

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: Core-shell structure of palladium carbide nanoparticles revealed by in situ EXAFS and XRPD	Experiment number: MA- 3710
Beamline: BM31	Date of experiment: from: 30.11.2017 to: 09.12.2017	Date of report: 02.03.2018
Shifts: 23	Local contact(s): Wouter Van beek (email: wouter@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Aram Bugaev* ^{1,2} , Oleg Usoltsev* ¹ , Alina Skorynina* ¹ , Andrei Tereshchenko* ¹ , Alexander Guda ¹ , Kirill Lomachenko* ³ , Jeroen van Bokhoven ⁴ , Carlo Lamberti ^{1,2} ¹ Southern Federal University, Zorge street 5, 344090 Rostov-on-Don, Russia ² University of Turin, Via P. Giuria 7, 10125 Turin, Italy ³ ESRF, 71 avenue des Martyrs, CS 40220, 38043 Grenoble, France ⁴ ETH Zurich, HCI E127, 8093 Zurich, Switzerland		

Report:

Part of the obtained results have been included in the recently published paper:

Bugaev et al. *J. Phys. Chem. C* **2018**, doi: 10.1021/acs.jpcc.7b11473

Abstract: The presence of a core/shell behavior in Pd nanoparticles (NPs) during the formation of the metal-hydride phase has recently been highlighted combining X-ray absorption and scattering experiments [*J. Phys. Chem. C* **2017**, 121, 18202]. In this work, we focus on the formation of the carbide phase in the bulk region and on the surface of supported palladium NPs because it affects the catalytic activity and selectivity in hydrogenation reactions. We present *in situ* X-ray absorption spectroscopy study of carbide formation and decomposition in 2.6 nm palladium nanoparticles supported on carbon during exposure to acetylene, hydrogen, and their mixtures at 100 °C, taken as a representative temperature for hydrogenation reactions. Fourier analysis of extended X-ray absorption fine structure (EXAFS) spectra was used to determine the average Pd–Pd bond distance in the NPs, reflecting the formation of bulk palladium carbide, while theoretical calculation of X-ray absorption near-edge structure (XANES) using the finite difference method allowed us to determine the PdC_y stoichiometry in the bulk region and at the surface of the nanoparticles. The difference in the XANES and EXAFS results indicated different behavior of bulk and surface carbide formation. In particular, exposure to pure acetylene leads to the immediate formation of surface Pd–C bonds and much slower growth of bulk carbide, resulting in the increase of Pd–Pd bond distance with respect to pure metallic palladium nanoparticles by only ~0.6% after 1 h of exposure. Vacuum conditions at 100 °C did not affect the carbide structure of both the bulk and surface of the NPs. However, exposure to H₂ at 100 °C cleans the surface of palladium, removing surface Pd–C bonds, without decomposing bulk carbide. After second exposure to acetylene, this fraction of lost Pd–C bonds is immediately restored, and the bulk carbide phase continues growing. Thus, we showed how the combination of near-edge and extended structures of the absorption spectra can be utilized to determine the properties of surface and bulk regions of palladium nanoparticles, which showed different behavior in formation of the Pd–C bonds.

1. Description of the experimental procedure and data analysis.

The idea of this proposal was to monitor core-shell structure of palladium carbide phase upon exposure of palladium nanoparticles to acetylene, ethylene and their mixtures with hydrogen. We used 3 types of samples: 1 nm particles that are considered to have only shell, 2.6 nm particles that can be virtually divided to core and shell regions, and bulk palladium that is considered not to have any shell. All the samples were exposed to acetylene at 50 and 100 °C, ethylene at 50 and 100 °C, and the mixture of ethylene with hydrogen at 80 °C. After formation of carbide phase the samples were exposed to hydrogen to test the stability of these carbides. The process of carbide formation and decomposition was monitored by simultaneous X-ray absorption and X-ray diffraction. First shell Fourier analysis was performed for the EXAFS data. Rietveld refinement was done for diffraction data. In addition, XANES spectra were analyzed by the following approach. We took the palladium carbide spectrum obtained in acetylene and subtracted from it a spectrum of pure palladium nanoparticles. Then we used this difference signal to fit difference spectra (carbide minus pure) of all other difference spectra thus quantifying the degree of carbonization. The difference spectrum was also fitted by theoretically calculated spectra and the C/Pd ratio was obtained. The result of XANES, EXAFS and XRPD analysis are presented below in Section 3 with comments written in the caption of each figure. Analysis of some data is still in progress. In particular, all the figures report the data for 2.6 nm particles only. To make EXAFS and XRPD results comparable with each other, we report not absolute values of interatomic distances and lattice parameters, but their relative increase with respect to pure metallic palladium.

