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ESRF

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.

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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.

ESRF	**Experiment title:** Core-shell structure of Pd nanocatalyst upon hydrogenation and semi-hydrogenation of alkynes (CRG for proposal Ref. No 34572)	**Experiment number**: 01-01-971
Beamline: BM01B	**Date of experiment**: from: 01.10.2014 to: 07.10.2014	**Date of report**: 31.01.2015
Shifts: 18	**Local contact(s)**: Hermann Emerich (email: ermano@esrf.fr)	*Received at ESRF:*

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Report:

Experimental Details

Pressure composition isotherms were obtained for Pd Hydride nanoparticles with average particle size about 3 nm deposited on carbon (see fig.1). Pd/C nanoparticles were packed in a 1mm thick capillary connetted to a pressurized system enabling to control hydrogen pressure. Vaccum pump was connected to the system for outgassing. Gas blower positoned above the sample was used to controll the temperature. Initial pretreatment of the sample was done at 125 °C in 200 mbar of hydrogen during 30 minutes. Pd foil and Pd black were used as reference samples.

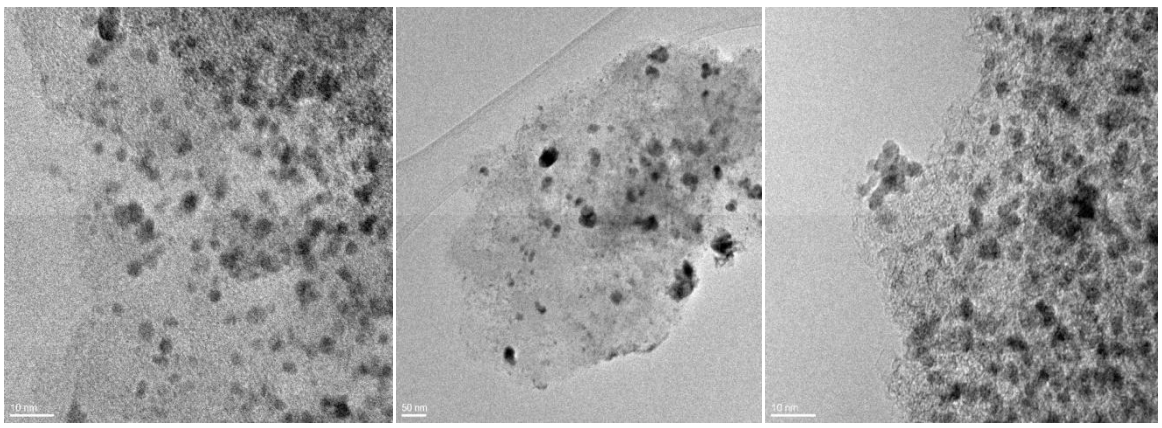

Fig.1. TEM images of Pd/C nanoparticles.

X-ray Absorption and X-ray Powder Diffraction data were collected at -10, 20, 50, 80 and 110 °C in a pressure range from 0 to 10000 mbar. X-ray Absorption Spectra at Pd K-edge were obtained in the transmition mode in the continuous scanning mode in the energy of the incoming photons from 24.1 to 25.4 keV. Pd foil was measured simultaneously for energy callibration.
X-ray diffraction images was collected by CMOS-Dexela 2D detector. The photon wavelength was set as 0.50544 Å. The values of wavelength and sample-to-detector distance were optimized using silicon poweder and lanthanum hexaboride. The geometry of the experimental setup resulted in a 2θ angles from 0 to 52 degrees. For better statistics 5 images and 5 dark images with time acquisition of 10 seconds were collected at each of the experimental points.

Data analysis
X-ray absorption spectra were proccessed using Demeter package. Backgroung removal, normalisation and energy calibration was performed in Athena program. Single-shell EXAFS analysis was performed in Artemis program in the real space range between 1.5 and 3.0 Å k in the k-range of 5-12 $Å^{-1}$.
X-ray diffraction images were integrated using Fit2D software to obtained I(2θ) data. Rietveld refinement was performed in Jana2006 code, giving the information on the cell parameter and fractions of α and β phases.

