DISTRIBUTION OF La AND O VACANCIES IN BULK AND SURFACE MODELS OF CERIA

A Thesis in
Chemical Engineering
by
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Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

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ABSTRACT

Dry reforming of methane is a significant alternative energy technology that can valorize two major greenhouse gases, methane and carbon dioxide, by converting them to synthesis gas. One of the major challenges involved in making dry reforming of methane a commercially viable process is to design a catalyst that would have high activity, selectivity, sulfur tolerance, and resistance to coking. Preliminary experimental and density functional theory (DFT) studies have shown that transition metal (TM) doped rare earth oxides (REOs) can provide better coking resistance and sulfur tolerance than conventional reforming catalysts by forming oxysulfide surfaces. Further atomistic scale understanding of these catalytic systems for dry reforming of methane calls for a thorough understanding of dopant and doping induced O vacancy distribution in the REO, to develop a reasonable model of the TM-doped REO.

This thesis utilizes DFT to study the distribution of La and O vacancies in bulk and surface models CeO$_2$. The La dopant and O vacancy preferences have been studied in the bulk by low and high level doping of La atoms in the CeO$_2$ fluorite supercell. We also consider La and O vacancy distribution on a 5 layered CeO$_2$ (111) surface slab. The energies and the probabilities for different possible configurations have been evaluated and used to identify the most stable arrangements of La and O vacancies in CeO$_2$ bulk and surfaces. Future reactivity studies using the most stable surface model developed from this study are discussed.
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CHAPTER 1

Background and Motivation

The availability of large shale gas reserves and developments in hydraulic fracturing and horizontal drilling technology have led to an increased attention on methane as a potential carbon source for the world’s growing energy needs\(^1\). Methane can be used for the generation of heat, electricity and, most relevant to this study, synthesis gas. Synthesis gas, also called syn gas, is a mixture of carbon monoxide and hydrogen that can serve as a building block for the production of liquid fuels and chemicals. Meanwhile, the combustion of fossil fuels to meet our energy demands has amplified carbon dioxide emissions causing significant concern over its effect on global warming and climate change. Dry reforming of methane (DRM) represents an innovative approach to utilize methane and carbon dioxide, two of the most predominant greenhouse gases, to make synthesis gas (Eq. 1). It serves as a sustainable alternative energy producing solution that can ease the impact of both the compounds as well as create valuable products.

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad (\Delta H_{298\text{ K}} = +247 \text{ kJ mol}^{-1})
\]  

(1)

DRM requires temperatures between 1073-1273 K\(^1\). The ratio of CO/H\(_2\) that this reaction gives makes it attractive for Fisher-Tropsch process that converts the synthesis gas to liquid fuels and in the manufacturing of chemicals like methanol and ammonia\(^2\). However, there are some challenges in making DRM a commercially practical process. First, the likely feeds for the process are raw or partly purified natural gas. These have sulfur containing compounds which are known to poison the catalyst used for the reforming
reaction. Second, DRM is inevitably accompanied by catalyst deactivation due to carbon deposition. The DRM main reaction (Eq. 1) is followed by three side reactions, methane decomposition (Eq. 2), carbon monoxide disproportionation (also called the Boudouard reaction) (Eq. 3), and the reverse water gas shift (RWGS) reaction (Eq. 4).

\[
\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2 \quad (\Delta H_{298 K} = +75 \text{ kJ mol}^{-1}) \tag{2}
\]

\[
2\text{CO} \rightleftharpoons 2\text{C} + \text{O}_2 \quad (\Delta H_{298 K} = -171 \text{ kJ mol}^{-1}) \tag{3}
\]

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{298 K} = 41 \text{ kJ mol}^{-1}) \tag{4}
\]

Studies on the thermodynamics of carbon deposition show that the first two side reactions are responsible for catalyst deactivation. Wang et al. reported that, the DRM reaction proceeds at temperatures in excess of 913 K and formation of carbon most likely takes place within the temperature range of 830 K – 973 K. To kinetically inhibit coke formation and to improve the DRM reaction rate, the choice of catalyst becomes very important. The third practical challenge for DRM is that, the high temperatures required for the reaction cause sintering of the active catalytic material. Therefore, the development of stable reforming catalysts with high activity, selectivity, sulfur tolerance, and resistance to coking would improve process energy efficiency, decrease cost, and allow DRM to reach economic feasibility.

A wide range of heterogeneous catalysts have been studied under various operating parameters for this purpose. A general agreement in these works is that traditional Ni based catalysts on metal oxide supports are not optimal and are prone to deactivation. Nobel metal catalyst like Rh and Ru show high resistance to carbon deposition. However,
their high cost, challenges their employment as an industrial DRM catalyst\textsuperscript{9,10}. Other transition metals (Pt, Co, Pd, Ir) supported on metal oxides (Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, MgO, CeO\textsubscript{2}, ZrO\textsubscript{2}), bimetallic catalysts (Ni-Co, Ni-Fe), perovskites, and structured catalysts like foams and monoliths are also some of the catalytic systems being studied for DRM\textsuperscript{1,3,4}.

