



## 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:** Size-dependent Pd Hydride Phase Diagrams

**Experiment number:**  
MA- 2530

**Beamline:**  
BM01B

**Date of experiment:**  
from: 01.07.2015 to: 06.07.2015

**Date of report:**  
10.09.2015

**Shifts:**  
15

**Local contact(s):**  
Michela Brunelli ( email: brunelli@esrf.fr)

*Received at ESRF:*

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

Aram Bugaev\*<sup>1,2</sup>, Alexander Guda\*<sup>1</sup>, Andrea Lazzarini\*<sup>2</sup>, Kirill Lomachenko\*<sup>1,2</sup>, Alexander Soldatov<sup>1</sup>, Jeroen van Bokhoven<sup>3,4</sup>, Carlo Lamberti\*<sup>1,2</sup>

<sup>1</sup>Southern Federal University, Zorge street 5, 344090 Rostov-on-Don, Russia

<sup>2</sup>Department of Chemistry, University of Turin, Via P. Giuria 7, 10125 Turin, Italy

<sup>3</sup>Institute for Chemical and Bioengineering, ETH Zurich, HCI E127 8093 Zurich

<sup>4</sup>Laboratory for Catalysis and Sustainable Chemistry (LSK), Swiss Light Source, Paul Scherrer Institute, WLGA 135 5232 Villigen

## Report:

### I. Palladium hydride phase diagram for Pd/C nanoparticles

The main results of the measurements concerning Pd-hydride phase diagrams complemented with the results of the beamtime CRG 01-01 971 (Oct 2014) were presented at XAFS16 conference and submitted to Journal of Physics: Conference Series. The extended version of the manuscript is in preparation.

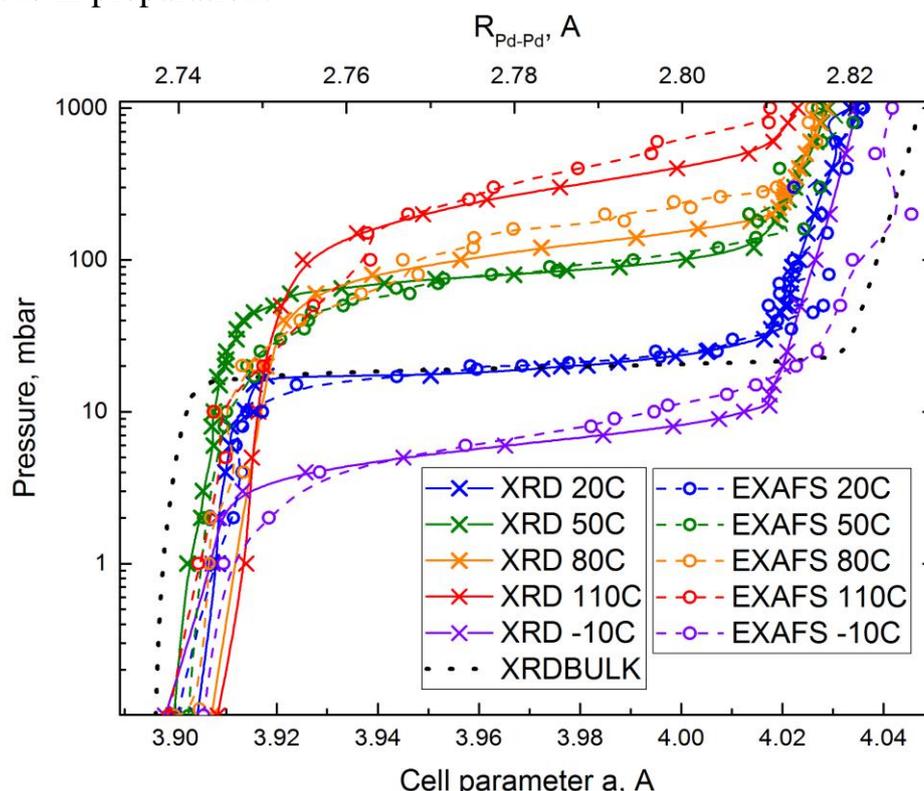


Figure 1. Results of EXAFS and XRD analysis.

The work represent a comprehensive study of the Pd hydride phase formation at different temperatures from -10 to 120 °C in the pressure range from 0 to 10 bar. At each point of the (P,T) space XRPD and EXAFS data was measured. Rietveld analysis of the XRPD data allowed to obtain cell parameters and concentration of bare and hydride phases. Single-shell analysis of EXAFS provided the evolution of Pd-Pd interatomic distances, which is in perfect agreement with XRPD results. All results are summarized in figure 1, where scatters represent experimental points. The results were complemented by laboratory BET measurements (Figure 2) which allows to estimate the hydrogen loading in the sample.

