Alkane Reforming on Partially Sulfided CeO₂ (1 1 1) Surfaces

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Abstract

Cleanup of biomass gasification effluent requires a catalyst that can reform methane and larger hydrocarbons while tolerating the presence of H_2S or, ideally, that can act as a sulfur sorbent while reforming hydrocarbons. We utilize density functional theory (DFT) methods to examine the impact of oxide sulfidation on the reforming of methane and the initial steps of propane reforming, using M-doped CeO_2 catalysts. On a ceria oxy-sulfide surface, surface oxygen atoms remain active for C-H bond activation via hydride abstraction whereas surface sulfur atoms are significantly less active. Methyl adsorption is slightly favored at a surface sulfur site, and though subsequent dehydrogenation steps remain viable, the final steps of methane decomposition may lead to carbon buildup on the surface. However, surface sulfur sites will be less active globally for the initial rate limiting H abstraction step, and these sites can nucleate carbon buildup. Doping CeO_2 with Mn accelerates C-H bond activation, aids eventual CO product desorption, and may induce sulfur tolerance by motivating CH_x intermediates to bind to surface O atoms rather than surface S atoms. This work represents an initial step in development of S-tolerant oxide catalysts for hydrocarbon reforming.

Keywords: ceria, DFT+*U*, sulfur, alkane, doped oxide

1. Introduction

Cleanup of gasifier effluents requires both reforming of hydrocarbons and removal of sulfur species. A single material capable of performing both cleanup steps at gasifier effluent temperatures would aid process integration [1, 2]. $\text{MO}_x\text{-CeO}_2$ materials can be used to adsorb sulfur [3-8] as well as reform hydrocarbons [8-13]. These two processes have mostly been studied independently from one another on oxides, though reforming in the presence of sulfur species has been examined on metal catalysts [14, 15]. There are several studies (both experimental and computational) examining hydrocarbon reforming over ceria, with most of them focused on methane [9-13, 16-18]. The overall mechanism to reform methane over a ceria surface is established [4, 11, 19]. The adsorption of sulfur using M-doped ceria has also been examined using both experimental and computational techniques [3-7]. Dooley and coworkers recently examined the impact of partial sulfidation of an oxide on reforming catalytic chemistry on ceria [8]. The mechanistic impact of partial sulfidation on hydrocarbon conversion catalyzed by CeO_x and $\text{MO}_x\text{-CeO}_x$ remains unclear. As an initial step towards developing oxides that can reform hydrocarbons in the presence of S, we use density functional theory (DFT) to examine the reforming of methane over M-doped ceria with sulfur present in the surface. We also further establish the electronic reduction state of the ceria surface with methyl intermediates (CH_3 , CH_2 , CH and C) adsorbed, both with and without sulfur present at the surface, and examine initial steps in propane oxidation.

Current biomass gasification cleanup processes first remove sulfur from the effluent then reform the methane and other larger hydrocarbons [1, 2]. Sulfur typically has to be removed prior to catalytic processes due its corrosive nature and its poisoning of many industrial catalysts. In gasifier effluent cleanup, the adsorption step is typically performed at temperatures lower than

those coming off the gasifier and subsequent catalytic steps, leading to process energy inefficiencies [1]. M-doped ceria has shown promise as a high temperature sulfur sorbent [3-7] as well as a hydrocarbon reforming catalyst [3, 9-13, 16-18]. Few studies have examined hydrocarbon reforming on CeO₂-based oxides in the presence of S-containing molecules. A Ni/Ce-ZrO₂/Al₂O₃, studied for steam reforming of both toluene and naphthalene, converted both completely at 1073 K with no carbon deposition [20]. In the presence of 250 ppm H₂S, the same catalyst maintained high activity after 7 h. Li et al. recently examined the reforming of tar (C₁₀H₈) with and without H₂S present over mixed oxides with ceria [8]. The presence of sulfur (H₂S) caused a partial deactivation of the catalyst for reforming of tars, though catalysts remained active for several turnovers. Mn-doped supported rare earth oxides (REOs) showed promise for tar reforming in the presence of sulfur as they exhibited high sulfur tolerance, less coking and less methanation than the typical Ni-based reforming catalysts.

Ceria adsorbs sulfur, forming oxy-sulfides, and doping ceria can increase its sulfur capacity [3-7]. CeO₂-ZrO₂ has a higher sulfur capacity compared to CeO₂ alone, and the additional sulfur capacity is thought to result from increased surface area and reducibility of CeO₂-ZrO₂ compared to pure ceria [7]. Ce_{0.7}La_{0.3}O_y has a greater sulfur capacity than either pure CeO₂ or pure La₂O₃ [5]. The addition of either MnO_x or FeO_x to CeO₂/La₂O₃ mixtures further increases the sulfur capacity [6]. Our group previously applied DFT methods to show that the greater sulfur capacity of La-doped CeO₂ compared to pure ceria is a result of the activation barrier of the H₂S adsorption and dissociation and can be associated with the fast surface kinetics over La-doped CeO₂ [4]. The Dooley and Janik groups have also shown that Mn-doped CeO₂ has an even greater sulfur capacity compared to La-doped CeO₂, which is a result of having more active oxygen vacancies for the adsorption of H₂S [3].

To our knowledge, DFT methods have not been previously employed to consider how the presence of sulfur affects the hydrocarbon oxidation/reforming ability of metal oxides. DFT studies have examined how sulfur affects hydrocarbon reforming over metals [14, 15]. The presence of sulfur on Ni (1 1 1) will deactivate the step sites on Ni, leaving only terrace sites active for the activation of methane [14]. Rh has a low sulfur resistance, which can be improved with the addition of Ni forming a bimetallic surface [15]. The impact of S absorption into oxides may be expected to be more complex, as surface S atoms may alter the surface redox properties, impact the binding of adsorbates on nearby O atoms, or themselves bind surface adsorbates.

Prior to considering the sulfidation impact on surface chemistry, we review relevant mechanistic details of hydrocarbon oxidation chemistry on doped ceria. Our previous DFT work has established the rate limiting step for the oxidation of methane on pure and M-doped CeO₂ to be the initial abstraction of a hydrogen from methane [16, 21]. This step reduces the surface, converting Mⁿ⁺ atoms to M⁽ⁿ⁻¹⁾⁺ through occupation of an electron in a localized *d*- or *f*-orbital. In the surface of ceria, certain dopants alter the reducibility of cerium atoms, while others become the reduction center. Whether it becomes the reduction center or alters the reducibility, all transition metal dopants lower the activation barrier compared to pure ceria [17]. We have also established the reforming mechanism for propane over Zr-doped CeO₂ [18].

