Towards Operando and real time 3D analysis of Nanomaterials in Environmental TEM

Thierry EPICIER

Université de Lyon, INSA-Lyon, UCBL Lyon 1, MATEIS, UMR 5510 CNRS, 7 Avenue Jean Capelle, 69621 Villeurbanne Cedex, France.

In the last decade, Environmental Transmission Electron Microscopy (ETEM) has become a new sharp blade of the 'TEM' Swiss Army knife for studying materials at the nanoscale in almost operando conditions. Spectacular technological improvements have been made for both dedicated ETEMs and E-cells [1, 2], enabling today to follow a chemical reaction under gas and in temperature down to the atomic level. Doing so, one of the scientific locks to be lifted is the temporal resolution required to follow the dynamic of the process to be studied. Another challenging topic is the need for 3D information during the evolution of the object when exposed to reactive conditions and more ambitiously, mechanical stimuli.

We will survey here several studies related mostly to nanocatalysts and conducted on the 80-300 kV Cs-corrected FEI-TITAN ETEM installed at CLYM in Lyon in 2013. In most of experiments, a Wildfire heating-holder (DENSsolutions) was used with 1300°C compatible Si/SiN_x nanochips. Its high tilting capability of ± 72° allows in situ nano-tomography. A high speed Oneview camera from Gatan capable of acquisition rates at several hundreds frames per second (100 fps in 2K) allows fast 'tilting' tomography at the minute and even second level [3], which opens the way to quantitative 3D kinetics studies of nanocatalysts under operando conditions. Illustrated works concern:

- The oxidation of soot by YSZ catalysts in the contest of Diesel motors depollution [4]
- A Quantitative atomic mobility at {100} surfaces of ceria (cerium dioxide CeO_2) nanocubes under different atmospheres, see figure 1 [5].
- Preliminary in situ nanocompression of nanoparticles (depending on time)

During this presentation, attention will be paid to the influence of the electron beam on the observed processes (irradiation effects). Some clues will be discussed regarding the development of routine '5-10 seconds' fast operando nanotomography in the ETEM. Big data issues (regarding storage and more importantly image processing) will also be evoked [6].

References

[1] J. Jinschek, *Chem. Commun.*, **50** (2014), 2696-2706; E.D. Boyes, P. Gai, *C. R. Physique* **15** (2014), 200-213; P.A. Crozier, T.W. Hansen, *MRS Bull.* **40** (2015), 38-45; S Takeda, Y Kuwauchi, H Yoshida, *Ultramicroscopy* **151** (2015), 178-190.
[2] "Controlled Atmosphere Transmission Electron Microscopy", ed. T.W. Hansen, J.B. Wagner (Springer, New York), (2016), 332 p.
[3] A. Serve, T. Epicier, M. Aouine, F.J. Cadete Santos Aires, E. Obeid, M. Tsampas, K. Pajot, P. Vernoux, *Appl. Catal. A*, **504** (2015) 74-80.
[4] L. Roiban, S. Li, M. Aouine, A. Tuel, D. Farrusseng, T. Epicier, *J. of Microscopy* **269**, 2 (2018), 117-126.
[5] M. Bugnet, S. H. Overbury, Z. Wu, T. Epicier, *Nano Letters*, **17** 12 (2017), 7652-7658.
[6] This work is largely based on ongoing projects involving several colleagues at Univ. Lyon: S. Koneti, L. Roiban, M. Bugnet, L. Joly-Pottuz, K. Masenelli-Varlot from MATEIS, INSA-Lyon; M. Aouine, F.C. Santos Aires, Philippe Vernoux, Diego Lopez-Gonzalez from IRCELYON, UCBL; T. Grenier, H. Banjak, V. Maxim from CREATIS, INSA-Lyon; I. Jenei, F. Dassenoy from LTDS, ECL).
The support of ANR through the project 3DCLEAN n°15-CE09-0009-01 is gratefully acknowledged. Thanks are due to CLYM (www.clym.fr) for the access to the Environmental microscope which was founded through a CPER project funded by the Rhône-Alpes region, the 'Great Lyon' and the CNRS.

