



Surface structure of catalytically-active ceria nanoparticles



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ABSTRACT

Catalytic mechanisms, and therefore activity, depend on the structure of catalyst surfaces. In turn, surfaces may reconstruct and/or exhibit local configurations that vary from bulk composition and structure. CeO₂ (ceria) is a redox catalyst of interest in numerous automotive, energy and, increasingly, biomedical applications. Previous studies aimed at understanding catalytic mechanisms on ceria have limited consideration to systems with bulk-like stoichiometric or sub-stoichiometric surfaces. Here we summarize previous computational studies on ceria surfaces, nanoclusters, and nanoparticles, and highlight challenges in constructing physically-representative ceria nanoparticle (CNP) structures. Setting aside assumptions of bulk-like stoichiometric or sub-stoichiometric ceria surface terminations, we report results of DFT + *U* calculations and show that sufficiently small CNPs are not bulk-terminated, but rather are stabilized by the formation of O_x^q groups ($-2 \leq q \leq 0$, $x \leq 3$) at corners, edges, and {100} facets. These surface structures, not the annihilation and regeneration of O-vacancies, may directly control reduction/oxidation catalysis at CNPs below a critical size. As anion groups other than O_x^q groups could be incorporated in stable CNP surfaces, this suggests the possibility of tailoring small CNP structures and mechanisms for particular catalytic reactions.

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1. Introduction

Catalysts are essential engineering materials used to promote specific chemical reactions in a host of applications and processes. Typical catalysts influence target reactions by enhancing the binding or localization of reactant molecules at catalyst surfaces while lowering reaction barriers and allowing desorption of product molecules. Ideal catalysts have high activity, specificity and stability, as well as low contamination rates under operating conditions. Various pure metals and, increasingly, metal oxides are widely applied as catalysts. Reversible reduction/oxidation catalysts have particular technological value in energy, environmental and biomedical applications. Cerium dioxide (CeO₂, ceria) has served as an excellent reduction/oxidation catalyst for 30 years. Ceria has been shown to have wide applications in environmental remediation, energy generation and biomedicine, in addition to other important applications in microelectronics, optical films, gas sensors, and polishing materials [1–13].

The effects of a catalyst on a chemical reaction are necessarily surface effects. That is, the physical and chemical action of a catalyst occurs at the interface between the catalyst and its

environment—namely, at the catalyst's surfaces. Enhancing or tailoring catalytic behavior, therefore, first requires an understanding of the structure and properties of the catalyst's surfaces. In ceria or ceria-supported catalysis the discovery that *bulk* cubic fluorite ceria can be reduced through the formation of O-vacancies and reversibly (re-)oxidized via the annihilation of O-vacancies has led to the development of a general understanding that the presence of (or potential to form) O-vacancies on ideal, bulk-terminated ceria surfaces drives the catalytic activity of ceria in reduction/oxidation reactions. In fact, explanations for the mechanism of ceria catalysis have, to date, assumed ideal, bulk-like ceria surface structures, or minor perturbations thereof. But does this picture apply to ceria *nanoparticle* (CNP) systems? Do the catalytically active surfaces of CNPs actually exhibit ideal, bulk-like surface terminations?

In this paper we report DFT + *U* calculation results demonstrating that sufficiently small CNPs are not bulk-terminated, but instead exhibit stable surface configurations characterized by the formation of chemically bound O_x^q groups. In presenting these results we summarize previous computational efforts to discern the detailed structures and properties of experimentally-relevant ceria facets and CNPs. We highlight how previous studies have generally limited consideration to structures with bulk-like surface terminations and primarily focus on the potential role of lattice O-vacancies as active surface sites for ceria catalysis. We discuss

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the inherent challenges in constructing physically-representative structures for computing CNP surface properties, and note that the complexity underlying these challenges motivates an exploration of CNP structures that is not limited by assumptions of bulk-like CNP surface terminations. We then give a detailed description of our computational methods, including a discussion of how initial CNP structures were generated and the computational tools and techniques used to relax these structures to their ground state (lowest energy) configurations. We derive a robust expression for the excess energy of formation capable of characterizing—and allowing comparisons between—the stability of surface configurations on CNPs of various shapes and sizes.

The present DFT + U results show that sufficiently small CNPs are stabilized by the formation of bound O pairs and triples at corners, edges and {100} facets in both O-rich and O-lean environments. We further show that a straightforward model accounting for formal charges and the non-stoichiometry of CNP corners, edges and {100} facets predicts a transition from larger, net reduced (CeO_{2-x}) particles which would exhibit bulk-like surface terminations (as assumed by the present understanding of ceria catalysts), to smaller, oxidized (CeO_{2+x}) particles with O_x^q -based surface terminations (shown to be stable here). The stability of O_x^q -terminated CNPs demonstrates that, below a critical size, the catalytic activity and O-storage capacity of CNPs is controlled not by the thermodynamics and kinetics of O-vacancies, but rather directly by surface structures that incorporate molecular anions. In turn, the detailed structures of catalytically-active CNP surfaces—specifically including the type and distribution of surface anion groups—are controlled by surface chemistry, and therefore by experimentally-controllable environmental conditions like solvent composition, pH, and CNP surface functionalization.

