

Combining environmental gas TEM and electron tomography

BAAZIZ, W.¹, BAHRI, M.¹, GAY, A.², VALETTE, S.³, ERSEN, O.¹ and Hirlimann, C.⁴

¹ IPCMS CNRS/UNISTRA, France, ² IFP-Énergie Nouvelle, France, ³ CREATIS - CNRS - INSA Lyon, France, ⁴ IPCMS-CNRS, France

The combination of several complementary TEM-based techniques on the very same nano-objects is one of the most suited tools for determining the structural characteristics and properties of the analyzed specimens. In the case of metal-based nanoparticles with potential as catalysts, the most important aspect is their structural evolution under activation and reaction conditions. These can be directly determined by making use of in-situ gas TEM in an environment as close as possible to that of regular catalytic reactors; however, when using only 2D projection images, the analysis of the in-situ data requires a significant number of hypotheses on the 3D characteristics of the particles such as for example the external shape, faceting and localization on a complex support. We present here a combination of environmental gas TEM at atmospheric pressure with electron tomography performed on the chosen particles before and after the thermal treatment under the reactive gas at atmospheric pressure. The measurements were done on a JEOL 2100 F microscope equipped with tomography capabilities and an Atmosphere™ gas cell from the Protochips Company.

The system of interest is the core-shell Pd@SiO₂ in which Pd particles with size between 15 and 20 nm and shapes octahedral or icosahedral, are confined inside a porous silica shell. Some typical areas containing such nanostructures were followed under H₂ gas at atmospheric pressure during a thermal heating up to 400°C with tomographic data acquired before and after the thermal treatment. The first observation was the formation of new Pd particles with a size of 1±0.5 nm inside the silica shell due to a diffusion mechanism activated around 300°C. One of the original findings was the evidence of a very strong thermal dependence of the shape and faceting parameters of the initial crystallographic structure of the particles. The single crystal octahedral NPs were found to be quite unstable: the thermally activated atomic diffusion leads to a decrease in the particle size and induces a high migration kinetic towards the silica shell. As a consequence, new palladium particles have been formed inside the shell and also on their outer surface. The icosahedral-polycrystalline NPs showed a better thermal stability with morphology and faceting globally unchanged: this can be explained by a significant diffusion effect "within" the particle, in agreement with the higher amount of crystallographic defects compared to the single crystal NPs. In this last case, new particles were observed only inside the silica shell and no additional sintering was evidenced.

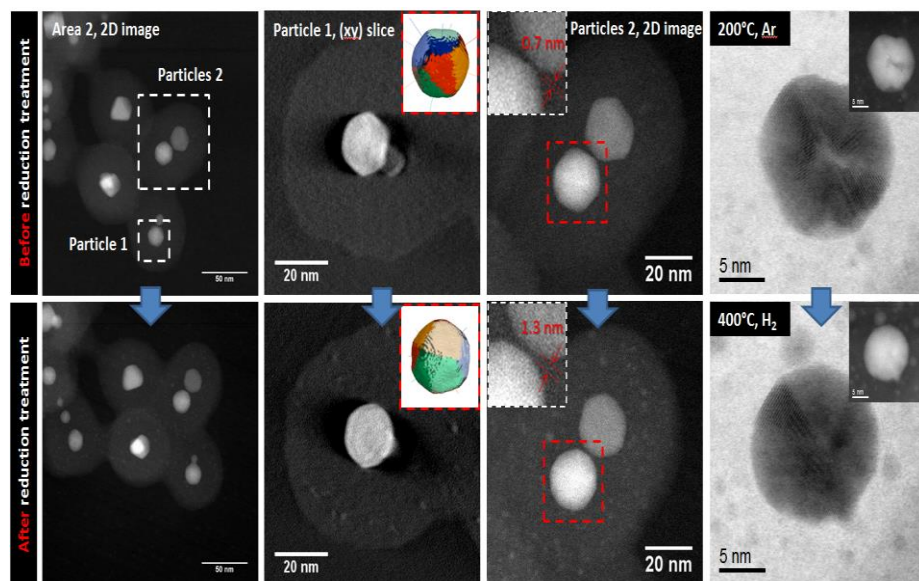


Figure1: Combined environmental TEM - electron tomography of second type Pd@SiO₂ nanostructures containing icosahedral multiple twinned Pd particles. *Top:* TEM data before the reduction treatment; *Bottom:*

after the treatment under hydrogen. *Left:* chosen area for the combined analysis, squares point to the particles analyzed in detail. *Middle:* corresponding slices extracted from the volume reconstructions of one nanostructure, before and after the treatment, illustrating similar facetings (inset) and the formation of new small Pd nanoparticles in the silica shell after the treatment. *Right:* thermal evolution of the nanostructure containing two Pd nanoparticles within the same shell.