



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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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: High Energy X Ray Diffraction studies of the dehydrogenation catalytic reaction in LOHC technology	Experiment number: CH-6393
Beamline:	Date of experiment: from: 2/11/2022 to: 6/11/2022	Date of report: 10/02/2023
Shifts:	Local contact(s): Andrea Sartori	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Ms. Olvido Irrazábal Moreda*, ESRF Dr. Jakub Drnec*, ESRF Proff. Olaf Magnussen, University of Kiel (Christian-Albrechts-Universität zu Kiel)		

Report:

Introduction:

Liquid organic Hydrogen Carriers (LOHC) are an efficient alternative for storing and transporting hydrogen, safely, at ambient conditions, and reusing the existing infrastructure for liquid fossil fuels. The hydrogen gets chemically bonded to the carrier, benzyltoluene in this case, via a catalytic exothermic reaction. When and wherever the hydrogen is needed to produce energy, it can be released via another catalytic reaction, endothermic, that we refer to as dehydrogenation. This technology is already commercially deployed by our partners Hydrogenious LOHC Technologies GmbH, in Germany. Nonetheless, the dehydrogenation efficiency could be improved if the catalyst life were to be extended, as at the moment it gets slowly poisoned and deactivated. What causes the deactivation and the processes going on at the catalyst surface during the reaction are currently unknown, and these scientific questions are the core of this collaboration project, part of InnovaXN.

Experiment design:

This is the first official beamtime allocated for our measurements, where we have tested for the first time our recently designed reactor to carry the dehydrogenation reaction. This reactor (Figure 1a) is built in a commercial scale, to replicate realistic conditions of temperature (260 °C) and pressure (2 bar), but at the same time compatible with the X-Ray requirements for operando measurements, which means that is mostly transparent to X-Rays, in this case made of quartz glass. The setup (Figure 1b) consists of a packed bed of catalyst, that gets heated at 260 °C, through which the hydrogenated benzyltoluene (liquid) flows through at a slow rate, controlled by a pump, and comes out of the reaction partially dehydrogenated (liquid), together with the produced hydrogen (gas), that get cooled down and collected separately. The setup also includes a system for collecting liquid samples of the product, that allows us to measure the reaction rate together with the measured hydrogen flow.

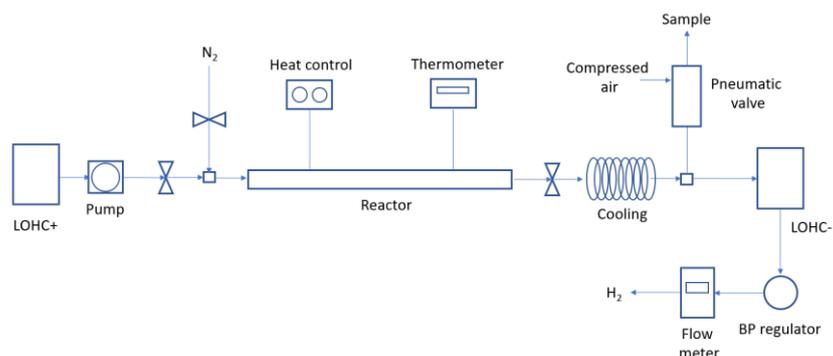
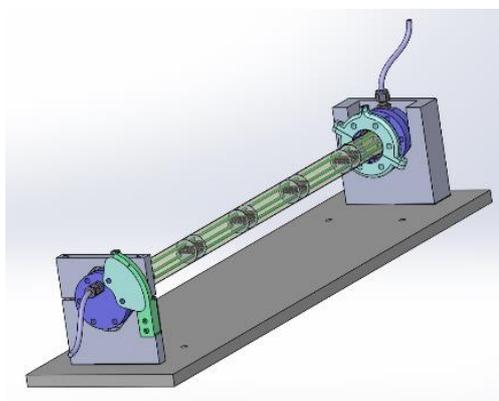


Figure 1. a) Reactor 3D model, made of quartz glass and with place for the catalyst beds, with an inlet and outlet connected to Swagelok fittings through flanges that are cooled down during the reaction. b) Reactor complete setup scheme.

Our goal was to collect X Ray diffraction (XRD) patterns of the catalyst during the reaction, meaning inside of the reactor and while the benzyltoluene is flowing and the hydrogen is being generated. For this purpose, we used, also for the first time, a model catalyst that replicate the commercial one in the form of pellets (Figure 2a), but in a form of a single crystal (Figure 2b) that allows us to measure the XRD. This catalyst is made of platinum nanoparticles (around 2 nm) supported on aluminium oxide (Al_2O_3) single crystal wafers, and accordingly treated to reduce the acidity and the formation of secondary products.



Figure 2. a) Commercial catalyst of $\text{Pt}/\text{Al}_2\text{O}_3$ provided by Hydrogenious. b) Model catalyst of Pt supported on single crystal Al_2O_3 .

