Ceria chemistry at the nano-scale

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Reducible oxide are particularly challenging to describe using theoretical chemistry/physics methods because they easily toggle between different oxidation states, so that both the electronic structure and the geometric structure are important. We are currently developing a *multi-scale approach* to unravel the chemistry of ceria (CeO_2 and CeO_{2-x}), going from DFT=> DFTB (tight-bindning DFT) => Force-field simulations (ReaxFF reactive force-field).

Our current application is ceria nanoparticles and the oxygen chemistry on them. The chemical composition, shape and structure of small metal-oxide nanoparticles (NPs) can be strongly affected by their surrounding environments. In a recent study [1], we demonstrated how reduced ceria nanoparticles could be stabilized in an oxidative environment through the adsorption of many O_2 molecules. Rather than being re-oxidized to form a CeO_2 nanoparticle, such reduced particles become supercharged with O_2^- species leading to a dramatically enhanced oxygen storage capacity.

In the current work, we study the chemical composition, shape and structure of ceria nanoparticles in reducing, oxidative and humid environments. We search for the global minimum structures using a force-field based evolutionary algorithm. From the initial screening, candidate structures are further geometry-optimized using density functional calculations and the effect of the environment is introduced through standard thermodynamic relations. Based on our calculations, we predict that small stoichiometric ceria nanoparticles will have a very limited stability range in both oxidative and humid environments. Instead, as illustrated in **Fig. 1**, the reduced ceria nanoclusters are stabilized through the adsorption of oxygen molecules in the form of superoxo species and water in the form of hydroxo species.

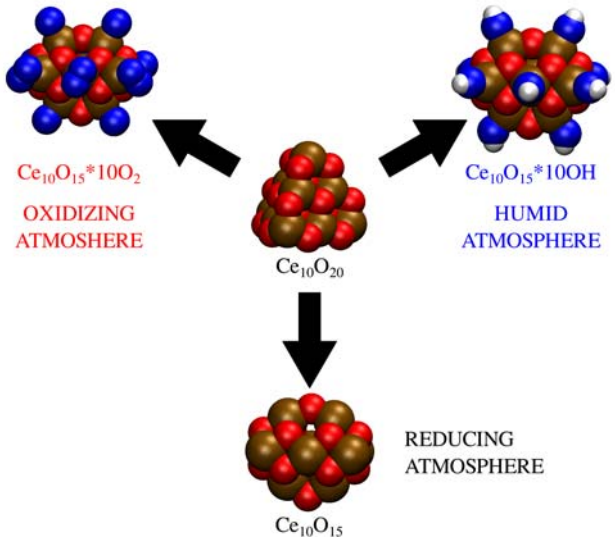

Fig. 1 Our calculations predict that stoichiometric clusters have limited stability and readily transform into reduced clusters in oxidizing, humid and reducing atmospheres. This is exemplified in this figure for the $Ce_{10}O_{20}$ (stoichiometric) and $Ce_{10}O_{15}$ (reduced) clusters.

References:

[1] Kullgren, J., Hermansson, K., and Broqvist, P., *J. Phys. Chem. Lett.* **4**, 604−608 (2013)