Catalytic Propane Reforming Mechanism over Mn-Doped CeO₂ (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 CeO₂ (1 1 1) surface. A plausible set of elementary reaction steps are identified for conversion of propane to CO/CO₂ and H₂/H₂O 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/CO₂ 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.

Keywords: ceria, DFT+U, manganese, doped oxide, reforming

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 CeO₂ increases catalytic activity and lessens deactivation from HCl and Cl₂.¹ 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 CeO₂ will have a high rate for oxidation of methane.⁴ MnO_x/CeO₂ has also been shown to oxidize volatile organic compounds,⁵ toluene,⁶ tars (C₁₀H₈),⁷ hydrocarbons with chlorine (trichlorophenol⁸ and trichloroethylene¹), and CO.⁹ Though the ability of Mn-doped CeO₂ 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 CeO₂ and identify key intermediate steps. The overall reaction path for the decomposition of propane over the surface of Mn-doped CeO₂ is found to be similar to the reaction path over Zr-doped CeO₂.¹⁰ 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 CO₂ 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 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 H₂O and CO/CO₂ 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 CO₂. 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 CeO₂ (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 $5s^2 5p^6 6s^2 4f^1 5d^1$, manganese is $3d^6 4s^1$, oxygen is $2s^2 2p^4$, carbon is $2s^2 2p^2$, and hydrogen is $1s^1$. The Monkhorst Pack scheme²⁵ was used for k -point sampling of (2 x 2 x 1), with the third vector perpendicular to the surface. Structural optimizations were performed by minimizing forces on all atoms to below $0.05 \text{ eV} \cdot \text{\AA}^{-1}$. We have previously shown that using a force criteria of $0.05 \text{ eV} \cdot \text{\AA}^{-1}$ is sufficient to provide converged structure and energetics compared with a force criteria of $0.02 \text{ eV} \cdot \text{\AA}^{-1}$.¹³

The DFT+ U approach was utilized due to the difficulties standard DFT has in representing the nature of the $4f$ 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, Figure 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 CeO₂ 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 CeO₂ 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 Ce⁴⁺. As described in our previous paper, the site projected charge method is utilized to identify the number of cerium atoms reducing from Ce⁴⁺ to Ce³⁺.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 CeO₂ 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 under even the most

oxidative conditions considered herein. As Mn-doped CeO₂ is more reducible than Zr-doped ceria, we would expect that hydrocarbon oxidation on Mn-doped CeO₂ oscillates about redox states without reaching the fully oxidized MO₂ stoichiometry. Though the propane oxidation path is considered here on an H-free surface, the inclusion of surface re-oxidation steps in our analysis allows determination of the point in the mechanism at which the extent of surface reduction is consistent with the reaction environment oxygen chemical potential. Prior to this point, a greater degree of surface reduction may actually be present, making elementary C-H and C-C bond breaking steps less favorable.

2.3. Reaction and Free Energies

The elementary reactions and the formulas for their reaction energy are the same as utilized in our previous paper, and are given in Table S1 (Supplemental Information).¹⁰ As a first analysis, the reaction path is determined only using the elementary reaction energies and free energies and transition states are not considered. All of the reaction energies use free energies of all gas phase species and the chemical potential of all gas phase species was calculated using an *ab initio* thermodynamics approach.¹⁰ Though DFT overestimates the O-O binding energy of oxygen, the DFT energy of O₂ is utilized.³⁷ A correction term can be added, however it would only offset the absolute oxygen partial pressures and temperatures rather than the observed trends.

