Palladium-based catalyst has proven to be an excellent catalyst in the automotive catalyst and for the combustion of natural gas. Due to the oxygen involvement and the temperature range of catalytic reaction, PdO and/or Pd can play an important role in catalytic reaction. Understanding of the redox of Pd is essential for manipulation and control of the catalyst. Abundant studies have been done on redox of palladium by different techniques: thermogravimetric analysis (TGA), surface techniques such as: X-ray Photoelectron spectroscopy; Auger-Electron Spectroscopy (AES); Low Energy Electron Diffraction (LEED); Scanning tunneling Microscopy (STM), and Transmission Electron Microscopy (TEM), but most of this information is obtained under conditions far from the actual catalytic reactions in automotive applications because these techniques require for instance a limited gas pressure, limited temperature, limited resolution, limited detection depth etc. An analytical tool that can operate at realistic gas pressures, reaction temperatures, and can monitor the changes of particles morphology, nanostructure and chemical composition measurement at the same time, will give us no doubt unique information on the catalyst. Here we present the in-situ TEM results on reduction and oxidation of ~20 nm Pd nanoparticles in different gases O₂, H₂ and He with pressure of 0.5-0.65 bar, temperature range from room temperature to 800 °C using a static nanoreactor. When heating from room temperature to 800 °C in O₂, the morphology of initial metal particles changes in different way depending on their initial structures. Void formation, wetting, de-wetting and sintering of particles occur. All the changes demonstrate that, during heating, there exists a drastic interaction at gas-solid and solid-solid interface (figure 1). Particles, which were first hydrogenated to the beta phase under 0.55bar, released hydrogen in an oxygen atmosphere first at around 130 °C and oxidized at a higher temperature. Reduction and oxidation of Pd nanoparticles can also be induced by the electron beam depending on oxygen gas pressure and temperature.

Acknowledgement: This work is supported by ERC NEMinTEM Project 267922.
Fig. 1: Image sequences of Pd nanoparticles oxidation during heating in O₂ 0.6 bar. Heating rate: 13K/min. (a)RT. (b) 195 °C. (c)265 °C. (d) 540 °C. In general, during heating, particles show de-wetting, facet formation, voids appearance and disappearance, wetting and growth. 4 particles numbered show typical type of changes in their morphologies.