Nano-Tomography in Environmental TEM: towards a fast 3D characterization of the evolution of nano-materials under dynamic gas and temperature conditions

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1. INTRODUCTION

Modern environmental Transmission Electron Microscopes (ETEM) enable chemical reactions to be directly observed, which opens wide perspectives in the operando characterization of nano-materials. However, morphological features are essentially missing in 2-dimensional observations, thus nano-tomography under environmental conditions is a new promising challenge. Obviously, the essential condition to achieve this goal is to run fast tilt series acquisitions as compared to the kinetics of the reactions which are followed in situ in the microscope.

This contribution will show that such experiments are possible, and we will present results obtained on the same object followed in 3D at different temperatures under gaseous environments in a Cs-corrected ETEM (FEI-TITAN).

2. RESULTS

2.1 Simulations

Firstly, simulations were performed on ghost models in order to appreciate the influence of the goniometer rotation speed during image acquisition on their quality (sharpness and blurring effects). We used a typical TEM micrograph of the nano-objects of interest (see section 2.2) as a starting 2D model. Their 1D projections were then calculated according to different conditions intending to reproduce the effects of a continuous tilt during the acquisition. Typical results are illustrated by figure 1 and 2.

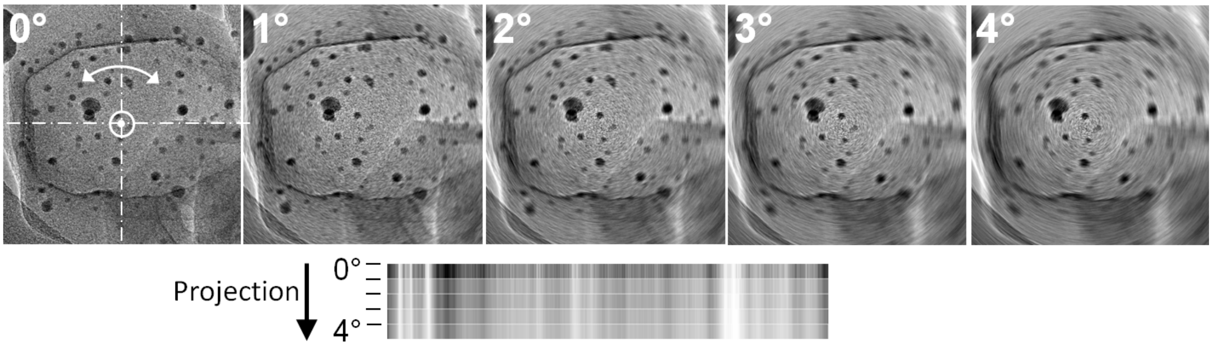

Figure 1. The top line shows the ghost model used for simulations (Ag nanoparticles in a hollow silicate cage). The first image labeled 0° is the starting 2D model perpendicular to the tilt axis; other images (1 to 4°) are calculated images assuming the indicated angular rotation during the acquisition as it will occur when rotating continuously the goniometer during a real acquisition in the microscope. The bottom picture shows the projections of the different top images (for better visibility, each 1D-projection has been repeated over several pixels in height).

Figure 1 shows that even if images are acquired with a high rotation speed of the goniometer, the resulting motion-blur recorded in the projection does not produce a significant artifact as compared to the correct projection without any motion (the 0° projection from the 0° image). To give an order of magnitude, a 120° rotation which would be performed in 1 minute with acquisition of images every second without interrupting the rotation would lead to an angular blur of only 2° in each image, which is clearly acceptable, although somewhat subjective range.

Figure 2 compares reconstructions using different conditions; it can be seen that the reconstruction obtained from a continuous tilt series leading to a 2° blur in each projection is not very different form that obtained from the conventional step-by-step acquisition scheme applied to the same total angular amplitude.

