Gaseous Environmental TEM: a complementary study of nanocatalysts using a combined "dedicated ETEM vs E-cell" approach

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Since a few decades, technological developments have allowed various approaches to perform environmental studies under gas at high temperature in a TEM (Transmission Electron Microscope). On the one hand, a dedicated ETEM (Environmental TEM) consists in a differential pumping system around the pole pieces region in the column of the microscope; on the other hand, a closed E-cell (Environmental cell) mounted on a specific sample holder allows to confine the environmental atmosphere between two thin membranes sealing the object of interest. It is the purpose of the present contribution to perform a complementary study on some nanocatalytic systems using both tools: a dedicated objective Cs-corrected 300 kV FEI-TITAN ETEM equipped with a DENS Solutions 'Wildlfire' heating specimen holder, and a Protochips 'Atmosphere' E-cell mounted on a probe Cs-corrected 200 kV JEOL 2100F. Both microscopes are also equipped with a Tridiem GIF (Gatan Imaging Filter) and EDX (Energy-Dispersive X-ray spectroscopy) analyzers.
We report on metallic (Pd and Ni) nanoparticles supported on delta- alumina. These systems of high interest for heterogeneous catalysis have been studied in conditions approaching their working conditions up to about 900°C either under oxidizing and reduction atmospheres to study the calcination and reduction steps while preparing the catalysts, or under a gas mixture H_2/CO_2 to study the methanation of CO_2.
Two sets of results will be presented: firstly, and despite the intrinsic differences between the two microscopes, comparative results that can be obtained under very similar imaging (low mag and high resolution conventional TEM and HAADF: High Angle Annular Dark Field, and bright field STEM: Scanning TEM), temperature and low pressure (typically around 10 mbar) conditions as reported in figure 1. Secondly, complementary results as permitted by the specific performances of each approach concerning EELS (Electron Energy-Loss Spectroscopy) analysis, tomography and studies at atmospheric pressure [1].

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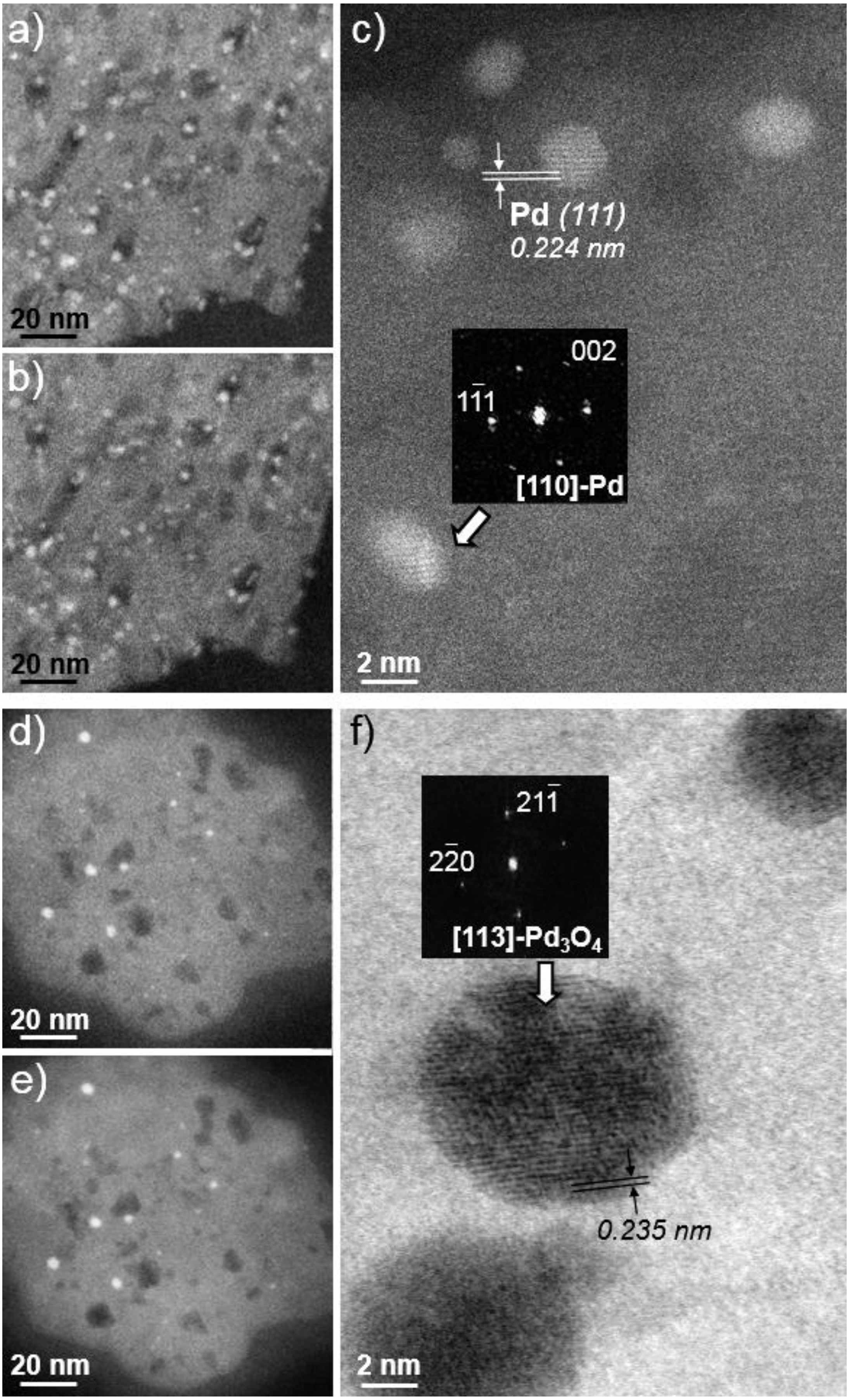

Figure 1: ETEM (a-c) and E-cell (d-g) HAADF-STEM results on the Pd / delta-Al_2O_3 system. a-b): images corresponding respectively to the calcination state (11.8 mbar of oxygen at 450°C after 1h15') and the reduced state (11 mbar of hydrogen at 200°C after 1h40'); c): High resolution dark field STEM image showing metallic Pd nanoparticles identified during the in situ reduction. d-e) E-cell observations similar to a-b) respectively under 12 mbar of oxygen at 450°C after 1h13' (d) and 12 mbar of hydrogen at 200°C after 1h. f): E-cell High resolution bright field STEM image showing oxidized Pd nanoparticles identified during the in situ calcination.