

## 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: In situ and real-time study of kinetics and mechanisms of mechanochemical milling reactions by simultaneous X-ray diffraction, temperature and pressure monitoring</b>	<b>Experiment number:</b> CH-4023
<b>Beamline:</b> ID15B	<b>Date of experiment:</b> from: 18 Jun 2014 to: 23 Jun 2014	<b>Date of report:</b> 31 Aug 2014
<b>Shifts:</b> 15	<b>Local contact(s):</b> Simon Kimber	<i>Received at ESRF:</i>

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## Report:

This is a preliminary report.

The data acquired in experiments carried out within the proposal are still in the process of analysis. We do have some preliminary results which are described below. We collected a huge amount of data (ca. 1 TB). We have carried out around 140 milling experiments and monitored the evolution of crystalline species during milling. Each experiment resulted in ca. 400 diffraction patterns.

We have carried out a series of investigations introducing variations to reaction conditions of separate systems. We have investigated a number of mechanochemical reaction for the formation of porous metal-organic frameworks (MOFs) as listed:

- (1) pillared MOFs based on zinc, terephthalic acid and diazabicyclooctane where we have investigated templating effects of sulphate and nitrate anions.
- (2) HKUST-1 formation under different LAG conditions. Here we have observed remarkable reactivity influenced by different liquid additives (protic, polar and apolar liquids).
- (3) We have monitored mechanochemical formation of the magnesium MOF-74, a well known material for its high ability to bind carbon dioxide at free metal sites.
- (4) We have conducted experiments of the formation of zeolitic imidazolate framework material, ZIF-8, under an elevated pressure of carbon dioxide (up to 5 bar). These experiments were preliminary and the reaction conditions were not very well controlled. This is the experiment which we would like to repeat in the next proposal. In the meantime we expect to have the reaction apparatus improved.
- (5) We have observed remarkable amorphisation of nascent ZIF-8 under aqueous wet grinding. This finding is in strong contrast to previously reported stability of ZIF-8 in water.

For experiments under (1) we have established remarkable selectivity of mechanochemical formations of different MOF frameworks (which are otherwise isomeric) using even minute amounts of anionic additives – sulphate vs. nitrate (in the form of ammonium salts). A series of experiments revealed the sulfate-templated hexagonal framework to be kinetically controlled while the tetragonal nitrate framework is thermodynamically stable under the investigated conditions. We have indications, which could nevertheless still be resolved from the current data, that a short lived hexagonal- resembling intermediate phase, possibly a two dimensional crystal acting as a seed, is the first product which further grows into the hexagonal framework which persist for some time before it is converted into the more stable tetragonal framework. The tetragonal framework is obtainable immediately if nitrate anions (e.g. ammonium nitrate) are used as additives.

For (2) we have established that different liquid additives result in substantially different reactivity. Even similar simple alcohols result in different reactivities. For instance, using ethanol, we have observed an intermediate phase while with methanol no intermediate was observed and the reaction was an order of magnitude faster. With polar aprotic liquids we have observed also different reactivities. For instance, acetonitrile directly and very fast gave the desired HKUST-1 framework while nitromethane resulted in very poor and slow reactivity. The reaction is occurring, albeit extremely slowly even with no liquid present as was the case also when chloroform was added as the liquid additive.

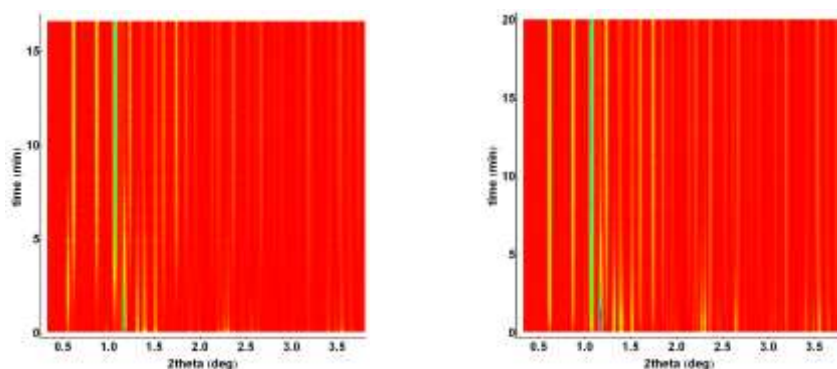


Figure. Preliminary results on comparison of HKUST-1 formation with ethanol (left) and methanol (right) as the liquid additives. All reaction conditions are otherwise the same.

For (3). For MOF-74 we have observed that the reaction is highly dependent of the temperature of the reaction mixture resulting in reaction 10 to 20 times faster if the reaction is conducted at 60 degrees Celcius instead of at room temperature. Formation of magnesium MOF-74 was even not possible at room temperature while it formed easily at higher temperatures. These results could have strong implications for commercial manufacture of this and other MOF materials.

For (4) the experiments were carried with a completely solvent-free procedure in mind. With only gaseous carbon dioxide to fill the pores, the ZIF-8 preparation could be performed in an even cleaner fashion than so far. These experiments have shown some promising results but the experiments could not be carried out in optimal manner and would need to be repeated using an improved apparatus for the control of atmosphere in the reaction vessel.

For (5). Previously, there have been numerous reports of ZIF-8 preparation. ZIF-8 is surely among the most popular porous frameworks studied today. We have observed its formation under wet milling conditions where the added liquid was pure water. Remarkably, the nascent ZIF-8 gradually became amorphous. This result is significant in respect that this is the first direct observation of crystallisation – amorphisation mechanism in mechanochemical reactions as well a simple route to amorphous ZIF-8 which was thus far hard to produce and required harsh conditions of elevated pressure or very specific precursors (nanocrystalline ZIF-8). In future proposals, we plan to extend on this investigation to other metal-organic porous materials and potentially develop the general method of preparation of amorphous metal-organic materials.