

Electron localization in cerium oxide-based materials

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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. Moreover, the well-known strong influence of the support on the reactivity of ceria supported vanadium oxides (VO_x) in several important oxidation reactions is yet not understood. To this end, we apply density-functional theory (DFT) with the HSE hybrid functional as well as the DFT+U approach to study the $\text{CeO}_2(111)$ surface¹ and $\text{VO}_n/\text{CeO}_2(111)$ model catalysts ($n=0-4$).^{2,3} To compare their catalytic activity in oxidation reactions, we calculate the energy of oxygen vacancy formation (which relates to the reaction energy), and the energy of hydrogenation (which relates to the energy barrier of the rate determining step). We show that subsurface vacancies at the $\text{CeO}_2(111)$ surface are energetically more favourable than surface ones, and thus provide support for the most recent experimental result.⁴ Additionally, we combine DFT with statistical thermodynamics and discuss the stability of VO_n species as function of the oxygen partial pressure and temperature. We argue that the high catalytic activity of vanadia supported on ceria has its origin in the ability of ceria to stabilize reduced states by accommodating electrons in localized f-states, which is promoted by the supported vanadia species. We further show that the preference for subsurface vacancies and the stabilization of the +5 oxidation state of vanadium upon reduction, are the result of defect-induced lattice relaxation. The relaxation effects are crucial to the localization of the electrons left behind upon oxygen removal driving the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ reduction. Besides, we find that vacancies at the $\text{CeO}_2(111)$ surface are likely to be bound to Ce^{4+} ions rather than to Ce^{3+} as priorly suggested.

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