In determining a reaction path, possible C-H breaking, C-C breaking, intermediate desorption, and surface re-oxidation steps are considered. Formation of C-C bonds to form C₄⁺ intermediates towards coking/oligomerization was not considered. Surface re-oxidation is first considered, and an O atom is added to the surface if re-oxidation is found to be exoergonic. The

preference among C-H breaking, C-C breaking, and desorption is then considered, with all non-symmetric C-H and C-C breaking possibilities considered. Desorption is considered preferred relative to surface reaction only if the 0K desorption energy is more favorable than surface reaction. The 0K desorption energy is used rather than the desorption free energy because the 0 K value is considered a reasonable approximation of a desorption barrier. The desorbing species would not yet attain the entropic freedom of the desorbed species at the desorption transition state. Using this procedure, the effective desorption barrier is being compared with the surface reaction energy, rather than barrier, in deciding which step is preferred. Despite this imprecision in mechanism determination, we find, under oxidizing conditions, that desorption of all C_z intermediates is at least 1.5 eV higher in energy than subsequent surface reaction energies until CO or CO_2 is reached. We, therefore, conclude the only major C-containing products are CO and CO_2 , and that this conclusion is robust despite the imprecision of comparing desorption barriers with surface reaction energies. Mn-CeO₂ is not a selective partial oxidation catalyst for formation of C_2 and C_3 intermediates. Section 3.5 further discusses the possible desorption of reaction intermediates.

We consider desorption of surface H (as H₂O), formed from C-H bond breaking, to occur immediately following surface hydroxyl formation. Desorbing as H₂O is thermodynamically preferable relative to H₂ desorption under this gas phase environment.¹⁰ The oxidative desorption of a surface H atom forms the mechanistically awkward “half of a water molecule” leaving “half of an oxygen vacancy” in the surface to be re-oxidized by “one fourth of an O₂ molecule.” Our mechanistic analysis effectively considers these steps equilibrated when considering what portion of the mechanism limits the overall reaction, thereby allowing use of these awkward stoichiometries when comparing reaction sequences.

2.4 Apparent reaction barrier and rate limiting step estimation

Without a detailed microkinetic model, we utilize the procedure outlined by Murdoch to estimate the apparent reaction barrier and rate limiting reaction process.³⁸ Murdoch's procedure involves breaking the reaction energy diagram into sections terminated by an intermediate more stable than that which began the section. The apparent barrier of each reaction section is then estimated as the difference in energy between the initial intermediate of the section and the highest energy state in the section. The rate limiting process is the section with the highest apparent energy barrier. Though we compute only reaction free energies rather than barriers, conclusions as to limiting sequences can be considered only preliminary. As discussed below, we do find this sufficient in most instances to estimate the limiting process. Initial C-H breaking or CO/CO₂ desorption often limit the rate, for which we present reasonable estimates of the barriers.

3. Results and discuss

3.1. Propane reforming in an oxidizing environment (0.1 atm O₂)

The initial step for propane oxidation over Mn-doped CeO₂ is a secondary hydrogen abstraction. This state forms a secondary propyl radical in the gas phase and a hydrogen bound to a surface oxygen atom. The energy of this state likely represents closely that of the C-H activation transition state, as previously shown for methane activation.¹³ We refer to this as a pseudo-transition state. The 0 K energy for the secondary hydrogen abstraction is 0.63 eV. Following the hydrogen abstraction, the secondary propyl radical binds to a surface oxygen atom (shown in Figure 2a), with an adsorption energy of -2.67 eV. The overall reaction free energy

diagram for the reforming of propane over Mn-doped CeO₂ in an oxidizing environment is contained in Figure 3, and structures of all intermediates are illustrated in Figures S1-S2 (Supplemental Information).

For the secondary alkyl adsorbate, breaking a C-H bond or a C-C bond, desorption, and the possibility of re-oxidizing the surface with oxygen was considered. The following step after adsorption of the secondary propyl radical is the abstraction of a hydrogen atom from one of the primary carbon atoms and the bonding of the same carbon atom to a surface oxygen atom, forming C*H₂C*HCH₃. The asterisks refer to carbon atoms bound to surface oxygen atoms. The following two steps, after H₂O desorption and oxygen vacancy refilling, involve the abstraction of a hydrogen from the primary carbon bound to the surface, and then the abstraction of the hydrogen on the secondary carbon atom forming C*HC*CH₃ (Figure 2b). Next, the abstraction of a hydrogen from the primary carbon atom not bound to a surface oxygen occurs, forming C*HC*CH₂. Another hydrogen is abstracted from the primary carbon atom not bound to the surface and the carbon atom forms a bond with a surface oxygen atom, C*HC*C*H. A surface re-oxidation occurs next with the oxygen atom forming a bond with both of the primary carbon atoms forming an oxete like structure (Figure 2c).

