EUROPEAN**S**YNCHROTRON**R**ADIATION**F**ACILITY

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.

ESRF	**Experiment title:** Size-dependent Pd Hydride Phase Diagrams	**Experiment number**: MA- 2930
Beamline: BM01B	**Date of experiment**: from: 13.04.2016 to: 19.04.2016	**Date of report**: 20.10.2017
Shifts: 18	**Local contact(s)**: Michela Brunelli (email: brunelli@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Aram Bugaev*[1,2], Alexander Guda*[1], Budnyk Andriy*[1], Kirill Lomachenko*[1], Bjoern Tore Loenstad Bleken[3], Koen Bossers[3], Sigurd Oien[3], Alexander Soldatov[1], Carlo Lamberti*[1,2]

[1]Southern Federal University, Zorge street 5, 344090 Rostov-on-Don, Russia

[2]Department of Chemistry, University of Turin, Via P. Giuria 7, 10125 Turin, Italy

[3]Department of Chemistry, University of Oslo, Norway

Report:

Part of results obtained during this experiment was published in the following papers:

1) Vera V. Butova, Andriy P. Budnyk, Alexander A. Guda, Kirill A. Lomachenko, Aram L. Bugaev, Alexander V. Soldatov, Sachin M. Chavan, Sigurd Oien-Odegaard, Unni Olsbye, Karl Petter Lillerud, Cesare Atzori, Silvia Bordiga, Carlo Lamberti "Modulator effect in UiO-66-NDC (1, 4-naphthalenedicarboxilic acid) synthesis and comparison with UiO-67-NDC isoreticular MOFs" Crystal Growth & Design **2017** *17* (10) 5422-5431 **(Journal Cover)** DOI: 10.1021/acs.cgd.7b00892
2) L. Braglia, E. Borfecchia, A. L. Bugaev, A. V. Soldatov, S. Øien-Ødegaard, U. Olsbye, K. P. Lillerud, K. A. Lomachenko, G. Agostini, M. Manzoli, C. Lamberti "The duality of UiO-67-Pt MOFs: connecting treatment conditions and encapsulated Pt species by operando XAS" Physical Chemistry Chemical Physics **2017** *19* 27489-27507 DOI: 10.1039/C7CP05185A

The next part of the data reported below is not published yet, the manuscript is in preparation

Formation and catalytic activity of palladium nanoparticles inside metal-organic framework

The sample of UiO-67 metal-organic framework functionalized by palladium was loaded in 1.5 mm glass capillary and heated in the 50 ml/min flow of 6% H_2 in He (47 ml of He and 3 ml of H2), from room temperature to 350 °C ramp 5°/min. The amount of sample was about 10 mg. We repeated this activation procedure twice (on different samples).
During one ramp we measured only EXAFS, and we see progressive formation of Pd particles, that can be seen from Fourier-Transforms shown in Figure 1.

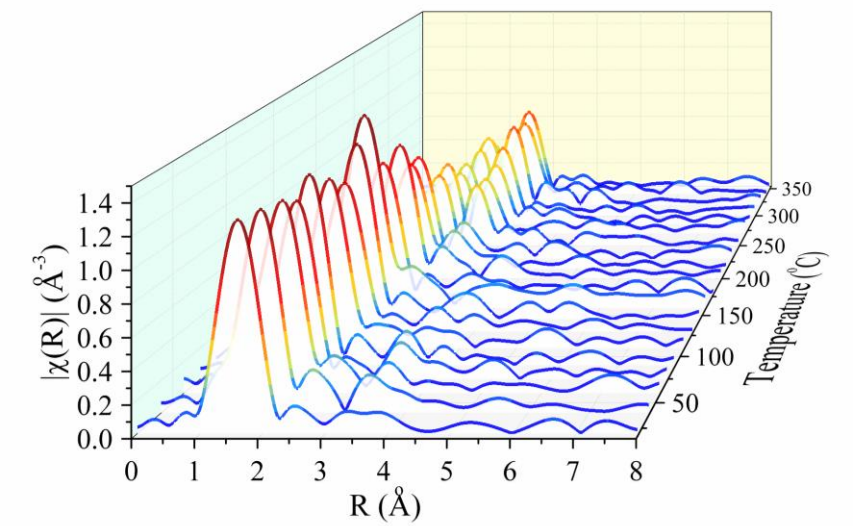

Figure 1. FT-EXAFS during formation of Pd particles inside UiO-67.