To examine the impact of surface sulfidation on alkane oxidation processes, we first need to develop a reasonable model of a partially sulfided, M-doped CeO₂ surface. In our previous work with pure, La-, Tb-, and Mn-doped ceria (1 1 1) surfaces, we established the thermodynamic equilibrium in the presence of biomass gasifier effluent to be CeO_{1.25}S_{0.25} for pure ceria surface region and M_{0.25}Ce_{0.75}O_{1.25}S_{0.25} for the M-doped ceria surface region [3, 4]. The equilibrium CeO₂ (1 1 1) 2x2 surface cell has one surface oxygen atom replaced by a sulfur

atom, with one surface and one subsurface oxygen vacancy. The M-doped ceria structure also has one surface oxygen atom replaced with a sulfur atom, with two oxygen vacancies, one surface and one subsurface, and two of the cerium atoms substitutionally replaced with the dopant atom (one surface and one subsurface) [3, 4]. Further sulfidation of the surface and subsurface layers is endogenic, such that this reduced oxysulfide surface would be stable under gasifier effluent conditions.

In addition to the ab initio thermodynamics analysis that suggests this surface model is stable under gasifier effluent conditions, this model is supported by a series of experimental observations. The 25% dopant concentration in the surface region of the model surface cell is in the range of bulk dopant concentrations at which La [22-24], Tb [25, 26], and Mn [3, 27-31] have been shown to form fluorite-structured mixed oxides with CeO_2 , and a reasonable representation of the surface dopant concentration given the established tendency of lower valent dopants to surface segregate [22-24]. The presence of $\text{Mn}^{2+}/\text{Mn}^{3+}$ ions within a mixed $\text{Mn}_{0.05-0.2}\text{Ce}_{0.95-0.8}\text{O}_x$ phase has been established by EPR, DR-UV, XPS, and XANES analysis [27, 28], together with XRD and Raman spectroscopy confirming the lack of separate MnO_x phases [28-31]. The oxygen vacancy level is consistent with that observed by Ce L_{III}-edge XAFS that indicates a first shell fit of 6 (versus 8 in CeO_2) for $\text{Mn}_{0.2}\text{Ce}_{0.8}\text{O}_x$ samples at 923 K after reduction in syngas, and this high level of reduction was confirmed by TPR [3]. XANES, XPS, XRD, and TPD analysis have all indicated that La and Tb induce vacancy formation beyond that in pure CeO_2 and consistent with the vacancy concentrations used in our surface model [22, 25, 26, 32].

The ratio of 1 S atom per 4 M atom in the surface is consistent with the experimentally observed S absorption capacities. Using experimental surface areas and approximating the

surface as only exposing (111) facets, the absorption capacity in the computational model corresponds to a capacity of 0.4 mmol g^{-1} , in close agreement to the experimentally observed 0.3 mmol g^{-1} for $\text{Mn}_{0.2}\text{Ce}_{0.8}\text{O}_x$ at 923 K and 10^{-3} atm H_2S in a syngas mixture [3]. Greater absorption capacities (1.7 mmol g^{-1}) have been observed for $\text{Mn}_{0.25}\text{Ce}_{0.75}\text{O}_x$, though at higher H_2S pressures (10^{-2} atm), lower temperature (873 K), and no water in the CO feed [33]. High surface area LaCeO_x was reported to have 2.6-3.6 S atoms per nm^2 in the presence of syngas [5, 34], placing our model (1.9 S nm^{-2}) slightly lower than this experimental range. Sulfidation of these complex mixed oxides has not been extensively investigated with surface science methods to provide direct comparison between our surface model and surface characterization. Mullins and McDonald examined $\text{CeO}_2(111)$ films, and used sXPS to indicate that there are between 1-2 (oxidized film) and 3-4.5 (mostly reduced film) sulfur atoms per nm^2 , with S atoms mainly at O vacancy sites [35].

Herein, we utilize the aforementioned thermodynamically stable surface models to compare the reforming of methane and the initial steps of reforming propane over sulfided and un-sulfided pure and M-doped $\text{CeO}_2(111)$ ($\text{M} = \text{La, Tb, Mn}$) surfaces. Single crystal model oxysulfide surfaces are used to consider alkane oxidation chemistry. To our knowledge, comparable experimental single crystal studies do not exist. Our intent is to construct a model system that allows consideration of the impact of sulfidation on oxide alkane conversion catalysis, though practical mixed oxide systems will surely offer a much wider array of surface terminations and local compositions than considered here. Our goal is to determine whether oxysulfide surfaces formed due to S absorption will retain activity for methane oxidation. We show that sulfidation reduces the number of highly active surface sites for C-H activation, though the reforming energetics of methane over the partially sulfided surfaces are similar on

remaining O atoms, suggesting hydrocarbon conversion activity would remain. We also further examine how the state of the reduction of the ceria surface changes along the methane reforming path.

2. Theory

2.1. Electronic structure method

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 [36-38]. A plane wave basis set was used to represent the valence electrons with a cutoff of 450 eV. The core region was represented using the projector augmented wave (PAW) method [39]. The valence configurations were $5s^25p^66s^24f^15d^1$ for cerium, $5s^25p^65d^16s^2$ for lanthanum, $4f^9$ for terbium, $3d^64s^1$ for manganese, $2s^22p^4$ for oxygen, $3s^23p^4$ for sulfur, $2s^22p^2$ for carbon, and $1s^1$ for hydrogen. All DFT calculations were spin polarized. The exchange and correlations energies were represented using the Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) [40]. The Monkhorst Pack k -point sampling scheme was utilized with a (2 x 2 x 1) grid, with the third vector perpendicular to the surface [41]. All forces were converged to $0.05 \text{ eV}\cdot\text{\AA}^{-1}$ for structural optimizations, and previously a force criteria of $0.02 \text{ eV}\cdot\text{\AA}^{-1}$ was tested and both the structures and energetics were converged at the coarser value [17].

We applied the DFT+ U approach due to well established difficulties that DFT has in representing the nature of the $4f$ orbitals of cerium [42-44]. A Hubbard U -correction adds an on-site Coulombic interaction term that penalizes non-integer occupation of localized orbitals [45, 46]. This correction effectively penalizes the delocalization of Ce f electrons. We utilized a U -

value of 5 eV on the f orbitals of cerium which is consistent with previous DFT studies of ceria [9-13, 16-19, 21, 47-49]. The oxygen vacancy formation and methane activation energies depend on the value of U chosen for the f -states of Ce in CeO_2 and $\text{M}_x\text{Ce}_{1-x}\text{O}_2$. The two energies increase in exothermicity linearly with increasing the U -value on the f -states of Ce, though there is only a slight slope when the M atom serves as the reduction center [16]. With the dependence of vacancy formation and methane activation energies on the chosen U -value, the quantitative analysis presented herein is U -dependent. Utilizing a U -value of 5 eV provides an accurate description of the electronic structure of reduced ceria and provides reliable qualitative results for alkane adsorption with and without sulfur present, however, the transferability of U values across chemical systems is not absolute and introduces a possible error in all results that is difficult to quantitatively estimate.

