Identifying Ce^{3+} sites at the CeO_2 (111) surface with water and AFM imaging

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Water interactions with oxygen-deficient cerium dioxide (CeO_2) surfaces are central to hydrogen production and catalytic redox reactions, but the atomic-scale details of how local defects influence adsorption state (either molecular or as a hydroxyl pair, Figs. 1a-b) and reactivity remain elusive. Here, we unveil how water adsorbs on partially reduced CeO_{2-x}(111) using cryogenic atomic force microscopy (AFM) with chemically sensitive, oxygen-terminated tips, combined with first-principles calculations [1]. Our AFM imaging (Fig. 1c) reveals water molecules as sharp, asymmetric boomerang-like features -radically departing from the symmetric triangular motifs previously attributed to molecular water. Strikingly, these features localize near subsurface oxygen vacancies, implicating local charge redistribution and lattice distortions in directing adsorption. While the imaging is carried out at low temperature to enable atomic resolution, water was introduced at room temperature, capturing configurations relevant to initial adsorption events in catalytic processes. Density functional theory identifies Ce^{3+} sites adjacent to subsurface vacancies as the thermodynamically favored adsorption sites, where defect-induced symmetry breaking governs water orientation. Force spectroscopy and simulations further distinguish Ce^{3+} from Ce^{4+} centers through their unique interaction signatures (Figs. 1d-e). By resolving how subsurface defects control water adsorption at the atomic scale, this work demonstrates the power of chemically selective AFM for probing site-specific reactivity in oxide catalysts, laying the groundwork for direct investigations of complex systems such as single-atom catalysts, metal-support interfaces, and defect-engineered oxides.

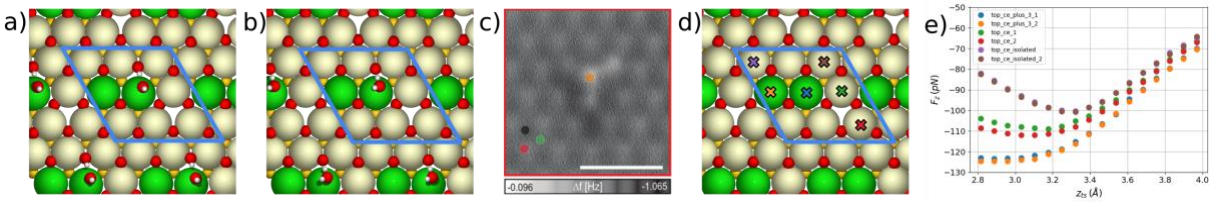

Figure 1. Dissociated (a) and molecular (b) water adsorption configurations (unit cell outlined in blue). (c) Experimental constant-height AFM image of a CeO_2(111) surface with adsorbed water. The three atomic sites of CeO_2 are identified: oxygen (red), cerium (white), and coordination vacancy (green), with water (orange) serving as a site marker. (d) Reduced CeO_{2-x}(111) surface sites with corresponding DFT force vs tip-surface distance curves (e). Ce^{3+} sites appear more attractive than Ce^{4+} atoms.

Reference

[1] O. Custance, M. González-Lastre, K. Kim, E. Fernandez-Villanueva, P. Pou, H. Sepehri-Amin, D. Katsube, M. Abe, S. Kawai, M. V. Ganduglia-Pirovano, R. Pérez (2025, submitted)