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Catalytic propane reforming mechanism over Mn-Doped CeO_2 (111)

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ABSTRACT

MnO_x/CeO_x mixed oxide systems exhibit encouraging hydrocarbon oxidation activity, without the inclusion of a noble metal. Using density functional theory (DFT) methods, we examined the oxidative reforming path of propane over the Mn-doped CeO_2 (1 1 1) surface. A plausible set of elementary reaction steps are identified for conversion of propane to CO/CO_2 and H_2/H_2O over the oxide surface. The rate-limiting reaction process may vary with redox conditions, with C-H dissociation limiting under more oxidizing conditions and more complex reaction sequences, including surface re-oxidation, limiting under highly reducing conditions. The possibility of intermediate desorption from the surface during the reforming process is low, with desorption energies of the intermediates being much less favorable than further surface reactions until CO/CO_2 products are formed. The reforming paths over Mn-doped ceria are similar to those previously identified over Zr-doped ceria. The extent of surface reduction and the electronic structure of the surface intermediates are examined.

1. Introduction

MnO_x/CeO_x mixed oxides can catalyze rapid hydrocarbon oxidation without the addition of noble metals. Ceria itself is an efficient oxidation catalyst that is cheap and can convert volatile organic compounds (such as methane, methanol and propane) [1]. The addition of MnO_x to CeO_2 increases catalytic activity and lessens deactivation from HCl and Cl_2 [1]. Solid solutions of MnO_x-CeO_x are stable at relatively high concentrations with no presence of an MnO_x phase seen in x-ray diffraction (XRD) [2]. Density functional theory (DFT) studies have suggested that Mn can be doped into the fluorite lattice of ceria when there are oxygen vacancies present [3], and Mn-doped CeO_2 will have a high rate for oxidation of methane [4]. MnO_x/CeO_2 has also been shown to oxidize volatile organic compounds [5], toluene [6], tars ($C_{10}H_8$) [7], hydrocarbons with chlorine (trichlorophenol [8] and trichloroethylene [1]), and CO [9]. Though the ability of Mn-doped CeO_2 to oxidize hydrocarbons is well established, the lack of mechanistic information limits further active site optimization. We employ DFT to analyze the reaction path for the oxidative decomposition of propane over Mn-doped CeO_2 and identify key intermediate steps. The overall reaction path for the decomposition of propane over the surface of Mn-doped CeO_2 is found to be similar to the reaction path over Zr-doped CeO_2 [10]. We also examine the extent of reduction of the surface and the electronic configuration of surface-bound intermediates at each step during the oxidation path.

A number of studies have demonstrated that MnO_x/CeO_x mixed oxides have activity for hydrocarbon oxidation and stability at high temperatures (over 1000 K) [6]. MnO_x and CeO_x combined nanorod structures were very active for the total oxidation of toluene to CO_2 at temperatures as low as 225 °C [6]. The catalytic activity of the total oxidation of *n*-hexane on MnO_x/CeO_x supported on alumina is also high [11]. Mn-doped ceria has shown promise in reforming tars (modeled as $C_{10}H_8$) from gasifier effluents, converting tars to methane and in some conditions to CO and H_2 [7]. The addition of MnO_x to CeO_2-ZrO_2 mixtures increases the activity of reforming methane [4]. MnO_x/CeO_x mixtures have shown promise in the low temperature catalytic combustion of volatile organic compounds (VOCs) [1,5,8,12]. At moderate conditions (100–140 °C), MnO_x/CeO_x mixed oxides oxidize VOCs to HCl, Cl_2, CO_2 and small amounts of CO [8,12]. The Mn in the mixture may help to remove chlorine species from Ce active sites, allowing for a higher stability of the surface [1].

Many transition metals can substitutionally dope for Ce atoms in the CeO_2 structure and enhance oxidation activity by increasing the surface reducibility. Compared with other oxides and metals that can be mixed with CeO_2, MnO_x can increase the stability of the catalyst [6], and is less expensive than other metals (Ag, Au, Pt, Pd) that can increase the activity of ceria [13–16]. Cen et al. [17], Gupta et al. [18], and Tang et al. [19] all showed that the addition of Mn to the ceria surface increases the reducibility of the surface. Mn will dope into the lattice of ceria with oxygen vacancies present and also increases the reducibility and catalytic activity of the surface [3,13].

