

## 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> Elucidating Pd leaching behaviour at the solid-liquid interface	<b>Experiment number:</b> CH-3316
<b>Beamline:</b>	<b>Date of experiment:</b> from: 20 July 2011 to: 27 July 2011	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Dr. Mark NEWTON.	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

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 Dr. Klaus Hellgardt,<sup>a,\*</sup> Dr. Mark NEWTON<sup>b</sup>

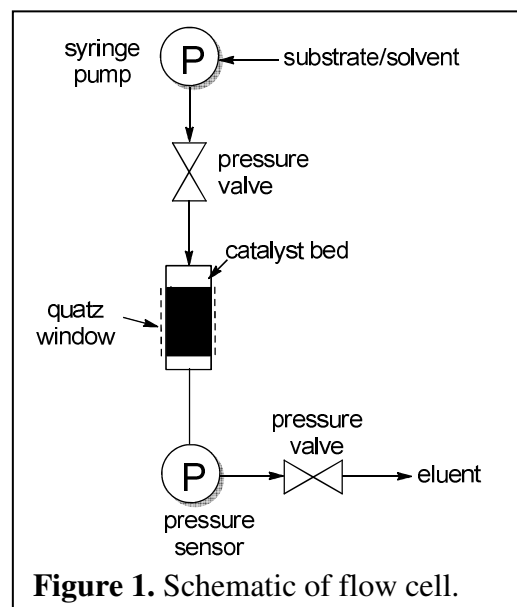
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**Report:**

A new sample environment was designed and constructed at Imperial College London specifically for this experiment (figure 1), which enables the delivery of reactants and solvents via a syringe pump, through a catalyst bed mounted in a quartz tube, which can be heated and pressurised. Different heterogeneous Pd catalysts, including PdEncat (encapsulated Pd(0) and Pd(II) in a polyurea matrix), Pd/Al<sub>2</sub>O<sub>3</sub> (1-10 mol% loading) were tested for their catalyst activity prior to arrival at ESRF (to verify real reaction conditions).

The experiments use the vertical focus of the beam, with the recently acquired QuEXAFS, as well as scanning EXAFS, to examine the transformation of heterogenised Pd(0) and Pd(II) species, when they are exposed to reaction mixtures, as well as the reaction solvent (in this case, ethanol). The sample environment was mounted on beamline BM23 on a Huber motor.

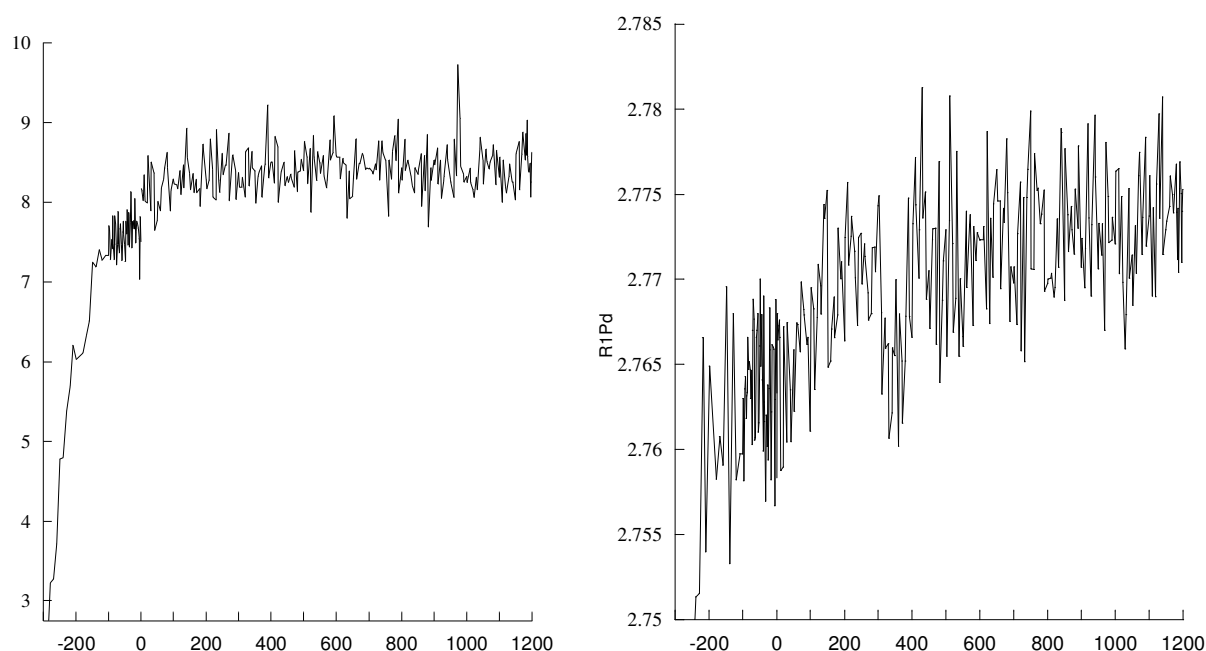


**Figure 1.** Schematic of flow cell.

Reaction examined and results:

1. Heterogenised Pd species were initially examined using scanning EXAFS and used as reference for later examinations. Pd(OAc)<sub>2</sub> encapsulated in a polyurea matrix (EnCat30) and Pd(II) (predominantly hydroxide) deposited on an alumina support show discernable differences, both from each other and from their comparable Pd(0) catalysts – nanoparticulate palladium encapsulated in a polyurea matrix (EnCatNP) and the same alumina supported palladium which had been calcined (2 h, 500 °C) and reduced under H<sub>2</sub>.

