Study of redox reactions to split water and carbon dioxide

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STUDY OF REDOX REACTIONS TO SPLIT WATER AND CARBON DIOXIDE

By

DARWIN ARIFIN
B.S., University of Wisconsin-Stevens Point, 2008

A thesis submitted to the
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has been approved for the Department of Chemical and Biological Engineering

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
The development of carbon-neutral, environmentally-sustainable energy carrier is a technological imperative necessary to mitigate the impact of anthropogenic carbon dioxide on earth’s climate. One compelling approach rapidly gaining international attention is the conversion of solar energy into renewable fuels, such as H$_2$ or CO, via a two-step thermochemical cycle driven by concentrated solar power. In accordance with the increased interest in this process, there is a need to better understand the gas splitting chemistry on the metal oxide intermediates encountered in such solar-driven processes. Here we measured the H$_2$ and CO production rates during oxidation by H$_2$O and CO$_2$ in a stagnation flow reactor. Redox cycles were performed over various metal oxide chemistries such as hercynite and ceria based materials that are thermally reduced by laser irradiation. In addition to cycle capacity evaluation, reaction kinetics intrinsic to the materials were extracted using a model-based analytical approach to account for the effects of mixing and dispersion in the reactor.

Investigation of the “hercynite chemistry” with raman spectroscopy verifies that, at the surface, the cycle proceeds by stabilizing the reduced and oxidized moieties in two different compounds, which allows the thermal reduction reaction to occur to a greater extent at a temperature 150 °C lower than a similarly prepared CoFe$_2$O$_4$-coated m-ZrO$_2$.

Investigation of the ceria cycle shows that the water splitting reaction, in the range of 750 – 950 °C and 20 – 40 vol.% H$_2$O, can best be described by a first-order kinetic model with low apparent activation energy (29 kJ/mol). The carbon dioxide splitting reaction, in the range of 650
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CHAPTER 1
MOTIVATION, BACKGROUND & SCOPE

1.1. Motivation

One of the most difficult challenges that we face in the 21st century is supplying the world with clean, reliable, and renewable energy source. Projected growth in global population and continued industrialization of developing countries will increase total world energy consumption by 50% between 2008 and 2035.\(^1\) Approximately 85% of this need is fulfilled by burning fossil based fuel, a non-renewable energy source that is inhomogeneously distributed under the earth’s surface. This trend is not sustainable as it contributes to the increase in anthropogenic carbon in the atmosphere and often fuel geopolitical conflicts to control the dwindling fossil fuel resource.

Atmospheric anthropogenic carbon is a significant concern due to its effect on warming the biosphere. Since the advent of the industrial revolution, the global average temperature has increased by 0.6 °C. While this does not sound alarming, in actuality, this value represents a drastic regional warming trend; exemplified by the 10% decrease in snow and ice cover in most mid and high latitude regions since the 1960’s. Currently, this warming trend is projected to continue to increase. In fact, the rate of warming has doubled in the past 40 years when compared to the time period from 1910 to 1945; which makes this warming rate greater than any other time in the past 1000 years.\(^2\) The global warming trend is largely caused by chemically stable, long lived, greenhouse gases such as carbon dioxide, methane and nitrous oxide that increase atmospheric absorption of outgoing solar radiation. As of 2005, the concentration of carbon dioxide in the atmosphere has increased by 35%, to 379 ppm. This is higher than any
pre-industrial time period recorded in the glacial-interglacial ice core data, dating back 650,000 years.³

Energy independence and geopolitical stability is another important reason why transition from the dwindling fossil fuel energy economy is important. By the middle of the 20th century, the United States’ energy consumption has exceeded its domestic production. While the recent development of advanced crude oil production technologies continue to increase domestic oil production, United States still imports approximately 45% of its oil needs.⁴ This large dependence in foreign oil supply frequently leads to supply disruption, price volatility, and often allow oil to be used as leverage in political coercion. For example, the recent democratic uprising in numerous countries in the Middle East and Northern Africa, the increased tension with Iran, and strained diplomatic relationship with South American countries such as Venezuela has posed threats to the world’s oil supply, and is detrimental to the already weakened economy recovery in Europe and the U.S. Therefore, improved energy diversification and creation of larger spare energy capacity to safeguard against supply disruption needs to be attained, and can be accomplished by shifting to a renewable domestic energy production.

Currently, only 8% of the U.S. energy consumption is fulfilled by renewable resources. Of the various renewable resources, solar energy is particularly promising and is available in great abundance. In 2012, the annual world’s energy consumption is approximately 5.5 X 10²⁰ J.¹

In one hour, the amount of energy from the sun that hits the earth is approximately 4.3 X 10²⁰ J.⁵ Therefore, there’s enough energy in the sunlight that hits the earth in ~1.3 hours to power human activities for one year. Despite this abundance, less than 0.1% of electricity and less than 1.5% of biomass derived fuels are provided from solar sources.⁵ The biggest challenge with utilizing solar energy is the relatively diffuse nature of the solar flux, with an energy density of
approximately 1270 W/m$^2$, depending on the latitude and cloud cover. Therefore, to be cost competitive with fossil fuel, the capture, conversion, and storage of solar energy must be done in a highly efficient manner utilizing low cost materials.