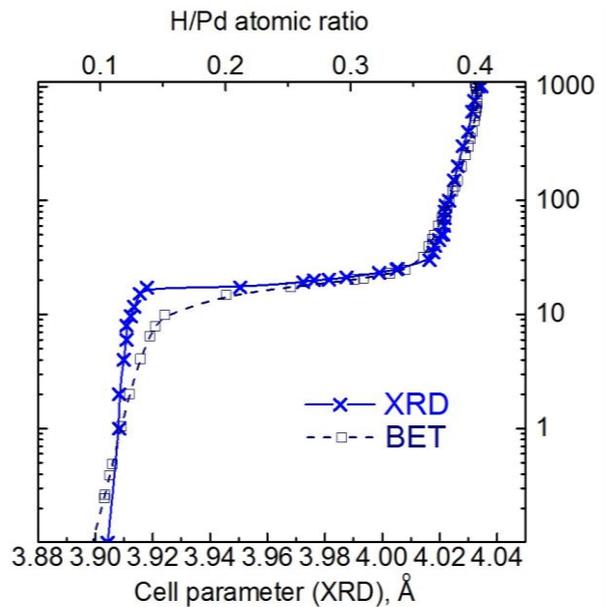


Figure 2. Comparison of XRD results with volumetric measurements at RT.

## II. Temperature-dependent hydrogen desorption kinetics in Pd/C nanoparticles

We applied powder XRD to study the process of H<sub>2</sub> desorption in carbon supported Pd nanoparticles. The data was collected by 2D image plate at BM01B of ESRF. The setup allowed to collect reliable data with temporal resolution of 3 shots per second. We studied the kinetics at in the temperature range from -10 to 30 °C. The sample was initially exposed to 300 mbar of hydrogen that is quite above the beta-phase formation region (10-20 mbar) for all the studied temperatures. The evacuation of hydrogen was performed by opening the valve which connects the capillary with vacuum pump (we did not estimate the speed of outgassing). For all the temperatures desorption process saturates in less than 10 seconds.

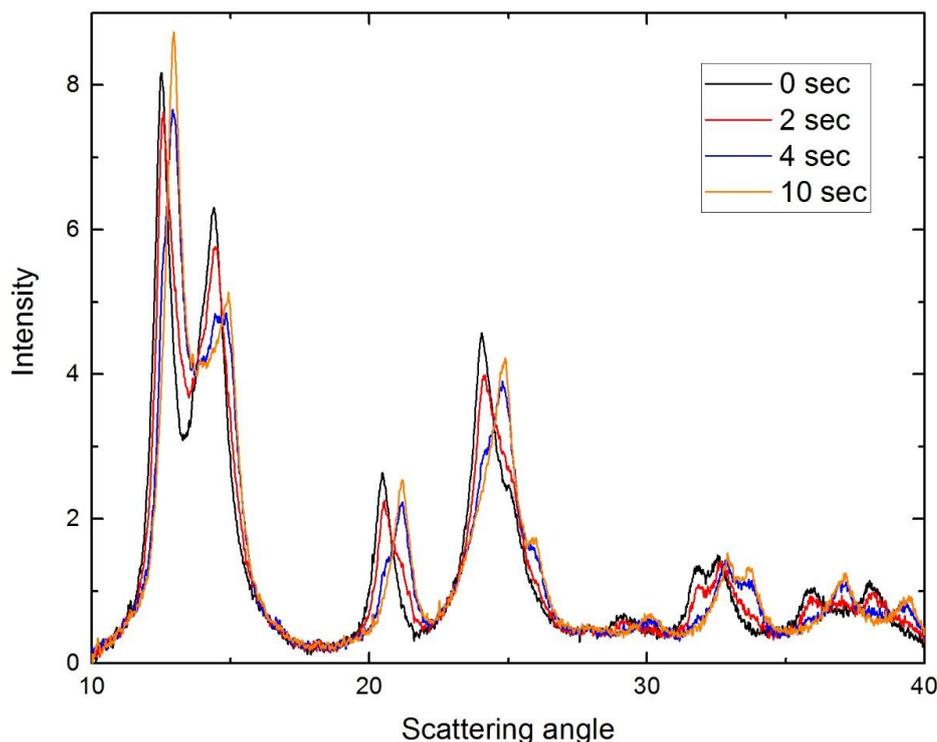


Fig.3. Time evolution of the XRD patterns during hydrogen desorption at -10 °C.

