

Water interaction with CeO₂(111) and its defect structure

M. Verónica Ganduglia-Pirovano

Institute of Catalysis and Petrochemistry-CSIC, Madrid, Spain

Ceria surfaces are important for many applications, particularly catalysis. The importance relies to a large extent on its facile reducibility and the associated ability to release lattice oxygen with the control of the density and the nature of oxygen vacancies providing a means for tailoring the reactivity of ceria-based catalysts. Furthermore, water is present in every realistic environment and surface hydroxylation can have a significant effect on its reactivity. To this end, we apply density-functional theory (DFT) to study the reduced CeO₂(111) surface^[1,2] and the H₂O/CeO₂(111) system.^[3]

It has been generally accepted that the electrons left behind upon oxygen removal from CeO₂ surfaces, driving the Ce⁴⁺ → Ce³⁺ reduction, localize on cationic sites in next-neighbor distance to the defect. We apply DFT with the HSE06 hybrid functional as well as the DFT+U approach and predict that vacancies are likely to be bound to Ce⁴⁺ ions rather than to Ce³⁺ as priorly suggested.^[1] This prediction has been recently confirmed by means of STM imaging and spectroscopy and DFT based simulations.^[2] We further find that subsurface vacancies are energetically considerably more favourable than surface vacancies, and thus provide support for a recent experimental result.^[4] Defect-induced lattice relaxations are used to explain the findings.

For the H₂O/CeO₂(111) system, we apply DFT with the HSE06 hybrid functional as well DFT+U with van der Waals (vdW) density functionals and find that on the clean surface complete water dissociation can be ruled out, and water can be found either in a molecular state or as a hydroxyl pair. Both states are found to be consistent with the triangular protrusions associated with water in STM and AFM images.^[5,6]

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