ESRF	**Experiment title:** Capturing changes at the interface of ceria nanoparticles supported on nanoporous gold using in situ ptychography	**Experiment number**: **CH- 4290**
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Names and affiliations of applicants (* indicates experimentalists):

S. Baier [1,*], F. Benzi [1,*], G. Tofighi [1,*], M. Scholz [2,*], R. Hoppe [3,*], A. Wittstock [4], C. D. Damsgaard [5,*], C. G. Schroer [2, 6] and J.-D. Grunwaldt [1,7]

[1] *Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, D-76131Karlsruhe, Germany*

[2] *DESY Photon Science, D-22607 Hamburg, Germany*

[3] *Institute of Structural Physics, Technische Universität Dresden, D-01062 Dresden, Germany*

[4] *Angewandte und Physikalische Chemie, University of Bremen, Germany*

[5] *Center for Electron Nanoscopy and Center for Individual Nanoparticle Functionality, Technical University of Denmark, DK- 2800 Kgs. Lyngby, Denmark*

[6] *Department Physik, Hamburg University ,D-20355Hamburg, Germany,*

[7] *Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, D- 76344 Eggenstein-Leopoldshafen, Germany*

Report:

To understand the function of heterogeneous catalysts and to improve the catalytic properties, a structure-activity relationships are required which make it inevitable to study the catalysts during reaction conditions.[1-3] In order to get highly resolved images, X-ray ptychography, can be used.[4-5] Starting from the 1980s, gold became an interesting element for heterogeneous catalysis. One example is nanoporous gold (np-Au), which is composed of a sponge-like three-dimensional network.

Np-Au has been modified to be suitable for different reactions such as CO oxidation, oxidation of alcohols or water gas shift reaction,[6-9] and has been used to form “inverse catalysts”, where a metal oxide is supported on a pure metal. Like for traditional catalyst systems, also in these “inverse catalysts”, an important issue is the thermal stability and the metal oxide prevents coarsening of the gold nanostructure[10] at high temperatures. In order to follow the coarsening of the np-Au at different temperatures and gas environments, *in situ* ptychography was used to study the coarsening of np-Au at different temperatures of an annealing treatment. The study was performed in the specially designed *in situ* cell.

Commercial 50 nm gold particles, pure np-Au and CeOx/np-Au were used to perform the in situ ptychography study. The newly developed *in situ* cell is based on a sample holder composed of a Protochips E-chip® and a cell body with X-ray transparent windows. To realize a special reaction environment, the cell has a gas inlet and outlet. Heating is realized by resistive heating within the E-chip which is connected to a current source. Using the E-chip, the user benefits from the thin electron transparent window within the chip, which enables TEM measurements on exactly the same sample. To close the cell body, another window is realized by a Kapton® foil.

The *in situ* ptychography experiment was carried out at the nanofocus endstation of the beamline ID13 at the European Synchrotron Radiation Facility (ESRF). The *in situ* cell was mounted on a kinematic mount and was scanned under the nanofocused beam (FWHM ~ 150 nm) at 14.9 keV. Far field diffraction patterns were recorded with a Maxipix detector with a sample - detector distance of 1 m for np-Au and CeOx/np-Au samples and 2 m for the 50 nm Au samples. An area of 2 µm x 2 µm was scanned with a step width of 50 nm.

First, as a model sample, 50 nm Au particles were studied to show the feasibility of *in situ* ptychography. Exemplarily, in *situ* measurements during heating and with a gas flow are shown here on np-Au. The study was performed on a crack (gained by milling with the FIB) on np-Au at different temperature steps with a flow of 3 ml / min of synthetic air which is shown in Figure 1.