2. Preliminary conclusions.

From the analysis that have been already performed some interesting conclusions can be already made. First of all we observed the discrepancy between EXAFS and XRPD results: the degree of lattice expansion is systematically smaller in EXAFS than in XRPD. This observation correlates with our previous results obtained for palladium hydride systems (mainly in experiment MA-2530, published in [*J. Phys. Chem. C* **2017**, *121*, 18202]). The possible explanation of this fact is that the creation of “carbon defects” which is the incorporation of carbon atoms into the palladium lattice is more difficult in the surface than in the bulk. Thus, the main goal of the proposal, to reveal core-shell structure of PdC_y particles is already achieved. But more detailed analysis is of course required.

Then, we observed that at 50 °C the lattice expansion is ~ 3 times smaller than at 100 °C, which means that less carbon can be introduced inside the lattice. However, XANES spectra, which are sensitive to the amount of Pd-C bonds, indicate that C/Pd ratio is lowered by only ~ 1.5 times. The possible explanation of this fact is that at lower temperature we observe surface adsorbed acetylene and ethylene molecules, that do not increase lattice parameter, but do contribute to the XANES region.

Some expected but still important results are that 1) the carbide formation in ethylene is slower than in acetylene, and 2) the carbide formation at high temperatures is faster.

Finally, the most surprising result was that carbide can continue to form from the already adsorbed acetylene, even if the sample is left in He (Figure 6).

3. Results of the data analysis

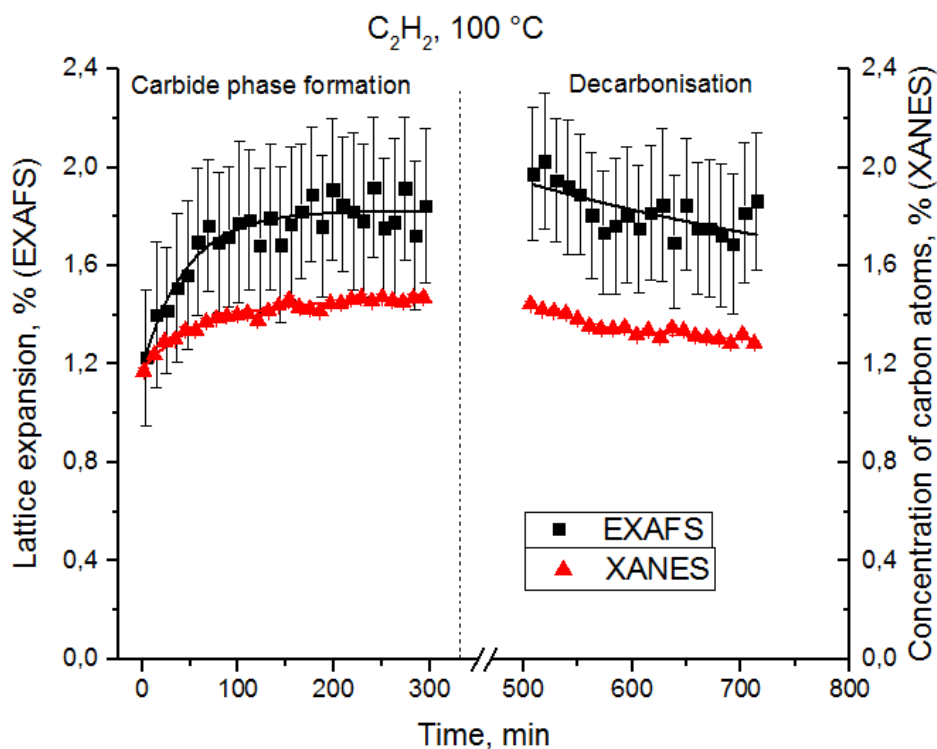


Figure 1. The sample was exposed to acetylene at 100 °C (left part) and then to hydrogen at 100 °C (right part). Black squares correspond to the lattice expansion from EXAFS (black squares left axis) and red triangles reflect the concentration of carbon atoms (rough estimation) determined by XANES (red triangles, right axis).

