

In-situ TEM on (de)hydrogenation and oxidation/reduction of Pd

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In order to understand the mechanism of chemical reactions based on catalytic effects, such as, hydrogen (de)absorption and oxidation on a metallic crystal, it is important to study the processes at the atomic level. In-situ transmission electron microscopy (TEM) at pressures (1-10 bar) of gas is expected to provide the most direct information. Such a pressure in combination with the high vacuum of the TEM can be achieved by the use of a nanoreactor, which is a novel way to perform in-situ TEM with atomic resolution at ambient gas pressure [1], thus allowing the study of all kinds of chemical reactions under industrially relevant gas pressures.

Here, we report an in-situ TEM study on (de)hydrogenation and oxidation of crystalline palladium using a nanoreactor operated at hydrogen and oxygen gas pressures of 0.5 - 4.5 bar and 0.7 bar, respectively, and temperatures between 20 and 700 °C. The MEMS based nanoreactor is composed of two Si chips with square-shaped 1 μm thick SiN windows which contain very thin (about 15 nm thick) SiN membranes about 10 μm in diameter. One of the chips contains a Pt heater and has an inlet and outlet for the gas. Pd was deposited as a 10 nm thick thin film on the chip that did not contain the heater. The Pd film was annealed at higher temperature, which resulted in mainly (111)-oriented grains. The specimen holder includes O-rings to obtain leak tight connections between the holder and the nanoreactor. We have developed a gas supply system to allow any gas pressure between 0 and 10 bar to pass via the TEM holder through the nanoreactor. Various measurements were taken to reduce contamination originating from hydrocarbons, which may for instance originate from the gas container.

We have performed in-situ TEM (using a Philips CM30T at 200 and 300 kV) of (de)hydrogenation on palladium by varying the hydrogen gas pressure and/or by changing the temperature (Fig.1(a-f)). In electron diffraction mode we observed reproducibly a crystal lattice expansion (α -phase \rightarrow β -phase, Fig.1(a-c)) and shrinkage (β -phase \rightarrow α -phase, Fig.1(d-f)) owing to hydrogenation and dehydrogenation, respectively. In general, within one to two seconds all Pd particles are hydrogenated, but within this time frame one can observe that some particles are hydrogenated quicker than others [2].

In-situ TEM of the oxidation of Pd has been performed with 0.3 bar oxygen gas. Figures 2 (a-d) are bright field images taken during oxidation of Pd islands. It has been observed at 600 °C that the oxidation fronts propagate along the direction indicated by the blue arrows (Fig. 2). The oxidation front propagates with a speed of about 5 nm/s. Figures 2(e) and 2(f) show electron diffraction patterns taken before and after this specific oxidation process, respectively. In Fig. 2(e) only the reflections from Pd are visible. In Fig. 2(f) relatively strong PdO reflections can be seen. We could also observe reduction of PdO using hydrogen gas at around 0.2 bar where the reflections from PdO indicated by the red arrows have disappeared [3].

In conclusion, we succeeded to (de)hydrogenate and oxidize crystalline palladium and observe the lattice changes in diffraction and bright-field image mode. This result shows that this is a fast method to investigate metal hydrides and oxides with information at the nanometer scale.

References

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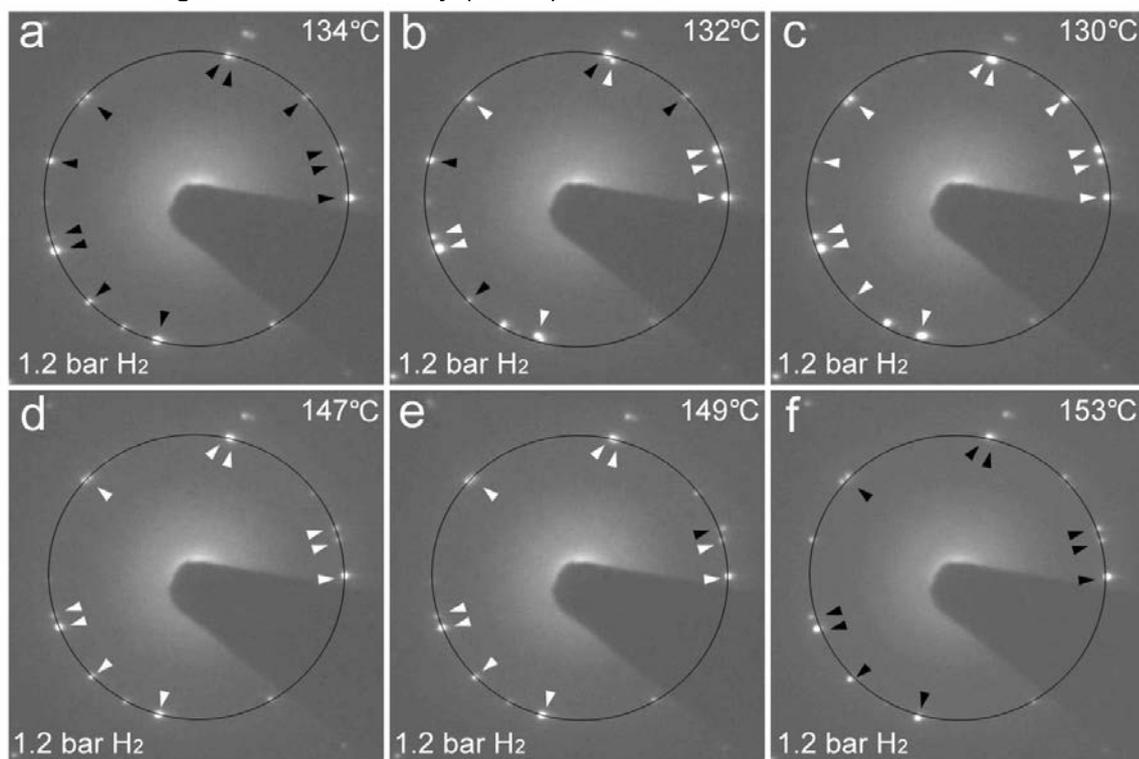