DFT with typical GGA exchange-correlation functions is also known to have difficulties representing localized d -states on metal oxides [50, 51]. Therefore, we included a U -value of 4 eV on the d -states of Mn. This U -value provided reasonable agreement with a series of experimental values for MnO_x species [37]. This U -value also correctly predicts the oxidation states for Mn in the intact and oxygen vacant Ce- MnO_x mixed oxides, as shown through comparison with XANES results, and provides a relative energy between Mn^{2+} and Mn^{3+} states in agreement with a HSE06 hybrid functional [52]. We did not include a U -value on either the La or Tb dopants, because these dopants retain their 3+ oxidation state throughout the hydrocarbon oxidation catalytic process. We again note that despite the qualitative and quantitative agreement of DFT+ U methods for CeO_x , MnO_x , and Ce- MnO_x systems, absolute transferability across the mixed oxide systems considered cannot be established.

2.2. Surface models

The cubic fluorite structure of ceria is utilized as in our previous studies [3, 4, 16, 18, 21, 52] and the bulk lattice constant is reproduced within 1% of experimental values [16]. A $p(2 \times 2)$ ($\text{Ce}_{16}\text{O}_{32}$) unit cell expansion (Figure 1) is used with 4 CeO_2 layers (12 atomic layers) which are converged to surface formation and oxygen vacancy formation energies as shown in our previous paper [17]. Mirrored slabs were used to minimize the slab-to-slab interactions that could result from a net surface dipole due to reduction of metal atoms. The (1 1 1) surface is used because it is the lowest energy surface among single crystal terminations of ceria [16, 53, 54]. This termination of ceria results in four oxygen atoms per side of the unit cell and four cerium atoms in the layer below. 15 Å of vacuum space is utilized perpendicular to the surface.

The sulfided surfaces used in this study would be in thermodynamic equilibrium with effluent from a biomass gasifier (1100 K, 0.35 atm of H_2 , 0.03 atm of H_2O , 10^{-2} atm of H_2S), as shown previously with an *ab initio* thermodynamic approach [4]. This sulfided structure has one oxygen atom replaced by a sulfur atom. Our previous work concluded that the stable surface under these conditions would attain this level of sulfidation, and that this reasonably matched the high S absorption capacity observed experimentally for these materials [4]. Two oxygen vacancies are included in the surface slab, one in the outermost surface layer and one in the first subsurface layer, as the *ab initio* thermodynamic analysis found this extent of reduction as the equilibrium surface state under biomass gasifier effluent conditions. The doped surface has two cerium atoms substitutionally replaced with a dopant atom (Tb, La, or Mn), with one of the replaced cerium atoms in the first layer and the second atom in the layer below. This gives a dopant level similar to that used experimentally (M:Ce of 1:3 to 1:6) in our previous work [4]. During the catalytic cycle for the reforming of methane, the surface will cycle between two states, as the reforming of methane (desorption of CO) removes a lattice oxygen atom. We use an

initial surface modeled with one sulfur replacing a surface oxygen atom and one subsurface oxygen vacancy (Figures 1c-d). Reaction transforms the surface to the thermodynamic equilibrium state with two oxygen vacancies. Another choice, cycling through the thermodynamic equilibrium state and the further reduced state, would reduce the surface to an extent that would be physically unreasonable given our surface model with 16 CeO₂ units. The un-sulfided model surface also has one subsurface oxygen vacancy, matching the state of reduction in the sulfided case (Figures 1a-b). The presence of an oxygen vacancy in the un-doped ceria surface causes reduction of two cerium atoms (Ce³⁺). In the doped system, the oxygen vacancy allows both of the dopant atoms to have a 3+ oxidation state, and none of the cerium atoms are reduced. As we have previously shown, Mn will not dope into the ceria surface or be stable unless an oxygen vacancy is present (Mn²⁺ or Mn³⁺) [52]. The level of doping, with a high concentration (25%) of dopant in the near surface and pure CeO₂ in deeper sublayers, was considered low enough not to affect the lattice parameters.

We did not consider the potential for partial hydroxylation (dissociative H₂ desorption) of the surface under reaction conditions. Though we compute the free energy for H₂ dissociative adsorption on the surface as exoergonic, determination of the steady state coverage of H* under reaction conditions is beyond the scope of this study. As the objective of this study is to consider the impact of dopants and partial sulfidation on methane conversion chemistry, the use of a non-H covered surface is a reasonable approximation to allow comparison among the surfaces studied.

2.3. Reaction Energies

All chemical reactions and their reaction energy formulas considered in this study are listed in Table 1.

The variables used in Table 1 are listed below:

E_S is the energy of the surface slab.

$E_{S/(n-1)V_O}$ is the energy of a surface unit cell with $(n-1)$ oxygen vacancies on each side of the unit slab.

E_{S/nV_O} is the energy of a surface unit cell with n oxygen vacancies on each side of the unit slab.

$E_{S/C_zH_y^*}$ is the energy of the surface slab with a hydrocarbon molecule bound to the surface.

E_{S/H^*} is the energy of the surface slab with a hydrogen bound to the surface.

E_{O_2} is the energy of a gas phase O_2 molecule.

E_{H_2} is the energy of a hydrogen molecule in the gas phase.

$E_{C_zH_y}$ is the energy of a hydrocarbon molecule in the gas phase.

$E_{C_zH_{y-1}^{\bullet}}$ is the energy of a hydrocarbon radical in the gas phase.

E_{S/C^*} is the energy of the surface slab with a carbon atom bound to the surface.

The factors of 2 listed in the reaction energies of Table 1 are a result of using mirrored slabs. Even though it is known that DFT overestimates the O_2 binding energy, in Equation 1 the DFT energy for O_2 is utilized [51]. We did not add in a correction to better match the experimental binding energy because we are using the oxygen vacancy formation energies for qualitative trends and a constant correction term would not alter these trends. For all gas phase molecules, the ZPVE and temperature dependent free energy terms were not added. All energies reported herein are used to compare between the sulfided and un-sulfided surfaces and these corrections would only alter the absolute adsorption energies and not the differences between these two cases. The dehydrogenation of CH_x^* intermediates on the surface would produce surface bound H^* atoms that would then pair and desorb as H_2 during a reforming process. As our emphasis is on the hydrocarbon surface chemistry, we consider dehydrogenation ($CH_x^* \rightarrow$

CH_{x-1}^*) to directly produce half of an H_2 molecule without considering the H_2 desorption process. This allows us to isolate the impact of sulfidation on H^* or CH_x^* adsorbates without considering co-adsorption of both in the same unit cell. The desorption energies (Equation 5) can represent desorption of a CO molecule or of a CS molecule (for which desorption is highly unfavorable) from the sulfided surface.