2. The reaction solvent (ethanol) was subsequently passed through the catalyst bed, at ambient, as well as elevated (80 °C) temperatures. At ambient temperature, this had no discernable chemical effect on the palladium. At elevated temperatures reduction of the palladium occurs. A controlled ramp of the temperature shows this process only begins to take place above approximately 40 °C. QuEXAFS were initially used to track the changes in the coordination and oxidation state of the Pd species at a fixed point of the bed, followed by a full mapping of the bed using scanning EXAFS.



**Figure 2.** Observed changes in Pd-Pd coordination number (left) and first shell Pd-Pd distance (right) during the reduction process of reduction at 75 °C.

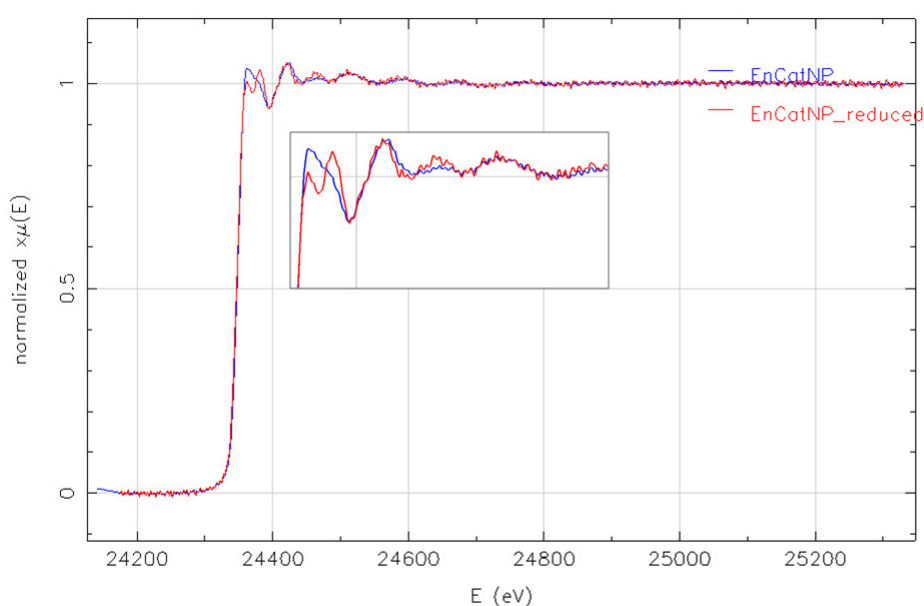
Clear reduction of Pd(II) to Pd(0) can be observed when the catalyst bed is exposed to solvent, or a reaction mixture (consisting of aryl bromide, aryl boronic acid and base).. Preliminary results revealed some highly unusual observations (figure 2). Initial assessment seem to suggest that the reduction process initially led to the formation of Pd nanoparticles of approximately 3-4 nm in size (<300 scans). With subsequent exposure to the reaction mixture (>300 scans), the Pd-Pd bonds lengthen quite significantly. This could be suggestive of numerous things (including the formation of bulk PdC and PdH phases) but is important in that it demonstrates that under reaction conditions the Pd nanoparticles display physical characteristics that are not, a priori, expected.

Catalyst leaching was also observed at the top of the catalyst bed, which may be captured by the introduction of a pristine bed of Al<sub>2</sub>O<sub>3</sub>.

3. In contrast, the PdENCAT catalyst displayed very different behaviour. Firstly, the encapsulated  $\text{Pd}(\text{OAc})_2$  (PdENCAT30) appear to undergo a much slower reduction to  $\text{Pd}(0)$ . The nature of the final  $\text{Pd}(0)$  also appear to differ significantly from the  $\text{Pd}(0)$  species obtained from the reduction of  $\text{Pd}(\text{OAc})_2$  supported on  $\text{Al}_2\text{O}_3$ . Furthermore, no catalyst leaching was observed in this system, suggesting that PdENCAT may be more robust to reaction conditions than Pd on an inorganic supported.

4. Rather unexpectedly, with subsequent mapping of the catalyst beds, it appears that there is *spatial speciation of Pd species at the beginning and the end of the catalyst bed*. This is also a very exciting result which has never been previously observed, as it suggests that spatial-temporal mapping of the reduction process may be possible. This will form the basis of a further proposal.

5. We next examined the supported  $\text{Pd}(0)$  nanoparticles, also encapsulated in polyurea (PdENCATNP) and supported on  $\text{Al}_2\text{O}_3$ . The reduction of the surface palladium oxide ( $\text{PdO}$ ) was observed by passing heated ethanol through both catalyst beds (for example, figure 3). However, reduction to  $\text{Pd}(0)$  appears to be much more complete with the catalyst supported on alumina. The precise nature of the reduced species, and temporal evolution data will require further analysis.



**Figure 3.** PdEncatNP ( $\text{PdO}$ ) before and after reduction.

In summary, a number of very interesting observations have been made during the performance of these experiments with different Pd catalyst, which revealed very important dependence of catalyst activation, and subsequent leaching on the type of heterogeneous support used. Although this observation is not new, the data acquired will allow us to delineate, for the first time, the key molecular interactions that determines these processes, which certainly warrant further experimentation and analysis. Further follow-up work will also be conducted at Imperial, to correlate the catalyst activation/leaching process, with the above observations. We expect that our preliminary work (on the evolution of Pd-Pd distances) will be the first to be communicated via a publication, as well as disseminated by

Dr. Hii at the meeting she has been invited to speak at, in December 2011 (McBain Medal Lecture, SCI, London).