Rare earth oxides (REOs) have been studied for their catalytic properties. Several experimental investigations revealed that the addition of REOs to Ni based reforming catalysts result in improved catalytic activity\textsuperscript{11} as well as resistance to carbon formation\textsuperscript{12–15}, and sulfur poisoning\textsuperscript{16–18}. Ceria is one of the common REOs examined due to its ability to readily transition between oxidation states that makes it a good redox catalyst\textsuperscript{19}. Transition metal (TM) oxide – CeO\textsubscript{2} mixed materials can be used to adsorb sulfur\textsuperscript{20–22} as well as reform hydrocarbons\textsuperscript{23–25}. Dooley et al. studied TM-doped REOs for tar reforming and observed that, at temperatures > 1100 K, TM-doped REOs exhibit higher tolerance to sulfur and lesser coke accumulation than Ni based catalysts\textsuperscript{23}. Doping ceria with transition metals like Mn, La, Tb, and Zr, alter the surface reducibility, catalytic activity and sulfur adsorption capacity\textsuperscript{21,26–29}. Recent computational studies on CeO\textsubscript{2} and TM- doped CeO\textsubscript{2} surfaces for alkane reforming suggest that these systems may form thermodynamically stable oxysulfide surfaces where sulfur substitutes some of the surface oxygen sites\textsuperscript{30}. Though this reduces the number of sites available for the activation of the C-H bond, it does not alter the activity of the remaining surface oxygen atoms. The study also suggests that by doping ceria with TM, it is possible to destabilize carbon forming intermediates.

Based on these preliminary studies, we hypothesize that TM-doped REOs are promising catalytic systems for DRM that may provide coking resistance and retain activity.
in the presence of sulfur by forming oxysulfide surfaces under reforming conditions. However, there is a lack of understanding of several significant aspects of these catalytic systems such as the mechanism of dry reforming over the unsulfided and oxysulfided surfaces of TM-doped REOs, effect of dopant properties on reactivity, surface structure and stability relative to phase segregation under reforming conditions, CH₄ and CO₂ activation over oxysulfide surfaces, tendency for carbon-carbon bond formation and how surface sulfidation alters reforming and coking kinetics. Hence it is important to apply atomistic scale simulation methods to gain fundamental insights on the nature of these oxysulfide surfaces. Such studies are necessary, not only to develop a mechanistic rationale for how surface sulfidation affects DRM and coke formation over model TM-doped REOs, but also to identify key factors that can help design better catalysts for the process.

An essential step in computational examination of TM-doped REOs for dry reforming of methane is model development. Surface properties evaluated using model TM-doped REOs are strongly affected by the distribution of the dopants and oxygen vacancies in the model. This necessitates a thorough evaluation of the atomistic scale distribution of dopants and oxygen vacancies in REOs and the identification of stable configurations for studying DRM.

In this work, we have chosen to examine the distribution of La dopants and O vacancies in CeO₂. Initial density functional theory (DFT) analysis of this system suggest that it exhibits a reasonable ability to activate methane. Theoretical and experimental studies on H₂S adsorption on ceria-lanthanide mixtures indicate that it is a good sulfur sorbent with the potential to form stable oxysulfide surfaces. La-doped CeO₂ forms
stable fluorite-structured mixed oxides up to dopant concentrations of 60% and La exhibits a tendency to surface segregate\textsuperscript{31}. Experimental analysis indicate that La doping can induce vacancies beyond that in pure CeO\textsubscript{2}\textsuperscript{32}. Theoretical calculations and adsorption spectroscopy suggest that the dopant ions and oxygen vacancies do not disperse randomly but are likely to form clusters\textsuperscript{33,34}. An NMR investigation suggested that two La ions are always accompanied by a vacancy\textsuperscript{35}. Conversely atomistic simulations show that La ions prefer to take second neighbor positions with respect to the vacancy\textsuperscript{36}.

Thus, literature reports on the distribution of the La dopants and oxygen vacancies are not consistent enough to use it to develop a reasonable model of the doped oxide system under reforming conditions. In addition to this, an understanding of the stability, electronic structure and properties of La-doped CeO\textsubscript{2} is of paramount importance to be able to know its utility in other applications such as ion conducting electrolytes for solid oxide fuel cells, automotive exhaust catalysis, oxidation catalysis etc.