As noted in Table 1, reaction type B, we use a “pseudo-transition state” to approximate the activation barrier for the initial C-H activation of methane. We have demonstrated previously across a number of M-doped ceria systems that the transition state for this step is well-approximated by an adsorbed H^* atom and a separate gas phase CH_3 radical, as the actual transition state is late in the H-abstraction process [17]. The use of the pseudo-transition state saves significant computational time with little loss of quantitative accuracy. Transition state searches are not reported herein, as these were computationally intractable for the number of surfaces and elementary steps explored. Assessments of reactivity presume activation barriers for similar reactions (C-H dissociation) generally correlate with reaction energies.

2.4.Determination of oxidation states

We utilize the site projected charge method to identify the number of cerium atoms in the Ce^{4+} and Ce^{3+} oxidation states, as described in our previous study [17]. The formal oxidation states of La and Tb were assigned to 3+, as the formation of a single oxygen vacancy with two La/Tb doped into the surface did not reduce the cerium atoms, but did increase the electron density on the La and Tb atoms. The formal oxidation state of Mn was identified using the site projected charge method (RWIGS of 0.7 for Mn) and the spin state of each Mn atom. Using this method, obtaining the number of valence electrons on the Mn to be ~ 3.5 indicated the Mn^{3+}

oxidation state and ~3.7 electrons indicated an oxidation state of Mn^{2+} . The change of site-projected charge on Mn from 3.5 to 3.7 occurs with formation of a localized gap state on Mn and a change in spin consistent with integer reduction of the Mn atom. We refer the interested reader to the Supplementary Information of our previous publication [17] for extensive discussion of the use of site-projected charges with small radii for identifying oxidation state changes in doped ceria. For all structures, metal oxidation state changes were clear and localized orbitals appeared in the band gap region, indicating surface reduction occurred through reduction of localized metal centers.

3. Results and discussion

3.1. Initial C-H bond activation

Table 2 reports the hydrogen abstraction, methane decomposition and propane decomposition energies, with and without partial sulfidation of the oxide surface. The initial hydrogen abstraction from methane (or any alkane) onto the surface of M-doped CeO_2 leaves a hydrogen bound to an oxygen atom (labeled O1-O4 in Figure 1) on the surface and a methyl (alkyl) radical in the gas phase. The energy to abstract a H atom on a surface oxygen has only a slight variance if a nearby O atom has been replaced with a S atom. However, abstraction of the first hydrogen from the methane on a sulfur atom (Figures 2a-b, Reaction Type B in Table 2) causes the extraction to be less favorable by 0.34-0.46 eV than abstraction onto an oxygen atom in the same position (O1/S1). As this H-abstraction energy is used as a pseudo-activation barrier for the initial C-H bond activation [17], this increase is kinetically significant and we conclude substitution of surface oxygen atoms by sulfur atoms will leave less active sites (sulfur atoms) for the methane abstraction. This will impact the overall rate of alkane oxidation through

lowering the number of sites, but the barrier on the remaining active sites (surface oxygen atoms) is unperturbed by sulfidation. Our previous thermodynamic analysis suggested the surface saturates with 25% substitution of oxygen to sulfur under typical biomass gasifier effluents, though the extent of surface sulfidation would be temperature dependent. Sulfidation will effectively remove surface oxygen sites for C-H bond activation. All structures for the adsorption of H* on the surface can be seen in Figures S1 and S4.

A thermodynamic cycle decomposition of the process involved in the abstraction of a hydrogen/alkyl fragment from a hydrocarbon is given in Figure 3. The overall reaction abstracts a hydrogen/alkyl fragment from a hydrocarbon, and we term this abstraction energy as E_{act} given the pseudo-transition state assumption. Table 3 contains the energies associated with each step of Figure 3 for the abstraction of a hydrogen from methane for pure, La-, Tb- and Mn-doped CeO₂ (1 1 1). For the abstraction of a hydrogen from methane, R₁ would represent CH₃ and R₂ would represent H.

We decompose formation of the pseudo-transition state into two steps, (1) forming of a CH₃ radical and a hydrogen radical in the gas phase and the (2) adsorption of the hydrogen on an oxygen or sulfur in the surface. Step 1 does not depend on the surface and the energy required to break this bond is therefore independent of whether the surface is partially sulfided. The energy for reaction 2 will depend on whether the hydrogen binds to a sulfur or an oxygen atom. We further split step 2 into 3 processes: (2a) removing an oxygen (or sulfur) from the surface forming a vacancy, (2b) oxidizing (or sulfiding) the hydrogen radical in the gas phase, and (2c) adsorbing the hydroxyl (or sulfided radical) into the surface vacancy. The O-H bond in the gas phase is 0.42 eV stronger than an equivalent S-H bond (both forming radicals in the gas phase, step 2b.) This step is surface independent. The difference in the overall hydrogen abstraction

energy occurring on a surface sulfur versus oxygen on the four surfaces ranges from 0.34 to 0.46 eV. This difference is similar to the O-H and S-H bond energy difference. There is a large energy difference between the sulfur and oxygen atoms for steps 2a (breaking M-S or M-O interactions) and 2c (reforming the M-S or M-O interactions), however the difference in the sum of steps 2a and 2c for oxygen versus sulfur ranges from -0.08 to 0.04 eV. The difference in absolute energies between 2a and 2c result from differences in the surface redox processes, as forming an oxygen vacancy (2a) is a 2 electron reduction process whereas adsorbing OH* (SH*) is a one electron process. We conclude from this analysis that the preferable (faster) abstraction of hydrogen from hydrocarbons on surface oxygen atoms versus surface sulfur atoms occurs due to the stronger O-H versus S-H bond formed.

Contrasting the surface O-H/S-H bonding, adsorbing a methyl species onto a surface sulfur atom (S1) is slightly more favorable than adsorbing to the methyl group onto an oxygen atom (O1). We can again use the thermodynamic cycle in Figure 3 to analyze this difference, with R₂ now representing the methyl species and R₁ representing a H atom. Steps 1 and 2a are unchanged from surface H abstraction. The O-CH₃/S-CH₃ difference in step 2b is surface independent, and, as for the O-H/S-H, the O-CH₃ bond is 0.46 eV more stable than the S-CH₃ bond. Contrary to H abstraction, the differences in energy for steps 2a and 2c do not cancel for methyl adsorption. For methyl adsorption, the sum of 2a and 2c is 0.46 to 0.59 eV more stable on the sulfided surface. This leads to CH₃ preferential adsorption on the sulfur atom versus an oxygen atom. The slightly stronger adsorption of CH₃ to surface sulfur atoms over oxygen atoms may lead to eventual carbon buildup on the sulfided surface, as discussed in Section 3.2. All structures for reforming of methane on the surface can be seen in Figures S2 and S5.