A hydrogen abstraction occurs next and the oxete like structure is disrupted. The dehydrogenated primary carbon atom has two carbon-oxygen bonds, with one resembling a carbon-oxygen double bond (Figure 2d). The C-C bond to the primary carbon atom then breaks, forming a desorbed CO₂ molecule, leaving behind C*HC* on the surface and forming an oxygen vacancy. The surface is re-oxidized again with an oxygen atom that forms a bond with the dehydrogenated carbon atom. The last hydrogen atom is abstracted, following by a re-oxidation. The carbon-carbon bond is then broken forming 2 CO₂ molecules, leaving behind an additional 2

surface oxygen vacancies (4 total). Completing the catalytic cycle, the surface is then re-oxidized with 3 oxygen atoms, re-oxidizing the surface to the initial starting surface (one surface oxygen vacancy present). A detailed examination of the electronic structure of surface intermediates is contained in Section 3.5.

Reforming of propane over the Mn-doped CeO₂ (1 1 1) surface produced 3CO₂ and 4H₂O molecules with an overall reaction free energy of -21.83 eV, similar to the reaction energy calculated from tabulated energies of formation (-22.00 eV).³⁹ The overall reaction rate for oxidation of propane over Mn-doped CeO₂ would be mostly dictated by the initial first hydrogen abstraction from the propane forming a secondary propyl radical in the gas phase (0 K barrier of 0.63 eV, and free energy barrier relative to gas phase propane of 1.07 eV) and the final product desorption of CO₂ (1.00 eV). As discussed in our previous paper, the surface would not be bare fully-oxidized surface under these reaction conditions.¹⁰ We neglected that the surface present under reaction conditions may have H* bound to surface oxygen atoms. Including surface hydrogen coverage would lead to a higher degree of surface reduction and could raise the barrier to propane activation. Co-adsorbed H atoms could also make desorption of the CO partial oxidation product competitive with further oxidation.

3.2. Propane reforming in a reducing environment (1×10^{-17} atm O₂)

Figure 4 illustrates the reaction energy diagram under reducing conditions, and Figures S3 and S4 contains all structures along this reforming path. The specific partial pressure of O₂ was chosen to represent reducing conditions, but at an intermediate O₂ pressure relative to the oxidizing and extremely reducing conditions considered in sections 3.1 and 3.3. In a reducing environment, the elementary steps are the same as under oxidizing conditions until the formation of C*HC*C*H. The paths diverge at this point. At higher oxygen chemical potential, the surface

re-oxidized once this intermediate was formed. In the reducing environment, the abstraction of the final two hydrogen atoms (forming a 3 carbon ring) is preferred over re-oxidizing the surface. The first and second re-oxidation steps occur next, forming a carbon-oxygen bond with each of the primary carbon atoms. One of the carbon-carbon bonds is then broken, allowing the desorption of a CO₂ molecule from the surface and forming an additional oxygen vacancy. The surface is then re-oxidized again, forming a carbon-oxygen bond. Next, the carbon-carbon bond is broken and two CO₂ molecules desorb from the surface forming an additional two surface oxygen vacancies (4 total). The catalytic cycle is then completed by the re-oxidation of the surface with 3 oxygen atoms.

Under the reducing conditions presented here, there are three CO₂ and four H₂O molecules formed during the reforming of propane. The first hydrogen abstraction is not the highest energy sequence, as for the oxidative environment. A series of steps in the middle of the overall reaction, completing with the first C-C dissociation and CO₂ desorption, gives an apparent barrier of 1.89 eV. This limiting reaction sequence involves the refilling of an oxygen vacancy from H₂O desorption and re-oxidizing the surface. The final C-C breaking step in this sequence contributes 0.75 eV to the apparent barrier. This reforming path is very similar to the path in an oxidative environment, with the only major difference being the point at which the surface re-oxidizes. Though CO formation is expected rather than CO₂ formation under these reaction conditions, CO₂ adsorption is found to occur. This discrepancy is likely due to the lack of surface hydrogen in the surface model. The additional hydrogen on the surface would increase the overall reduction of the surface, which would prefer to desorb less oxidized products.

