

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.

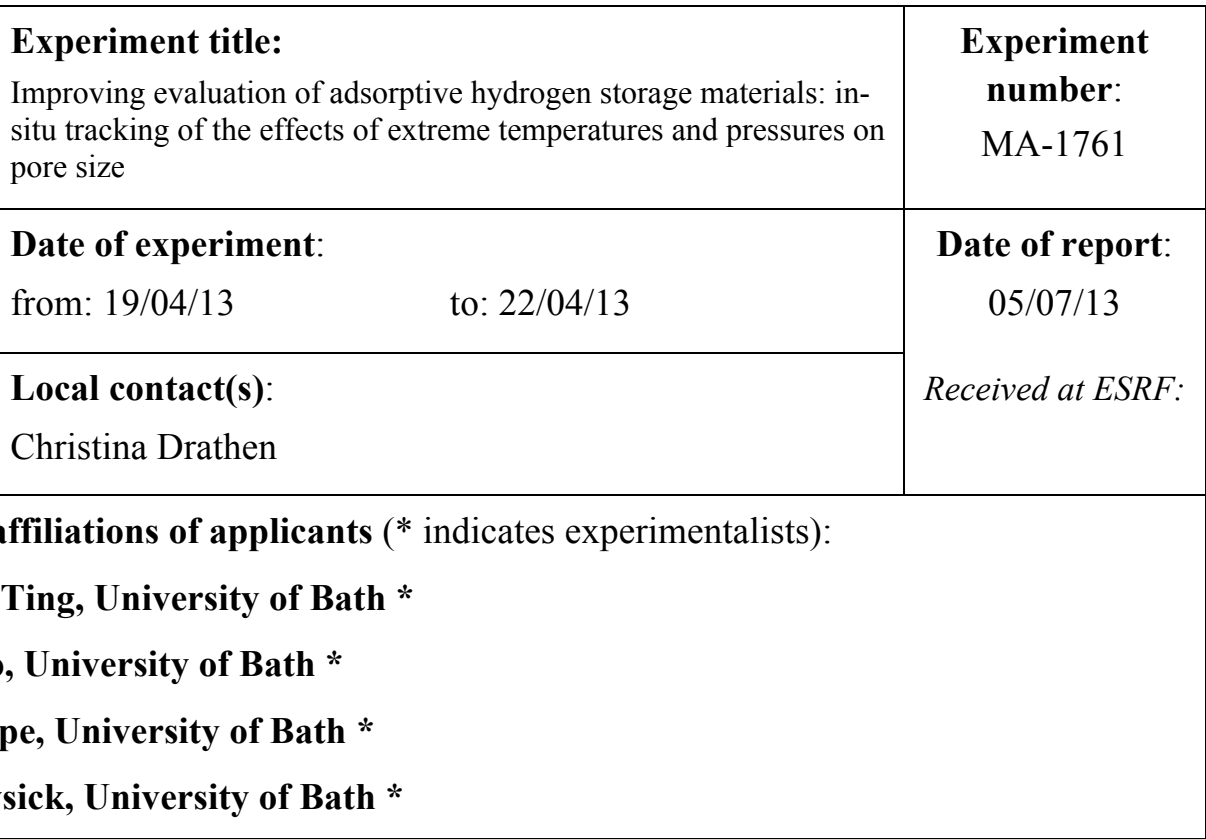
Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

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.



While hydrogen (as a sustainable alternative to fossil fuels) can currently be stored as a compressed gas at high pressures or a liquid at extremely low temperatures, there are concerns about the safety and energy efficiency of such storage methods. As an alternative storage method, adsorption of hydrogen into the pores of solid materials such as metal-organic frameworks (MOFs) causes densification of the hydrogen so that greater amounts can be conveniently stored in smaller volumes under milder storage conditions of temperature or pressure. Certain MOFs have been observed to be flexible with the inclusion of an adsorptive, and so show a variation in pore volume with pressure. The pore volume is a particularly important quantity in the modelling of the H₂ adsorption process, and when calculating the total amount of hydrogen in the system (a quantity which cannot easily be determined experimentally, and yet is vital for engineering evaluations) the pore volume is routinely assumed to be constant. If this assumption is false, this could result in inaccurate estimates of the H₂ storage capacity of porous materials. This experiment was designed to use synchrotron-based powder diffraction methods to directly measure the effects of H₂ on these materials at the extreme low temperatures and high pressures – conditions that favour H₂ storage and were expected to show the largest effects in the pore volume – to check the validity of this assumption for a range of materials.