The data in Table 2 allows for consideration of how La-, Tb-, or Mn-doping impact C-H bond activation kinetics. Using the H* pseudo-transition state assumption, Tb- or La-doping increases the activation barrier relative to pure CeO₂ (1 1 1) on all surface oxygen atoms or sulfur atoms, with an average increase of 0.31 eV (0.70 eV for sulfur) for La-doping and 0.05 eV (0.12 eV for sulfur) for Tb-doping. As H abstraction is occurring on a surface with a subsurface oxygen vacancy already present, La- and Tb-dopants are reduced to a 3+ state prior to C-H activation. La- and Tb- doping appear to increase the activation barrier by making the adjacent Ce atoms slightly less reducible. Doping often increases surface area as well, so the overall impact on activity cannot be ascertained from the barrier alone. Contrarily, Mn-doping lowers the barrier for H abstraction on O1 (S1), O3 and O4. Prior to H abstraction, Mn atoms are in a 3+ oxidation state, but their accessible 2+ state helps promote C-H bond activation. The barrier for H abstraction on O2 for the Mn-doped surface is higher than pure CeO₂. O1 (S1), O3 and O4 are all nearest neighbors to the Mn dopant and O2 is a next nearest neighbor (doesn't share any bonds with the Mn atom). This suggests that Mn-doping promotion of C-H activation is a local affect, only promoting C-H activation on oxygens bound to surface-doped Mn atoms.

3.2. Complete methane dehydrogenation with and without sulfur present

Figure 4 contains the reaction (free) energy diagram for methane reforming over pure CeO₂ (1 1 1) and sulfided CeO₂ (1 1 1), given both as 0 K ΔE values and ΔG values under approximate biomass gasifier effluent conditions. All CH_x species are taken to adsorb on O1 or S1. The pseudo-transition state (for hydrogen abstraction on a sulfur and oxygen) as described in the section before, is included on the reaction energy diagram. H abstraction on a surface sulfur or oxygen can lead to CH₃* formation on either site, as the radical may move along the surface to find a binding site. The 0 K reaction energy diagram of Figure 4 suggests CH₄ surface

decomposition and subsequent CO desorption is highly unfavorable, uphill in energy by ~ 4 eV. This should not be taken to indicate a lack of favorability under reforming conditions. The free energy values in Figure 4 show a reduction in the reaction energy, with the reaction free energy to form CO and H₂ still unfavorable. Figure 4 does not show the complete catalytic cycle, as an additional oxygen vacancy remains in the surface in the final product. Refilling this vacancy is favorable, making the overall reaction free energy for methane reforming to CO and H₂ -0.08 eV at the considered conditions. The standard state reaction free energy to partially oxidize methane to carbon monoxide and hydrogen is -0.89 eV (exergonic) [55], which we compute as -0.25 eV with the difference mainly due to the known DFT error in overestimation of the O₂ bond energy [37]. Though the use of reaction free energies better convey the favorability of the overall reaction, we use 0 K energies in the remainder of the paper to allow for simple and consistent comparison between dehydrogenation of the different CH_x species, and between the sulfided and un-sulfided surface, at the expense of providing realistic energetics at reaction conditions.

The CH₃* species has a small preference to adsorb at a surface sulfur atom. The CH₂* product of the second hydrogen abstraction also has a small preference to bond to a sulfur atom. The subsequent CH* and C* intermediates show a strong preference to bond to surface oxygen atoms, indicating complete methyl decomposition will be less favorable on surface sulfur sites. The CH₂* species is stabilized relative to the CH* and C* species on the sulfided surface, suggesting sulfidation can increase the concentration of the CH₂* species that can facilitate coking. The largest difference between methane decomposition on an oxygen atom compared to a sulfur atom is the desorption of the final products, with the desorption of the CO molecule being 1.13 eV more favorable than desorption of the CS molecule. Desorption of the CS product is so unfavorable that this product would not be observed. The large discrepancy between these

two desorption energies is a result of stronger M-S versus M-O bonds and may also stem from the adsorbed CS molecule having an unpaired electron on the carbon atom, suggesting significant electronic structure reorganization needed for desorption. The electronic structure of all C_1 intermediates including CS will be discussed in the next section. The similar first and second hydrogen abstraction energies on an oxygen atom compared to a sulfur atom suggest that methane can be dehydrogenated on either surface atom. However, after the first two abstractions, the energies of the second two hydrogen abstractions and product desorption are much higher on the sulfur atom compared to the oxygen atom, which can lead to irreversible formation of these surface intermediates on S atoms. We did not explore C-C bond formation, but the stability of these intermediates suggests that they could nucleate formation of larger bound hydrocarbons on partially sulfided ceria surfaces.

For methyl decomposition on an oxygen site, the oxygen atom bound to the carbon is always towards the surface, see Figure 5. For the CH_3^* , CH_2^* and CH^* intermediates on the sulfur atom, the sulfur is in the same orientation as for oxygen bound intermediates. However, for the C^* bound to a sulfur atom (CS^*) the CS molecule is flipped and has the carbon atom pointing towards the surface.

The supporting information contains the 0 K reaction energy diagrams for methane decomposition over the sulfided and the un-sulfided La- and Tb-doped CeO_2 (1 1 1) surface. The reaction energy diagrams for La- and Tb-doped CeO_2 (1 1 1) are very similar to the reaction energy diagram for pure CeO_2 . The adsorption of CH_3^* and CH_2^* intermediates has a slight preference on the sulfur atom and the adsorption of CH^* and C^* intermediates has a strong preference on the oxygen atom. Reaction on a surface O atom produces CO which can desorb, whereas C binding to surface S atoms results in surface CS species.

The 0 K reaction energy diagram is illustrated in Figure 6 for the methane decomposition over the sulfided and the un-sulfided surface of Mn-doped CeO₂ (1 1 1). A significant difference between the Mn-doped surface and the pure CeO₂ or Tb, La-doped surfaces is that the initial C-H activation barrier is low and the initial CH₃* adsorption is more favorable by 0.15 – 0.5 eV. The CH₂* state is also more stable on the un-sulfided Mn-doped CeO₂ (1 1 1) surface, though the sulfided surface shows less difference. The CH₃* (slightly) and the CH₂* (considerably) prefer to bind to surface oxygen atoms on Mn-doped ceria, suggesting Mn-doping may induce a sulfur tolerant property. The CH* species is less stable on the Mn-doped surface than the other dopants. The C* species is more stable on the Mn-doped surface, and the CO or CS product, leaving a surface oxygen vacancy, is significantly preferred on the Mn-doped surface due to its significantly more favorable oxygen (sulfur) vacancy formation energy. As for the other dopants, desorption of the CS molecule is more endergonic compared to desorption of the CO molecule. Most of these differences can be accounted for by the difference in electronic behavior between the Mn-doped surface and the three other surfaces, as described in the following section.