3.3. Propane reforming in an extremely reducing environment (8×10^{-22} atm O₂)

The equilibrium between H_2O and H_2 at 1000 K, $P_{\text{H}_2} = 0.234$ atm, and $P_{\text{H}_2\text{O}} = 0.05$ atm would give an oxygen partial pressure of 8×10^{-22} atm. These conditions are similar to the effluent from a biomass gasifier.² Under these conditions, the reforming path for propane is the same as the reducing environment, up until the surface re-oxidizes. The reaction free energy diagram under these extremely reducing conditions is contained in Figure 5, with all structures in Figures S5 and S6. Instead of the surface re-oxidizing, one of the carbon-carbon bonds break forming a CO in the gas phase and a surface oxygen vacancy. This is followed by the breaking of the other carbon-carbon bond, forming two more CO molecules and two more surface oxygen vacancies.

Under these extremely reducing conditions, the products are three CO and four H_2O molecules in the gas phase. As in the reducing environment, the initial hydrogen abstraction is not the highest energy sequence. The highest energy sequence (3.35 eV uphill) is the refilling of the oxygen vacancy from H_2O desorption followed by desorption of the first CO molecule. This process is contributed by C-C breaking and the CO 0 K desorption energy. The major differences between the extremely reducing environment and the previous two environments is the lack of surface re-oxidation and the production of CO instead of CO_2 . The large endothermicity in the high energy sequence is a result of using an over oxidized surface as the initial model. In actuality, there would be more surface oxygen vacancies present, along with hydrogen adsorbed on the surface. Further surface reduction would increase the kinetic importance of the initial hydrogen abstraction, alter the reaction path, and lower the CO desorption energy. The presented reforming paths in oxidizing and reducing environments are reasonable, however, in an extremely reducing environment the path is inaccurate due to misrepresentation of the initial surface oxidation state. The use of a constant initial surface oxidation state across redox conditions allows analysis of how the O chemical potential impacts reaction paths, and was

motivated by the large computational requirements of elucidating such complex paths. As such, our analysis might be considered equivalent to an initial reaction path analysis on metal surfaces that neglects coverage effects.

3.4. Differences between Mn- and Zr-doped CeO₂

The overall propane oxidation paths on Zr-doped CeO₂ and Mn-doped CeO₂ are similar, with a few notable differences. The initial hydrogen abstraction is lower in energy on the Mn-doped CeO₂ by 0.05 eV, suggesting the Mn-dopant will promote, though slightly, initial C-H activation. This 0.05 eV promotion comes despite beginning with an oxygen vacancy present in the Mn-doped surface, and this difference would be more pronounced if the Zr-doped surface also initially included an oxygen vacancy. The first difference in the path occurs at the third hydrogen abstraction step. On the Zr-doped surface, the third hydrogen abstraction involves the removal of a hydrogen from a primary carbon that is not bound to an oxygen atom, and following hydrogen abstraction the carbon binds to a surface oxygen atom. On the Mn-doped surface, the third hydrogen is abstracted from a carbon that is already partially dehydrogenated and bound to the surface. After the third dehydrogenation, one of the three carbon atoms are not bound to the Mn-doped surface whereas all 3 carbon atoms are bound to the Zr-doped surface. The primary carbon that is not bound to an oxygen binds to an oxygen during the sixth hydrogen abstraction, forming C*HC*C*H on the surface, later than for the Zr-doped catalyst. In the oxidative and reducing environments, the point at which the surface first re-oxidizes is much later on the Mn-doped CeO₂ surface (after formation of C*HC*C*H in an oxidative environment) compared to the Zr-doped surface (after formation of C*H₂C*HC*H in an oxidative environment). This signifies that the Mn-doped surface is easier to reduce compared to the Zr-doped surface, despite the initial Mn-doped surface model already including an O-

vacancy. The final products realized in the different reaction environments did not differ between dopants.

