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Role of vacancy and metal doping on combustive oxidation of Zr/ZrO_2 core-shell particles

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ABSTRACT

We studied self-propagated combustion synthesis of transition-metal-doped tetragonal ZrO_2 (t-ZrO_2) with first principles-based one-dimensional diffusion reaction model. The optimal reaction condition for the combustion process was investigated by calculating energetic stability and surface reactivity of oxygen vacancy defects on (101) surface termination of t-ZrO_2 using first-principles density functional methods. In the first-principles model, the surface was doped with 14 different metal impurities in the 4th and 5th row of the periodic table to examine the role of transition-metal doping on the combustion process. Results indicate that there are clear trends in the defect stability and reactivity depending upon the type of metal impurity and their relative location with respect to the oxygen vacancy. Surface density of states and charge density information also show that there is a trade-off between the vacancy stability and chemical activity of the surface defect states. Based on the thermodynamic information obtained from first principles, we analyze the combustion process of a Zr metal particle by using a one-dimensional diffusion-reaction model. The competition between the vacancy-assisted chemisorption and the vacancy diffusion results in an optimal point for rate of combustion reaction with respect to the vacancy stability. From this, we suggest a plausible screening strategy for metal-doping which can be applied at different temperatures and pressures, as well as with different particle sizes. Our analysis indicates that first-principles calculation provides key information that can be subsequently used for an optimization of the reaction rate for a self-sustained combustion process. An explicit inclusion of rates of defect and ionic transport will be introduced into our model in future work.

1. Introduction

Zirconium oxide is a technologically important material that is used in a wide range of applications such as in thermal barrier coatings, support for catalysts, and sensor applications due to its high ionic conductivity and high-temperature stability. Polymorphic variations of ZrO_2 are well known. At ambient pressures, ZrO_2 has a monoclinic structure. At temperatures higher than 1450 K, phase transition from monoclinic to tetragonal crystal structure takes place. Subsequently, a phase transition from tetragonal to cubic structure occurs at 2650 K [1]. The high-temperature forms of ZrO_2 are known for their mechanical strength in addition to good ionic conductivity. Low-temperature stabilization of metastable ZrO_2 has immense technological importance. The most widely known method of stabilization is the cationic doping with yttrium to form yttria-stabilized cubic zirconia (YSZ) [2]. More recently, methods beyond the extrinsic cation doping have been suggested such as size-induced [3,4] and vacancy-induced stabilizations [5]. Theoretical studies of the high-temperature ZrO_2 crystal suggest that stabilization of the metastable phase is possible by enhancing oxygen vacancy concentrations in the crystalline lattice [5–8]. Some of the nanoscale stabilization may also be owing to a balance between costs for surface termination and vacancy concentrations on or near the surface layers.

The structural, electronic, and mechanical properties of the defect stabilized zirconia have been widely studied [5,6,9–12]. A majority of the recent studies involve the cubic structured zirconia stabilized with extrinsic cation doping [13–16]. Tetragonal ZrO_2, on the other hand, has not been as extensively investigated as the cubic ZrO_2 despite its similar mechanical strength and exceptional ionic conductivity. For bulk crystal, it was reported that a stable form of tetragonal zirconia could carry up to 0.4 mol% of oxygen vacancy concentration at around 1200 °C without doping [7,17,18]. The oxygen vacancy concentration is also closely related to the doping concentration of less-coordinated cationic impurities (e.g. by doping Y_2O_3). With a typical yttria concentration of 2–8 mol%, [27] the vacancy concentration up to 2 mol% can be achieved. For combusting particles, the rapid oxidation of metallic phase causes much higher vacancy concentration than in the bulk. The large extrinsic concentration of oxygen vacancies provides tetragonal ZrO_2 a great potential in electrochemical applications such as catalysts support in solid-oxide fuel cells (SOFC).

The vacancies on surface also play important role in combustion of metal particles by improving oxygen chemisorption via surface

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sites. Tetragonal ZrO_2 for example can be conveniently synthesized using combustion synthesis process [19]. During this self-propagating reaction, the metal surface reacts with oxygen to produce a thin layer of oxide. The oxygen molecules are then adsorbed on the oxide surface with a certain defect concentration and are transported through the oxide layer via vacancy diffusion mechanism until they reach the metal/oxide interface needed to propagate the oxidation of the metallic core. However, a premature termination of the oxidation reaction due to fast saturation of vacancy sites in the oxide layer can prevent total conversion of the metal core. Since it is critical to sustain the vacancy defect concentration to prevent such termination, understanding reaction chemistry of tetragonal ZrO_2 surface and particle size plays an important role in the combustion synthesis of nanoscale zirconia.

Understanding the behavior of oxygen vacancies in the tetragonal ZrO_2 surface is thus essential for both room temperature stabilization and improved performance as a nanoscale combustion medium. Most experimental studies of metastable ZrO_2 surfaces have been focused on their electrochemical properties for its application as catalytic substrate [20,21]. First-principles studies of structural and electronic properties of cubic and tetragonal phases with and without the presence of defects have been reported in the literature [22–26]. First-principles electronic structure calculation of yttrium-doped tetragonal ZrO_2 [27] indicates that the atomistic scale understanding of cationic doping is essential to predict the properties of oxygen vacancy at the metastable ZrO_2 system. A number of experimental works showing the significance of doping tetragonal zirconia with transition metal elements other than yttrium have also been reported. Doping of yttria-stabilized tetragonal zirconia with Sc (10 mol%) and Ce (1 mol%) [28] as well as Fe (8 mol%) and Co (5 mol%) [29] was investigated to assess SOFC operating conditions with the compositional effects on electrodes. V-doped (2.5–15 wt.%) [30] and Fe-doped (0.5 wt.%) tetragonal zirconia [31] was prepared to characterize the materials' catalytic performance. Ti was doped in zirconia (up to 16 mol%) to stabilize the tetragonal phase of zirconia [32]. However, detailed first-principles-based analysis on the effect of cationic doping and the mechanism of vacancy stabilization on the tetragonal ZrO_2 surface are not clearly explored to date in the literature.