3.3. Electronic structure analysis during methane dehydrogenation

Lewis structures for each surface intermediate along the decomposition of methane over the sulfided and un-sulfided surfaces of pure CeO₂ (1 1 1) are illustrated in Figure 7. Table 4 contains the number of reduced (3+) cerium atoms at each intermediate, along with Figures S9 and S10 containing the total density of states for each intermediate. The adsorption of the methyl radical on the ceria surface forms a C-O (C-S) bond and reduces one cerium atom to Ce³⁺. Abstracting the second hydrogen from the C₁ intermediate to form CH₂* leaves an unpaired electron on the carbon atom. All efforts to motivate H₂C=O (H₂C=S) formation and localize the unpaired electron to form an additional Ce³⁺ were unsuccessful and we conclude that the CH₂•

adsorbed state is more favorable than the state with a $\text{H}_2\text{C}=\text{O}$ ($\text{H}_2\text{C}=\text{S}$) double bond and two reduced cerium atoms. The third hydrogen abstraction forms a $\text{HC}=\text{O}$ ($\text{HC}=\text{S}$) double bond and leaves a lone pair of electrons on the carbon atom. No additional cerium atoms reduce. The O-C-H bond angle is indicative of an sp^2 hybridized carbon atom. Conversion of CH_4 (g) to $\text{CH}^* + \frac{3}{2} \text{H}_2$ leads to only a 1 electron reduction of the surface, occurring upon O- CH_3 /S- CH_3 formation.

In progressing to the CH^* species, the surface and adsorbate electronic structure did not differ between the O- CH_x^* or S- CH_x^* species. The last hydrogen abstraction from the C_1 intermediate bound to the oxygen atom forms a CO molecule, “ C^* ”, with the CO species having little interaction with the surface. An additional cerium is reduced (2 Ce^{3+}) on converting CH^* to $\text{C}^* + \frac{1}{2} \text{H}_2$. C^* on a sulfur atom prefers instead to flip to put the carbon end down, and the CS species is bonded to a cerium atom with an unpaired electron on the carbon atom. Product desorption of the CO molecule, forming a surface oxygen vacancy, maintains the same extent of surface reduction (2 e^- reduction) as the previous C^* state. Desorption of the CS molecule breaks the C-Ce bond and reduces an additional Ce (2 Ce^{3+}). After either desorption, the surface has a vacancy with 2 reduced cerium atoms. La- and Tb-doped ceria showed no difference in the state of reduction or character of surface intermediates from the pure CeO_2 surfaces.

For the Mn-doped surface, the initial CH_3^* adsorption reduces a Mn atom from 3+ to 2+ rather than reducing a Ce atom. The Mn-doped ceria surface, compared to pure CeO_2 or La-, Tb-doped CeO_2 (1 1 1), shows additional differences in electronic structure after the second hydrogen abstraction (CH_2^*) (Table 4). For CH_2^* , the unpaired electron localized onto a cerium atom rather than the adsorbate C atom. This allowed the formation of a double bond between the carbon and the oxygen atom in the surface. The next hydrogen abstraction left a lone pair of electrons on the sp^2 hybridized carbon atom and maintained its double bond with the oxygen

atom. The cerium atom reduced in the CH_2^* state re-oxidized to Ce^{4+} in the CH^* state. Contrary to the pure CeO_2 surface, the final C^* (in either CO or CS formation) has two electrons reducing atoms in the surface and both adsorbates have an interaction with the surface. Collectively, the main impacts of Mn-doping for CH_4 conversion is the initial reduction of Mn^{3+} to Mn^{2+} on C-H abstraction and in stabilizing the eventual oxygen vacancy when CO/CS is formed. The accessible Mn^{2+} oxidation state also facilitates various propane oxidation intermediates, as discussed below.

3.4. *Initial reforming of propane over a sulfided surface*

The surface chemistry of propane oxidation is more complex due to the potential for adsorbates with multiple points of surface interaction and the mixing of C-H and C-C dissociation with C-O formation and surface re-oxidation. We have examined this complex reaction process over Zr-doped CeO_2 (1 1 1) previously [18]. Here, we consider only the initial steps of propane oxidation to explore the impact of a partially sulfided surface. Energetics of surface intermediates are reported in Table 2 and two key intermediates are included in Figure 2. Table 4 includes the extent of surface reduction for each propane-derived surface intermediate. All structures for the first three steps of propane reforming can be seen in Figures S3 and S6.

The dissociative adsorption of propane, forming $\frac{1}{2} \text{H}_2$ and a propyl species adsorbed to O4 through the secondary carbon atom, is slightly more favorable when there is sulfur present in the surface. The second hydrogen abstraction is from a primary carbon, and when the hydrogen is abstracted the primary carbon forms a bond with a second surface oxygen atom (O3), forming the $\text{C}^*\text{H}_2\text{C}^*\text{HCH}_3$ intermediate and $\frac{1}{2} \text{H}_2$ (g). Our previous paper showed this was more favorable than C-C dissociation [18]. This second hydrogen abstraction is less favorable with sulfur present. We did not examine the binding of these intermediates with surface sulfur atoms.

For the abstraction of a 3rd hydrogen atom, we considered: (1) abstracting the hydrogen from the primary carbon already bound to an oxygen atom, (2) abstracting the hydrogen from the other primary carbon atom and binding the 3rd carbon atom to an oxygen atom, and (3) abstracting the hydrogen from the other primary carbon atom and binding it to a sulfur atom (Figures 2c-d). The subsequent H abstraction (either removing H from the primary carbon bound to the surface ($C^*HC^*HCH_3$), or forming an additional carbon-oxygen bond with the other primary carbon ($C^*H_2C^*HC^*H_2$ on O2, O3 and O4)), is slightly more favorable on the sulfided surface for the pure CeO_2 and Mn-doped CeO_2 (1 1 1) surfaces, but less favorable on the La- and Tb-doped CeO_2 (1 1 1) surfaces. Removal of the third hydrogen, either forming a C-O or a C-S bond with the other primary carbon, is more favorable on the sulfur atom, except for the Mn-doped CeO_2 surface.

4. Conclusions

The presence of sulfur in the partially sulfided CeO_2 or M- CeO_2 (1 1 1) surfaces will decrease the number of active sites for the activation of hydrocarbons. Surface sulfur sites are less active for the rate limiting step of C-H activation, though partial sulfidation has little effect on the remaining surface oxygen atoms. While H^* formation preferably occurs on surface oxygen atoms, there is a slight preference for CH_3^* species to bind to surface sulfur atoms. The subsequent dehydrogenation of CH_3^* to surface CH_xS species represents a potential deactivation route, as desorption of these species is significantly less favorable than CO desorption. The highly endergonic desorption energy of CS will result in stable surface carbon species that could accelerate carbon buildup compared to the un-sulfided surface. La- and Tb-doping have little effect on the surface chemistry, though Mn-doping accelerates C-H activation through Mn^{3+}

reduction to Mn^{2+} . Mn-doping similarly promotes eventual CO product desorption, and also shows a greater preference for some hydrocarbon species to bind to surface oxygen atoms versus sulfur atoms, suggesting the potential for enhanced tolerance against surface poisoning. The complete catalytic cycle with all free energies computed under reaction conditions, including the refilling of oxygen vacancies, was not considered here. The complete cycle would be necessary to definitively conclude whether Mn-doping truly accelerates the oxidation rate.

