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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:** A new approach to studying heterogeneous and homogeneous catalysis utilising time resolved in situ EDXAFS/UV-Vis and Raman spectroscopies.	**Experiment number**: CH-1986
Beamline: ID24	**Date of experiment**: from: 02 November 2005 to: 08 November 2005	**Date of report**: 1 December 2005 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr Mark A Newton	

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Report:

During this experimental time we were able to further develop a setup for obtaining combined *in situ* ED-EXAFS, UV-Vis and Raman spectroscopy in order to study heterogeneous catalysts under real working conditions. To our best knowledge, this is the first in situ device which couples three spectroscopic techniques in one reactor which focuses on the same spot of a metal oxide catalyst under true reaction conditions and is capable of delivering sub second time resolution. The acquisition times for the three techniques ranged from 50-2000 ms for 1 scan although in order to improve the signal-to-noise ratio multiple spectra were recorded and summed. Typically for these experiments the acquisition times used were 400 ms for EDXAFS data, 1 s for Raman, 2 s for the UV-Vis and 10 s for the mass spectrometer. However due to the time delay for read out from the Princeton detector and the need to shutter the Raman laser in order to avoid saturation of the UV-Vis signal the time resolution between each acquisition was reduced to approximately 4-5 s for the EDXAFS, 10 s per UV-Vis and 15 s per Raman spectra.

In order to test this setup we carried out a series of studies using 13 - 3 wt% Mo/Al_2O_3 and Mo/SiO_2 incipient wetness impregnated catalysts during successive reduction (5% C_3H_8 in Helium)/oxidation (5% O_2 in Helium) cycles at 550°C. Since the three techniques are sensitive to changes in the molybdenum oxidation/coordination states it was possible to obtain complementary information on the catalysts behaviour and therefore the set-up allows us to discriminate between the dynamics of both catalysts under reaction conditions, as well as to identify the active site and the deactivation pathways.

Propane dehydrogenation over a 13 wt% Mo/Al$_2$O$_3$ catalyst.

In Figure 1 we show data collected using the three techniques in tandem during the first propane dehydrogenation cycle for the 13 wt%_Mo/Al$_2$O$_3$ catalyst. The initial features observed in the spectra included a distinct 1s-4d pre-edge feature at 20001.5 eV in the Mo K-edge ED-XANES, a strong LMCT band at 470 nm in the UV-Vis and a band in the Raman spectra at 1350 cm^{-1} (BN internal standard). The results are consistent with the presence of Mo^{6+} species dispersed on the catalyst surface probably in a mixture of tetrahedral/distorted octahedra environments. Only significant changes in the UV-vis absoprtion were observed to occur in the first 10 minutes of the propane dehydrogenation step although a small decrease in the baseline intensity in the Raman was observed and very small changes in the ED-XANES data (which included a decline in pre-edge peak intensity, an increase in the 1s-5p transition feature at 20021.7 eV) which continued until the reaction ceased some 20 minutes later. The changes observed in the Raman and UV-Vis data appear to be associated with the formation of coke on the catalyst surface.

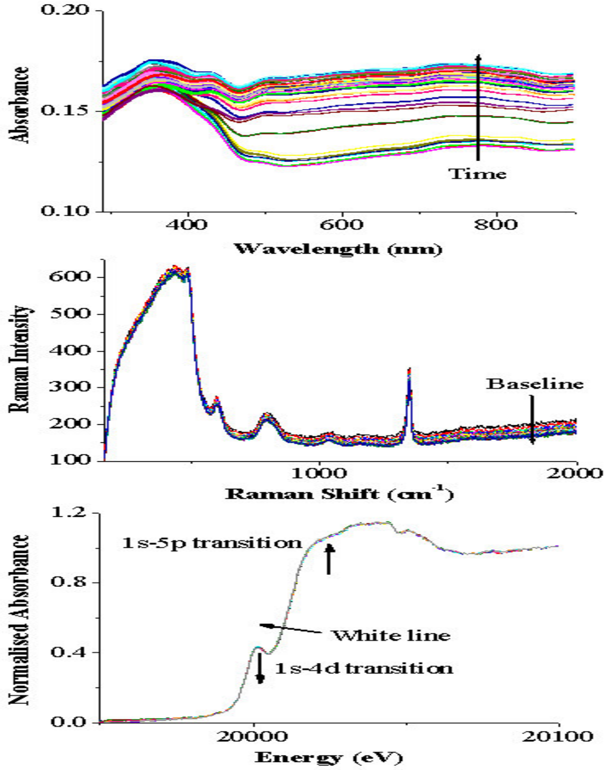

Figure 1. UV-Vis (top), Raman (middle) and ED-XANES (bottom) data acquired during PC1 for the Mo/Al$_2$O$_3$ catalyst. The observed increase in UV-Vis absorption coincided with a decrease in the intensity of the Raman bands corresponding to the background fluorescence. The appearance of bands at 420, 470, 680 and 780 nm in the UV-Vis data and the bands at 445, 485, 610, 830 and 1040 cm^{-1} in the Raman data are from the quartz reactor.

We were able to repeat these measurements twice more (after oxidative regeneration) and found that due to changes in the catalyst local structure the performance differed. Furthermore we also studied the behaviour of the corresponding lower loaded Mo/Al$_2$O$_3$ material and Mo/SiO$_2$ material and compared their catalytic performance under the same conditions. An early analysis of the results suggested that there were differences in redox behaviour between the different loadings on the catalysts and on the different types of support but critically this combination of techniques is able to show why this is so. Further data analysis is currently in progress.