

## Visualizing and Quantifying the Cationic Mobility at {100} Surfaces of Ceria: Application to CO<sub>2</sub> Adsorption/Desorption Phenomena in the Environmental Transmission Electron Microscope

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Environmental transmission electron microscopy in a dedicated instrument allows ultimate spatial resolution with chemical analysis capabilities similar to high resolution transmission electron microscopes (HRTEMs), while retaining partial pressures up to 20 mbar around the specimen [1]. Such instruments provide an optimized approach to study the early stages of catalytic reactions, which can start from very low partial pressure, at the atomic-scale.

In this work, gas-surface interactions induced by the partial pressure and temperature within a dedicated FEI Titan 80-300 Cs-corrected environmental transmission electron microscope (ETEM) are investigated on CeO<sub>2</sub> nanocubes. Ceria is a fundamentally interesting compound, which is widely studied in the field of heterogeneous catalysis, both as catalyst and catalyst support, at the laboratory scale and for industrial applications [2]. In high vacuum TEMs, ceria is prone to electron-beam induced reduction, hence limiting, and sometimes preventing, the analysis of ceria-based materials. However, proper control of the atmosphere in the ETEM allows tuning the redox state of CeO<sub>2</sub> [3]. Furthermore, atoms at {100} surfaces of ceria are inherently mobile in high vacuum, and their mobility must be assessed for a better understanding of the temporal evolution of the atomic structure of facets [4, 5]. Nevertheless, in-depth atomic scale surface analysis in environmental conditions (gas, pressure, temperature) is lacking, and is now addressed here.

Recently, we have shown how the mobility of Ce and O atoms could be directly visualized using HRTEM under various atmospheres [5]. Using a last generation fast CMOS Gatan Oneview<sup>TM</sup> detector, a frame rate of 25 frames/s (4k\*4k) is sufficiently high to detect the mobility of Ce and O surface atoms, and quantify the mobility of Ce cations as shown in Figure 1a. In thin surface regions of CeO<sub>2</sub> nanocubes, where kinematic conditions are fulfilled, the atomic column occupancy is taken as proportional to the inverse of the intensity of “black atoms” atomic columns in HRTEM images. The mobility of cations is evaluated under HV, O<sub>2</sub>, and CO<sub>2</sub> atmospheres, and decreases strongly when the atmosphere changes from HV to O<sub>2</sub>, and even further when CO<sub>2</sub> is introduced around the specimen in the ETEM. The presence of adsorbed carbonates at the surface is confirmed by electron energy-loss spectroscopy when the surrounding atmosphere is CO<sub>2</sub>. Subtle effects such as variations of atomic mobility along the facet are observed, in agreement with previous theoretical predictions [6].

The evaluation of the atomic mobility is further used as a tool to investigate CO<sub>2</sub> adsorption/desorption phenomena at {100} surfaces of CeO<sub>2</sub>. The desorption of adsorbed carbonates is detected through the recovery of {100} atomic mobility when increasing the temperature, as shown in Figure 1b. Differences are observed between the desorption temperature at reduced surfaces vs stoichiometric ceria. To confirm these results, *in situ* diffuse reflectance FT-IR spectroscopy (DRIFTS) [7] was undertaken under similar atmospheres and temperatures, as shown in Figure 1c. Both data sets appear to be well-consistent.

This work demonstrates the direct visualization of the atomic scale mobility at {100} surfaces of ceria in the environmental TEM, its quantification, and its application to the monitoring of adsorption/desorption phenomena of CO<sub>2</sub>. These findings open a field of study for direct visualization and control of atomic scale phenomena at surfaces, such as single atom catalysis and interaction of molecular species with solid surfaces [8].

## References:

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