The single-shell Fourier-analysis of the resulting spectrum taken after activation and cooling down in 6%H_2/He gives the Pd-Pd interatomic distance $R_{Pd\text{-}Pd}$ = 2.79 ± 0.01 Å, with respect to 2.74 for bulk Pd, which indicates that the nanoparticles are in the Pd-hydride phase. After flowing He the interatomic distance to 2.75 ± 0.01 Å. The determined coordination number is 8.5 ± 1.0 with respect to 12 for bulk Pd, which indicates the formation of small particles.

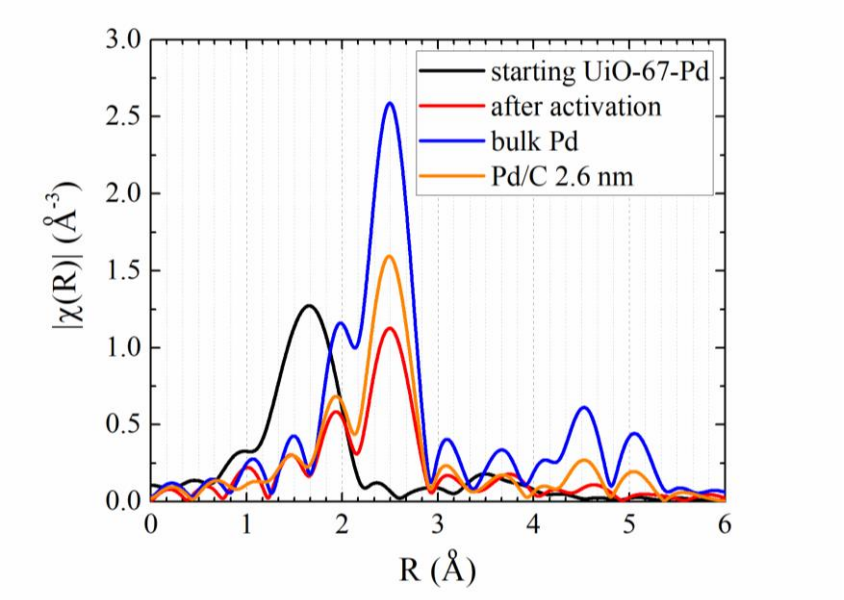

Figure 2. Phase uncorrected FT-EXAFS of UiO-67-Pd before (black) and after (red) activation in H_2 in comparison with bulk Pd (blue) and Pd nanoparticles on carbon with d~2.6 nm (orange).

In the non-activated material palladium is coordinated with both N and Cl atoms, as shown in figure 3, with $R_{Pd\text{-}N}$ = 2.05 Å and R_{Pd_Cl} = 2.29 Å. More detailed analysis will be done on the spectra measured for the pelletized sample.

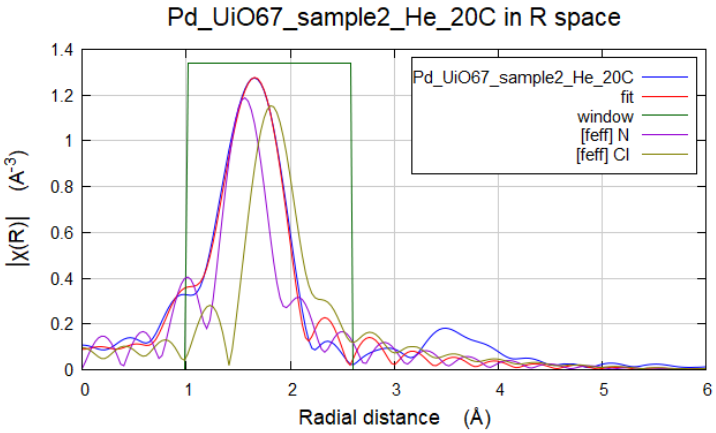

Figure 3. EXAFS analysis of the initial sample.

The linear combination fit of XANES spectra was performed using two reference states obtained in He before and after activation.

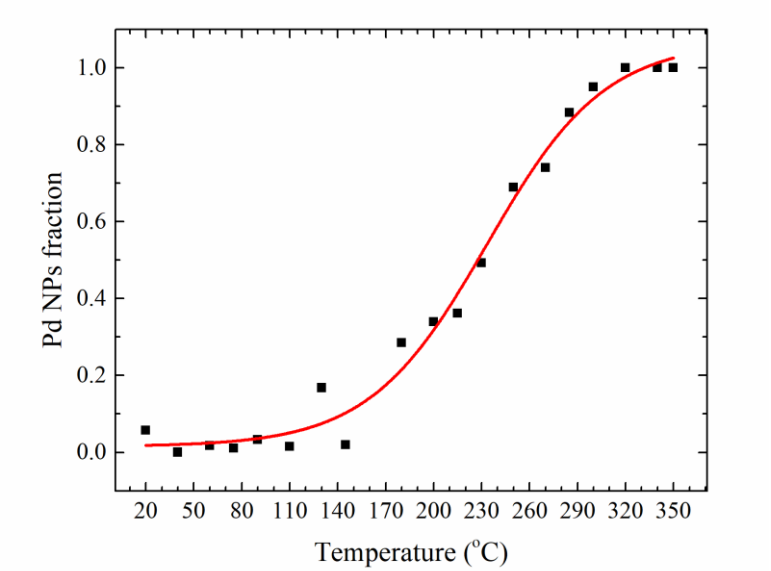

Figure 4. Evolution of the Pd nanoparticle fraction as a function of activation temperature, obtained from linear combination fitting.