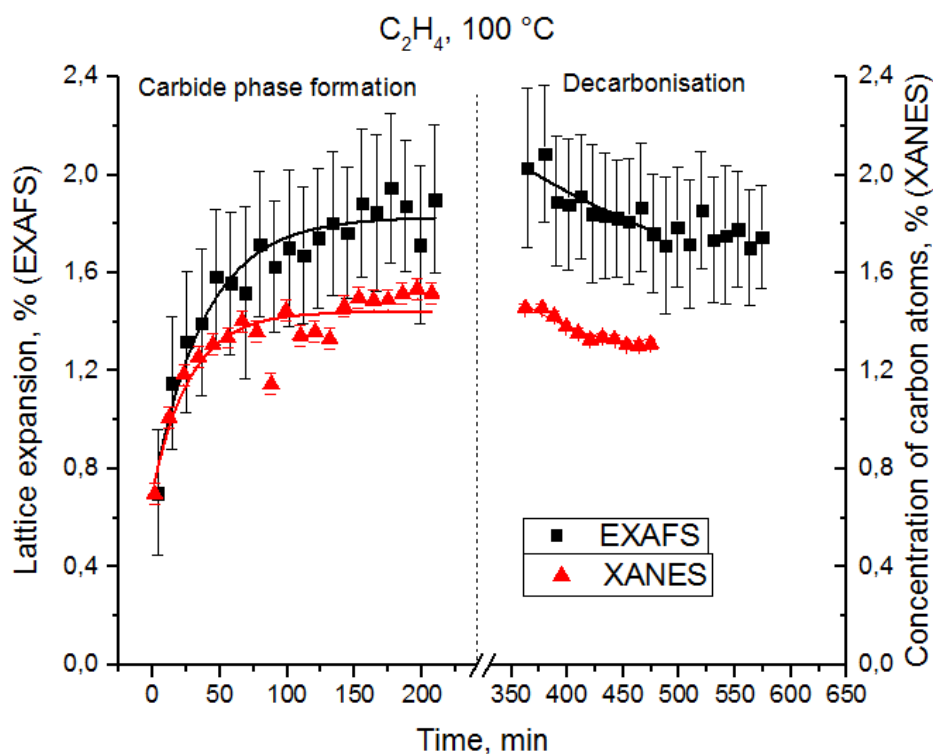


Figure 2. The same as figure 1, but for ethylene at 100 °C.

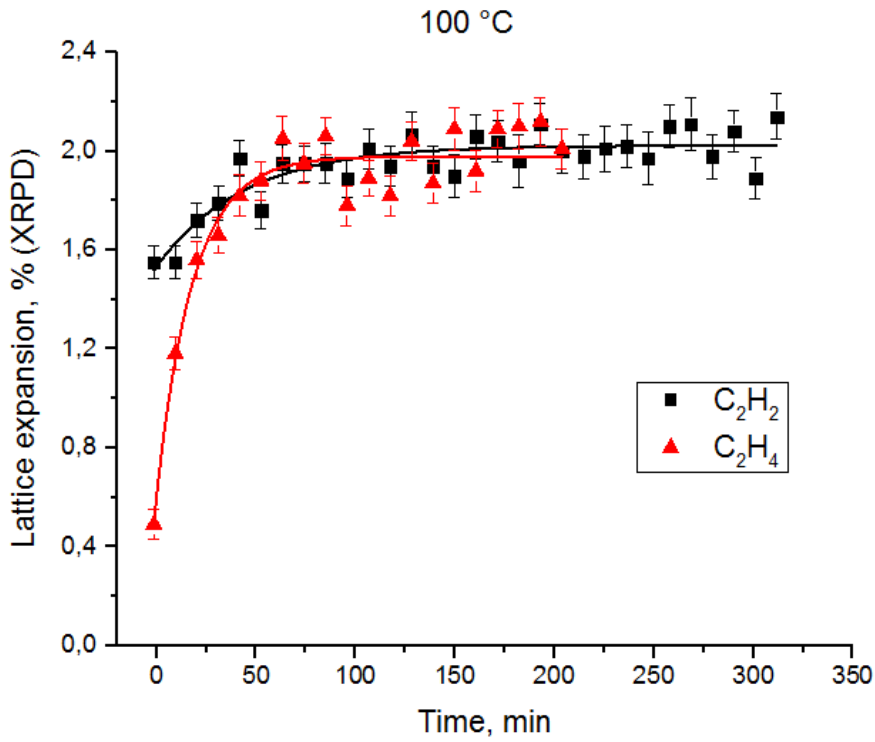


Figure 3. Comparison of lattice expansion by EXAFS for samples exposed to acetylene (black) and ethylene (red) at 100 °C.