Herein, we have used density functional theory to study the La and O vacancy distribution in bulk and surface models of CeO\textsubscript{2}. We aim to combine the existing knowledge about these systems with insights gained from atomistic scale modelling techniques to propose a defendable model of La-doped CeO\textsubscript{2} surface that can be adapted for future DFT studies of surface reaction processes.
CHAPTER 2

Distribution of La and O Vacancies in Bulk and Surface Models of CeO₂

2.1 Introduction

Lanthanum-Ceria mixed oxides are potential materials for use as desulfurization adsorbents, solid-oxide fuel cell (SOFC) electrolytes and oxidation catalysts. LaₙCe₁₋ₓOₙ hydrocarbon reforming catalysts can be sulfur tolerant with higher resistance to carbon deposition than Ni-based catalysts. Atomistic scale understanding of the kinetics and thermodynamics of sulfide formation, coke formation and reforming over La-doped CeO₂ surfaces is essential to develop better reforming catalysts. A necessary step for carrying out computational surface catalytic studies using La-doped CeO₂ is, building a reasonable atomistic model of the system. The atomic arrangement of La and O vacancies, however, is not clearly established. The molecular level distribution of La and O vacancies can have significant effects on the bulk and surface properties of the material. In this work, we use density functional theory to examine the distribution of La and O vacancies in bulk and surface models of LaₙCe₁₋ₓOₙ.

Experimental phase relation studies of CeO₂-La₂O₃ solid solutions have established that LaₙCe₁₋ₓOₙ materials form a stable mixed oxide fluorite structure up to La atomic fractions of x = 0.6 under conditions where fluorite is the stable CeO₂-δ structure. Surface characterization of these materials reveal that La exhibits a strong tendency to surface segregate. Doping of CeO₂ with La induces charge compensating O vacancies in the fluorite lattice in order to take a La³⁺ formal oxidation state. XPS analysis of Ce₁₋ₓLaₓO₂₋δ nanosized solid solution by Reddy et al. revealed that the sample
contained both Ce\(^{4+}\) and Ce\(^{3+}\) atoms, indicating that doping with La can facilitate Ce\(^{4+}\) reduction\(^{48}\). An EXAFS study on La-doped CeO\(_2\) suggested that the dopants form a dopant-vacancy-dopant cluster\(^{34}\). Hayashi et al. also observed, in their molecular dynamics simulations of La-doped CeO\(_2\), that the vacancies prefer to cluster at nearest neighbor positions to the La\(^{3+}\). A kinetic Monte Carlo model of defect transport in La-doped CeO\(_2\) proposed that it is easier for the oxygen vacancy to migrate towards the La than away from it, thus exhibiting a tendency to cluster\(^{49}\). Heinmaa et al. conducted local structure evaluation of La-doped CeO\(_2\) using NMR and showed that, at low concentrations, about half of the La\(^{3+}\) ions are not directly bound to a vacancy and such clusters occur only at higher concentrations of dopant\(^{35}\). A study on defect structure in ferromagnetic nanocrystals of La-doped CeO\(_2\) also reports dopant vacancy clustering to occur at higher dopant concentration\(^{50}\). Contrary to these studies, Raman spectroscopy of Ce\(_{0.8}\)La\(_{0.2}\)O\(_2\)\(_{0.5}\) suggest that the La dopant appears as a MO\(_8\) – type complex, not directly adjacent to an O vacancy\(^{51}\). Minervini’s et al. atomistic scale simulations to study defect cluster formation in M\(_2\)O\(_3\) – doped CeO\(_2\) showed that, for La dopants, the oxygen vacancies prefer to segregate to next nearest neighbor sites\(^{36}\). Previous DFT studies have examined the electronic structure of La-doped CeO\(_2\), but have not evaluated the relative stability of various distributions of La and O vacancies\(^{32}\).

In summary, there is no conclusive determination of the atomic arrangement of La dopants and O vacancies in La-doped CeO\(_2\). In this work, we have used density functional theory (DFT) to evaluate the structural and energy changes in bulk and surface models of CeO\(_2\) upon doping with low and high concentrations of La. We have identified the La-La and La-O vacancy distribution preference in both bulk and surface models of La\(_x\)Ce\(_{1-x}\)O\(_y\)
by evaluating and comparing the energies associated with different possible configurations of La and O vacancies. We have used the relative energies to illustrate a probability distribution for both the bulk and surface structures of La$_x$Ce$_{1-x}$O$_y$.

2.2 Methods

2.2.1 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$^{52-54}$. A plane wave basis set was used to represent the valence electrons with a cutoff of 700 eV. The core region was represented using the projector augmented wave (PAW) method$^{55}$. The valence configurations were $5s^25p^66s^24f^45d^1$ for cerium, $5s^25p^65d^16s^2$ for lanthanum, $2s^22p^4$ for oxygen. All DFT calculations were spin polarized. The exchange and correlations energies were represented using the Perdew, Burke and Ernzerhof (PBE) version of the generalized gradient approximation (GGA)$^{56}$. The Monkhorst Pack k-point sampling scheme was utilized with a (3 x 3 x 1) grid, with the third vector perpendicular to the surface and a (3 x 3 x 3) grid for the bulk$^{57}$. All forces were converged to 0.05 eV•Å$^{-1}$ for structural optimizations, and a force criterion of 0.02 eV•Å$^{-1}$ was tested and both the structures and energetics were converged at the coarser value.

