (P1) appears to be an intermediate between the oxidized and reduced iron molybdate forms, whilst the second (P2) seems to represent a complete breakdown of the catalyst from which the material cannot be regenerated under oxidizing conditions. Whilst these anaerobic conditions are not experienced under general catalyst operation, the identification of these deactivation routes is important as these structure may form under less harsh conditions. The object of this work was to identify these exact conditions and to obtain more detailed information on the mature of P1 and P2.

Unfortunately, during the initial experiments it was found that it was not possible to reduce the amount of oxygen within the gas flow to an amount under which deactivation occurred in a reasonable time period with the mass flow controllers and gases available (i.e. even at the lowest oxygen flow rates deactivation did not occur). Therefore the work focused primarily on understanding the nature of the intermediate phases P1 and the temperature condition under which it formed.

This proved successful and we were able to use relatively low temperatures in the anaerobic environment to form the P1 phase (together with a small amount of fully reduced beta molybdate phase) and 'stabilize' it for long periods (figure 1a). Interestingly after the reduction of the initial FeMo phase to form P1 we note that formaldehyde formation (as observed by online mass spectroscopy) continued without further reduction of the catalyst (figure 1b). This is unexpected because under anaerobic conditions the formation of formaldehyde from methanol unusually produces a molecule of water with the additional oxygen being extracted from the catalyst phase in a Mars-van Krevelen type manner (as there is no gaseous oxygen).

It seems then that under these mild conditions, and in the presence of the P1 phase, formaldehyde can be produced without further reduction of the catalyst, which would result in total deactivation. Therefore formaldehyde production may here occur *via* a different mechanism to that described preciously. Work is ongoing to confirm this data using full gas chromatography measurements, however if correct this observation could have important implications for the operation of iron molybdate type catalysts.

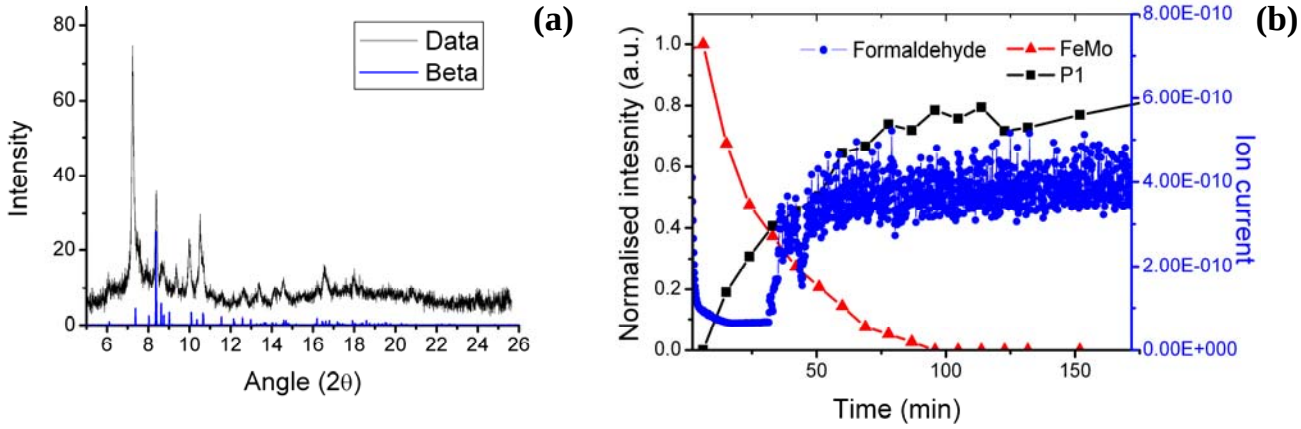

Figure 1: The formation of the stabilized P1 phase along with some beta was observed at 250°C (a). The evolution of this phase along with the initial FeMo demonstrates its stability even under the reducing anaerobic conditions, whilst the mass spectrum data demonstrates continued production of formaldehyde.

Conclusion

Although the conditions under which the phases P1 and P2 formed could not be identified we have used temperature variation to 'stabilize' the P1 intermediate and demonstrated that formaldehyde can be produced over this material under anaerobic conditions. This is of significant interest as it may suggest an alternate route to formaldehyde production at low temperatures over this 'intermediate' and further detailed catalytic test on these materials remains ongoing to confirm these observations.

References

(1) Soares A. P. V., Portela M. F., Kiennemann A., *Catal. Rev. Sci. Eng.* 47, 125, **2004**

(2) O'Brien M. G., Beale, A. M. ,Jacques S. D. M. Weckhuysen B. M.. *Top. Catal.* 52, 1400, **2009**