



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: Operando XAS spectroscopy of methanol conversion	Experiment number: CH 1788
Beamline: BM 26 A	Date of experiment: from: 17/02/2005 to: 22/02/2005	Date of report: 28/02/2005
Shifts: 12	Local contact(s): S. NIKITENKO	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

S. Cristol, M. Capron, C. Dujardin

Laboratoire de Catalyse de Lille

UMR CNRS 8010

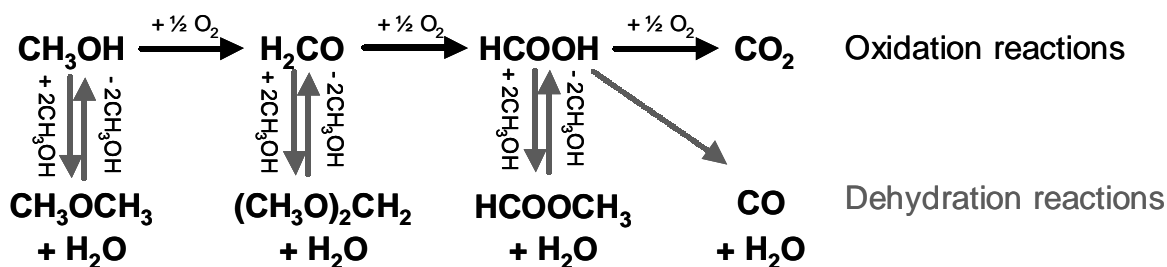
Bat. C3 USTL

F-59650 VILLENEUVE D'ASCQ

France

Report:

Introduction : Analysis techniques such as XPS and HREELS are generally used to characterize the surface state of heterogeneous catalysts but they cannot be used under working conditions. Infrared and Raman vibrational spectroscopy represent an attractive alternative as they can be applied to probe the catalyst under reaction or Operando conditions. The combination of Raman and IR spectroscopies can then give a better insight into catalytic systems under steady state conditions enabling to obtain information on the nature of the adsorbed species, the nature of the active phase and on the nature of their interaction. The oxidation state of active sites can also be characterized using bulk analysis techniques such as EPR and XAS to obtain data on an atomic scale. Molybdenum oxide based catalysts are used industrially for the partial oxidation of hydrocarbons such as methanol. The partial oxidation of methanol is of great interest for industrial applications¹ but is also a probe reaction to test the catalytic properties of new preparations⁴. Indeed, numerous studies have shown that methanol oxidation is very sensitive to the nature of active sites and can be used to study the acidic and oxidation properties of catalytic surfaces^{ii,iii,iv}. The possible pathways for the reaction of methanol on a bulk or supported metal oxide catalyst are summarized in Scheme 1.



Scheme 1: Reaction pathways in methanol transformation on MoO₃ catalysts⁴.

The oxidative-reductive processes lead to oxidized species such as formaldehyde (F), formic acid (FA) and carbon oxides (CO_x) whereas acid-base functions mainly lead to the dehydration product (dimethylether - DME). Successive dehydrations of oxidation products can yield dimethoxymethane (DMM) or methyl formate (MF)⁴. Hence, the distribution of the reaction products gives indications on the functionalities present on the catalyst surface. Moreover, oxidation of methanol is well adapted for spectroscopic studies^{v,vi} and has been described on various materials^{vii,viii}.

We have focused the present study on the characterization of the active phase and adsorbed species with Raman/Infrared and EPR spectroscopies during the oxidation reaction of methanol on a well-designed polymolybdate deposited on γ -alumina.

The beam time on the BM26A beam line (proposal # CH 1788: OPERANDO XAS SPECTROSCOPY OF THE METHANOL CONVERSION) was dedicated to the observation of the active phase through the molybdenum probe.

Experimental:

For the experiments, an in-situ and Operando home-made cell was built (figure1)^{ix}. It is made in boron nitride, a material completely transparent at the Mo k-edge with a good thermal conductivity coefficient. We have characterized the Mo/Al₂O₃ (20 wt% and 3 wt% Mo) compounds by EXAFS and XANES at the Mo K-edge using the transmission mode. We have first follow the catalysts activation, i.e. its evolution as a function of the activation conditions: nature of the gas phase (air or O₂) and temperature. Then, the structural catalysts evolution was studied during the oxidation reaction itself at different temperature. The effluent products were monitored with a Quick gas chromatograph (μ -GC, SRA).