The reaction set up, as described, was installed at the ID31 beamline, with the reactor on top of the microstation, with an additional translation motor that allowed us to move along different reactor positions. Underneath the reactor we placed a custom-made tray to prevent any possible leakage to go into the microstation, and we also used safety tray for placing all the liquid reservoirs. The beamline setup can be seen in Figure 3.

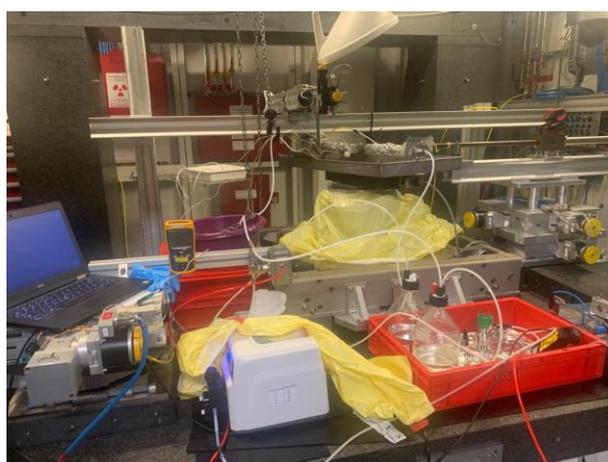


Figure3. Experiment setup at the ID31 experimental hutch.

The model catalysts were aligned for grazing incidence XRD measurements using the Pilatus detector. At the same time, we arranged the Dexela detector and corresponding beamline setup to be able to measure also grazing incidence small angle X ray scattering (GISAXS). The beamstop robot available at ID31 can be used for covering the Al_2O_3 reflections allowing us to see exclusively the Pt of our catalyst.

Results:

During the allocated beamtime we were able to successfully carry the dehydrogenation reaction, extracting the hydrogen out of the benzyltoluene thanks to our reactor. At the same time, we were able to collect diffraction patterns at grazing incidence of our model catalyst, observing and tracking the Pt Bragg peak to study its changes during the reaction. At different moments during the reaction, we were also able to collect GISAXS images. Unfortunately, the original reactor design couldn't be used as intended, since the fragile quartz tube broke during its assembly at the chemistry lab. This forced us to use a replacement tube made of stainless steel. Although the high energy still allowed us to see the Pt peaks, the steel scattering gave a high intensity background that made us cover around 80% of the Pilatus detector with lead instead of using the beamstop as it was planned. Moreover, the reactor holder that supported our model catalyst inside of the tube was not stable enough in the turbulent reaction conditions, which made us lose the alignment of the sample continuously, and our heating device (electrical heating cord) did not provide stable heating (Figure 4a). As a result of the sample instability, we lost a lot of time re-aligning the sample, and the constant misalignments made the data acquisition challenging and the signal was rather weak (Figure 4b).

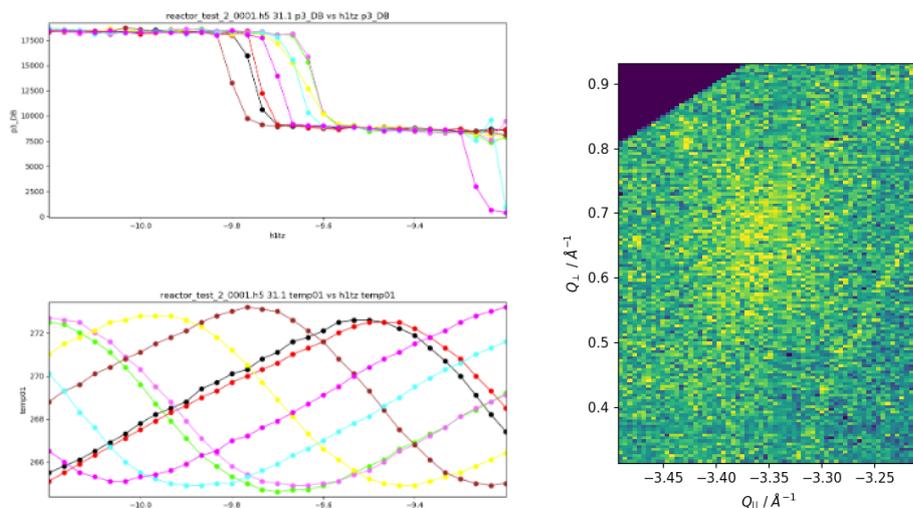


Figure 4. a) Sample height position changes (above) due to the temperature instability (below). b) Pt Bragg peak noisy image due to the constant sample misalignment.