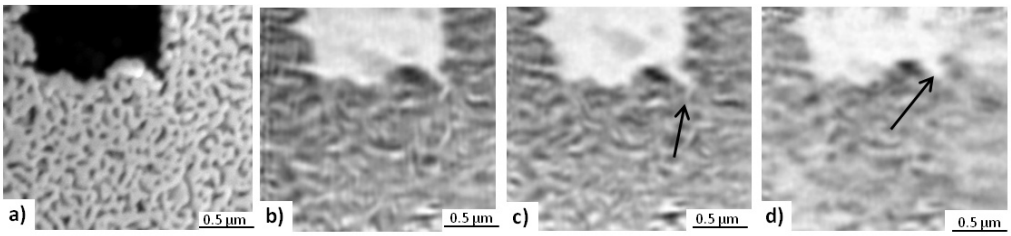

Figure 1: Np-Au on a SiN membrane studied by SEM (SE contrast) and ptychography at different annealing steps with a flow of 3 ml / min synthetic air. a) Ex situ SEM image in SE contrast before any thermal treatment, b) phase contrast image of the same area in the ptychographic measurement at room temperature, c) phase contrast image at a power of 59 mW d) phase contrast image at a power of 130 mW.

As it is visible in Figure 1 b), the structure gained by ptychographic reconstruction at room temperature during gas flow is in good agreement with the SEM image. Structures of 35 nm, i. e. the width of crack marked in 1 c), could be resolved. While heating at 59 mW (see Figure 2 c)), either the first changes which are marked by an arrow already occurred at this relatively low temperature or the resolution became slightly worse, which could happen due to thermal vibrations. However, heating at 130 mW (Figure 1 d)) clearly lead to changes in the structure, which are marked as well.

The design and application of an *in situ* cell for ptychography has been demonstrated on a model sample of 50 nm Au particles and for real catalyst samples based on np-Au. Real *in situ* measurements with a gas flow and at elevated temperature have been achieved for the first time with a closed cell up to temperatures of approx. 660 °C.
By this study, it has been shown, that coarsening of pure np-Au already starts at relatively low temperature below 300 °C. This is a good basis for future studies which at aim at high resolution using the new detector available at ID13 also uncovering more detail in the expected differences for the pure and the inverse catalyst.

References

[1] J.-D. Grunwaldt, C. G. Schroer, Chemical Society Reviews, 39, 4741-4753, (2010).
[2] B. M. Weckhuysen, Chemical Communications, 97-110, (2002).
[3] J.-D. Grunwaldt, J. B. Wagner, R. E. Dunin-Borkowski, ChemCatChem Reviews, 5, 62-80, (2013)
[4] J. M. Rodenburg, H. M. L. Faulkner, Appl. Phys. Lett., 85, 4795-4797, (2004).
[5] R. Hoppe, J. Reinhardt, G. Hofmann, J. Patommel, J. D. Grunwaldt, C. D. Damsgaard, G. Wellenreuther, G. Falkenberg, C. G. Schroer, Appl. Phys. Lett., 102, 203104-203104, (2013).
[6] Y. Iizuka, A. Kawamoto, K. Akita, M. Daté, S. Tsubota, M. Okumura, M. Haruta, Catalysis Letters, 97, 203-208, (2004).
[7] V. Zielasek, B. Juergens, C. Schulz, J. Biener, M. M. Biener, A. V. Hamza, M. Baeumer, Angewandte Chemie-International Edition, 45, 8241-8244, (2006).
[8] A. Wittstock, V. Zielasek, J. Biener, C. M. Friend, M. Baeumer, Science, 327, 319-322, (2010).
[9] J. Shi, A. Schaefer, A. Wichmann, M. M. Murshed, T. M. Gesing, A. Wittstock, M. Bäumer, The Journal of Physical Chemistry C, 118, 29270-29277, (2014).
[10] M. Bagge-Hansen, A. Wichmann, A. Wittstock, J. R. I. Lee, J. Ye, T. M. Willey, J. D. Kuntz, T. van Buuren, J. Biener, M. Bäumer, M. M. Biener, The Journal of Physical Chemistry C, (2014).