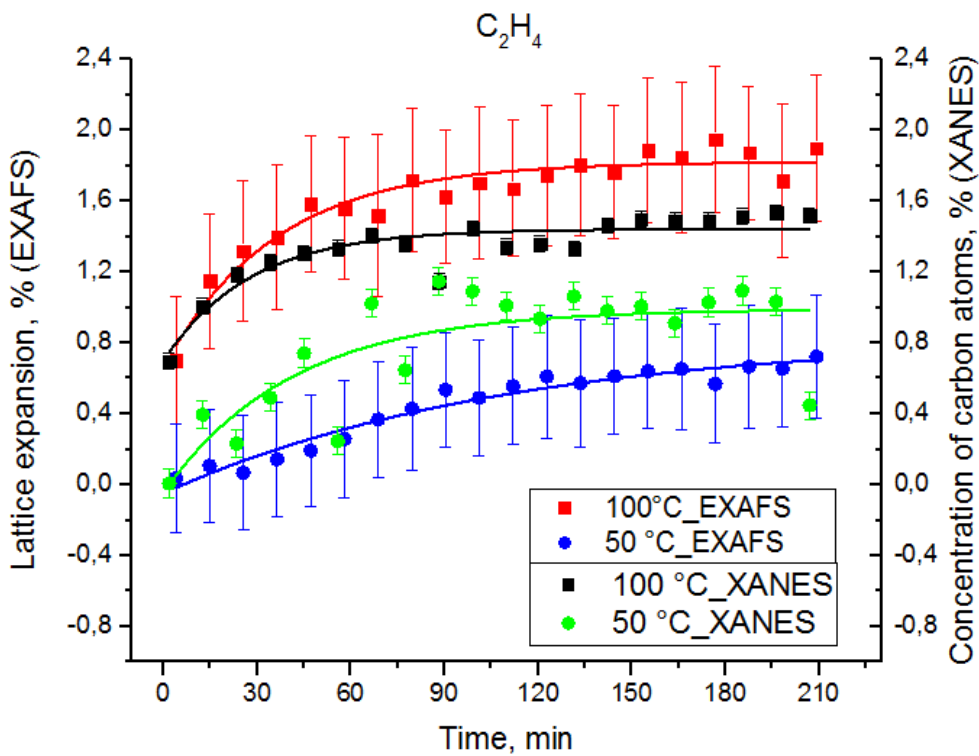


Figure 4. Comparison of lattice expansion by EXAFS (squares) and C/Pd ratio by XANES (circles) for samples exposed to ethylene at 50 (blue and green) and 100 °C (red and black).