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6. Supporting Information Available:

Structures of hydrogen adsorption and methane reforming, along with additional reaction energy diagrams are included in the supporting information and total density of states for methane reforming.

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Tables & Figures

Table 1. Reaction types and reaction energy definitions for all reactions included in this paper.

Reaction Type	Chemical Reaction	Reaction Energy
(A) Oxygen Vacancy Formation	(A) $M_xCe_{1-x}O_{2-(n-1)} \rightarrow M_xCe_{1-x}O_{2-n} + \frac{n}{2}O_2(g)$	$\Delta E_{vac} = \frac{E_{S/nV_O} + E_{O_2} - E_{S/(n-1)V_O}}{2} \quad (1)$
(B) Pseudo-Transition State	(B) $C_zH_y(g) + * \rightarrow H^* + C_zH_{y-1}^{\bullet}(g)$	$E_{act} = \frac{(E_{S/H^*} + 2*E_{C_zH_{y-1}^{\bullet}}) - (E_S + 2*E_{C_zH_y})}{2} \quad (2)$
(C) Hydrocarbon Adsorption	(C) $C_zH_y(g) + * \rightarrow C_zH_{y-1}^* + \frac{1}{2}H_2(g)$	$\Delta E_{ads} = \frac{(E_{S/C_zH_{y-1}^*} + E_{H_2}) - (E_S + 2*E_{C_zH_y})}{2} \quad (3)$
(D) Hydrogen Abstraction	(D) $C_zH_y^* \rightarrow C_zH_{y-1}^* + \frac{1}{2}H_2(g)$	$\Delta E_{abs} = \frac{(E_{S/C_zH_{y-1}^*} + E_{H_2}) - (E_{S/C_zH_y^*})}{2} \quad (4)$
(E) Desorption of species	(E) $C^* \rightarrow CO(g) + * + V_o$	$\Delta E_{CO} = \frac{(E_{S/nV_O} + 2*E_{CO}) - (E_{S/C^*})}{2} \quad (5)$

Table 2. Adsorption, dehydrogenation and oxygen vacancy formation energies for methane and propane reforming on sulfided and un-sulfided surfaces of pure, La-, Tb- and Mn-doped CeO₂ (1 1). The oxygen numbers refer to which oxygen the species is bound using the labels in Figure 1. O1 is the sulfur atom position in the sulfided cases. The * represents the carbon(s) or hydrogen bound to an oxygen or sulfur atom. Reaction types are defined in Table 1.

Reaction Type	Product Surface Species	Oxygen Sites	CeO ₂		La-Doped CeO ₂		Tb-Doped CeO ₂		Mn-Doped CeO ₂	
			Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)
A	O Vacancy	O1 (S1)	3.19	3.27	3.23	3.14	3.22	3.01	1.53	1.47
A	O Vacancy	O2	3.09	3.10	3.16	3.06	3.17	3.20	1.51	1.23
A	O Vacancy	O4	3.07	2.89	2.98	2.82	2.79	2.64	2.10	1.33
A	O Vacancy	O3	3.67	2.55	3.59	2.53	3.27	3.10	2.02	1.75
B	H*	O1 (S1)	1.28	1.64	1.61	1.95	1.30	1.76	0.84	1.23
B	H*	O2	1.22	1.15	1.54	1.52	1.38	1.45	1.51	1.34
B	H*	O4	1.24	1.13	1.48	1.40	1.23	1.19	0.98	0.75
B	H*	O3	1.27	1.22	1.62	1.60	1.30	1.40	0.83	0.77
C	C*H ₃	O1 (S1)	0.13	0.00	0.41	0.33	0.24	0.20	-0.13	-0.14
D	C*H ₂	O1 (S1)	1.81	1.85	1.99	1.76	1.91	1.69	0.29	1.25
D	C*H	O1 (S1)	1.48	1.69	1.01	1.94	1.13	2.43	2.18	2.43
D	C*	O1 (S1)	0.19	0.42	0.53	0.24	0.26	-0.22	-0.39	-0.33
E	Desorb CO/CS	O1 (S1)	0.56	1.70	0.17	1.32	0.35	1.44	0.06	0.67
C	CH ₃ C*HCH ₃	O4	-0.09	-0.35	0.07	0.00	-0.21	-0.19	-0.51	-0.60
D	C*H ₂ C*HCH ₃	O3,O4	0.49	1.18	0.45	1.04	0.32	0.83	0.15	0.23
D	C*HC*HCH ₃	O3,O4	0.48	-0.06	0.34	0.85	0.50	0.66	0.79	0.43
D	C*H ₂ C*HC*H ₂	O2,O3,O4	0.30	-0.33	0.33	-0.26	0.51	0.02	0.63	0.46
D	C*H ₂ C*HC*H ₂	O1,O3,O4	0.47	0.02	0.96	0.21	0.74	0.35	0.38	0.41

Table 3. Energies associated with the thermodynamic cycle decomposition of the abstraction of a hydrogen from a methane forming a methyl radical in the gas phase and a hydrogen adsorbed on the surface (on O1 for un-sulfided or S1 for sulfided) for pure, La-, Tb- and Mn-doped CeO₂ (1 1 1). This cycle is represented graphically is Figure 3, if the R₁ represents CH₃ and R₂ represents hydrogen. Step 2 is the sum of steps 2a-c and E_{act} is the sum of steps 1 and 2. Steps 2b and 2c are the energies associated with the thermodynamic cycle breakdown for the adsorption of a methyl radical on the surface.

	CeO ₂		La-Doped CeO ₂		Tb-Doped CeO ₂		Mn-Doped CeO ₂	
	Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)	Un-Sulfided (eV)	Sulfided (eV)
Step 1	4.81	4.81	4.81	4.81	4.81	4.81	4.81	4.81
Step 2a	3.53	1.80	3.48	1.74	3.25	1.69	1.37	0.02
Step 2b for H*	-1.66	-1.24	-1.66	-1.24	-1.66	-1.24	-1.66	-1.24
Step 2c for H*	-5.41	-3.72	-5.02	-3.36	-5.10	-3.49	-3.68	-2.36
Step 2 for H*	-3.54	-3.17	-3.20	-2.86	-3.51	-3.05	-3.98	-3.58
E _{act}	1.28	1.64	1.61	1.95	1.30	1.76	0.84	1.23
Step 2b for CH ₃ *	-1.41	-0.96	-1.41	-0.96	-1.41	-0.96	-1.41	-0.96
Step 2c for CH ₃ *	-4.52	-3.38	-4.19	-2.99	-4.13	-3.07	-2.62	-1.74
Step 2 for CH ₃ *	-5.94	-4.33	-5.61	-3.94	-5.55	-4.03	-4.04	-2.70

Table 4. The number of reduced cerium atoms and the oxidation state of the dopant atoms for methane and propane reforming surface intermediates over sulfided and un-sulfided surfaces of pure, La-, Tb- and Mn-doped CeO₂ (1 1 1). La- and Tb-doped ceria had the same extent of reduction at the surface for every step and the dopant is represented by M. The oxygen numbers refer to which oxygen the species is adsorbed to, using the labels in Figure 1. O1 is the sulfur atom at the sulfided surfaces. The * represents the carbon or hydrogen bound to an oxygen or sulfur atom, and the oxygen numbers represent the oxygen (sulfur) to which the carbon or hydrogen is bound.

