Adsorption/desorption phenomena of carbonates at {100} surfaces of ceria revealed from direct visualization and quantification of atomic mobility 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 image-corrected environmental TEM (ETEM) are investigated on CeO_2 nanocubes. In high vacuum (HV) TEMs, CeO_2 is prone to electron-beam induced reduction, hence limiting or preventing the analysis of ceria-based materials. However, proper control of the atmosphere in the ETEM allows tuning the redox state of CeO_2 [2]. Furthermore, atoms at {100} surfaces of CeO_2 are inherently mobile in HV, and their mobility must be assessed for a better understanding of the temporal evolution of the atomic structure of facets [3, 4]. 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 [4]. Using a fast CMOS Gatan Oneview™ detector, a frame rate of 25 frames/s (4k*4k) is sufficient to detect and quantify the mobility of Ce surface atoms (Fig.1). In thin surface regions, 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 decreases from HV to O_2, and even further when CO_2 is introduced around the specimen in the ETEM. In the latter case, the presence of adsorbed carbonates at the surface is confirmed by electron energy-loss spectroscopy. Subtle effects such as variations of atomic mobility along the facet are observed, confirming previous theoretical predictions [5].

The evaluation of the atomic mobility is further used as a tool to investigate CO_2 adsorption/desorption phenomena at {100} surfaces of CeO_2. The desorption of adsorbed carbonates is detected through the recovery of atomic mobility when increasing the temperature (Fig.2a). Differences are observed between the desorption temperature at reduced surfaces vs stoichiometric ceria, as confirmed by *in situ* diffuse reflectance FT-IR spectroscopy (Fig.2b).
This work demonstrates the direct visualization of the atomic scale mobility at {100} surfaces of ceria in the ETEM, its quantification, and its application to the monitoring of adsorption/desorption of CO_2. 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.

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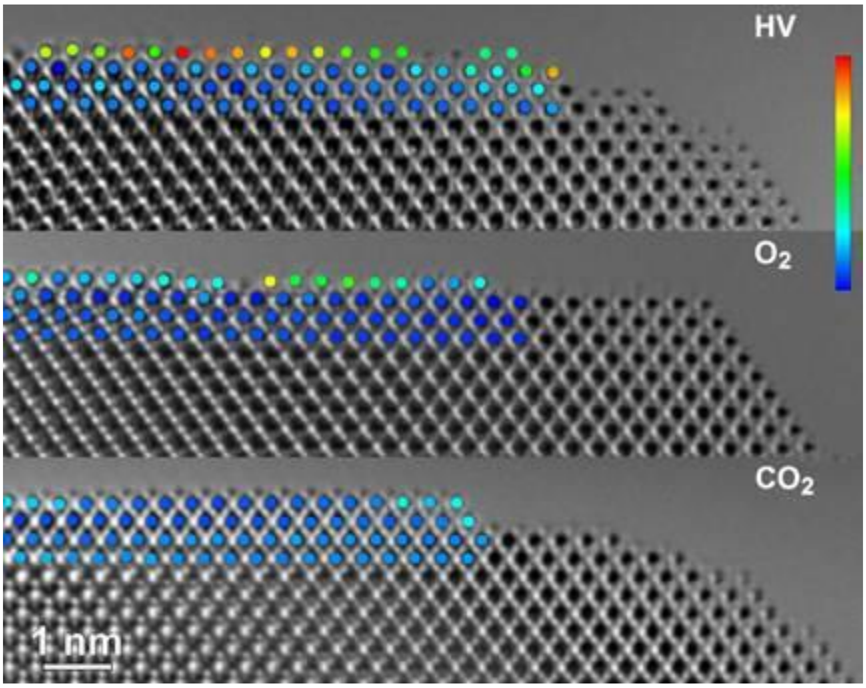

Figure 1. ETEM study of the atomic mobility on (100) facets of ceria (CeO_2) seen edge-on along [110]. Each image is the first frame of video sequences of 420 images recorded in the HR mode at 25 fps. Superimposed colour dots represent the atomic mobility as measured during the spanned timeframe (see details in [4]); a much higher surface mobility (red) is observed under HV in comparison with oxidizing gaseous environments.

a. b.

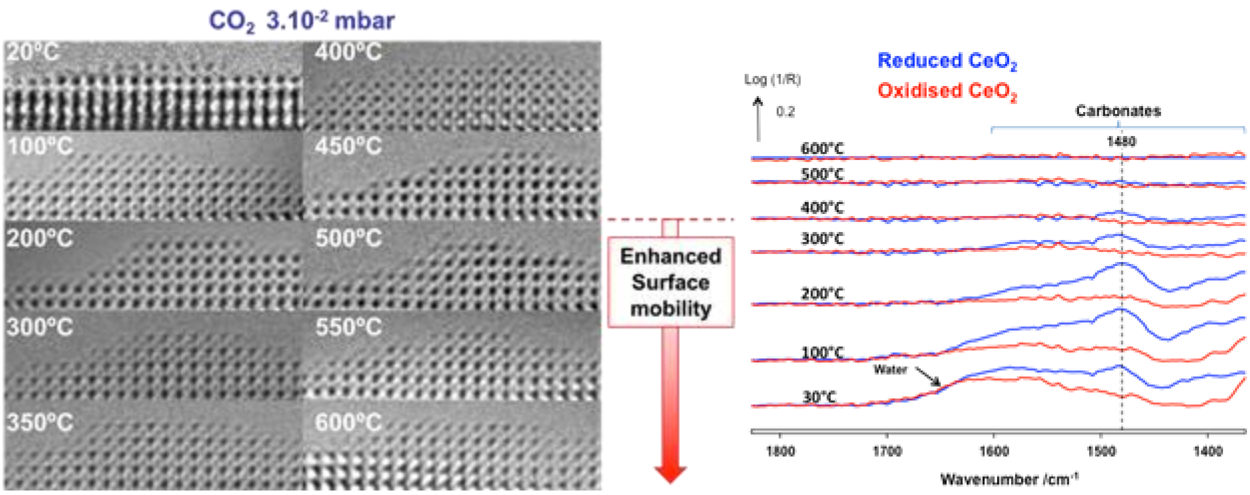

Figure 2a. Individual frames recorded on pre-oxidized CeO_2 at different temperatures, with CO_2 partial pressure; the atomic mobility is recovered at 500C, corresponding to the desorption of carbonates. **b.** Confirmation of b. from *in situ* DRIFTS spectra collected over pre-reduced (blue), and pre-oxidized (red) CeO_2, in the presence of 100 ppm of CO_2 at various temperatures.