We applied the DFT+$U$ approach due to well established difficulties that DFT has in representing the nature of the 4f orbitals of cerium$^{58-60}$. A Hubbard $U$-correction adds an on-site Coulombic interaction term that penalizes non-integer occupation of localized orbitals$^{61,62}$. This correction effectively prevents the delocalization of 4f electrons in
reduced ceria. We utilized a $U$-value of 5 eV on the $f$ orbitals of cerium which is consistent with prior DFT work on ceria$^{25,26,28,32,63–68}$. As discussed in previous studies, the absolute reduction energies depend on the choice of $U$ value, though trends in reduction energetics are preserved with varying $U^{26,30,64}$. Also, without an experimental benchmark, it is not possible to conclusively determine if the choice of the $U$ value reproduces the experimental reduction energy$^{67}$. Thus, the quantitative analysis presented herein is $U$-dependent and the absolute energies may not exactly match experimental values. However, a $U$ value of 5 eV provides an accurate description of the electronic structure of reduced ceria to qualitatively understand trends in $\text{La}_2\text{O}_3/\text{CeO}_2$ mixing and distribution of La and O vacancies.

2.2.2 Bulk Models

To model the bulk, a cubic fluorite unit cell of ceria ($\text{Ce}_4\text{O}_8$) and a 2 x 2 x 2 expansion of the cubic fluorite unit cell ($\text{Ce}_{32}\text{O}_{64}$) were used. The bulk lattice constant evaluated after optimization is 5.482 Å, within 1.5% of the reported experimental values$^{31,43,69}$. To study the distribution of La atoms and O vacancies in ceria, Ce atoms were substituted by La and stoichiometric O vacancies were created. The distribution was studied using the $\text{Ce}_{32}\text{O}_{64}$ supercell at low and high La concentrations containing 6.25% ($\text{La}_2\text{Ce}_{30}\text{O}_{63}$) and 25% ($\text{La}_8\text{Ce}_{24}\text{O}_{60}$) La atoms.

2.2.3 Surface models

A p(2 x 2) ($\text{Ce}_{20}\text{O}_{40}$) unit cell expansion is used with 5 CeO$_2$ layers (15 atomic layers) which are converged to surface formation and oxygen vacancy formation energies as shown in our previous study$^{26}$. To minimize the effect of any surface normal net dipole moment on energetics, a dipole correction was added to the calculations within the self-
consistent field cycle \cite{70,71}. The (1 1 1) surface is used because it is the lowest energy surface among single crystal terminations of ceria \cite{19,64,72}. 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 distribution of La in the surface of CeO$_2$ was studied by substituting 2 Ce atoms with La atoms and creating a stoichiometric vacancy in different surface layers.

2.2.4 Definition of Energetics

The O vacancy formation reaction (Eq. 5) and the formula used to evaluate the vacancy formation energy, $E_{\text{vac}}$, in the Ce$_4$O$_8$ unit cell in this study are:

$$La_xCe_{4-x}O_{8-(n-1)} \rightarrow La_xCe_{4-x}O_{8-n} + \frac{1}{2}O_2$$

(5)

$$E_{\text{vac}} = E_{La_xCe_{4-x}O_{8-n}} + \frac{1}{2}E_{O_2} - E_{La_xCe_{4-x}O_{8-(n-1)}}, n \geq 1$$

$E_{La_xCe_{4-x}O_{8-(n-1)}}$ is the energy of the unit cell before creating an oxygen vacancy.

$E_{O_2}$ is the energy of a gas phase O$_2$ molecule.

$E_{La_xCe_{4-x}O_{8-n}}$ is the energy of the unit cell after removing an oxygen atom.

The probability of occurrence of a configuration i, $P_i$, is given by:

$$P_i = \frac{J_i e^{-E_i/RT}}{\sum J_i e^{-E_i/RT}}$$

(6)

$J_i$ is the degeneracy of the configuration i.

$E_i$ is the energy of the configuration i relative to the most stable configuration.
$R$ is the gas constant whose value used here is 0.00831 kJ mol$^{-1}$ K$^{-1}$.

$T$ is temperature. We calculate the probability distribution at 1000 K as this value lies in the temperature range at which these materials are calcined and tested for high temperature reactions$^{23,43}$.

2.3 Results and Discussions

DFT was used to examine the distribution of La and O vacancies in bulk and surface models of CeO$_2$. Section 2.3.1 considers bulk La-doped CeO$_2$, represented with both a Ce$_4$O$_8$ unit cell and a Ce$_{32}$O$_{64}$ supercell. First, the effect of La doping on the O vacancy formation energy using the Ce$_4$O$_8$ cell is examined in Section 2.3.1.1. This is followed by Section 2.3.1.2, which elucidates the distribution of La and O vacancy at low dopant levels using the Ce$_{32}$O$_{64}$ supercell. We then examine the distributions at a higher dopant level in Section 2.3.1.3. In Section 2.3.2, we examine the segregation of La and O vacancies in a CeO$_2$ (111) surface. First, the segregation of La atoms on CeO$_2$ (111) surface at fixed O vacancy positions is examined in Section 2.3.2.1 to identify the stable configurations of La dopants on CeO$_2$ surface. The O vacancy distribution is then evaluated in these stable La-doped CeO$_2$ surface configurations in Section 2.3.2.2.

