

The Merits of *In situ* Environmental STEM for the Study of Complex Oxide Catalysts at Work

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While high resolution scanning transmission electron microscopy (STEM) is a well-established imaging method for the study of complex functional oxides via precise quantification of atomic intensity and displacements to enable the identification of novel phenomena[1], it is so far mainly limited to high vacuum imaging. However, some complex oxides, for example the MoVNbTe oxide (M1 phase), are excellent heterogeneous catalysts whose state and reactivity is dependent of the reaction environment. Environmental imaging is thus the only characterization tool that can offer insights into their atomic-sites specific behavior during reactions. In this work, we developed an *in situ* ESTEM protocol to investigate the working structure of the M1 complex oxide catalyst at the atomic scale. Employing a dedicated Titan ETEM operated at 300kV with a differentially pumped (DP) gas cell, a low-angle annular dark field ESTEM setting ($\alpha = 9.9$ mrad and $\beta = 20.9 \sim 71$ mrad) offers directly interpretable atomic images with intensity $I \sim Z^\alpha$ ($\alpha \sim 1.1$). More importantly, as shown in Fig.1, the atomic contrast remains sharp and the atomic SNR (signal-to-noise ratio) of M1 remains above 7 ($>$ the Rose criterion) up to 10 mbar in N₂. These observed low gas-induced scattering noise and high sample SNR are enabled by the nature of incoherent annular dark field STEM imaging[2], which makes ESTEM the optimum technique for imaging complex oxides in gases.

With this persisting sample SNR in gas obtained by ESTEM, atomic image quantification that conventionally performed to vacuum images is now feasible to environmental images for complex oxides. Fig. 2 presents the line profiles performed to quantify the changes in Te atomic intensity and Te-Te atomic distance at the M1 active centers, and the outcomes of these atomic quantifications as a function of the gas environments at reaction temperature 400°C. Aided with STEM image simulation, the observed decrease in Te atomic intensity as well as the Te-Te distance suggest Te reduction and depletion with time on stream. More interestingly, the degree of Te depletion, and the mean oxidation state of the remaining Te (as indicated by Te-Te distance) were found in dependent of the oxygen partial pressure of the gas feed (He < ethane/O₂ /He < O₂). DFT calculations suggest that this slightly reductive atmosphere during ethane selective oxidation can lead the emission of Te and O species from the 1D channels, thus depleting the n-type character of the M1 surface. This electronic structure change facilitates a new cooperative activation mechanism for ethane oxidization over complex oxides. The application of *in situ* ESTEM free of intensity loss while maintaining a good SNR at the atomic resolution opens up opportunities for quantitative investigation of functional nanomaterials with

complex structures in technologically relevant environments [4].

References:

- [1] SJ Pennycook, M Varela, *Journal of Electron Microscopy* **60** (2011), S213.
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 [3] Y Zhu *et al*, *Journal of the American Chemical Society* **139** (2017), p. 12342.
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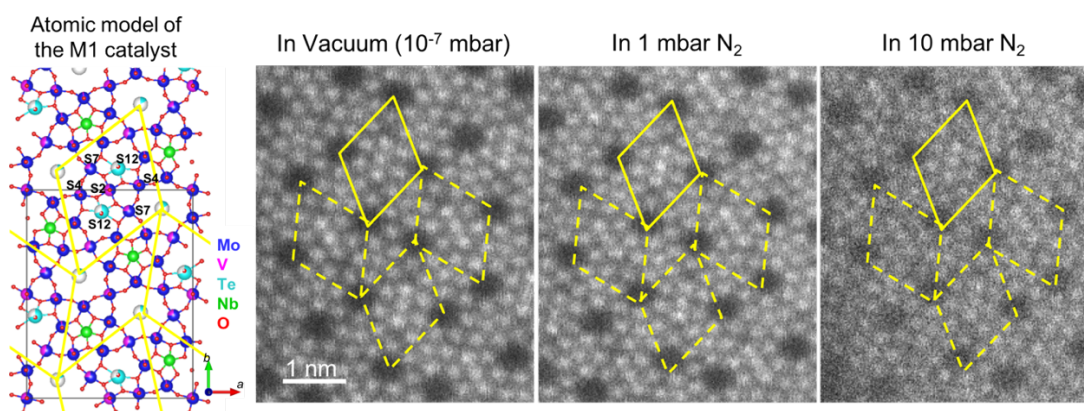


Figure 1. The Atomic model of the MoVNbTe complex oxide (M1 phase) catalyst, along with atomic ESTEM images (raw) of its (001) basal plane in microscope vacuum, in N₂ gas of 1 mbar and 10 mbar.

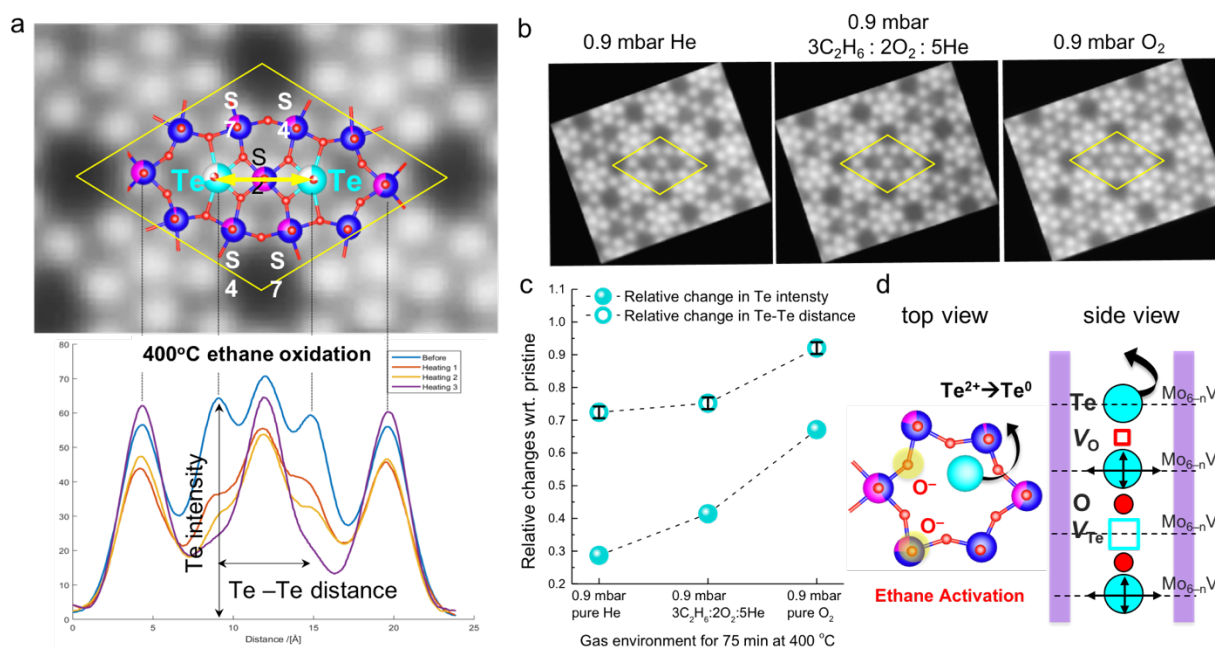


Figure 2. a) Schematics of the line profiles performed to quantify the changes in Te atomic intensity and Te-Te atomic distance. b) Averaged ESTEM images of three M1 catalyst particles after 75 min at 400°C in three different gas environments. c) Normalized Te intensity and distance as a function of gas feed. d) Schematic rendering of the cooperative activation process based on ESTEM observations.