	Oxygen Numbers	CeO ₂		La/Tb-Doped CeO ₂ ^a		Mn-Doped CeO ₂			
		Un-Sulfided	Sulfided	Un-Sulfided	Sulfided	Un-Sulfided		Sulfided	
		# Ce ³⁺	# Ce ³⁺	# Ce ³⁺	# Ce ³⁺	Mn States	# Ce ³⁺	Mn States	# Ce ³⁺
Starting Surface	-	2	2	0	0	2 Mn ³⁺	0	2 Mn ³⁺	0
H* On O1(S1)	O1	3	3	1	1	2 Mn ³⁺	1	2 Mn ³⁺	1
H* On O2	O2	3	3	1	1	2 Mn ³⁺	1	2 Mn ³⁺	1
H* On O3	O3	3	3	1	1	2 Mn ³⁺	1	2 Mn ³⁺	1
H* On O4	O4	3	3	1	1	2 Mn ³⁺	1	2 Mn ³⁺	1
C*H ₃	O1	3	3	1	1	1 Mn ²⁺ & 1 Mn ³⁺	0	1 Mn ²⁺ & 1 Mn ³⁺	0
C*H ₂	O1	3	3	1	1	1 Mn ²⁺ & 1 Mn ³⁺	1	1 Mn ²⁺ & 1 Mn ³⁺	1
C*H	O1	3	3	1	1	1 Mn ²⁺ & 1 Mn ³⁺	0	1 Mn ²⁺ & 1 Mn ³⁺	0
C*	O1	4	3	2	1	1 Mn ²⁺ & 1 Mn ³⁺	1	1 Mn ²⁺ & 1 Mn ³⁺	1
Desorb CO/CS	O1	4	4	2	2	1 Mn ²⁺ & 1 Mn ³⁺	1	1 Mn ²⁺ & 1 Mn ³⁺	1
CH ₃ C*HCH ₃	O4	3	3	1	1	1 Mn ²⁺ & 1 Mn ³⁺	0	1 Mn ²⁺ & 1 Mn ³⁺	0
C*H ₂ C*HCH ₃	O3, O4	4	4	2	2	2Mn ²⁺	0	1 Mn ²⁺ & 1 Mn ³⁺	1
C*HC*HCH ₃	O3, O4	5	5	3	3	2Mn ²⁺	1	2Mn ²⁺	1
C*H ₂ C*HC*H ₂	O2, O3, O4	5	5	3	3	1 Mn ²⁺ & 1 Mn ³⁺	2	1 Mn ²⁺ & 1 Mn ³⁺	2
C*H ₂ C*HC*H ₂	O1, O3, O4	5	5	3	3	1 Mn ²⁺ & 1 Mn ³⁺	2	1 Mn ²⁺ & 1 Mn ³⁺	2

^aLa- and Tb-dopants remained in the 3+ oxidation state in all intermediates along the methane/propane decomposition paths.

Figure 1. Top and side views of the $p(2 \times 2)$ unit cell expansion of sulfided M-doped CeO₂ (1 1 1). (a) side view, and (b) top view. The X is the position of the subsurface oxygen vacancy (the X denotes an oxygen vacancy in front of the labeled oxygen). The oxygen /sulfur atoms 1-4 labels are used in referring to surface adsorbate positions. Ce is displayed at tan (light), M as light blue (light gray), O as red (dark) and S as yellow (dark gray).

Figure 2. Four selected structures of hydrogen and a propyl derivative adsorbed onto the surfaces of sulfided and un-sulfided M-doped CeO₂. (a) H* (on O1) on the un-sulfided surface, (b) H* (on S1 (O1 position)) on the sulfided surface, (c) C*H₂C*HC*H₂ (on O1, O3, and O4) on the un-sulfided surface, (d) C*H₂C*HC*H₂ (on S1 (O1), O3, and O4) on the sulfided surface. Ce is displayed as tan (light), M as light blue (light gray), O as red (dark) and S as yellow (dark gray).

Figure 3. Thermodynamic cycle decomposition of the steps involved in the abstraction of R_2 from R_1 , forming a R_1 radical in the gas phase. For the sulfided surface where R_2 is bound to a sulfur, the O would be replaced with S.

Figure 4. Reaction energy (and free energy) diagram of methane decomposition over sulfided and un-sulfided surfaces of pure CeO_2 (1 1 1). For 0 K, ΔE values, the solid lines represent each hydrogen abstraction (product desorption) on the un-sulfided surface and the dotted lines are for the sulfided surface. ΔG values are labeled with long dash lines for the un-sulfided surface and the long-short dash for the sulfided surface. For the pseudo-transition state ($\text{CH}_3\bullet + \text{H}^*$), the long dash represents H abstraction on a sulfur atom and the short dash represents abstraction on an oxygen atom. The free energy values were calculated at biomass gasifier effluent conditions, 0.234 atm H_2 and 0.32 atm CO/CS at 1000K, with a methane partial pressure of 0.25 atm. The final product of this diagram has an additional oxygen vacancy formed upon CO (CS) desorption, and with vacancy refilling, the overall computed free energy of reaction for methane reforming to CO is -0.08 eV.

Figure 5. Structures of methane decomposition intermediates over (a-e) un-sulfided and (f-j) sulfided (1 1 1) surfaces of pure CeO₂. Isodensity surfaces representing isolated electron states on adsorbates are displayed in (b-c) and (g-i). They represent states appearing in the ceria band gap in the energy ranges of (b) -0.72 to -0.60 eV, (c) -1.24 to -1.10 eV, (g) -0.48 to -0.36 eV, (h) -0.55 to -0.35 eV, and (i) -0.36 to -0.13 eV (relative to the Fermi level). Total density of states for these structures are given as Figures S9 and S10. Ce is displayed as tan (light), O as red (dark), S as yellow (dark grey).

Figure 6. Reaction energy diagram of methane decomposition over sulfided and un-sulfided surfaces of Mn-doped CeO_2 (1 1 1). The solid lines represent each hydrogen abstraction (product desorption) on the un-sulfided surface and the dashed lines for the sulfided surface. For the pseudo-transition state ($\text{CH}_3^\bullet + \text{H}^*$), the long dash represents H abstraction on a sulfur atom and the short dash represents abstraction on an oxygen atom.

Figure 7. Lewis structures for methane decomposition surface intermediates over (a-e) surface oxygen atoms and (f-j) surface sulfur atoms over pure CeO_2 (1 1 1). Every image corresponds to the structure with the same letter displayed in Figure 5.

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