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Structure of oxygen vacancies and electron localization on CeO₂(111)¹

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In the many applications of ceria-based materials in heterogeneous catalysis, the reducibility of ceria is essential to the catalytic function. Thus, having a theoretical approach that is able to describe the changes in the oxidation state of the multivalent cerium atoms appears desirable. The use of density functional theory with hybrid functionals is shown to be adequate [1]. 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 density-functional theory (DFT) with the HSE06 hybrid functional as well as the DFT+U approach and predict that vacancies on CeO₂(111) are likely to be bound to Ce⁴⁺ ions rather than to Ce³⁺ as priorly suggested. This prediction has been recently confirmed by means of STM imaging and spectroscopy [3]. We further find that subsurface vacancies are energetically preferred when compared to surface vacancies by up to 0.5 eV, and thus provide support for the most recent experimental result [4]. Defect-induced lattice relaxations are crucial to the electron localization on more distant cation sites to the defect and to the subsurface preference.

[1] J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, G. Kresse, Phys. Rev. B 75, 045121 (2007)

[2] M. V. Ganduglia-Pirovano, J. L. F. Da Silva, J. Sauer, Phys. Rev. Lett. 102, 026101 (2009).

[3] J. F. Jerratsch, X. Shao, N. Nilius, H-J Freund, C. Popa, M. V. Ganduglia-Pirovano, J. Sauer, unpublished.

[4] S. Torbrügge et al., Phys. Rev. Lett. 99, 056101 (2007).

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