The obtained XRD patterns were refined in Java2006 program using 2 palladium phases. The cell parameters of  $\alpha$ - and  $\beta$ - phases and their relative concentration was determined (fig.4).

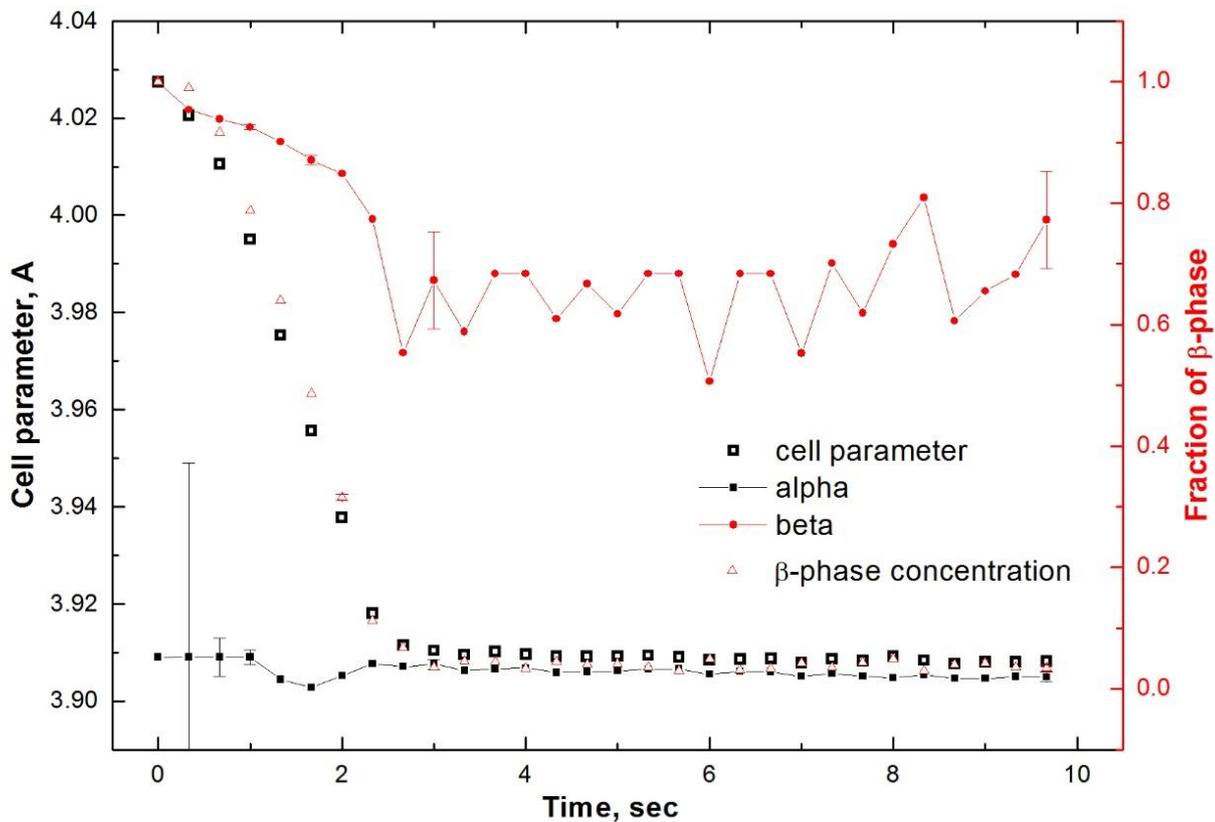


Fig.4. Results of Rietveld refinement of the XRD obtained during H2 desorption at -10 °C.

The averaged cell parameter normalized to (0,1) is used to describe the kinetics of the process, shown in figure 5.