2. Background

2.1. Ceria catalysis

The excellent catalytic properties of ceria were first harnessed in the late 1970s when ceria was utilized for the treatment automobile exhaust, serving as a key component in three-way catalysts (TWC) [14,15]. During the same time period, studies on the phase diagram of the cerium oxide system were carried out. It was discovered that bulk ceria (cubic fluorite CeO_2) can be reduced at elevated temperatures to form a range of O-deficient, non-stoichiometric oxides (CeO_{2-x}), referred to collectively as “reduced” ceria. In addition, it was shown that ceria is able to reversibly transform among these various reduced phases [16–18]. Further studies [19–21] directly exploring these transformations found that bulk ceria retains a cubic fluorite structure despite removal of 25% of lattice O atoms when subjected to reduction below 900 K. While these studies noted an anomalous lattice expansion during reduction, they found that O-vacancy-containing reduced ceria could be completely recovered to stoichiometric CeO_2 when exposed to an oxidizing environment, even at room temperature.

These discoveries implied that ceria can store O by adsorbing it (via the annihilation of O-vacancies) under O-rich conditions, and controllably release it by (re-)forming O-vacancies under O-poor or reducing conditions. The number of O^{II} anions (per volume or unit mass) that can be reversibly extracted and recovered during a particular reaction (e.g., oxidation or reduction of CO/CO_2) is quantitatively characterized as the “oxygen storage capacity” (OSC) of a ceria system [22,23]. Hence, ceria has two related, technologically important capabilities: the ability to strongly catalyze redox reactions, and the ability to serve as a solid state oxygen buffer for redox reactions.

Since the 1970s substantial experimental and computational effort has been expended to understand, control, and ultimately optimize ceria’s natural ability to both support [24,25] and directly catalyze [26–31] redox reactions. Over the course of these investigations the experimentally measurable OSC of ceria and ceria-containing systems has become a kind of litmus test for catalytic activity. That is, the realizable potential of a ceria system to form and annihilate O-vacancies during reduction and oxidation has become both the lens through which the general catalytic properties of all ceria-based materials are viewed, and the default basis for understanding all reduction/oxidation mechanisms in such materials.

For bulk ceria systems, the existence of O-vacancy-containing cubic fluorite “reduced ceria” phases and low-barrier reversible transformation paths between them (simply the formation/annihilation of O-vacancies) suggests a straightforward, “four-step” mechanistic hypothesis explaining ceria’s excellent catalytic activity: (1) formation of bulk O-vacancies and associated Ce^{III} cations, (2) migration of bulk Ce^{III} cations to a ceria surface, (3) adsorption of O-molecules at surface Ce^{III} cations, and (4) interaction of reactant molecules with adsorbed O-molecules leading to catalyzed product formation and (re-)oxidation of (surface) Ce^{III} cations.

The above “four-step” mechanism assumes two key points: (i) that reactive Ce^{III} cations are present only in conjunction with vacant O^{II} lattice sites, and (ii) that the intrinsic ceria surface itself has no direct role in catalytic reactions—that is, redox catalysis by ceria requires that a vacant O lattice site must migrate, along with its concomitant Ce^{III} cations, to the surface, and that this (surface) defect structure, not any intrinsic feature of the stable surface itself, is catalytically active. These assumptions have important consequences, namely implying that optimizing the activity of ceria catalysts requires increasing the concentration of surface O-vacancies (e.g., by reducing surface O-vacancy formation energies, or increasing bulk O-vacancy concentrations). Given that these implications have driven much of the recent research on optimizing or enhancing ceria and ceria-supported catalysts, it is worth considering under what conditions the assumptions leading to the “four-step” mechanism are applicable.

The first assumption (that Ce^{III} cations are present in conjunction with O-vacancies) is well-justified in bulk ceria systems with fixed charge, where reducing bulk ceria (that is, generating Ce^{III} cations) while maintaining charge neutrality requires the formation of one lattice O-vacancy for every two Ce^{III} cations. On this basis, it is a general practice to consider the reduction of ceria, the creation of Ce^{III} cations, and/or the creation of lattice O-vacancies to be equivalent processes in bulk ceria. The existence of large numbers of reactive Ce^{III} cations in ceria systems is itself justified by the existence of a range of sub-stoichiometric cubic fluorite reduced ceria phases (CeO_{2-x}) which can be reversibly oxidized or reduced [16–21].

The second assumption upon which the “four-step” mechanism is based, that catalytically-active surface sites are Ce^{III} cations present as lattice O-vacancies on ceria surfaces, implies by extension that stable ceria surface structures do not intrinsically exhibit Ce^{III} cations, and that no other stable surface structures (other than surface Ce^{III} cations) are catalytically active. An argument can be made that this assumption is applicable for ideal, bulk-terminated surfaces on semi-infinite ceria samples, particularly on the basis of STM images of such surfaces revealing ideal, unreconstructed structures populated with finite concentrations of vacant lattice O sites [32]. The “four-step” mechanism of ceria catalysis (and the assumptions it is based upon) is therefore well-supported for bulk samples (or more correctly, for structures with surfaces well-approximated as ideal, unreconstructed, semi-infinite and stoichiometric bulk cuts). But the direct translation of the above assumptions to nanoparticle structures ignores the possibility of

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