2.3.1 Bulk Models of La-doped CeO$_2$

2.3.1.1 Effect of La doping on O vacancy formation energy

The effect of La doping on the oxygen vacancy formation energy of ceria was studied using Ce$_4$O$_8$ cells. Table 2-1 shows the oxygen vacancy formation energies evaluated for un-doped and La-doped CeO$_2$. The energies suggest that La doping significantly reduces the oxygen vacancy formation energy in ceria. This observation is
consistent with previous studies on La$_x$Ce$_{1-x}$O$_y$ materials$^{32}$. The oxygen vacancy formation energies in the Ce$_4$O$_8$ cells with one La and two La indicate that there is a strong preference for the La to be doped as pairs of La with a charge compensating stoichiometric vacancy, allowing both La to have a 3+ oxidation state. The creation of a vacancy beyond the stoichiometric vacancy in the doped cells leads to the reduction of Ce from Ce$^{4+}$ to Ce$^{3+}$. This was confirmed by the DOS provided in Figure 2-1, showing spin up f state on Ce atom as well as Bader charge differences reported in Table 2-2, showing charge accumulation on the Ce atom. Doping with La reduces the energy needed for this sub stoichiometric reduction relative to reduction in Ce$_4$O$_8$, thereby enhancing the reducibility of pure ceria and supporting the experimental observation made by Reddy et al.$^{46}$.

**Table 2-1.** Vacancy formation energies (E$_{\text{vac}}$) evaluated using M$_4$O$_8$ cell.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E$_{\text{vac}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_4$O$_8$ → Ce$_4$O$_7$ + $\frac{1}{2}$O$_2$</td>
<td>3.77</td>
</tr>
<tr>
<td>Ce$_4$O$_7$ → Ce$_4$O$_6$ + $\frac{1}{2}$O$_2$</td>
<td>2.94</td>
</tr>
<tr>
<td>LaCe$_3$O$_8$ → LaCe$_3$O$_7$ + $\frac{1}{2}$O$_2$</td>
<td>1.53</td>
</tr>
<tr>
<td>La$_2$Ce$_2$O$_8$ → La$_2$Ce$_2$O$_7$ + $\frac{1}{2}$O$_2$</td>
<td>-0.20</td>
</tr>
<tr>
<td>La$_2$Ce$_2$O$_7$ → La$_2$Ce$_2$O$_6$ + $\frac{1}{2}$O$_2$</td>
<td>2.76</td>
</tr>
</tbody>
</table>
Figure 2-1. The Total Density of States (TDOS) plotted vs Energy (referenced to Fermi level). The black arrow points to the peak that indicates presence of a spin up $f$ electron on Ce atom.

Table 2-2. Bader charge on Ce atoms in Ce$_4$O$_8$, La$_2$Ce$_2$O$_7$ and La$_2$Ce$_2$O$_6$.

<table>
<thead>
<tr>
<th></th>
<th>Bader Charge (e) on Ce atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_4$O$_8$</td>
<td>9.64</td>
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<tr>
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<td>9.64</td>
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<td></td>
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<td>9.64</td>
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</tbody>
</table>
2.3.1.2 La and O vacancy distribution in La$_2$Ce$_{30}$O$_{63}$ cell

The segregation of La dopants in ceria was studied using a 2x2x2 ceria supercell (Ce$_{32}$O$_{64}$). The different sites for La doping were identified which lead to 5 symmetry non-equivalent configurations for La$_2$Ce$_{30}$O$_{64}$ (Figure 2-2). The La atoms do not show much preference as to how they would like to distribute, with maximum energy difference of 0.05 eV across the five structures. The values are reported in Table 2-3. However, a stable structure would include stoichiometric oxygen vacancies that reduce all La to a formal oxidation state of 3+. For two La dopants, the relevant cell formulation to be studied is thus La$_2$Ce$_{20}$O$_{63}$. To identify the preferred sites for the creation of the stoichiometric vacancies, different configurations of La$_2$Ce$_{30}$O$_{63}$ were classified with the vacancies being nearest neighbor (NN), next to nearest neighbor (NNN) and far with respect to both the La atoms. The relative energies for these different configurations are shown in Figure 2-3. In agreement with the observations of Minervini et al., there is a slight preference for the vacancies to occur in the next nearest neighbor positions to both the La atoms. The energetic preference for structures where the vacancy is NNN to both La atoms is almost 0.35 eV relative to the structures where the vacancy is far from both of the La atoms. Figure 2-4 shows the probability of occurrence of each of these configurations evaluated using Eq. 6. The most probable arrangement of La and O vacancy is configuration 3 in which the O vacancy is NNN to both the La atoms and the La atoms are NNN to each other.
Table 2-3. Relative energies of La$_2$Ce$_{30}$O$_{64}$ bulk structures, with La dopant configurations 1-5 illustrated in Figure 2-2. Energies are relative to most stable configuration 3.