The DFT examination of complex oxidation paths of larger hydrocarbons (larger than C_1) over oxide surfaces is uncommon and challenging. The surface intermediates formed during hydrocarbon oxidation remain unclear. Our previous work has identified the rate limiting step

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for the reforming of propane on Zr-doped CeO_2 (1 1 1) as the initial breaking of the C-H bond under oxidizing conditions, and a series of steps in the middle of the oxidation path as limiting under reducing conditions [10]. As Mn-doping is expected to increase the oxidation activity, its effect on elementary reaction energetics is of interest.

Our previous publication discussed the many modeling and mechanistic questions that arise in considering complex redox reactions on oxides [10]. Large hydrocarbons may follow numerous (hundreds) of possible sequences of C-H and C-C breaking and C-O forming steps. A number of H_2O and CO/CO_2 products are formed that may desorb at different points along a reaction path. Surface re-oxidation may also occur at various points. Considering all of these possibilities in a reasonably sized DFT unit cell is challenging, as each step may cause oxidation or reduction of metal atoms that are not necessarily adjacent to the adsorbed intermediates. We previously presented a coupled DFT and ab initio thermodynamics procedure that considers a complete propane oxidation sequence and how the reactive environment's oxygen chemical potential impacts the reaction sequence [10]. For every surface intermediate, we consider if it is more favorable to (1) dissociate to $C_zH_{n-1}^* + H^*$, (2) to dissociate to $C_{z-1}H_{n-x}^*$ and CH_x^*, (3) to add an oxygen atom to re-oxidize the surface, or (4) to desorb $C_zH_nO_y$, CO, or CO_2. When comparing paths, we considered the most exoergonic free energy step as the more favorable step. Dissociation products formed through C-H or C-C breaking are placed in separate unit cells to maintain a reasonable degree of local surface reduction.

This study examines the reforming path for propane over the Mn-doped CeO_2 (1 1 1) surface. We determine a possible reforming path for propane over Mn-doped ceria in an oxidizing, reducing and extremely reducing environment. We include a surface oxygen vacancy in our initial surface model to better approximate the stable surface under reaction conditions. We compare the reforming path of propane on the Mn- and Zr-doped ceria surfaces. Lastly, we examine the desorption of possible intermediates and give a detailed picture of the electronic structure at every intermediate step during the path.

2. Methods

2.1. Electronic structure method

Density functional theory calculations were carried out using the Vienna *ab initio* simulation program (VASP), an *ab initio* total energy, and molecular dynamics program developed at the Institute for Material Physics at the University of Vienna [20–22]. Plane wave basis sets were used with an energy cutoff of 450 eV. The ion-core interactions were represented using the projector-augmented wave (PAW) method [23]. The generalized gradient functional of Perdew-Wang (PW91) was utilized to incorporate the exchange and correlation energies [24]. All calculations were spin polarized. The valence configurations of cerium is $5s^25p^66s^24f^15d^1$, manganese is $3d^64s^1$, oxygen is $2s^22p^4$, carbon is $2s^22p^2$, and hydrogen is 1 *s* [1]. The Monkhorst Pack scheme [25] was used for *k*-point sampling of $(2 \times 2 \times 1)$, with the third vector perpendicular to the surface. Structural optimizations were performed by minimizing forces on all atoms to below 0.05 eV•Å^{-1}. We have previously shown that using a force criteria of 0.05 eV•Å^{-1} is sufficient to provide converged structure and energetics compared with a force criteria of 0.02 eV•Å^{-1} [13].