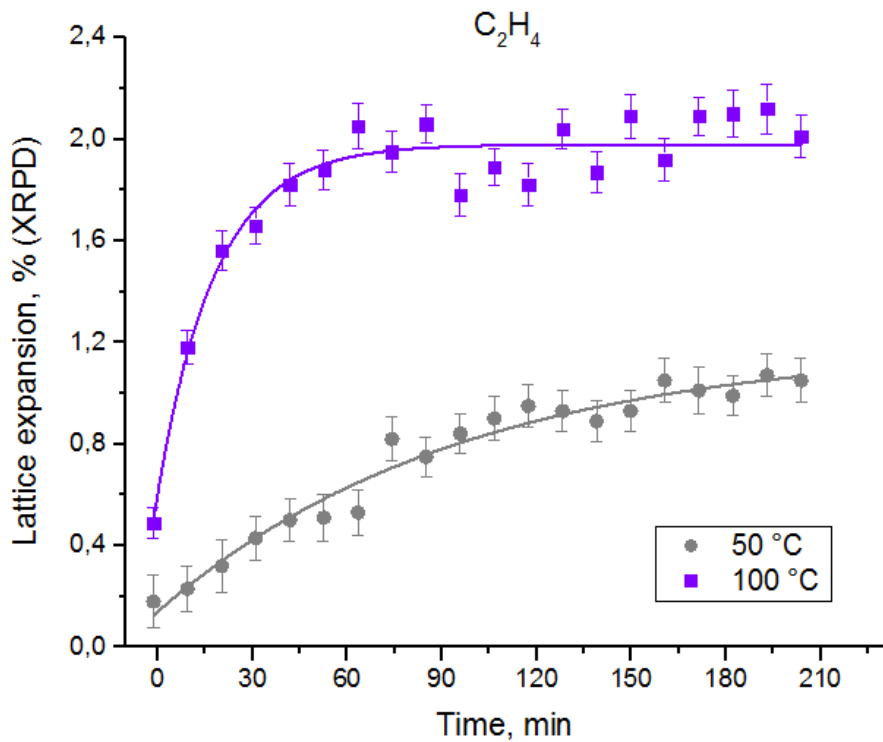


Figure 5. Comparison of lattice expansion by XRPD for samples exposed to ethylene at 50 (grey circles) and 100 °C (violet squares).

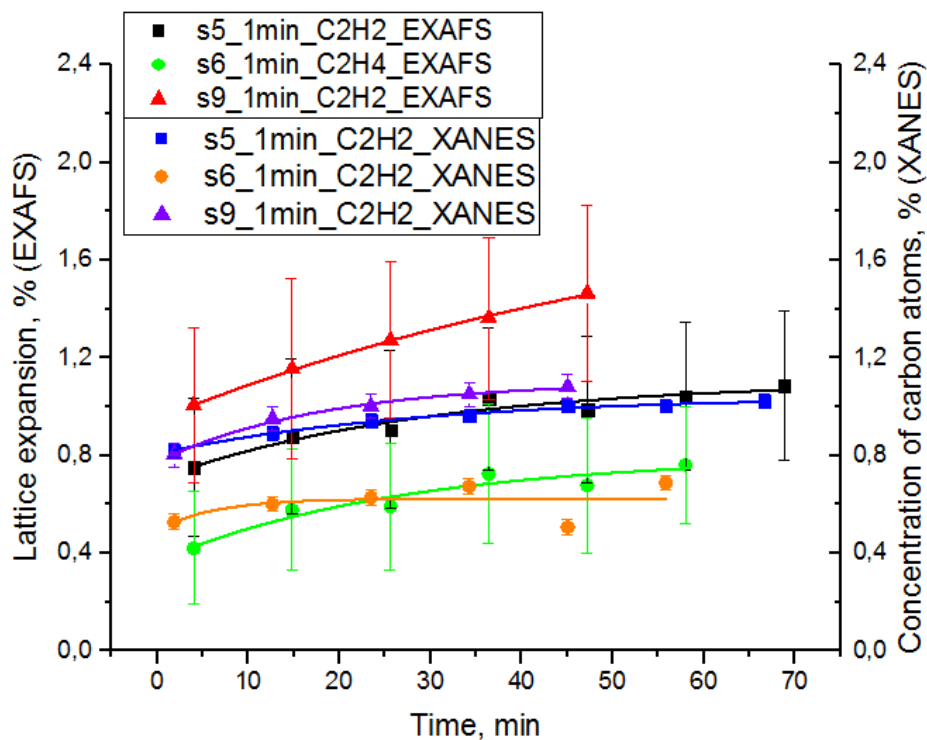


Figure 6. Comparison of XANES and EXAFS results for the samples that were exposed to acetylene and ethylene for a short time and then stayed in He.