<table>
<thead>
<tr>
<th>Configuration type</th>
<th>Relative Energy (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 2-2. Different configurations of 2 La dopants in La$_2$Ce$_{30}$O$_{64}$. 
Figure 2-3. Relative energies of the different La$_2$Ce$_{30}$O$_{63}$ bulk structures. La dopant configurations 1-5 are illustrated in Figure 2-2. Labels give O vacancy position relative to the 2 La dopants. NN and NNN indicate nearest neighbor and next nearest neighbor vacancy respectively. Energy is relative to most stable configuration (Configuration 1 with NNN-NNN vacancy).

Figure 2-4. Probability of occurrence of the different La$_2$Ce$_{30}$O$_{63}$ configurations.
2.3.1.3 La and O vacancy distribution in La$_8$Ce$_{24}$O$_{60}$ cell

The distribution of La and vacancies at a higher doping level was studied using a La$_8$Ce$_{24}$O$_{60}$ cell. There are too many configurations for the 8 La atoms to exhaustively consider all distributions. 4 configurations were chosen to observe trends in La and vacancy segregation. These configurations are shown in Figure 2-5 and their relative energies are shown in Table 2-3. In each of these configurations, stoichiometric vacancies can be created in an enormous number of combinations. A subset of these was chosen to observe relative stability of La$_8$Ce$_{24}$O$_{60}$ structures and vacancy ordering. Figure 2-6 illustrates the relative energies of these structures. Irrespective of the arrangement of the 8 La atoms in the supercell, the vacancies do not prefer to cluster. The energy of the structure is lowered by about 1.2 – 1.8 eV when a vacancy in a cluster is moved far from the cluster, resulting in a structure with a vacancy trimer (Comparing structure 1 and 6 in Figure 2-6). Of the configurations considered, the one with La atoms in configuration 3 and vacancies ordered along face diagonal (Figure 2-7) has the lowest energy and a high probability of occurrence of 0.86. The probability of occurrence of a La$_8$Ce$_{24}$O$_{60}$ structure with La atoms in configuration 2 and vacancies ordered along body diagonal (Figure 2-7) is 0.12. The probabilities of all other La configurations and vacancy ordering is negligible. Thus, there is a strong preference for vacancies to be ordered randomly along body or face diagonal relative to clustering or being far from each other, i.e. in the <110>, <101> or <111> direction. Similar ordering of vacancies has been observed through DFT studies in pure CeO$_2$ by Murgida et al. and EELS and SAED studies on Lanthanide (Sm, Gd, Dy and Yb)
doped CeO$_2$ by Ou et al$^{73,74}$. However, further experimental work on La-doped CeO$_2$ would be needed to confirm our DFT conclusion.

Figure 2-5. Different configurations of 8 La dopants in La$_8$Ce$_{24}$O$_{64}$.

Table 2-4. Relative energies of La$_8$Ce$_{24}$O$_{64}$ bulk structures, with La dopant configurations 1-4 illustrated in Figure 2-5. Energies are relative to most stable configuration 4.

<table>
<thead>
<tr>
<th>Configuration type</th>
<th>Relative Energy (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 2-6. Relative energies of the different La$_8$Ce$_{24}$O$_{60}$ bulk structures. La dopant configurations 1-4 are illustrated in Figure 2-5. Energy is relative to most stable configuration (Configuration 3 with vacancies along face diagonal).

Labels are defined as:
Cluster - four vacancies clustered together
Line - four vacancies ordered linearly
Dimer-Dimer - pairs of vacancies far away from each other
Far - all four vacancies far from each other
Body Diagonal – vacancies ordered along body diagonal of cubic sub lattice (Figure 2-7)
Trimer-Single – three vacancies clustered together and one far from the cluster
NN-NNN – four vacancies that lie in the NN and NNN shells of the La atoms
Face Diagonal - vacancies ordered along face diagonal of cubic sub lattice (Figure 2-7)
2.3.2. Surface Models of La-doped CeO$_2$

2.3.2.1 La segregation in La-doped CeO$_2$ (111) surface

To examine the La segregation in ceria surfaces, 2 La atoms were doped into a 5 layered CeO$_2$ (1 1 1) surface slab (Ce$_{20}$O$_{40}$) and a stoichiometric oxygen vacancy was created. The position of the stoichiometric oxygen vacancy was initially fixed in the surface layer and energies of 6 different surface structures, having La atoms distributed in surface, first subsurface and bulk layers, were evaluated. The surface configurations studied are illustrated in Figure 2-8. The relative energies of these structures are reported in Table 2-5. The probability of occurrence was evaluated for each of these surface configurations. The configuration with both the La atoms in the surface layer has a probability of 0.61. The configuration with one La atom in the surface layer and one in the first subsurface layer has a probability of 0.39. All other atomic arrangements, including both La atoms in subsurface and bulk layers, have negligible probability of occurrence. From the
probabilities and the relative energies, it is clear that La atoms have a strong preference to surface segregate, leaving with a 1:1 ratio of La:Ce on the surface layer or a 1:3 ratio in both the surface and first subsurface layers. This is in good agreement with several experimental studies on $\text{La}_2\text{O}_3$ – CeO$_2$ solid solutions$^{31,43,44}$.