In this paper, we report our analysis of the role of oxygen vacancy in altering combustion kinetics of tetragonal ZrO_2 in the presence of metal impurities. The first-principles electronic structure calculations are aimed at providing a better understanding of reactivity of defected crystal surface during the combustion reaction process when oxygen chemisorption is critical for sustaining such reactions. We report trends in the defect stability depending upon the type of a metal impurity doped at the surface. We also report charge compensation between the defect sites. The trend is analyzed using surface-projected local density of states. The combined information involving first-principles calculated defect stability, reactivity of oxygen chemisorption sites, and chemisorption barrier itself will be used to formulate a plausible screening strategy with the metal doping candidates that optimize the combustion dynamics of metal/metal oxide systems. The transport of defects and oxide ions on the surface and bulk are not explicitly treated in the current work for the high temperature combustion process. In future, we will augment the current model with transport information in doped ZrO2 systems discussed here. This understanding is important also for catalytic applications where such variations can alter the effectiveness of t-ZrO_2 as a support material.

2. Model

The oxide layer produced by fast combustion of metal particles contains substantial amount of defects. In zirconia structures, oxide vacancies can effectively diffuse through the oxide layer via ionic transport [8,33–35]. Once the combusting metal core is coated with the oxide layer by initial oxidation reaction, the combustion reaction can only proceed through the reduction of the oxygen vacancies at the surface.

The rate of surface oxidation is determined by two important factors — defect density on the oxide surfaces and their reactivity towards molecular oxygen. The former determines the thermodynamic stability and density of reactive sites and the latter determines the kinetic barrier of the reaction on the oxide surface. Other aspects such as the transport of oxygen vacancy through surface diffusion might still be relevant depending on the thermodynamic condition of the surface. However, we only consider the case where the extreme thermodynamic condition of the process allows us to assume that surface diffusion kinetics is not a rate-determining process. Based on this, we use an atomistic model derived using first-principles-based methods to study the energetic stability of the vacancy states at the surface and the electronic activity of the defect states at the surface.

We performed lattice optimization and formation energy calculations for bulk zirconia using periodic crystalline model with supercell geometry. Since combustion of zirconium is a rapid exothermic process that takes place at temperatures higher than 2000 K [36], we assume that the oxide layer formed during the combustion reaction will most likely exist as a tetragonal form (t-ZrO_2, space group P42/nmc), since it is the most stable structure of zirconia at around ~2000 K [25,37–39]. Lattice parameter of t-ZrO_2 structure was determined by minimizing the total energy of a primitive unit cell of t-ZrO_2. With $3\times3\times2$ k-point sampling with Monkhorst–Pack method, calculated lattice parameter was a = 6.89 Å and c = 9.95 Å. This agrees well with the values obtained from previous studies based on both theory [23,25,37–40] and experiment [41]. Based on the calculated lattice parameters, we constructed a periodic supercell geometry with $3\times3\times2$ t-ZrO_2 unit cell. Each periodic cell consists of 36 Zr atoms and 72 O atoms. For metal doped cases, one Zr site per periodic cell was substituted with one metal atom to model the metal impurity defect assuming that the impurities in metallic phase would form substitutional defects in the oxide when the doping concentration is dilute. The simple substitutional defect geometry with tetragonal crystal structure will not be feasible at much higher doping concentrations. The doping elements were introduced in place of Zr^{4+} and allowed to exchange electron from their coordination shell to attain their preferred oxidation state in a neutral unit cell. We modeled the oxygen vacancy by removing one oxygen from different positions in the supercell.

We constructed a slab surface model to calculate the electronic structure of doped t-ZrO_2 surfaces. Our method of generating the surface model is analogous to Christensen and Carter's [42], which uses the as-cleaved crystals and applies only local relaxations without allowing complex, long-range surface reconstruction. We took their lowest energy surface (101) to construct our surface model. Unlike the conventional slab models that allows two active sides of the surface by having a mirror plane in the middle of a slab, we keep only one side of the slab model (top-side). The other surface (bottom-side) is passivated with fictitious atoms [43]. Two types of passivating atoms were used. The core charges for the passivating atoms were set to be 1.5 and 0.5 for Zr and O passivation of the bottom surface, respectively. The role of passivating atoms is to remove the active surface states from the bottom surface and leave only one side of the slab electronically active. The method allows us to construct a thinner slab model without disturbing the electronic structure because the inactive surface at the bottom significantly reduces the interaction between the top and the bottom surfaces. The method has been used in the studies where the slab crystal structure is complex and therefore requires excessive computer time owing to the lack of symmetry operation in the middle plane [44].

The model was built with 2×1 surface primitive unit cell of (101) t-ZrO_2 surface. The vacancy formation energy at the surface was converged within 50 meV when compared with 2×2 unit cell surface. The distance between the vacancy sites from the periodic image was