ESRF	**Experiment title:** Nature of Pd species in Pd for acetylene semihydrogenation reaction	**Experiment number:** CH-6447
Beamline: BM30	**Date of experiment:** from: 13 Sep 2022 to: 19 Sep 2022	**Date of report:**
Shifts: 18	**Local contact(s):** Antonio Aguilar, Abdallah Nassereddine	*Received at ESRF:*

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Report:

The catalytic performance of single-atom catalysts (SAC) supported on amorphous carbon nitride was investigated to determine how the activation process in a reducing atmosphere affects the catalystic performance. The catalytic activity for acetylene conversion increased with decreasing temperature. The selectivities were excellent, with only approximately 5% ethane formed from no reduction sample to reduction at 300 °C. However, increasing the reduction temperature to 400 and 600 °C decreased the selectivity and increased ethane formation.

XANES and EXAFS spectroscopy were used to reveal the active phase formed during the reduction and how it changed during the acetylene semihydrogenation reaction. The experiments were conducted at different stages of the reaction: initial state at room temperature and atmospheric conditions, during reduction at 200, 400, 600, and 800 °C in a mixture of 1% C_2H_2 and 20% H_2 in N_2, after the reduction, during the reaction at 1 bar starting from 50 to 175 °C, the heating rate of 10 °C/min with a GHSV = 19.8 $Lh^{-1}g^{-1}$, and final state after the reaction in He.

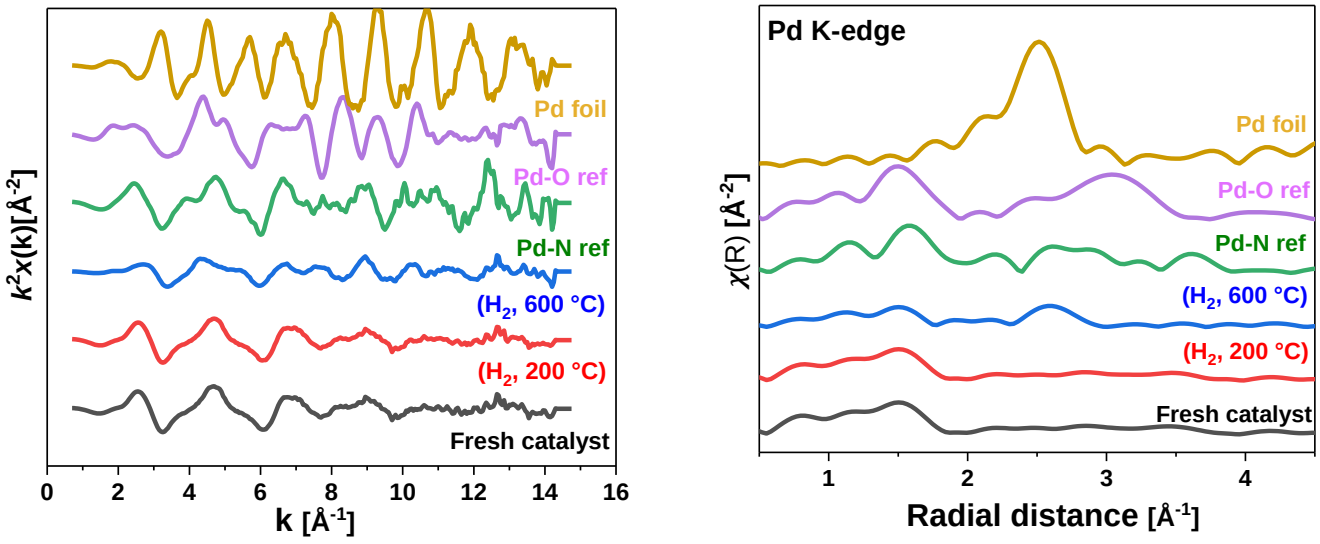

Figure 1: EXAFS spectra acquired at Pd K-edge measured for references, fresh Pd sample, sample after reduction at 200 °C and 600 °C.

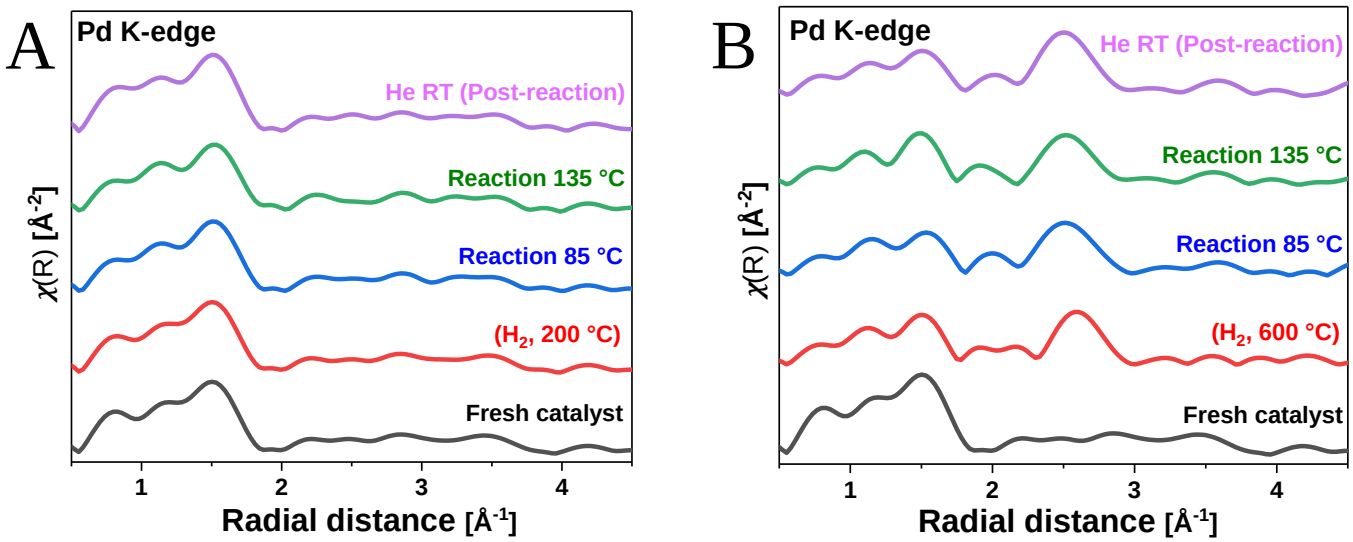

Figure 2: EXAFS spectra acquired at Pd K-edge measured during the catalytic cycle after reduction at 200 °C **(A)** and 600 °C **(B)**.

Figure 1 shows the EXAFS spectra of the Pd sample and references, indicating that Pd in the fresh sample was present only in the single-atom form. However, after reduction at 600 °C, the spectrum shows a clear fingerprint of the metallic Pd structure. Both these findings were confirmed by XPS and HAADF-STEM data. The *operando* EXAFS spectra of the reaction after reduction at 200 and 600 °C are presented in figure 2. After reduction at 200 °C, no noticeable changes were observed in the fine structure. However, after reduction at 600 °C and formation of nanoparticles, changes in the fine structure were observed.
Further analysis of the ensemble of XAS spectra will be conducted to provide a more comprehensive assessment and the results will be published.