Surface Oxygen Chemistry of Undoped and Doped Ceria

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Introduction
The redox nature of ceria makes it viable in a multitude of applications, such as automotive emissions regulators, thermal splitters, and heterogeneous catalysis [1, 2, 3]. Cerium’s ability to cycle between oxidation states by forming oxygen point defects while maintaining its fluorite crystal structure makes ceria an oxygen-buffering oxide [2, 3]. Developing a rigorous framework that elucidates the underlying surface chemistry of ceria is paramount to understanding the processes involving oxygen exchange. Our work describes a comprehensive first principles thermodynamics based investigation of the surface reducibility of undoped ceria in oxidizing and reducing environments, for a range of temperatures and pressures [4]. The methodology allows us to identify key descriptors governing surface transformations, which are harnessed in the exploration of different dopants altering the surface properties of ceria.

Methodology
Plane wave based density functional theory, as implemented in the Vienna Ab-Initio Simulation Package (VASP), was used to solve for the ground state energies at three levels of theory: semi-local (PBE), Hubbard modified (PBE+U, U =5 eV), and hybrid (HSE06) exchange-correlation functionals. A (2x2) symmetric slab model with an exposed (111) surface orientation was used to model the surface under various environments. The slab had 15 atomic layers, with the middle 3 layers fixed to simulate the bulk material and a vacuum of 15 Å ensuring non-interacting periodic images. A convergence criterion of 10−5 and 10−3 eV between consecutive electronic and ionic steps ensured the configurations reached optimized electronic and geometric structures. The oxygen content (potential) was varied systematically to represent the surface under different operating conditions. The relative surface energy was then used as a measure of thermodynamic stability. For doped ceria cases, a dopant was substituted for a cerium atom at the surface and its effect on the surface reducibility was investigated.

Results and Discussion
Figure 1a shows the ceria surface phase diagram [4]. Under nominal operating conditions, the ceria surface remains stoichiometric. Oxygen desorption and defect creation occurs only under harsh operating environments such as high temperatures or low oxygen partial pressures. The predicted phase transformation regions show excellent agreement with the literature experimental data. However, the presence of a reducing environment such as CO and H₂ favors surface reduction even under nominal operating conditions. Borne from this initial analysis, we identify the oxygen vacancy formation energy as the key descriptor of surface reducibility. Armed with this insight, we have explored the impact various dopant atoms across the Periodic Table could have on the oxygen vacancy formation energy (Figure 1b). The lower oxidation state elements favor oxygen vacancy formation while dopants with varying or similar oxidation states as cerium result in higher vacancy formation energy, thereby lowering the tendency for the formation of surface defects.

Figures

![Figure 1: a) Ceria surface phase diagram [4], b) Oxygen vacancy formation energy as a function of dopant.](image)

Significance
The framework developed here allows for rapid screening and development of novel catalytic materials, where properties could be tailored to target specific applications. Such a methodology with high fidelity predictions narrows the chemical domain search space for synthesis and testing.

References