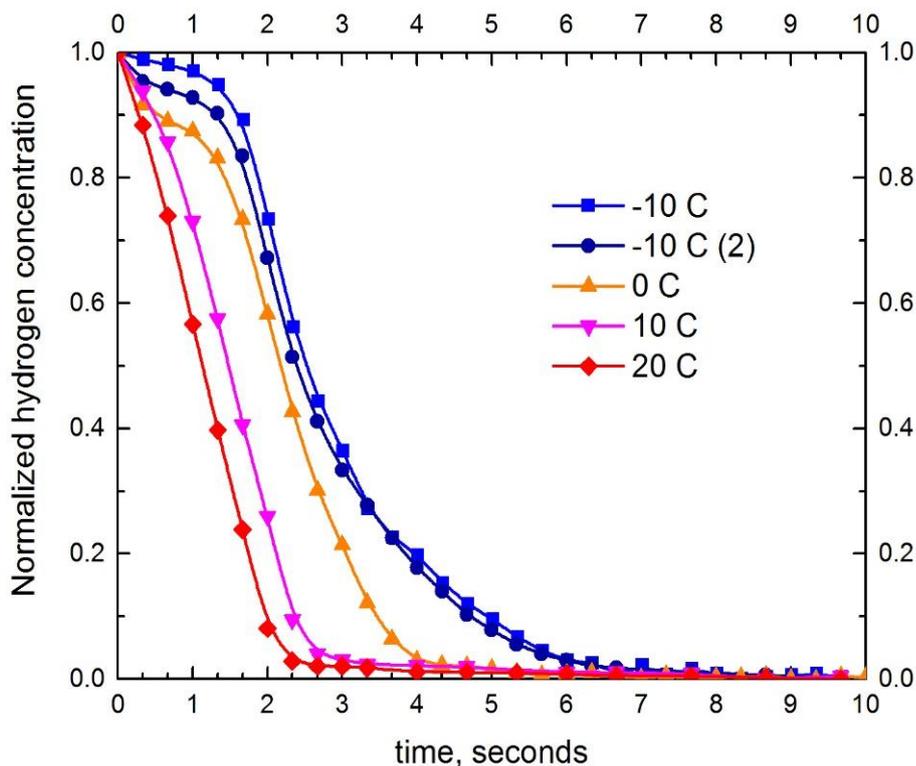


Figure 5. Temperature-dependent hydrogen desorption kinetics in Pd/C nanoparticles.

### III. Determination of the active phase of the catalyst during hydrogenation of ethylene.

We investigated how the catalytic performance of the palladium nanoparticles is affected by the formation of hydride and carbide phases. Mass-spectrometer was connected to the outlet of the capillary to monitor the conversion level. Figure 6 (left) shows how the fluxes of hydrogen and ethylene had been changing during the experiment. The grayscale reflects the conversion level (white – 0, black – 100%).

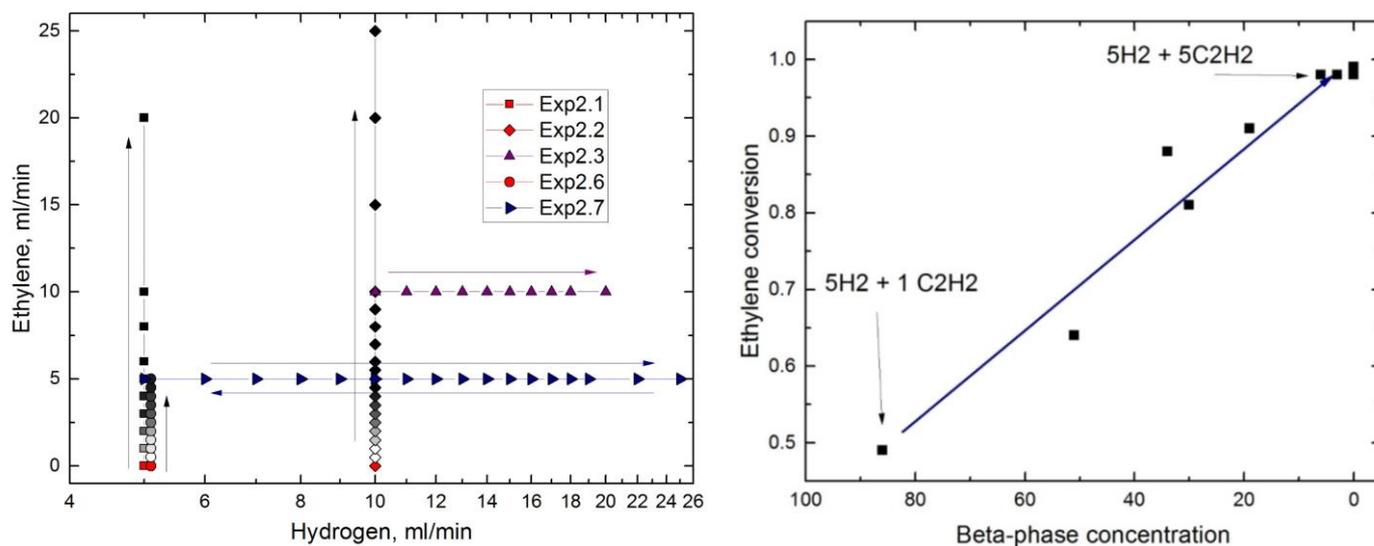


Figure 6. Left: Experimental conditions. Right: Changes of conversion depending on the structure of the nanocatalysts.

As indicated in figure 6 (right) an important result is that the conversion level increases when the sample is in pure and carbide states comparing with its hydride state.