

A First-Principles Study of Surface Doping of Ceria with Noble Metals for Hydrocarbon Conversion

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Introduction

Ceria (CeO_2) offers unique properties as a heterogeneous catalyst or catalyst support for a number of applications. The use of ceria is motivated by its ability to store and release oxygen, or more generally to readily transition between oxidation states. Ceria exhibits activity for the oxidation of hydrocarbons, making it suitable for catalytic combustion applications and as anode electrocatalysts for direct hydrocarbon solid oxide fuel cells (SOFCs). The addition of low levels of rare-earth or noble metals alters the redox properties and hydrocarbon oxidation activity of ceria-based materials. The surface structure of the metal- CeO_2 catalyst under operating conditions, and the impact of the surface structure on hydrocarbon oxidation activity remains unresolved. We use density functional theory (DFT), with the inclusion of an on-site Coulombic interaction (DFT+U), to examine the energetics of methane oxidation and oxygen vacancy formation over ceria surfaces with the addition of transition metals. The structure, stability, and oxidation activity of single noble metal atoms on ceria is explored. This model represents the limit of an ideally dispersed catalyst, however, experimental studies of ceria supported noble metals have suggested the catalytic relevance of single Au metal atoms, [1] oxidized Pd species, [2] and Pd substitution into Ce lattice sites of perovskites [3]. The preference for transition metal to substitution into the ceria lattice versus segregation to the surface as a single supported atom is evaluated. Methane oxidation and oxygen vacancy formation energetics as well as substitution thermodynamics are presented as a function of redox conditions. These results provide insight into the relationship between composition, surface reduction and catalytic activity of ceria-based metal oxides. Relevance to the design of mixed oxide anodes for direct hydrocarbon utilization in solid oxide fuel cells (SOFC) will be discussed.

Computational Methods

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP). The GGA+U methodology was employed to properly localize f-electrons in reduced ceria [4-5]. Sensitivity of the presented results to the choice of the U parameter will be discussed. An ab initio thermodynamics approach was used to determine the temperature and oxygen pressure dependence of the stability of various oxidation states of Pd atoms supported or incorporated on the low-energy surface planes of CeO_2 . Surface reaction energies and activation barriers were computed for methane oxidation, with transition states located using the climbing-image nudged elastic band method [6].

Results and Discussion

The relative energy of each of the single Pd-atom/ceria surface models illustrated in Figure 1a was computed as a function of temperature and oxygen partial pressure (Figure 1b, for the $\text{CeO}_2(111)$ surface). The relative energy can also be calculated as a function of the SOFC anode potential (ϕ_{anode} , relative to a standard oxygen electrode) by relating oxygen

partial pressure and potential through the Nernst equation. The shaded area represents an oxygen pressure/anode potential range over which it becomes favorable for Pd atoms to incorporate into Ce-lattice positions in the $\text{CeO}_2(111)$ surface.

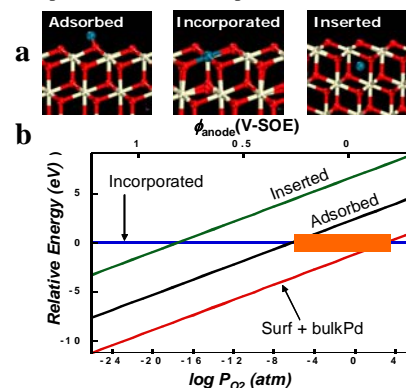


Figure 1. a) Three models used for single Pd atoms interacting with the $\text{CeO}_2(111)$ surface. b) Relative energy of the various structures as a function of oxygen pressure/SOFC anode potential.

Table 1. Activation barriers for dissociative methane adsorption over pure and Zr, Pd incorporated $\text{CeO}_2(111)$ surfaces.

Surface	E_{act} (eV)
CeO_2	1.40
Zr- CeO_2	1.06
Pd- CeO_2	0.22

Significance

Single noble metals atoms are shown computationally to be stable incorporated into the Ce-lattice positions of the $\text{CeO}_2(111)$ surface under a specific redox environment. These sites are further determined to provide enhanced C-H bond activation kinetics by providing reduction centers, rather than through direct activation of the C-H bond over the metal site. These computational results illustrate that the catalytic activity of oxide anode electrocatalysts for direct hydrocarbon use in SOFCs can be optimized by design of a mixed oxide with a surface reducibility properly chosen for the operating conditions at the cell anode.

References

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