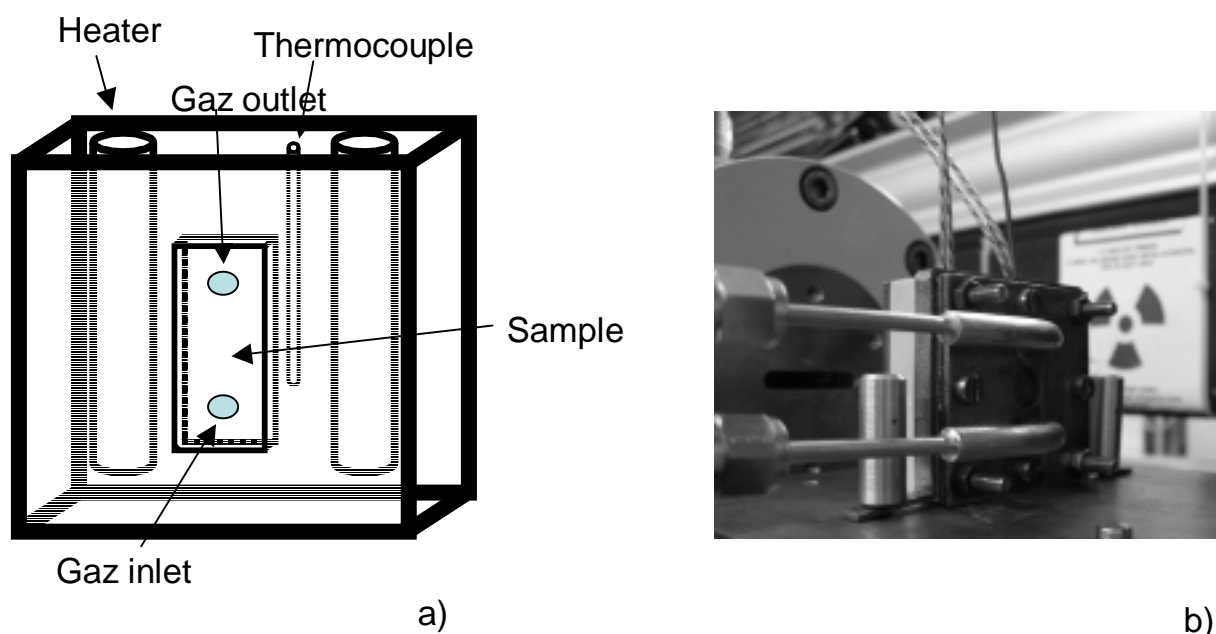


Figure 1: a) scheme of the home made cell dedicated to in-situ and Operando XAS spectroscopy b) picture of the cell.

Results:

The evolution of the XANES spectra for the high Mo loading catalyst with temperature under a He/MeOH mixture is present on the figure 1. A clear evolution of the XANES signal is seen. (see arrows on the figure). This evolution can be attributed to the reduction of the active oxomolybdic phase by methanol oxidation. Each increase of temperature is indeed characterized by the production of a small amount of formaldehyde as shown

by GC analysis. As there is no oxygen in the gas phase to reoxidized the reduced sites, the oxidative function of the catalyst quickly deactivates. If helium is substituted by oxygen in the reactive mixture, the catalyst is regenerated as shown by the production of formaldehyde. It can be seen on figure 3, that this regeneration of the oxidative function is characterized by an almost complete restoration of the signal obtained after activation of the catalyst. All these results are in agreement with previously obtained EPR data^x and the reduced signal can be attributed to Mo^V. The intensity of the pre-edge peak seems to correlate with the quantity of Mo^{VI}. A detailed analysis of the XANES and the EXAFS spectra is currently under progress in order to extract local structural data on the active phase.

The XANES spectra of the low Mo loading catalyst are presented on figure 4. The figure clearly shows that no evolution can be observed during the course of the reaction in agreement with the online gas analysis that only show dehydration products that are due to methanol reaction on alumina. The monomeric molybdenum centers that are present on the alumina surface at this low loading cannot perform methanol oxidation.

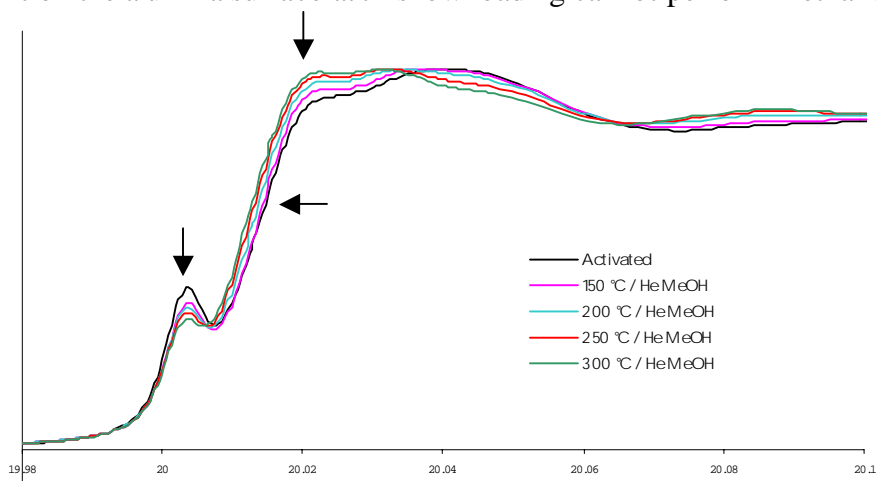


Figure 2: Evolution of the Mo₂₀ (20 Weight % of molybdenum) XANES spectra with temperature under He/MeOH.