Under more reducing conditions, where reactions sequences in the middle of the overall reaction path may limit the rate, Zr-doped CeO₂(111) shows a higher activity than Mn-doped CeO₂(111). The series of potentially limiting reaction steps occur later in the reaction path on the Mn-doped surface. In the moderately reducing conditions, the apparent barrier associated with the limiting series of steps on the Zr-doped surface is about 0.25 eV lower than on the Mn-doped surface. The desorption of CO₂, however, is 1.2 eV more favorable on the Mn-doped surface, and coupled with the slightly greater activity for C-H dissociation steps, may maintain Mn-doped ceria as more active. In the extremely reducing environment, the series of limiting steps on the Zr-doped surface includes a hydrogen abstraction, H₂O formation, and oxygen vacancy refilling. On the Mn-doped surface, the limiting process consists of refilling an oxygen vacancy and desorption of the first CO molecule. The energy involved on the Mn-doped surface is 3.35 eV (including the 0 K CO desorption energy) and on the Zr-doped surface is 2.03 eV, with the later CO desorption energy of 2.04 eV.

As the environment becomes more reducing, Zr-doped ceria becomes more competitive with Mn-doped ceria as an alkane oxidation catalyst. The Mn-doping is less effective in promoting oxidation as the surface becomes more reduced, as all Mn atoms are reduced to the 2⁺ oxidation state. A higher concentration of Mn-doping, allowing further reduction local to the reaction site, might allow for a greater degree of promotion.

3.5.Desorption of intermediates

For the reforming of propane in the oxidizing environment every hydrogen abstraction and re-oxidation step is exothermic in energy, with only the refilling of the ½ oxygen vacancy

formed after the desorption of H₂O and the desorption energy of CO₂ being endothermic. Table 1 contains C_z intermediate desorption, hydrogen abstraction and re-oxidation energies for the reforming of propane in an oxidizing environment. The 0 K desorption energies for all of the intermediate species on the surface are more endothermic than the following hydrogen abstraction or surface re-oxidation. Therefore, the surface will fully oxidize the propane to either CO or CO₂, depending upon reaction conditions, and will not partially oxidize the propane. Under reducing conditions, the surface will still fully oxidize the propane, as even though the energy to re-oxidize the surface with C*₃ is endothermic, the 0 K desorption energy is more endothermic. However, for the extremely reducing conditions, the 0 K energy for the desorption of the C*₃ species compared to the breaking of a C-C bond and desorption of the CO molecule is similar in energy (2.21 and 2.09 eV, respectively). This is most likely an artifact of not starting with a reduced surface when considering reactivity, and formation of gas phase C₃ is not expected.

3.6. Electronic structure analysis of surface intermediates

Figure 6 contains Lewis structures for surface intermediates formed during propane oxidation under oxidizing conditions. The order of structures follows the same reaction path as described in Section 3.1. The number of reduced metal atoms was determined as discussed in Section 2.2, and is listed in Figure 6 below the structure in each panel. The bond orders illustrated were assigned based on the bond lengths, the valency of the atoms, and using number of reduced metal atoms to determine the number of electrons remaining to participate in adsorbate and adsorbate-surface bonds. A number near a partial bond is the total number of electrons associated with that partial bond. Figures 6e, 6i and 6k all had a shared unpaired

electron between carbon and oxygen atoms; this has been signified by a partial bond between the atoms, along with an odd number of electrons associated with that bond. Oxygen atoms that are not doubly bound with a carbon atom, can be considered to retain a formal bond to the surface.

Unpaired electrons localized on the adsorbate or adsorbate/surface bonding region occur along the reaction path. The oxide surface has limited ability to delocalize charge, and participates only in integer reduction steps, compared with metals that can more readily delocalize charge. Though it may be surprising that these unstable species occur in an energetically viable oxidation path, both strong binding of these intermediates to the surface and the ability to somewhat delocalize electrons in adsorbate/surface bonding orbitals stabilizes these intermediates. Comparing the electronic structures presented with the reaction energy diagrams, unstable intermediates are identified, and the stabilization of these intermediates can be used as a computational parameter to test the potential activity of other surface compositions.

