

## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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**

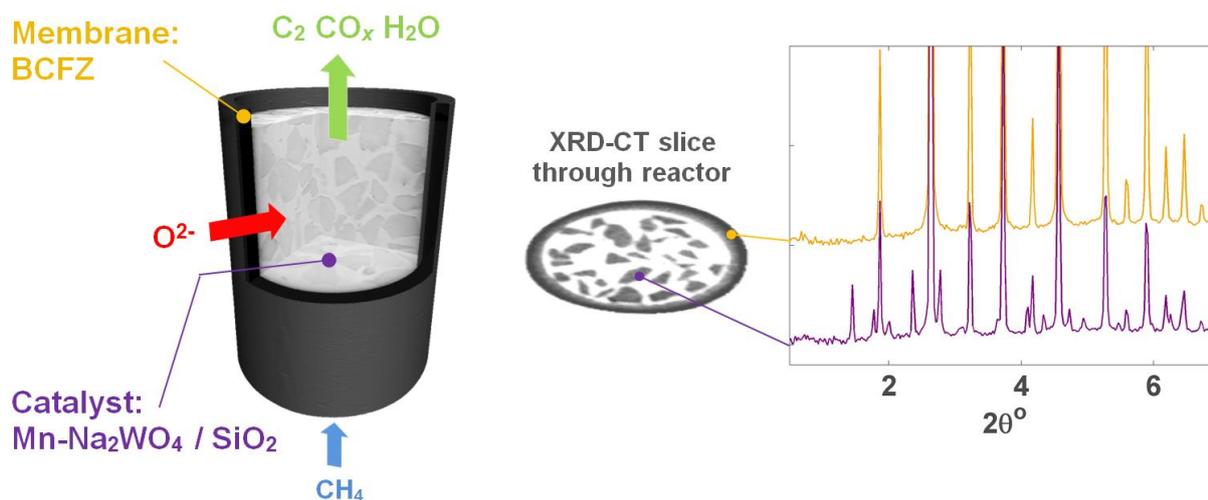
- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you 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.



	<b>Experiment title:</b> Operando XRD-CT study of a catalytic membrane reactor for the oxidative coupling of methane	<b>Experiment number:</b> CH-4148
<b>Beamline:</b> ID15	<b>Date of experiment:</b> from: 29 Oct 2014                      to: 04 Nov 2014	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Marco Di michiel ( email: dimichie@esrf.fr )	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *Dr Simon Jacques, School of Materials, Manchester University *Mr Antonios Vamvakeros, Department of Chemistry, University College London Dr Andrew Beale, Department of Chemistry, University College London		

## Report:

The aim in this study was to investigate the solid-state chemistry within a working catalytic membrane reactor (CMR) for the oxidative coupling of methane (OCM) to produce C<sub>2</sub> molecules, principally ethylene. We employed dynamic X-ray diffraction computed tomography (XRD-CT) and absorption micro computed tomography ( $\mu$ CT) to image the reactor in situ under preparation and operando conditions. In our study the CMR consisted of a hollow fibre dense ceramic membrane packed with a catalyst bed (see schematic in figure 1). The CMR was housed within a quartz tube and mounted onto a gas delivery stub such that a methane stream could be passed from the inner side and air stream could be controlled from the outer side of the membrane. The ceramic membrane is an oxygen transport membrane that activates at high temperature ( $>650^{\circ}\text{C}$ ) allowing selective diffusion of oxygen ions towards the catalyst within the membrane. The gas products were monitored in line by mass spectrometry. A number of reactor configurations were tested: (1)  $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$  with  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst; (2)  $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$  with  $\text{La-Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst; and (3)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  with  $\text{La-Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst. We also tested two fixed bed reactors with  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  and  $\text{La-Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalysts. In all cases, XRD-CT was performed as the reactors were heated to *expected industrial* operating conditions; XRD-CT were recorded at a set of fixed temperatures 675, 725 and 775 $^{\circ}\text{C}$ . At operating temperature (775 $^{\circ}\text{C}$ ) we varied the concentration of methane (5, 20, 50 and 100%) in helium.



**Figure 1:** *Left:* Image showing the CMR. *Top right:* Within an XRD-CT image each pixel has a corresponding diffraction pattern; the graph inset top right shows two selected diffraction patterns: one from the membrane (yellow trace) and one from the catalyst region (purple trace); note, here the purple trace also contains a signal from the membrane due to an absorption artefact which has yet to be corrected for. Images can be constructed that correspond to features (i.e. Bragg reflections) within the diffraction patterns.

Our analysis is in progress but here we report some initial results from the  $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$  with  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst. Figure 2 show  $\mu\text{CT}$  maps prior to and after OCM overlaid with phase maps constructed from the XRD-CT data including the cristobalite (purple),  $\text{Na}_2\text{WO}_4$  (red) and  $\text{BaWO}_4$  (green) phases; see figure panels A-F. It is important to state that the mass spectrometer showed that ethylene was indeed formed during the in situ OCM; see figure panel G. We observed the migration of W from the catalyst and subsequent formation of the  $\text{BaWO}_4$  at the inner side of the membrane. This is independently confirmed by post mortem SEM-WDS analysis which shows the presence of tungsten at the membrane surface; see figure panel H. A summed diffraction (from reconstructed XRD-CT data) from pixels of interest is shown in panel I over which the identified phases have been overlaid as stick intensities. These results are interesting as the formation of  $\text{BaWO}_4$  is likely to be inhibitory to the stability and performance of the catalytic membrane reactor. We have, of course, the corresponding XRD-CT and  $\mu\text{CT}$  data during reaction but this is not presented here as the analysis is on going.