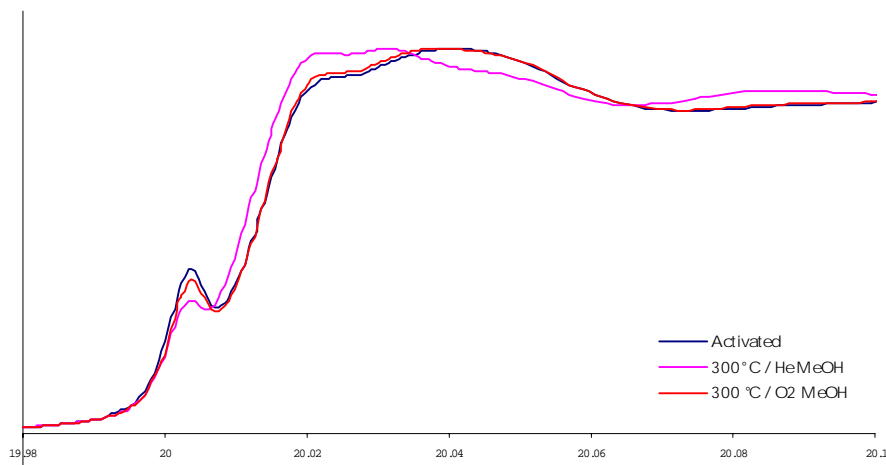


Figure 3: Evolution of the Mo₂₀ (20 Weight % of molybdenum) XANES spectra with the surrounding atmosphere.

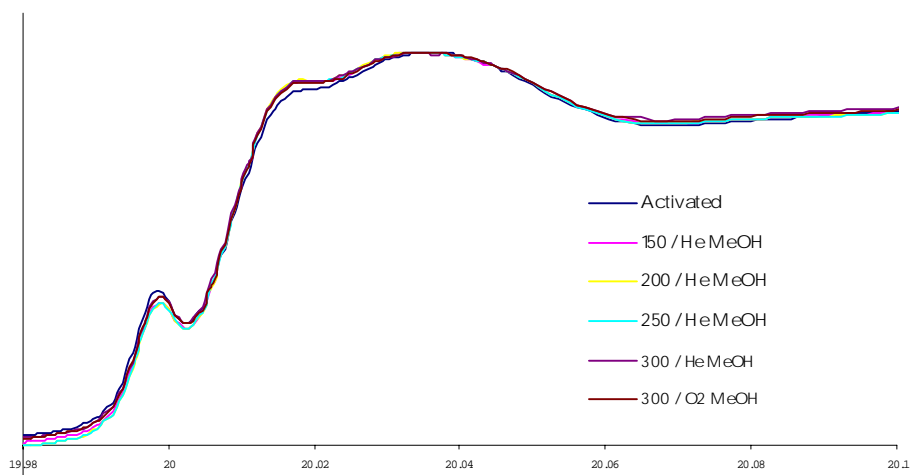


Figure 4: Evolution of the Mo₃ (3 Weight % of molybdenum) XANES spectra with temperature under He/MeOH

Conclusion:

In conclusions, these data show that a polymolybdate phase is required to perform methanol oxidation although the details of the reaction mechanism and the exact nature of the active phase evolution require a more in-depth analysis.

ⁱ E.J. Boake, A Boaks Roberts and Co, Patent # 110787 october 1917 ; H.W. Brandt, K. Flittard, J.P. Damand, R. Wambach, H.Wolz, BAYER society, Patent # 1 221 621 august 1964.

ⁱⁱ J.-M. Tatibouët, Appl. Catal. A : General 148 (1997) 213.

ⁱⁱⁱ Y. Matsuoka, M. Nywa, Y. Murakami, J. Phys. Chem. 94 (1990) 1477.

^{iv} L. E. Briand, W. E. Farneth, I. E. Wachs, Catal. Today 62 (2000) 219.

^v L.J. Burcham, M. Badlani, I. Wachs, J. Catal. 203 (2001) 104.

^{vi} J.C. Lavalley, Catal. Today 27 (1996) 377.

^{vii} H. Hu, I.E. Wachs, S.R. Bare, J. Phys. Chem. 99 (1995) 10897.

^{viii} Y. Yuan, H. Liu, H. Imoto, T. Shido, Y. Iwasawa, J. Catal. 195 (2000) 51.

^{ix} J.S Girardon et al. Journal of Synchrotron Radiation (submitted)

^x M. Brandhorst, S. Cristol, M. Capron, C. Dujardin, H. Vezin, G. Lebourdon and E. Payen, Catal Today (accepted)