In addition, during another ramp we collected both EXAFS and **XRD**, which is very interesting to be analyzed, because in the XRD patterns we also have an indication of Pd particle formation as very weak and smooth features are starting to appear exactly at the scattering angles which correspond to fcc Pd.

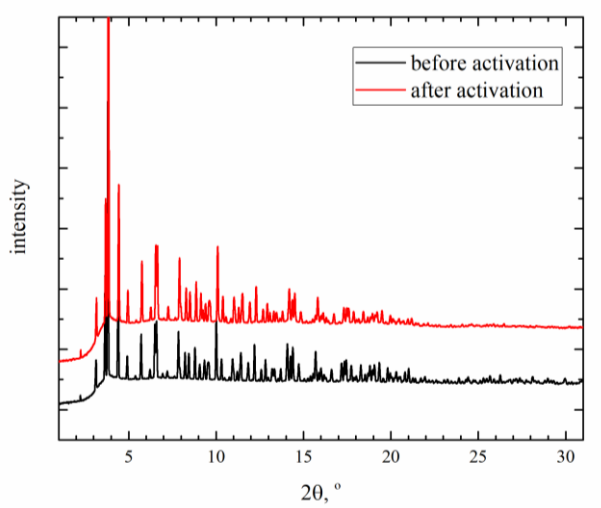

Figure 5. XRD data for UiO-67-Pd before (RT) and after (350 C) activation.

After formation of the nanoparticles we tested the catalytic activity of the sample in reaction of ethylene hydrogenation. This reaction was not performed on the material before activation. At 80 °C the conversion was very high, at 20 °C it was almost 0. The most interesting thing was that we found that after exposure to hydrogen and ethylene palladium nanoparticles form hydride and carbide phases similar to that we previously observed for 2.6 nm nanoparticles supported on carbon.

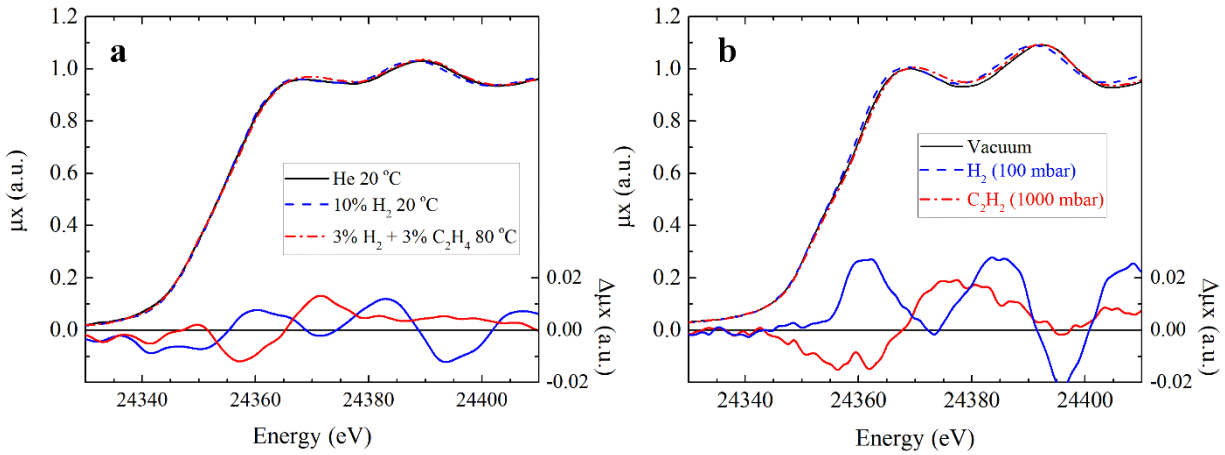

Figure 6. (a) XANES spectra of the activated sample after cooling down in He (black), exposure to H2 (blue) and to H2+C2H4 (red). The scale for the difference spectra is different and is shown on the right axis. (b) XANES spectra for Pd/C catalyst taken in similar conditions, published in Catal. Today, 2017, 119-126.