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Very Fast Tomography in the (E)TEM to Probe Dynamics in Materials during Operando and In Situ Experiments

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In situ and operando Transmission Electron Microscopy (TEM) is now an important area of important developments to probe properties and dynamics in nanomaterials subjected to external stimuli of various kinds, such as temperature and gas, liquid, electrical biasing or mechanical straining for the most common applications. However, specific obstacles still limit the efficiency of those approaches to permit a quantitative and relevant characterization of true and not only model systems. The purpose of this contribution is not review all of them, among which one can cite spatial resolution, sensitivity, chemical analysis capabilities, irradiation (electron beam) effects, and time resolution: it is aimed here to focus on the question of 3D information. Very intuitively, acquiring data giving access to a 3D knowledge at a pertinent scale must be a fast process as compared to the speed at which the sample evolves during the in situ or operando experiment.

We will show here the strategy recently developed at CLYM (Lyon F) to follow morphological changes of nanomaterials studied under gas at high temperature in a dedicated Environmental TEM (objective Cs-corrected FEI TITAN ETEM 80-300 kV) equipped with a CMOS-based 4K OneView camera from Gatan and a Wildfire S5 heating holder from DENS Solutions. The basic idea is to perform conventional tilt series acquisition as in conventional electron tomography, but speeding up both the sample rotation and the image recording to allow full data acquisitions in a few seconds (typically 4-10 seconds for a 140° rotation amplitude as permitted by the goniometer and camera performances) [1]. This strategy is today restricted to bright field imaging in conventional TEM since modern fast camera allow very short exposure times (a few ms or below) leading to a considerable gain of time and further enabling most of sample drifts and induced blur effects to be minimized if not suppressed. Such a fast operando nano-tomography offers two main advantages in terms of 3D characterization: firstly, it insures that no significant morphological changes occurs during the acquisition itself, leading to relevant tomograms. Secondly, it offers a tremendous gain of time during a complete treatment allowing 3D snapshots to be acquired, thus making it possible to follow the kinetics of the evolution of the same object along several hours and possibly under different temperatures and gases within a reasonable TEM session and without too much drastic irradiation [2].

Figures 1 and 2 illustrate applications mainly in the field of heterogeneous catalysis. One of the advantages of gaseous ETEM applied to nanocatalysts is that one can more or less slow down the speed of some reactions, like diffusion-based processes such as oxidation or reduction phenomena, with the control of both temperature and gas pressure. Accordingly, the required speed of the 3D acquisition may be adapted between a few seconds to even one or two minutes, which is then a comfortable degree of freedom to adapt the quality of data and the total duration of the in situ 3D analysis.

We will also address technical aspects of this approach by considering current limitations and adopted solutions especially regarding the mechanical instabilities (drifts and any kind of blur effects) of the sample (holder) during the rotation [3]. As a perspective we will also briefly discuss how we can dream of applying this fast tomography approach to electron sensitive materials and other kinds of in situ TEM experiments, and especially mechanical solicitations, which are certainly among the most challenging ones in this respect [4].

References :

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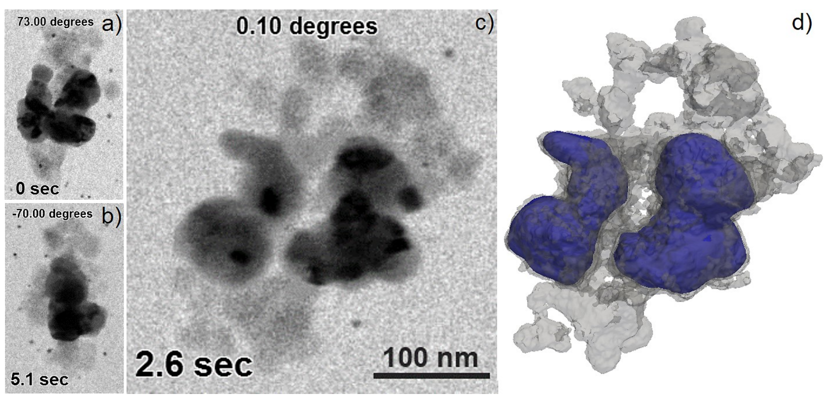

Figure 1. ETEM Fast tomography of a soot-ZrO_2 aggregate at 300°C under 5 10-5 mbar of oxygen. a): first projection at 73°, b) last projection at -70° over 511 images recorded at 100 fps (total recorded time 5.1 seconds), c) projection at zero tilt and d) corresponding 3D model of the tomogram reconstructed with an optimized SIRT-based algorithm [3].

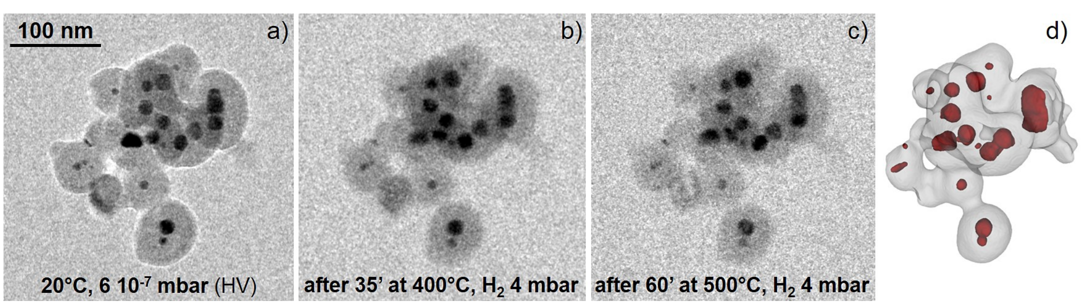

Figure 2. ETEM study of the resistance to sintering of Pd nanocatalysts (in dark) encapsulated in SiO_2 beads (grey areas) during a reduction treatment under hydrogen. a)-c): Zero tilt images of an aggregate at different temperatures and under different atmosphere conditions as indicated. d) : typical 3D model of the last state (c) after a tomographic acquisition of 7 seconds between 72 and -71°; tomograms have been obtained similarly at each state for a total beam exposure time less than 30 seconds.