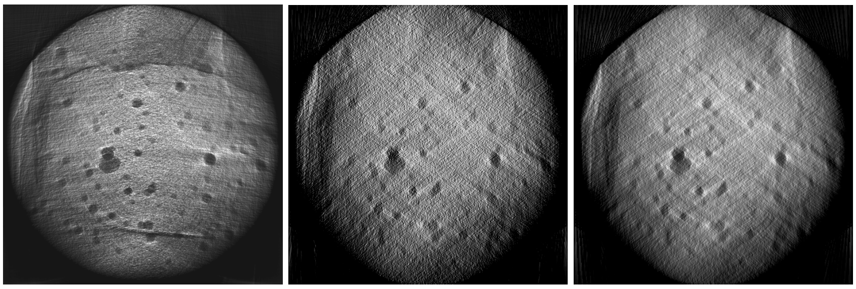

Figure 2. Typical reconstructions performed by Weighted Back Projection. Left: ideal reconstruction over -90-+90° with a step of 0.1° (1801 images); middle: conventional tomographic series between -60 and +60° with a step of 2° (61 images); right: reconstruction from a continuous tilt series leading to a blur of 2° per image.

2.2 Experimental ETEM results

A typical application of the environmental Nano-tomography is illustrated by figure 3. The calcination of hollow silicates containing silver nanoparticles was performed under oxygen partial pressure (up to 2 mbar) and at high temperature (up to 500°C) in the ETEM. These experiments have allowed to quantify accurately the evolution of the Ag NPs, which first coalesce in a medium temperature range to migrate out of the cages when they become oxidized.

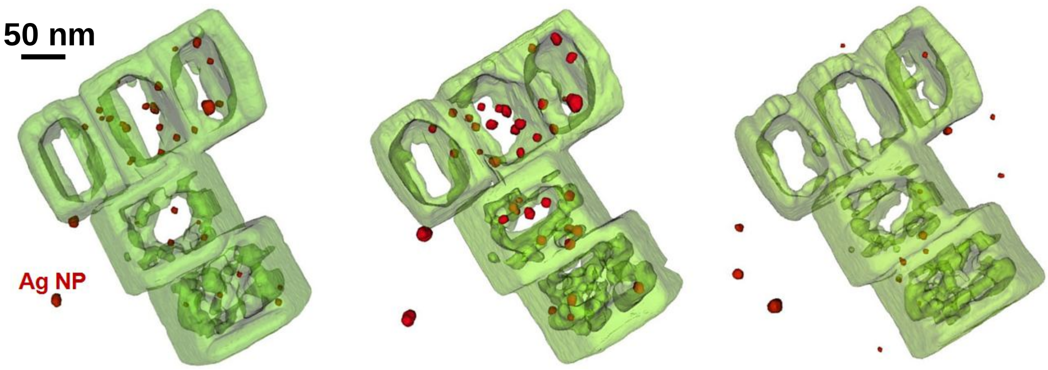

Figure 3. Models obtained from the volumes reconstructed in operando ETEM tomography. The experimental series were acquired at 20°C under high vacuum, 280°C and 450°C at 1.5 mbar of O_2 (respectively from left to right). The continuous tilt series were all recorded between -25° and 42° and respectively in 121, 106 and 116 seconds.

3. CONCLUSION

The present contribution demonstrates that rapid acquisition can lead to valuable results in order to provide 3D information on samples studied under dynamic conditions such as typically catalysts studied in an Environmental TEM. This rapid tomography approach can also be a great interest for beam sensitive samples where the material is generally not able to bear a long exposure to the electron beam without any specific and sometimes hazardous pre-treatment or preparation [1].

REFERENCES

[1] The CLYM (Consortium Lyon - St-Etienne de Microscopie, www.clym.fr) is acknowledged for its guidance in the ETEM project which was financially supported by the CNRS, the Région Rhône-Alpes, the 'GrandLyon' and the French Ministry of Research and Higher Education. The authors thank their colleagues from the University of Lyon S. Li, A. Tuel and D. Farrusseng (IRCELYON) for the synthesis of materials, and M. Aouine, F. Cadete Santos Aires (IRCELYON), N. Blanchard (ILM) and C. Langlois (MATEIS) for their technical contributions.