



| | | |
|---|--|---|
| | Experiment title: Following Facet-Resolved Shape- and Composition-Changes of Single PdPt Nanoparticles During Methane Oxidation by Operando CXDI | Experiment number: HC-4961 |
| Beamline: ID-01 | Date of experiment: from: 03 Oct 2022 to: 11 Oct 2022 | Date of report: 23. Feb. 2023 |
| Shifts: 18 | Local contact(s): Tobias Schüllli | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): D. Lapkin, I. Vartaniants, J.-C. Schober, D. Assalauova, J. Dwivedi, T. F. Keller, A. Stierle Deutsches Elektronen-Synchrotron DESY, D-22607 Hamburg, Germany | | |
| Participants: L. Bachmann*, J. Dwivedi*, G. Hinsley*, T. F. Keller*, A. Stierle* | | |
| Remote: D. Lapkin, I. Vartaniants | | |

Report:

We proposed to use operando Coherent X-ray Diffraction Imaging (CDI) in Bragg geometry to follow the structural evolution of a single PdPt nanoparticle (NP) during CH₄ oxidation. The aim was to track the shape and facet-resolved strain state changes in a single NP while heating the sample and dosing different gas compositions (inert and lean/rich catalytic reaction conditions), and thereby watch the catalytic activity of the sample by mass spectrometry in the gas outlet. Furthermore, we intended to identify NP surface facet sites and strain related surface compositions most relevant for methane oxidation for NPs with initial core-shell and alloy configuration.

The core-shell nanoparticles were prepared by dewetting a homogeneous, 50 nm thin Pt film at 1200 °C on a 100 oriented, Nb doped strontium titanate (STO) oxide single crystal in a tube furnace in air. The resulting nanoparticles were overgrown by molecular beam epitaxy (MBE) with 7 nm Pd at 250 °C under UHV condition. We investigated several pre-selected and pre-characterized single PtPd nanoparticles. The height was determined from the AFM topographic images and is between 80 nm and 100 nm for the selected particles. One example is shown in fig. 1a) and b) before and after the operando experiment, respectively. Hierarchically arranged Pt markers facilitates a simple relocation of the pre-selected NP.

The catalytic experiment was realized by a gas dosing system with a backpressure controller in the outlet. This system ensured a constant chamber pressure of 100 mbar throughout the whole experiment with a constant total flow of 50 ml/min of a gas or gas mixture. For this experiment CH₄, O₂, H₂ and Ar were used. A mass spectrometer in the outlet was tracking the gas composition in the chamber and the catalytic activity of the sample. Since the catalytic properties, i.e., partial and full methane oxidation are temperature-dependent, a heater was used to heat the sample up in steps in a temperature range between RT and 700°C, in lean and rich condition. The X-ray energy was 11.6 keV above the Pt_{L-III} edge, corresponding to a wavelength of 1.06888 Å, and the X-ray beam was focused by compound reflected lenses (CRLs, consisting of 18 Be lenses).

At the beginning of the experiment we had some technical issues with our complex gas dosing system, which were related to the connection of the latter to the backpressure controller in the outlet. We were able to solve this problem with assistance of the ESRF staff, so we could start the catalytic experiment. A fluorescence detector was used, not only to easily identify the marker, see fig. 1c), but also to find and track the particle during out-of-plane/in-plane rotations, and when moving between different Bragg reflections.