4. Conclusions

The reaction path for propane oxidation over Mn-doped CeO₂ (1 1 1) was evaluated using density functional theory calculations. Mn-doping promotes C-H bond activation relative to Zr-doping because Mn atoms serve as reduction centers. This effect is less pronounced when Mn-doping has already lead to oxygen vacancy formation and Mn⁴⁺ reduction to Mn³⁺. Propane activation then leads to Mn further reducing from Mn³⁺ to Mn²⁺. All possible intermediate desorption energies are more endothermic than further hydrogen abstraction or surface re-oxidation steps, consistent with CO/CO₂ and H₂/H₂O as the reaction products for propane conversion on MnO_x-CeO_x catalysts. Some of the surface intermediate species contain unpaired

electrons delocalized across the adsorbate and adsorbate-surface bonds, and stabilization of such intermediates may be expected to lead to more rapid oxidation.

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Tables & Figures

Table 1. Energies for C₃ intermediate desorption, C-H bond breaking of each C₃ intermediate, and to re-oxidize (through ½ O₂ adsorption) with each C₃ intermediate adsorbed.

C ₃ Intermediate	0 K Desorption Energy (eV)	Energy to Abstract Next Hydrogen (eV)	Energy to Re- Oxidize the Surface (eV)
C*HC*HCH ₃	2.91	-1.28	1.56
C*HC*CH ₃	1.73	-0.93	-0.75
C*HC*CH ₂	2.04	-1.37	0.43
C*HC*C*H	3.00	0.03	-0.39
C*C*C*H ^a	2.40	-1.17	-0.66
C*C*C* ^a	2.21	-	0.26

^a Energies based upon a reducing environment

Figure 1. Side and top views of a $p(2 \times 3)$ unit cell expansion of Mn-doped CeO₂ (1 1 1). Ce is displayed as tan (light), Mn as light blue (gray) and O as red (dark). The X's represent the location of the oxygen vacancy.

Figure 2. Four selected structures of propane reforming intermediates over Mn-doped CeO₂ (1 1). (a) CH₃C*HCH₃, (b) C*HC*CH₃, (c) C*HC*C*H (oxete like structure), (d) C*HC*C* (end C with 2 oxygens). Ce is displayed at tan (light), Mn as light blue (gray) and O as red (dark).

Figure 3. Propane reforming reaction energy diagram over Mn-doped CeO₂ (1 1 1) surface in a oxidizing environment (0.05 atm H₂O, 0.234 atm H₂, 0.1 atm O₂, 0.32 atm CO, 0.32 atm CO₂ and 0.1 atm propane at 1000 K). The blue (dark grey) denotes steps that are equivalent under more reducing environments in Figures 4 and 5.

Figure 4. Propane reforming reaction energy diagram over Mn-doped CeO₂ (1 1 1) surface in a reducing environment (0.05 atm H₂O, 0.234 atm H₂, 1x10⁻¹⁷ atm O₂, 0.32 atm CO, 0.32 atm CO₂ and 0.1 atm propane at 1000 K). The blue (dark grey) denotes the steps that follow the same sequence regardless of oxidation conditions considered (equivalent in Figures 3 and 5) and the red (light grey) denotes steps that are equivalent under the more reducing conditions of Figure 5.

Figure 5. Propane reforming reaction energy diagram over Mn-doped CeO₂ (1 1 1) surface in an extremely reducing environment (0.05 atm H₂O, 0.234 atm H₂, 8x10⁻²² atm O₂, 0.32 atm CO, 0.32 atm CO₂ and 0.1 atm propane at 1000 K). The blue (dark grey) denotes steps equivalent to the more oxidizing conditions used in Figures 3 and 4 and the red (light grey) denotes steps equivalent under the more oxidizing conditions in Figure 4.