Results
Single-shell EXAFS analysis with S02 set as 0.83 (determined initally for Pd-foil) determined a coordination number N = 9.7 which is consistent with the particle size. The increase of the Pd-Pd interatomic distance and Debye-Waller paremeter was observed during the increase of hydrogen pressure. EXAFS analysis performed for all of the measured spectra provided the pressure-composition isotherms of PdH nanoparticles are shown in figure 2. The solid curves presented on the plot correspond to the double-exponential fit of the experimental points:

$$f(d) = A\left(1 - e^{c(d-d_1)}\right) + Be^{k(d-d_2)}$$

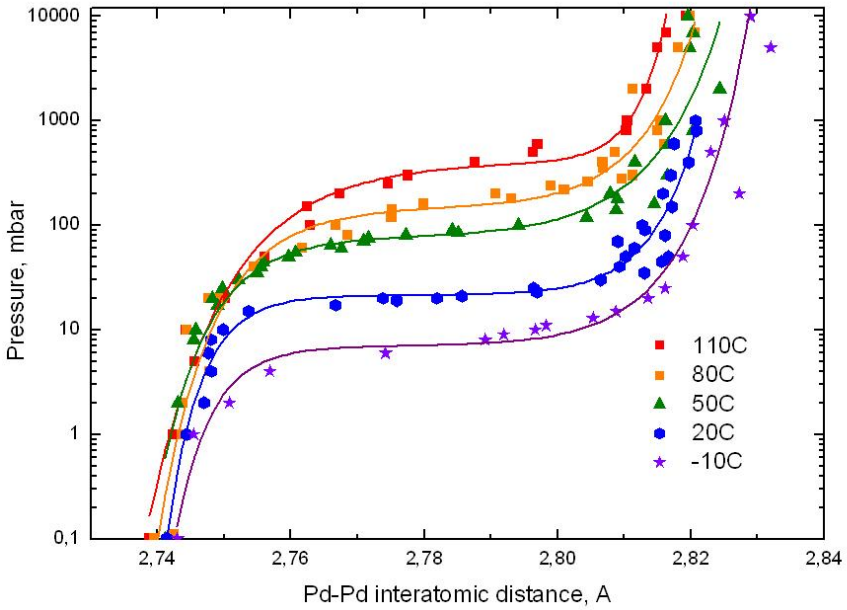

Figure 2. Pressure-composition isotherms obtained from EXAFS analysis.

Rietveld refinement of bare (P=0) and hydride (P=1000 mbar) Pd nanoparticles was run to optimize cell and profile parameters. The isotropic atomic displaced (Uiso) was discovered to be the same for both bare and hydride sample. Iт order to make the refinement of all the patterns with minimal number of variables, profile parameters were fixed as in bare sample, allowing only cell parameter and phase fraction to be refined. The example of the refinement result for the pattern obtained at 20 °C and 20 mbar of hydrogen, when α- and β- phases with slightly different lattice parameter coexisted in the sample is shown in figure 3.

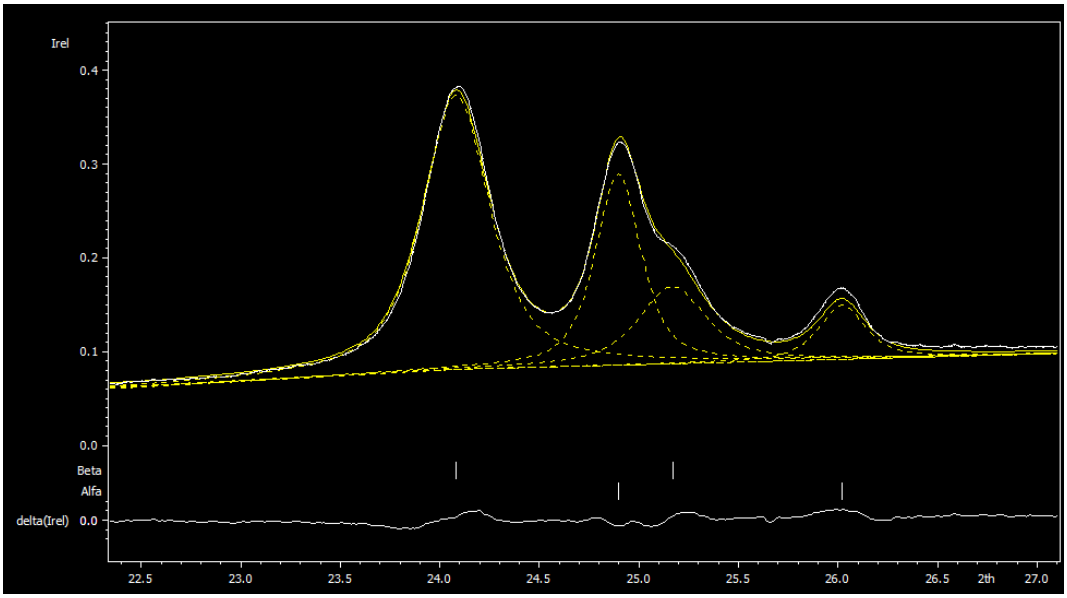

Figure 3. Example of the XRD pattern fitted with two Pd phases.