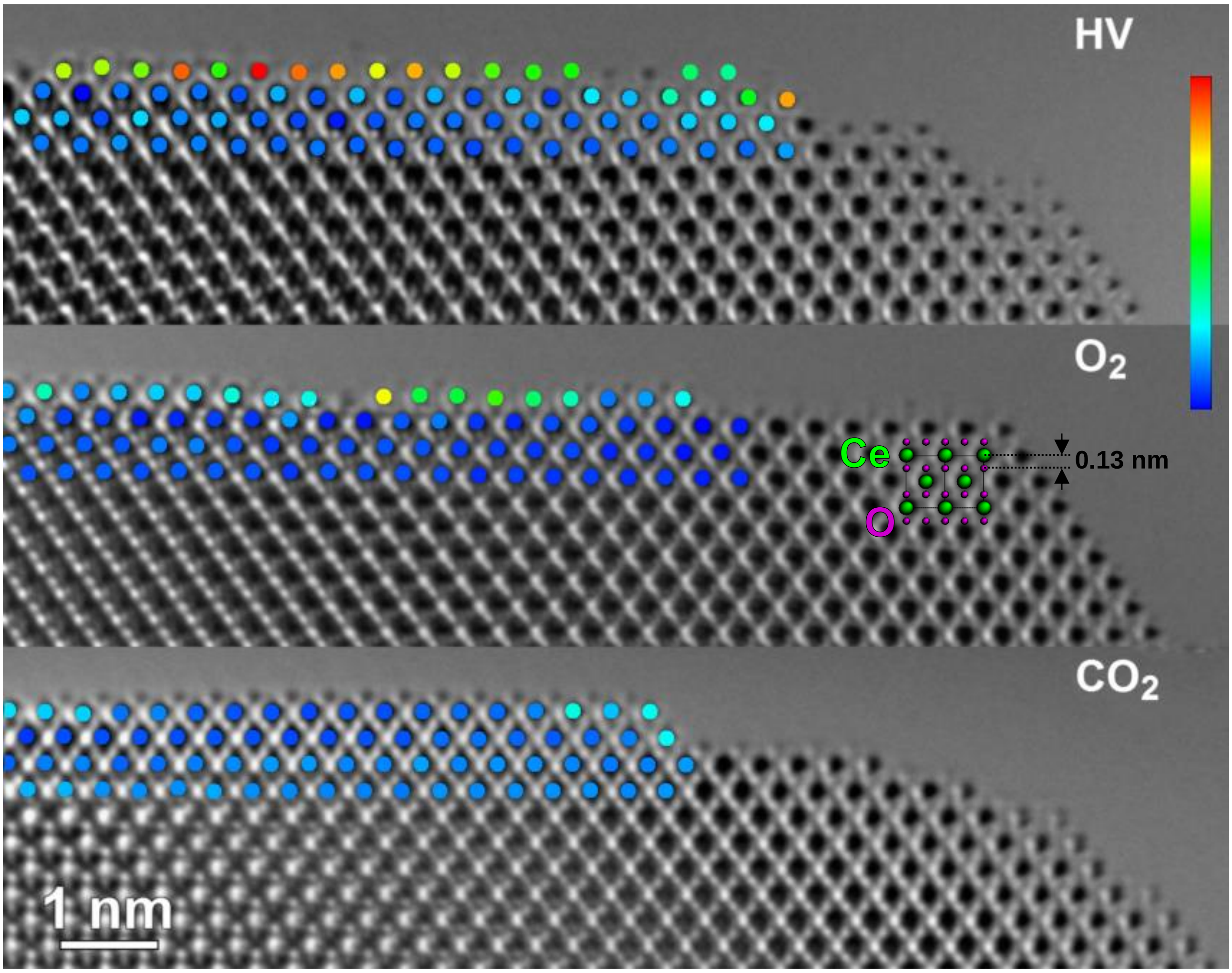

Figure 1: ETEM study of the atomic mobility on (100) facets of ceria (CeO_2) seen edge-on in the [011] azimuth. From top to bottom: in vacuum, under O_2 and under CO_2 respectively. Each image is the first frame of video sequences of 420 images recorded in the high-resolution mode at 25 fps. Superimposed colour dots represent the atomic mobility as measured during the spanned timeframe (see details in [5]); a much higher surface mobility (red) is observed under vacuum in comparison with oxidizing gaseous environments.