**Figure 2-8.** Surface configurations of $\text{La}_2\text{Ce}_{18}\text{O}_{39}$ (111) surface.
Table 2-5. Relative energies of La$_2$Ce$_{18}$O$_{39}$ surface structures. The energies are relative to the most stable configuration containing both La atoms on the surface.

<table>
<thead>
<tr>
<th>Position of La$_1$</th>
<th>Position of La$_2$</th>
<th>Relative Energy (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>Surface</td>
<td>0.0</td>
</tr>
<tr>
<td>Surface</td>
<td>Sub-surface</td>
<td>0.1</td>
</tr>
<tr>
<td>Sub-surface</td>
<td>Sub-surface</td>
<td>0.25</td>
</tr>
<tr>
<td>Surface</td>
<td>Bulk</td>
<td>1.15</td>
</tr>
<tr>
<td>Sub-surface</td>
<td>Bulk</td>
<td>1.47</td>
</tr>
<tr>
<td>Bulk</td>
<td>Bulk</td>
<td>3.22</td>
</tr>
</tbody>
</table>

2.3.2.2 O vacancy distribution in La-doped CeO$_2$ (111) surface

The preferred distributions of O vacancy in La-doped CeO$_2$ (111) surface was studied using models with the most probable surfaces configurations of La atoms found in the previous section. We considered both a model of La$_2$Ce$_{18}$O$_{39}$ with the two La atoms on the surface and a second model with one La atom on the surface and one in the subsurface. Henceforth these models are designated as Surf_Surf and Surf_SubSurf respectively. In these models, O vacancies were created in the surface, first subsurface, second subsurface, and bulk layers (bottom two trilayers of the (111) surface that were frozen during optimization). These layers are illustrated in Figure 2-9 using the Surf_Surf model of La$_2$Ce$_{18}$O$_{39}$. The relative positions of these vacancies with respect to the La atoms were either nearest neighbor (NN), next to nearest neighbor (NNN) or far from both the La atoms. The energies of the structures with different vacancy positions were evaluated for
each model. The relative energies are reported in Table 2-6. It becomes evident from the values reported in the table that the most stable arrangement of 2 La atoms and a O vacancy in CeO₂ (111) surface is the Surf_SubSurf model with an O vacancy in the subsurface that is NNN to both the La atoms. The probability of occurrence is also the highest for this arrangement with a value of 0.86. This model matches that used for La-doped CeO₂ in our group’s previous study of H₂S adsorption and alkane reforming, though the relative stability was not previously evaluated²¹,³⁰. The Surf_Surf model with a subsurface O vacancy that is NN to one La and NNN to the other has a probability of about 0.11. All other distributions of O vacancy in both the models have negligible probabilities.

![Illustration of surface layers in which O vacancies were created.](image)

**Figure 2-9.** Illustration of surface layers in which O vacancies were created.
Table 2-6. Relative energies of the different \( \text{La}_2\text{Ce}_{18}\text{O}_{39} \) structures using Surf_Surf and Surf_SubSurf models. The energies are relative to the most stable configuration (row 4, column 7).

<table>
<thead>
<tr>
<th>Vacancy Layer</th>
<th>Vacancy Position relative to La atoms</th>
<th>Relative Energy</th>
<th>Surf_Surf</th>
<th>Surf_SubSurf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>NN NN</td>
<td>0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NN NNN</td>
<td>0.52</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NNN NNN</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NN Far</td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Subsurface 1</td>
<td>NN NN</td>
<td>0.58</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NN NNN</td>
<td>0.18</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NNN NNN</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Subsurface 2</td>
<td>NN NN</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NN NNN</td>
<td>0.59</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NNN NNN</td>
<td>0.45</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Bulk</td>
<td>Far Far</td>
<td>3.06</td>
<td>2.77</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Conclusions

We have explored the distribution of La and O vacancies in bulk and surface models of \( \text{CeO}_2 \) using density functional theory methods. Using the \( \text{Ce}_4\text{O}_8 \) unit cell, we find that stable doped structures contain a charge compensating stoichiometric oxygen vacancy for each pair of La atoms. Bulk distributions of La and O vacancies were studied using a \( \text{Ce}_{32}\text{O}_{64} \) supercell. There is little inherent preference for specific distributions of La atoms, though O vacancy positioning can bias La atom distribution to allow for a small degree of vacancy ordering. There is a small preference of dilute La dopants and O vacancies
towards distributions that allow O vacancies at next nearest neighbor positions to the La atoms. At higher La dopant/O vacancy levels, again there is very little preference for specific distributions of La atoms. The position of O vacancies, however, drives the distribution of La into certain configurations. Oxygen vacancies prefer not to cluster or distribute randomly in bulk La-doped CeO$_2$. The most stable vacancy ordering is along the body or face diagonal of the O cubic sub lattice, i.e. in the $<110>$, $<101>$ and $<111>$ direction.