Variable pressure and temperature synchrotron XRD patterns were collected on a rigid zeolite (a MFI-type silicalite), a supposedly rigid metal-organic framework (MIL-101(Cr)), and a flexible metal-organic framework (MIL-53(Al)), in order to monitor the changes in both the size of the unit cell and the available pore volume under cryogenic temperatures and high pressures. The samples were dried at high temperature and high vacuum (10^{-7} mbar) prior to

collection of synchrotron powder XRD patterns at 0 bar hydrogen pressure at room temperature and at 100 K. The samples were then dosed with 100 bar of H₂ at these temperatures to investigate the pressure dependence of the structures. While there was slight contraction of the unit cell at lower temperatures (as would be expected through thermal expansion/contraction effects), increasing the hydrogen pressure resulted in no change in the peak positions was observed for either silicalite nor the MIL-101 MOF sample, confirming that the pore volume of the sample can be assumed to be independent of pressure with H₂ adsorption under these conditions (Figure 1).

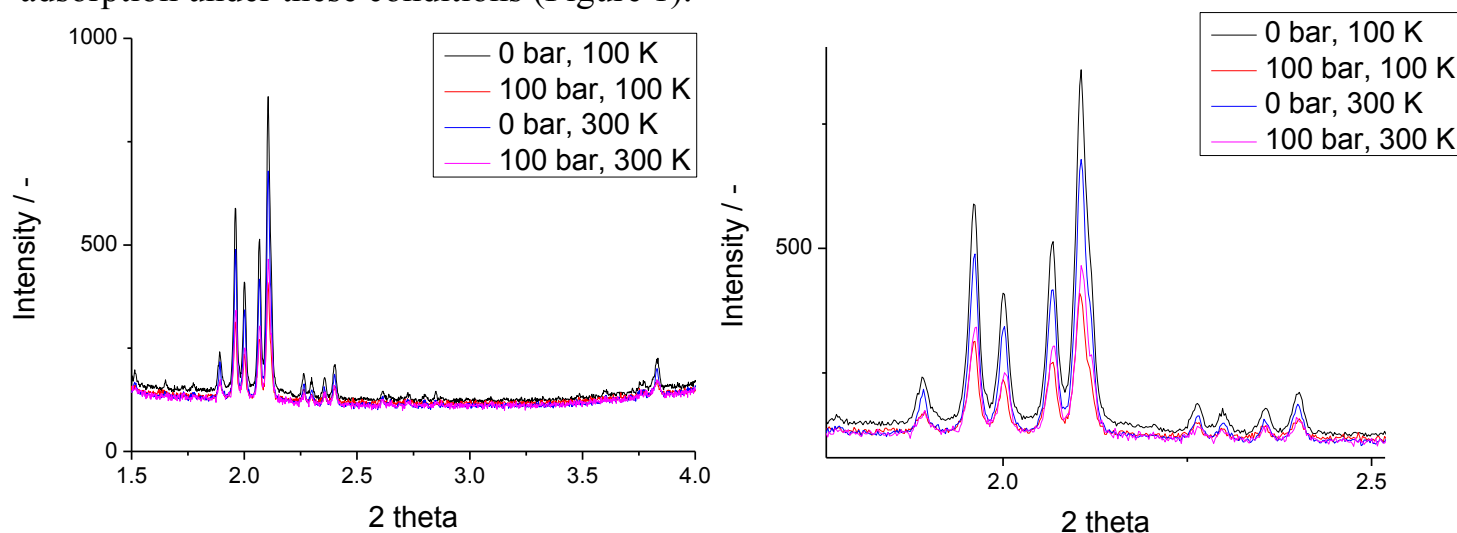


Figure 1 – The XRD patterns of MIL-101 at different pressures and temperatures showing no significant changes in peak position/unit cell (the spectrum on the right is a zoomed section of the spectrum on the left).

The flexible MIL-53 sample was then degassed at 423 K for 8 hours, before quick (5 min) scans were conducted at a variety of different temperatures and pressures (from 80-298 K, 0-100 bar H₂ pressure) to screen for changes in the structure. The spectra after initial H₂ dosing showed peaks that were inconsistent with that of the dry sample that was expected for the dry MIL-53 sample. Instead, the patterns observed were consistent with a wet phase of MIL-53(Al) with water inhabiting the pores. This phase persisted even after attempts to dry the sample in-situ with mild heating under vacuum. On returning to the University of Bath, we degassed the sample once more at 423 K for 4 hours and ran a powder XRD scan, which showed the pattern of dry MIL-53(Al) had been recovered. This indicated that there was water present in the H₂ supply used, which could not be removed from the sample by mild heating and the low vacuum available on ID31.

In conclusion, the high-resolution powder diffraction patterns of both silicalite and the MIL-101 material under conditions of high hydrogen pressure at 100 K showed no peak shifts up to 100 bar pressure, indicating that the structures remain rigid and therefore the pore dimensions remain constant with respect to increasing pressure. This information will be fed back into our models for adsorptive storage, which will ultimately lead to more accurate methods for evaluation of novel porous materials for gas storage, aiding in the assessment of their potential for use in practical applications. In the future, it would be very useful to repeat the experiment for the flexible MIL-53(Al) material, first ensuring the purity of the H₂ source and having access to a high vacuum to remove any adsorbed gas from the pores.