Quantitative study of the adsorption / desorption of CO_2 molecules at {100} ceria surfaces *via* atomic scale Environmental Transmission Electron Microscopy (ETEM) and Diffuse Reflectance FT-IR Spectroscopy (DRIFTS)

Matthieu Bugnet[a*], Steven H. Overbury[b], Zili L. Wu[b], Francisco Cadete Santos Aires[c], Frederic Meunier[c], Thierry Epicier[a]

[a] *University of Lyon, INSA-Lyon, UCBL Lyon 1, MATEIS, UMR 5510 CNRS, 69621 Villeurbanne Cedex, France.*
[b] *Chemical Science Division, Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.*
[c] *University of Lyon, UCBL Lyon 1, IRCELYON, UMR 5256 CNRS, 69100 Villeurbanne, France.*

* matthieu.bugnet@insa-lyon.fr

Transmission electron microscopy (TEM) is a well-established characterization technique to combine bulk and surface analysis of solids at the nanoscale. With a dedicated Environmental TEM (ETEM), the effect of the atmosphere on the reactivity of surfaces exposed to gas and temperature can be investigated *in situ*.

Our work focuses on ceria (CeO_2), a fundamentally interesting and technologically important catalyst and catalyst support [1]. With a strong tendency to be reduced under the electron beam, CeO_2 is also a challenging material in a High Vacuum (HV) TEM column, and offers a perfect field of play for redox state control in the ETEM. Whereas the redox properties of CeO_2 have been widely studied in the TEM using electron energy-loss spectroscopy (EELS), in-depth atomic scale surface analysis under environmental conditions is lacking and is now addressed here.

CeO_2 nanocubes [3] were observed in a dedicated Cs-corrected FEI Titan ETEM, equipped with a high-speed CMOS Gatan OneView^{TM} camera. In situ diffuse reflectance FT-IR spectroscopy (DRIFTS) was also performed using a setup described elsewhere [4].

The mobility of Ce and O atoms is monitored using high resolution TEM under various atmospheres, i.e. HV, O_2 and CO_2. A home-made image processing routine was developed to track and quantify the intensity of Ce columns, then the atomic mobility directly evidenced using video recording of atomic resolution 4Kx4K images at 25 fps [5]. The Ce mobility in HV is significantly higher on {001} surfaces than on other low-index {110} and {111} facets appearing at the edges of the nanocubes. Furthermore, the mobility decreases when the atmosphere changes from HV to O_2, then decreases even further when CO_2 is adsorbed on the surface as confirmed by EELS. The effect of temperature on the surface mobility under HV, O_2 and CO_2 is also investigated *in situ*. Significant differences in carbonate desorption temperatures were observed by DRIFTS between unreduced and reduced ceria, which are compared to ETEM results.

These findings open a field of study for direct visualization and control of atomic scale phenomena at surfaces such as adsorption and desorption of molecular species.

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