Figure 1. (a–c) SAED patterns of a few Pd particles taken at 1.2 bar and 134 °C, 132 °C and 130 °C, respectively. (d–f) Taken at 1.2 bar and 143 °C, 149 °C, and 153 °C, respectively. The (220) reflections indicated by the white and black arrows are from the α - and β -phases, respectively.

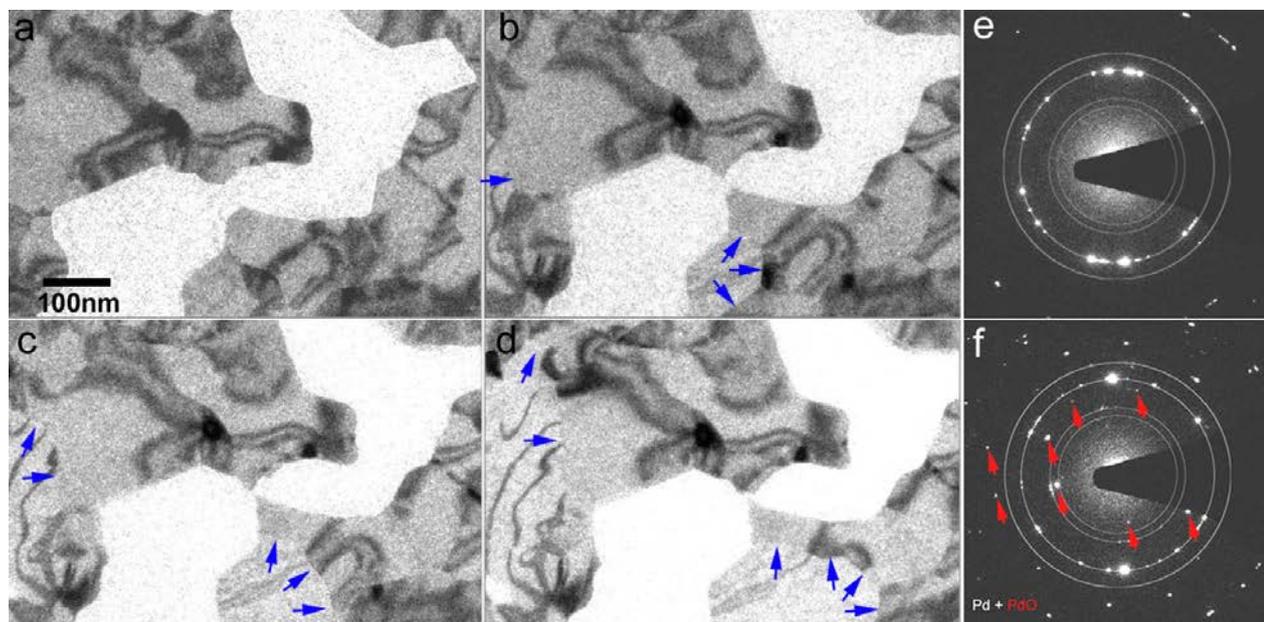


Figure 2. (a–d) Bright-field images taken during oxidation of Pd at 0.3 bar O_2 at 600 °C. (a) 0 sec, (b) 22 sec, (c) 32 sec and (d) 54 sec. Oxidation fronts are visible as faint but sharp line contrast indicated by blue arrows. Relatively broader and darker contrast areas are mainly due to bending contours. (e) and (f) SAED patterns taken from the Pd island in the right bottom corner before and after oxidation, respectively. The white rings correspond to the diffraction rings of the FCC lattice of Pd. The red arrows correspond to the reflections caused by tetragonal PdO.