Surface studies using a 5 layer CeO$_2$ (111) surface slab reveal that La atoms prefer to surface segregate, thereby confirming several experimental surface segregation observations. The two configurations of La$_2$Ce$_{18}$O$_{39}$ containing an associated vacancy that are stable include two La’s in the surface layer or one La in the surface layer and one in the first subsurface layer. The most stable distribution contains one La atom on the surface layer the other La atom in the first subsurface layer and the O vacancy in the first subsurface layer at a next to nearest neighbor position to both the La. The distribution preferences at the surface, therefore, are similar to the bulk, with an added tendency of La to segregate to the top two layers and O vacancy to segregate to the first subsurface layer.
CHAPTER 3

Future Work

One of the key issues in making dry reforming of methane a viable process is catalyst deactivation due to coke formation. C-H bond activation over TM-doped REOs has been previously studied\textsuperscript{26,64,66}. However, C-C bond breaking and formation over TM-doped REOs is a relatively unexplored area. The surface model of La-doped CeO\textsubscript{2} developed in this work can be utilized to understand C – C bond formation and coke formation kinetics. To develop an initial understanding of the tendency for C – C bond formation on La – doped CeO\textsubscript{2}, we have studied the surface reaction between adsorbed CH\textsubscript{3}\textsuperscript{*} and CH\textsubscript{2}\textsuperscript{*} to form C\textsubscript{2}H\textsubscript{5}\textsuperscript{*} using the La-doped CeO\textsubscript{2} surface model developed in this work. The reactant and product states are depicted in Figure 3-1.

The climbing image nudged elastic band method (CI-NEB)\textsuperscript{75–77} was used to isolate the transition state for this reaction. Within the CI-NEB method, a sequence of images along the reaction path are optimized and the highest energy image required to climb up in energy along the elastic band, a saddle point along the minimum energy path, is the transition state. Four equally spaced images between the reactant and the product state were created and CI-NEB optimization was carried out. The four reaction steps described by the images between the reactant and the product states are shown in Figure 3-2. Typically, the transition state is identified as the image with the maximum energy and absolute force tangent to the reaction coordinate less than 0.04 eV Å\textsuperscript{-1}. 
Figure 3-1. a) The reactant state with CH$_3$ and CH$_2$ species adsorbed on the surface. b) The product state with C$_2$H$_5$ adsorbed on the surface.

Figure 3-2. The CI-NEB optimized images used to find transition state for reaction between CH$_3^*$ and CH$_2^*$ to form C$_2$H$_5^*$ on the La-doped CeO$_2$ surface.
In the present study, image 2 with CH₃⁺ desorbing from the surface and becoming a free radical, satisfied this criterion. However, vibrational frequency calculations carried out on this state did not yield an imaginary frequency, confirming that it is not a transition state. Image 2 resembles a surface with a bound CH₂⁺ species and an unbound CH₃ radical. Hence, it suggests that C-C bond formation between CH₃⁺ and CH₂⁺ over La-doped CeO₂ goes via the formation of CH₃ radical and is not concerted. For future research, it may be of interest to investigate C-C bond formation using CHₓ⁺ species with other values of x, the stabilities of the surface CHₓ⁺ species and the C-C bond formation reaction barriers on La-doped CeO₂ surfaces. In addition, research efforts can be directed towards studying dry reforming and coking reactions over oxysulfide La-doped CeO₂ surfaces to generate fundamental insights for rational catalytic design for the process.
REFERENCES


reforming reaction over nickel supported on modified with CeO2 and/or La2O3 alumina catalysts.
14. Nandini A, Pant KK, Dhingra SC. K-, CeO2-, and Mn-promoted Ni/Al2O3 catalysts for stable
doi:http://dx.doi.org/10.1016/j.apcata.2005.05.016.
16. YU F, YUE B, WANG X, GENG S, LU X, DING W. Hydrocracking of Tar Components from
Hot Coke Oven Gas over a Ni/Ce-ZrO2/γ-Al2O3 Catalyst at Atmospheric Pressure. Chinese J
17. Laycock CJ, Staniforth JZ, Ormerod RM. Biogas as a fuel for solid oxide fuel cells and synthesis
gas production: effects of ceria-doping and hydrogen sulfide on the performance of nickel-based
20. Li R, Krcha MD, Janik MJ, Roy AD, Dooley KM. Ce-Mn Oxides for High-Temperature Gasifier


42. Ma L, Jia I, Guo X, Xiang L. Current Status and perspective of rare earth catalytic materials and


doi:10.1016/j.jeurceramsoc.2010.05.024.


doi:10.1021/cm903282w.


doi:10.1021/acs.jpcc.6b02817.


73. Murgida GE, Ferrari V, Ganduglia-Pirovano MV, Llois AM. Ordering of oxygen vacancies and