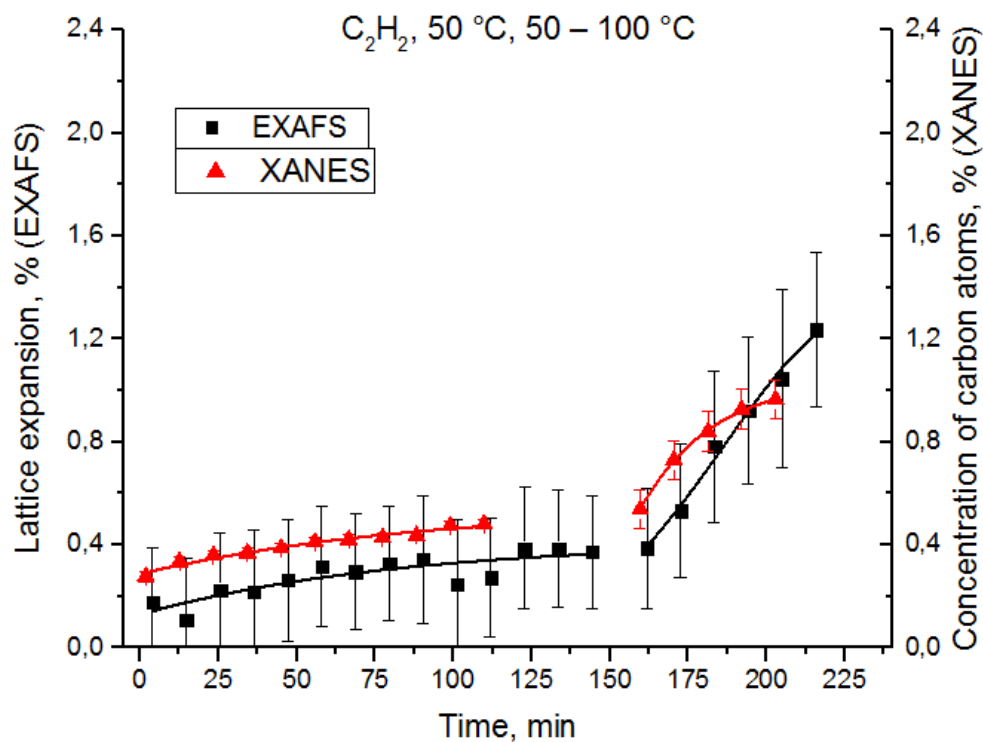


Figure 7. The sample was exposed to acetylene at 50 °C and after $t = 150$ min heated to 100 °C. Black squares correspond to the lattice expansion from EXAFS (black squares, left axis) and red triangles reflect the C/Pd concentration determined by XANES (red triangles, right axis).

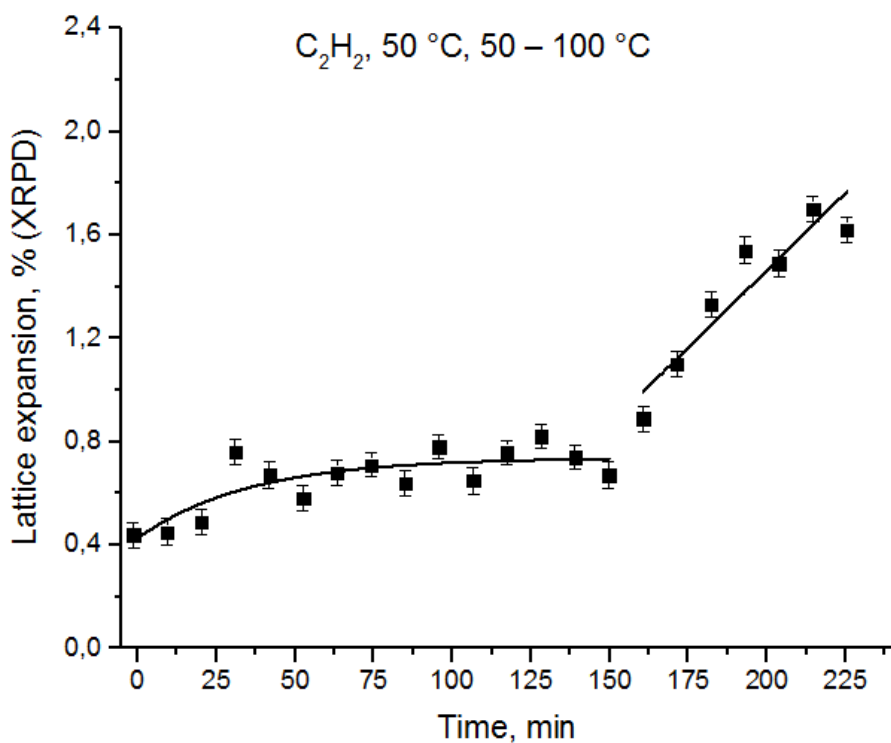


Figure 8. The same as Figure 7 but for the lattice expansion determined by XRPD.