The DFT + *U* approach was utilized due to the difficulties standard DFT has in representing the nature of the 4*f* orbitals in ceria [26–28]. This approach introduces an on-site Coulombic interaction (*U*-term) which penalizes non-integer occupation of localized orbitals, effectively penalizing delocalization of electrons. A *U*-value of 5 eV was utilized on the *f*-states of cerium, consistent with previous studies of ceria [2,3,13,29–33]. The oxygen vacancy formation and methane adsorption energies depend upon the *U*-value of the *f*-states of cerium [29]. The oxygen vacancy and methane adsorption energies decrease with increasing *U*-value for pure and Zr-doped CeO_2, with a slight increase in energies for Pd-doped CeO_2. With the dependence for oxygen vacancy and methane adsorption energies on the *U*-values chosen, the quantitative results presented herein dependent upon the *U*-value chosen. However, the majority of redox elementary reactions alter the oxidation state of Mn dopants rather than Ce atoms, such that the qualitative results presented herein will be reasonably correct with a *U*-value of 5 eV on the *f*-states of cerium.

For the Mn dopant in ceria, a *U*-correction for the Mn *d*-states must be added to correctly represent the electronic structure of Mn-doped CeO_2 [2,3,13,17–19,34]. A *U*-value of 4 eV on the *d*-states of Mn has been confirmed to properly represent the Mn oxidation state under reducing conditions, in agreement with both x-ray adsorption near edge spectroscopy (XANES) and DFT results using the hybrid functional HSE06 [2,3]. The choice of U value impacts reaction energies for steps that change the occupation of localized Mn or Ce states, and therefore the quantitative results presented are dependent on the choice of U value used. We have chosen U values that have previously provided redox energetics in agreement with experimental characterization, though the transferability of a constant U value across the numerous structures considered is not guaranteed. This is an inherent limitation in using a DFT-GGA approach for such a strongly correlated system. The impact of U parameter on hydrocarbon oxidation energetics has been discussed in our previous publications [29,35].

2.2. Surface models

The fluorite crystal structure of pure CeO_2 is the same as used in our previous studies, with a bulk lattice parameter of (5.466 Å) which is within 1% of experimental values [2,3,13,29–31]. The (1 1 1) surface was utilized as it is the lowest energy surface of ceria and will, therefore, represent a large portion of the surface of polycrystalline ceria [29,32,36]. The (1 1 1) termination of ceria results in surface termination of oxygen atoms with cerium atoms in the layer below, Fig. 1. A $p(2 \times 3)$ unit cell expansion is used to model the surface with 15 Å of vacuum space perpendicular to the surface. To remove any slab-to-slab interaction that might result from a net surface dipole upon propane adsorption and conversion, as well as formation of oxygen vacancies, mirrored slabs were utilized. 4 CeO_2 layers (12 atomic layers) were utilized for all optimizations with adsorbate/intermediates mirrored on top and bottom surfaces. All layers were allowed to relax during structural optimizations. The most stable surface of Mn-doped CeO_2 with one oxygen vacancy in a $p(2 \times 3)$ expansion includes two dopant Mn atoms along the short side (replacing Ce atoms and forming a continuous row of Mn) with an oxygen vacancy in the surface [3]. In this surface, the Mn atoms are in a 3+ oxidation state, and all cerium atoms remain as Ce^{4+}. As described in our previous paper, the site projected charge method is utilized to identify the number of cerium atoms reducing from Ce^{4+} to Ce^{3+} [13]. The oxidation state of Mn was also identified using the site projected charge method (RWIGS of 0.7), using both the total number of electrons counted on a Mn atom as well as the spin on each Mn atom. Using this method, a Mn atom in a 3+ oxidation state has ~3.5 electrons and in a 2+ oxidation state has ~3.7 electrons, and these oxidation states were verified by analyzing the system and atomic spins, the projected density of states, and orbital imaging. Though the site-projected charges do not return integer values, density of states and orbital imaging indicates that these site-projected charges are consistent with an integer change in oxidation state, which occurs through formation of localized gap states upon metal atom reduction. The use of atomic charges to determine oxidation step is preferred over the more detailed density of states analysis as it is rapid and has been verified to be consistent.

For the Zr-doped CeO_2 surface, we find that the stable surface under hydrocarbon reforming conditions is not a bare, fully oxidized surface [10]. Depending upon the conditions, the surface is either fully covered in hydrogen or there is a combination of surface oxygen vacancies and hydrogen on the surface. The Zr-doped surface was found to be reduced

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