As a result, we were able to collect some HE-SXRD data (Figure 5) during a few scans, but not at regular intervals of time. However, we gathered enough points to follow the evolution of sample structure during reaction. The collected data is rather noisy and good only for preliminary analysis. This shows clear differences in the lattice parameter shift during the reaction as a function of different treatments. Sulphur doped sample, typically the most active one, exhibit decrease in lattice parameter due to gradual transformation of the catalyst and/or different surface chemistry.

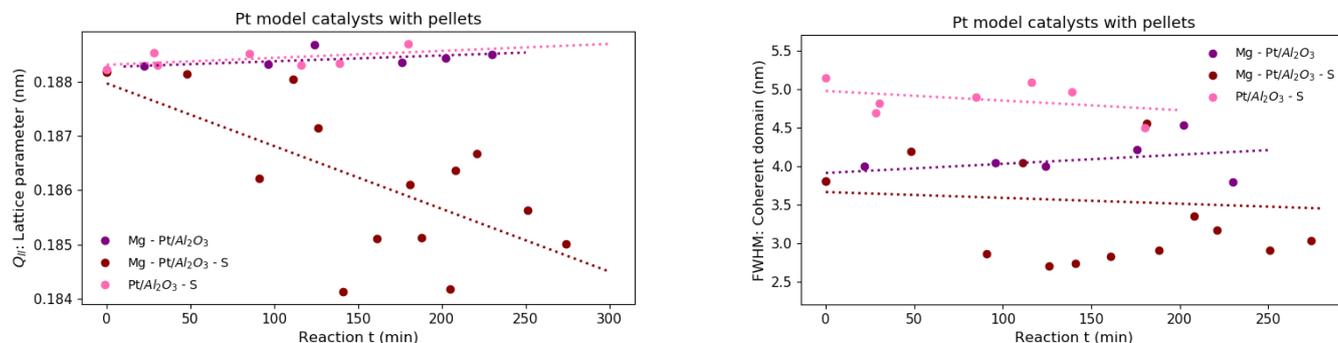


Figure 5. Data collected in one the reactions, where we can see that the misalignments and lack of points doesn't allow us to study the trend of the lattice changes.

As for the GISAXS, we were able to collect data at the beginning and the end of the reaction due to rapid misalignments. The data show rapid reorganization of the Pt shape at the onset of the reaction (Figure 6).

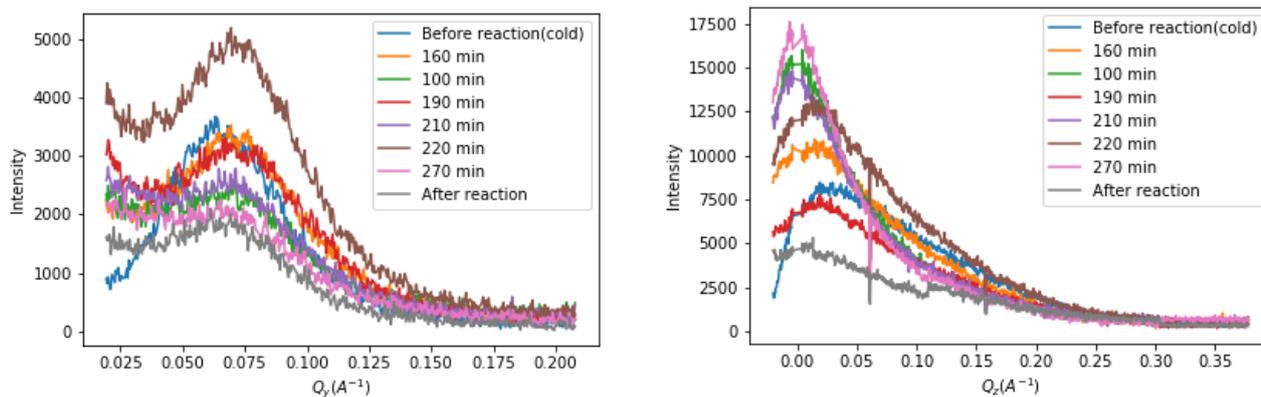


Figure 6. Preliminary data of the GISAXS measurements.

Unfortunately, we had no opportunity to ensure the reproducibility of the results by repeating the analysis on different equivalent samples.

Next steps:

This experiment has helped us to collect valuable preliminary data allowing first understanding of the system as well as to understand the limitations and requirements of the setup. We are already working on the improvements for a next experiment, including:

- A new reactor design that: i) simplifies the assembly reducing the risk of breakage, ii) blends together the stability of the steel and the alignment facility of the quartz glass, iii) ensures the sample stability with a much more robust sample holder, and iv) improves the thermal stability thanks to an insulated custom-made heating jacket.
- The pre-calibration of the sample position changes due to the temperature, to be able to follow its movements and avoid misalignment.
- The repetition of all the measurements at regular intervals and with good alignment, to gather more reliable datasets with better time resolution.
- The preparation of additional equivalent samples to ensure the reproducibility of the experiment.