

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.



Experiment title:

In situ XAS to unravel the catalytic cycle in oscillatory carbonylation reactions

Experiment number:

MA-3855

Beamline: ID26	Date of experiment: from: 30/01/2018 to: 7/02/2018	Date of report: 19/02/2018 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Dr Rafal Baran	

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Report:

Palladium-catalysed oxidative carbonylation (PCOC) is a unique reaction which demonstrates prolonged pH oscillations (up to a month) in a batch laboratory set-up without the need for addition of substrate. Beside this fantastic property, PCOC also exhibits temperature-dependent product selectivity and substrate diversity (including polymeric substrates). This extraordinary oscillatory reaction system has the major potential in the development of advanced self-oscillating polymeric architectures. However, the wide implementation of this reaction is associated with two major problems: (i) use of CO as a reactant and (ii) methanol as a solvent. In order to solve these two problems, we need to obtain a complete understanding of the mechanism of oscillations, especially of the catalytic processes involving palladium, so that benign, more environmentally friendly oscillatory reactions can be designed. So far, the knowledge in this area is poor and data are contentious.

To get an insight into palladium catalysis in PCOC, we aimed to collect XANES and EXAFS spectra at all stages of the reaction: from the so-called 'induction' period through to oscillations in pH. A highly novel reactor capable of sustaining prolonged pH oscillations was designed and manufactured to enable *in situ* XANES and EXAFS to be performed during PCOC (Figure 1). Five cells were run in parallel on a customised stirring stage to maximise performance and enable studies of two catalytic species at the same time - palladium acetate (PdAc) and palladium iodide (PdI₂).

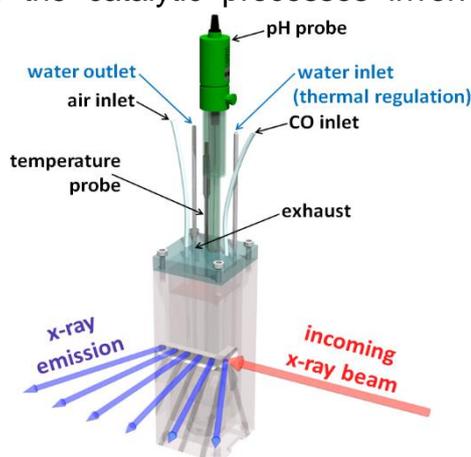


Figure 1. Reactor cell

This approach has enabled us to directly study, for the first time, the changes in oxidation state and atomic environment of palladium during catalysis. Although the data analysis is still in progress (beamtime performed in Feb 2018), we have captured the changes during the crucial ‘induction’ stage of the reaction, where Pd catalyst generated *in situ* (PdI₂/PdAc+KI) is purged with CO and air.

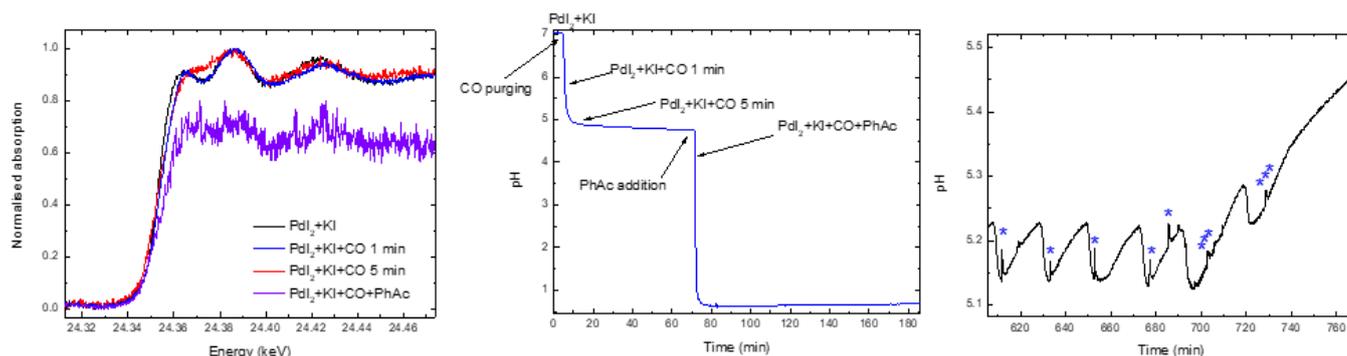


Figure 2. a) XANES spectra b) pH measured during induction stage c) radiation effect

Figure 2a shows evolution of XANES spectra at different stages of the reaction while Figure 2b gives recorded pH vs. time during the induction stage. Furthermore, after addition of substrate, phenylacetylene (PhAc), we observed a dramatic change in signal quality. Previously, it has been postulated that addition of substrate causes the first conversion stage, during which Pd²⁺ species (in solution) are converted into Pd⁰ species (insoluble/particulate). Thus, the changes in XANES spectra quality indirectly indicate that this assumption is correct. However, the collection of high-quality, fittable data in this case was challenging.

The reaction pH was monitored until the oscillations in pH occurred. Due to the low quality of the XANES data, we established a strategy of collecting samples at the bottom and top of oscillations and then binning them to obtain one good XANES spectrum for the two pH extremes. However, after binning 100 XANES spectra, the signal quality was still insufficient. Moreover, an unexpected effect of X-ray radiation on the reaction was observed. Radiating the sample for 60 s for a single XANES collection led to the appearance of spikes in the pH (labelled with single asterisks in Figure 2c), whereas multiple scans over short period of time, *i.e.* prolonged radiation (labelled with three asterisks), caused irreversible increase in pH. In the PdI₂-catalysed reaction, the starting oscillations ceased as soon as the reaction was irradiated with X-rays. This effect of X-rays on pH in palladium-catalysed reactions was only observed after the addition of substrate and is clearly associated with a species generated during conversion. These findings indicate that the radiation damage of the catalytic species occurring during the reaction prevents from collecting a full set of data in the reaction setup we used. However, findings also show that a continuous stirred-tank flow reactor (CSTR) with a flow-through cell for data collection is a suitable alternative set-up to prevent the radiation damage and gain acceptable signal.

As the induction period was not susceptible to radiation damage, quality *in situ* XANES data could be obtained during this phase of the reaction. The data obtained for the ‘induction’ stage is of incredible importance, since it sheds the light on the oxidative processes in palladium during CO incorporation. Consequently, during our beamtime we also studied other palladium catalysts [PdO, Pd (I)] during the ‘induction’ stage and we were capable to correlate changes in XANES spectra with the ability of each catalyst to generate oscillations in the pH. These findings are being prepared for a publication and, importantly, will form the basis of future work.