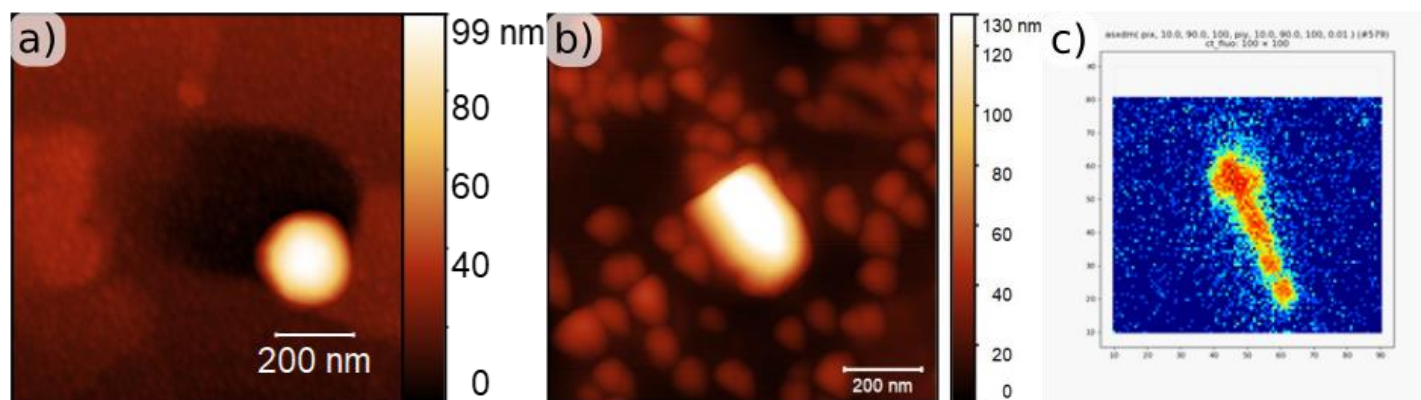


Fig. 1: a) Topographic AFM image of a PtPd NP. b) Topographic AFM image of the same NP after the operando experiment. c) Fluorescence detector image of a unique marker, helping to unambiguously find pre-selected NPs.

Our challenging operando X-ray experiment was further complicated by the beam shape having two big side maxima (fig. 2a), which lead to probing each NP three times (fig. 2b). Thus, the line profiles across each single NP had two side maxima (fig. 2c). This resulted into instable NP tracking during the CDI scans, because the automated alignment scripts easily picked the wrong maxima. By careful alignment combining the X-ray fluorescence signal and the Bragg signal on the maxipix detector it was still possible to collect BCDI datasets. Another impediment was that the center of rotation of eta and phi was about 35 μm apart, so it was not possible to bring the investigated NP into the center of rotation for both angles. Thus, for each angular movement the NP needed to be aligned in x and y. This was for example 0.0037 mm along the x direction for each degree of phi, as the calibration in fig. 2d) shows.

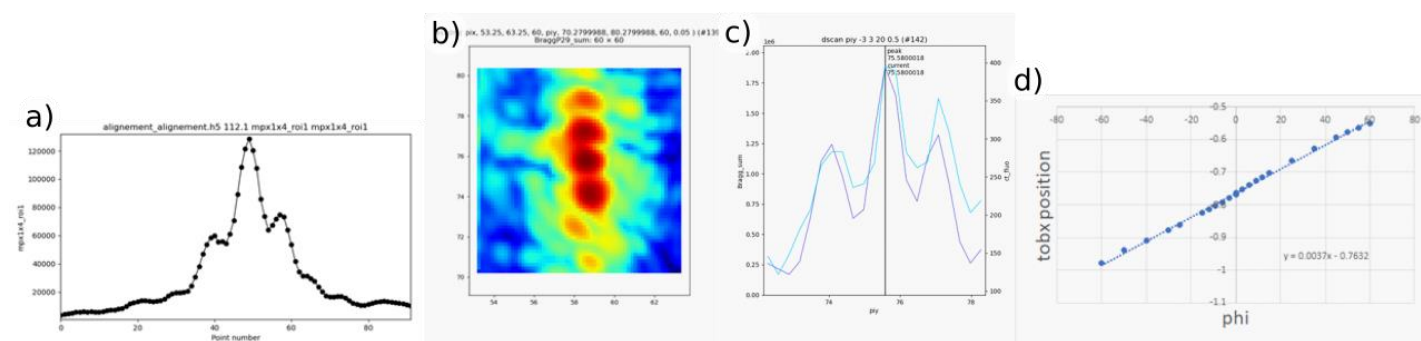


Fig. 2: a) beamprofil showing a central maximum of a width of 240 nm, and a total width of around 500 nm, b) fast continuous KMAP scanning image of a single NP c) a linescan through the same single nanoparticle shows three maxima, d) deviation from the center of rotation plotted as correction needed along x as function of sample rotation along phi.

During the experiment we collected altogether 5 BCDI datasets on a single particle at various states: the initial state (inert condition, in pure Ar), during and after partial CH_4 oxidation (CH_4 and O_2 at $400^\circ\text{C}/\text{RT}$) and during full oxidation (CH_4 and O_2 at 690°C). At the end of the experiment several BCDI datasets were taken at RT on different NPs. The analysis of the datasets is ongoing and is accompanied by extended experimental ex situ microscopy post-analysis at the DESY NanoLab including AFM (as shown in 1b), Scanning Auger Microscopy (SAM) and SEM with EDX and electron back-scatter diffraction (EBSD).