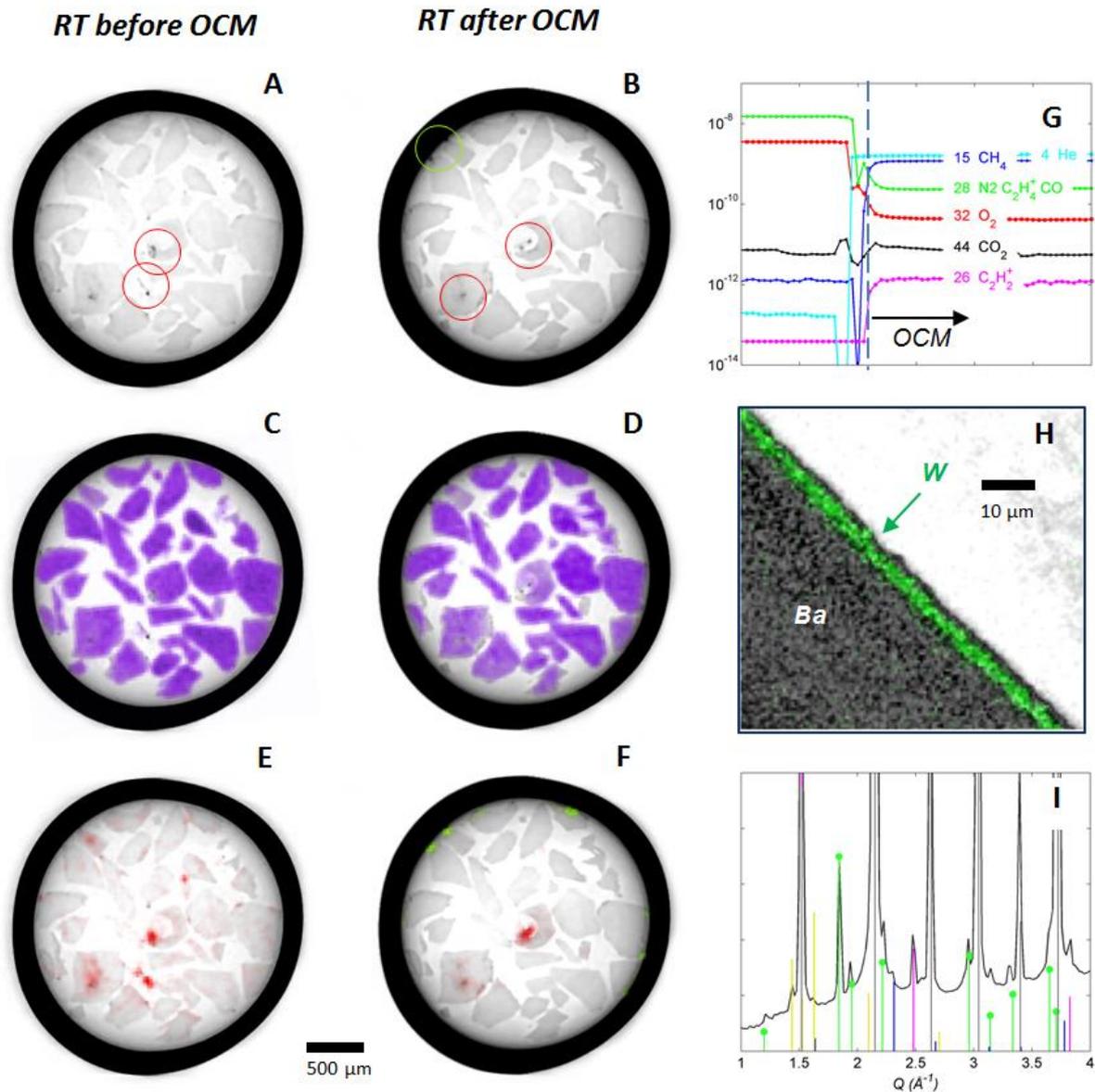


Figure 2. Panels A and B show reconstructed slices from micro-CT measurements of the CMR before and after the OCM2 experiment at room temperature. Panels C and D are the same images repeated with the distribution of cristobalite as found from XRD-CT overlaid in violet. Panels E and F, again contain the micro-CT slices but here overlaid with the distributions of  $\text{Na}_2\text{WO}_4$  (red) and  $\text{BaWO}_4$  (green). Panel G shows the mass spectroscopy data that correspond to the following masses: 4 (He - cyan), 15 ( $\text{CH}_4$  - blue), 28 ( $\text{N}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4^+$  - green), 32 ( $\text{O}_2$  - red), 44 ( $\text{CO}_2$  - black) and 26 ( $\text{C}_2\text{H}_2^+$  - magenta). Panel H shows the overlaid WDS elemental maps for Ba (grayscale) and W (green). Panel I shows a summed diffraction pattern from some selected green pixels. Overlaid on this pattern are sticks of database intensities for phases  $\text{BaWO}_4$  (green), cristobalite (magenta),  $\text{Mn}_2\text{O}_3$  (blue), tridymite (yellow) and BCFZ (grey).