To compare results obtained from diffraction with those of absorption an average cell parameter was calculated as $a=(1-n)a_{\alpha}+na_{\beta}$, where a_{α} and a_{β} are the lattice parameters of α and β phases, n – fraction of β phase determined by Rietveld refinement (see fig.4). The comparison of the resulting isotherms obtained from both XRD and EXAFS are shown in figure 5.

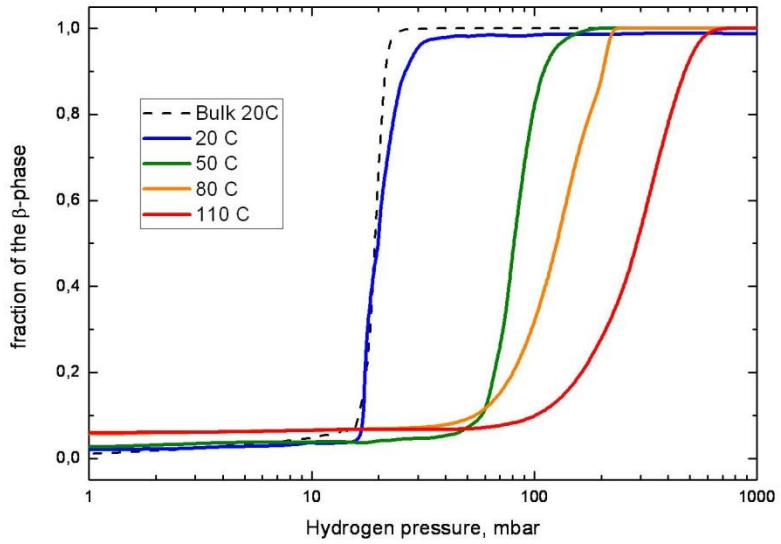

Figure 4. Concentration of PdH β-phase with increasing hydrogen pressure at different temperatures.

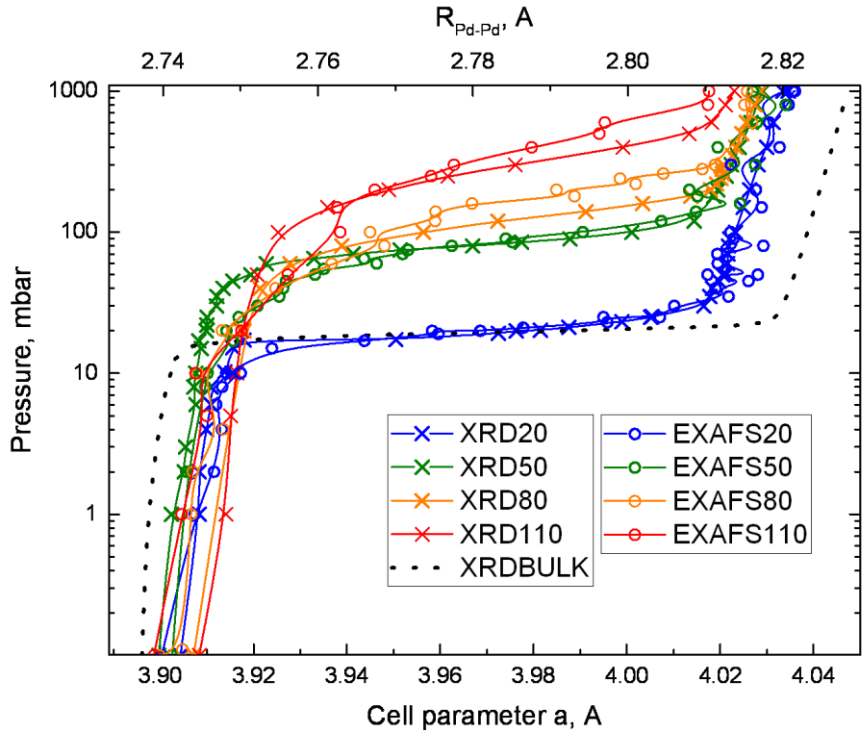

Figure 5. Comparison of the isotherms obtained from XAS and XRD. Black dashed curve corrrespond to Pd black sample.

Conclusion

We have a detailed analysis of hydride phase formation in Pd/C nanocatalysts using combined X-ray absorption and X-ray diffraction methods. Averaged Pd-Pd interatomic distance was obtained from EXAFS analysis and was accompanied with growing Debye-Waller parameter, while Rietveld refinement of diffraction data allowed to separate α and β Pd hydride phases. The averaged cell parameter calculated based on XRD results is in a good agreement with EXAFS results. Currently, we are going to perform XANES analysis following the strategy described in the paper *Bugaev et al. J. Phys. Chem. C. 2014*. Moreover, the obtained isotherms will be complemented by volumetric measurements for the same set of temperatures and pressure range.