EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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://wwws.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.

Names and affiliations of applicants (* indicates experimentalists):

Dr John B Brazier*
Dr King Kuok (Mimi) Hii
Dr Mark A Newton*

Report:

The aim of the experiment was to examine the changes along a catalyst bed (Pd/Al_2O_3) in a plug flow reactor. The spatial resolution allows an understanding of how solvents change the nature of the catalyst bed, what these changes are and where in the bed the changes take place.

In particular we were interested in:

1. the effect of changing the solvent passed through the catalyst (different organic solvents or different proportions of organic solvent and water)
2. the effect of changing the size of the nanoparticles in the catalyst (through different catalyst loadings)

There is a drive towards using "greener" solvents for industrial processes. Water and simple aliphatic alcohols are considered good candidates for replacing less environmentally friendly solvents, however, the

effects of such solvents upon catalysts is poorly understood. This work aims to identify what changes occur in the catalyst due to solvents and if they are uniform.

Our custom built sample environment was mounted on the beamline sample stages. Spectra (EXAFS) were recorded at the Pd K-edge in transmission mode with simultaneous recording of a Pd foil standard. A spot size of 3 mm × 0.35 mm (w × h) was employed to allow interrogation of the spatial resolution of the catalyst bed. A macro was used to record sequential spectra scanning up and down the catalyst bed over approx. two hours (typical experiment) although some measurements of longer duration were also made. The *in situ* Raman facilities were also employed, but the required acquisition time was too long for useful *in operando* measurements to be made on our samples. However, some off-line measurements were made to obtain end-point spectra.

The number of experiments and the volume of data collected will take time to fully process. We are looking at analysis of both XANES (edge jump & linear combination fitting, Fig. 1) and EXAFS (co-ordination number, Pd–Pd interatomic distance and Debye-Waller factor).
Main observations:

(i) Solvent effects:
   Reduction occurs only with 1º and 2º alcohols. Addition of water changes the rate and end point of the reduction.

(ii) Particle size:
   Larger nanoparticles reduce more quickly and to a greater degree than small particles. In addition, where metallic Pd phases are produced the first-shell Pd-Pd bond distances are unusually large given the dimensions of the Pd nanoparticles. This strongly suggests that atomic hydrogen is being stored within the reduced particles. The degree of hydrogen storage depends on the Pd loading and the Pd precursor used to make the catalysts.

(iii) Catalyst preparation:
   The precursor used in the preparation of the catalyst may also have a profound effect on the reduction of the Pd-np. Pd catalysts derived from Cl containing precursors are reduced at significantly faster rates than those that are Cl free This is currently attributed to the presence of chloride anions – further experiments have been planned to verify this hypothesis.
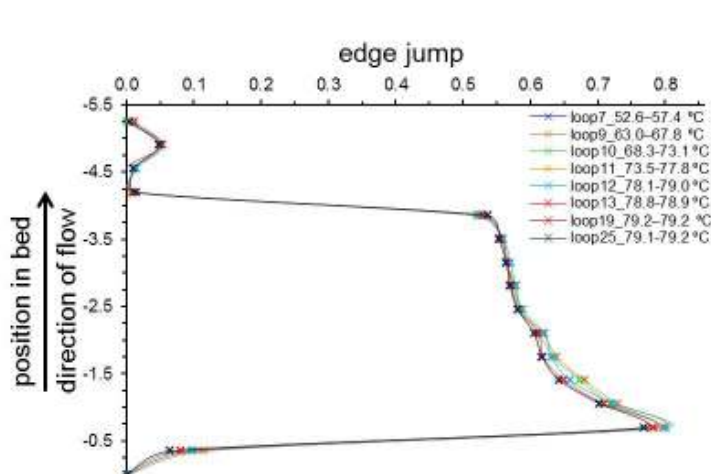

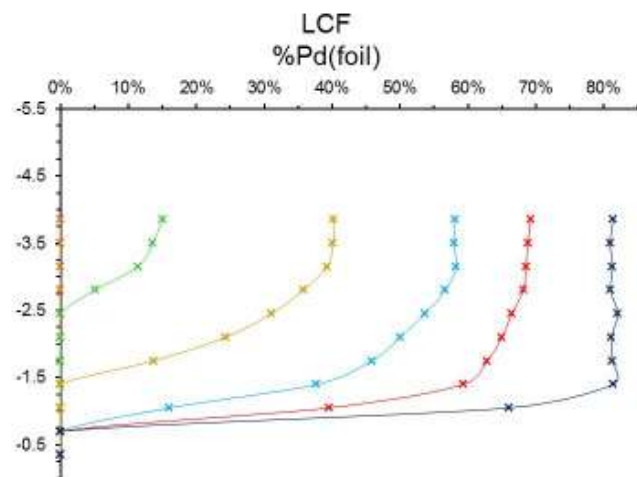**Figure 1a** Edge jump along catalyst bed.   **Figure 1b** Linear combination fitting of XANES.
(5% Pd/Al$_2$O$_3$, 50:50 EtOH, H$_2$O, 1 ºC/min to 80 ºC)

Each of our experiments run at the beamline (typically 400 spectra) produced a single output file which could not be read by any standard analysis software. Although a stand alone program has been written on the beam line to convert the output files from the beamline to a more standard format, this program is not transferable to other computers (a copy was made, but does not run on computers at our institutions). The need to run this program on all output files before they can be read by any standard analysis software is a major problem.

Due to time pressures, we did not convert data from two experiments using this program. The data from these two is therefore currently unusable to us. Further, the format of the "split up" files generated by this

stand alone program is not readable by the software required for batch EXAFS data analysis. The manual editing of files such that they can be read into software for the batch EXAFS analysis is not practical due to the large number of spectra which our experiments generate.

We have contacted Dr Emmerich regarding how to resolve this problem. He has communicated that he can write an executable file which will process the data to give a data format suitable to reading into our software. However, at the time of writing this report we are still waiting to receive this and remained blocked in terms of a deeper analysis of the large amount of high quality data that our visit to BM01 resulted in.

We hope that this can be sorted out in short order in 2015 such that we might make best use of the excellent data the beamline has provided us with and publish accordingly.