One method to capture and utilize solar energy is to convert it into a more fungible chemical fuel such as hydrogen. Hydrogen has emerged as an attractive alternative to fossil fuel, specifically for transportation fuel, since it has high energy density (120 MJ/Kg) and can potentially be produced in large quantities using abundant and renewable resources.$^5$ In general, there are three pathways to convert solar energy to renewable hydrogen. The first is to utilize photovoltaic cells to produce electricity to drive an electrolyzer, and produce hydrogen. This process has an overall solar to chemical efficiency of approximately 12%; due to the low efficiency of the PV cells (18%) that is coupled with losses incurred at the electrolytic system (approximately 70% efficient). The second pathway is to produce electricity with concentrated solar power (CSP), where concentrated solar energy is used to heat a working fluid, produce electricity, and subsequently use this electricity to drive an electrolyzer to produce renewable hydrogen.$^7, \, ^8$ The overall solar to chemical efficiency of this process is approximately 12% as well; due the low efficiency of the CSP process (18%), coupled with losses at the electrolyzer. Both processes are based on mature technologies available today; however, due to their low efficiencies, and the diffuse nature of solar insolation, are not currently cost competitive with traditional fossil fuel based fuel.$^9$

The third path to produce sustainable hydrogen is the solar thermochemical process. In recent years, the solar thermochemical process has emerged as an attractive alternative method to produce hydrogen. Unlike the aforementioned processes, the solar thermochemical route directly captures concentrated solar flux to drive a highly endothermic thermochemical process; thereby
bypassing the solar to electricity conversion and thus has the potential to achieve higher efficiency. In fact, the prototypical iron oxide based solar thermochemical cycle can theoretically achieve 36% efficiency without heat recuperation.\textsuperscript{10} Typically, the solar thermochemical process consists of two or more steps utilizing a metal oxide intermediate. In this work, we will focus our discussion on the two-step process since it can be carbon neutral, does not require difficult and expensive separation process, does not involve corrosive and toxic chemical species, can operate at higher thermal efficiencies, and requires less land and water to operate when compared to other processes such as biomass production and processing, artificial photosynthesis, photovoltaic-driven electrolysis, and other multi-step processes.\textsuperscript{10-14} Furthermore, the two-step solar process can be implemented for the capture and sequestration of carbon dioxide, which can be further used as feedstock to produce carbon monoxide for synthetic hydrocarbon fuel production.\textsuperscript{7, 10, 15-17} The ability to renewably produce hydrocarbon fuel with this cycle is an important consideration that allows conservation of our natural fossil fuel reserve before a full transition to a hydrogen-based fuel economy becomes a reality.

Despite the higher potential efficiency, practical implementation of the solar thermochemical process has not been achieved. The field faces numerous engineering and technical challenges from solar collector, reactor, and metal oxide design. To achieve optimum efficiency, minimize initial capital and operational cost, the metal oxide intermediate has to have high thermodynamic capacity, fast kinetics, and longevity in order to be cycled thousands of times before replacement/replenishment is necessary. And currently, the prototypical cycle with ferrite based chemistry is impractical due to the limited thermal stability (melting point).\textsuperscript{6} Therefore, it is imperative that we develop fundamental understanding of the various
thermochemical aspects of the metal oxide chemistry; to improve reactor design and solar to fuel productivity.

1.2. Scope

The objective of this research is to contribute towards the development of non-volatile metal oxide materials as intermediates in the two-step solar thermochemical for water or carbon dioxide splitting for fuel (H₂ or CO) production. In general there are three types of redox chemistries for the non-volatile metal oxide intermediate: the solid solution chemistry such as the traditional ferrite materials, a displacement type chemistry such as the hercynite chemistry, and the non-stoichiometric redox represented by CeO₂ based materials. This study focused on the latter two chemistries; the investigation of the hercynite chemistry and the kinetics of the non-stoichiometric ceria based material, with three specific aims: 1.) Contribute towards a better understanding of the thermochemical aspects of different chemistries of metal oxides; 2.) Develop a detailed kinetic model of the water and carbon dioxide splitting of non-stoichiometric metal oxide such as CeO₂; 3.) Investigate possible physical and chemical changes to CeO₂ that can improve cycle capacity.

To achieve these aims, thermochemical cycles of hercynite and ceria based materials were performed in a stagnation flow reactor (SFR), which was designed to operate under ideal flow conditions and at temperature ranges that is applicable for thermochemical conditions. The SFR is located in the Combustion Research Facility at Sandia National Laboratory in Livermore, CA, and is equipped with a near IR laser to simulate concentrated solar flux application that provides rapid heating. In order to accurately study the oxidation/fuel production kinetics, a rigorous quantitative data reduction algorithm, coupled with the solid state kinetics model, was developed to model fuel production over the entire reaction domain, and to determine the rate
governing mechanism and oxidation kinetic parameters of the water splitting (WS) and CO₂ splitting (CDS) reactions.¹⁸ The algorithm allowed for the separation of material specific fuel production behavior from experimental effects such as finite detector time lag and gas phase dispersion. Solid state kinetics theory were chosen because it allowed us to determine the rate governing mechanism of the heterogeneous oxidation reactions without delving into the elementary steps of the oxidation process, which can be computationally expensive. Once detailed oxidation kinetics mechanism for various ceria based material were obtained, they can be used to determine the optimum material and reactor design for solar thermochemical application.

This work has filled a critical gap in the knowledge base necessary to develop detailed computational models for the development of hercynite and ceria based solar receiver reactors. Due to limited solar availability in a day; it is important to maximize the solar to fuel conversion efficiency, and that requires optimization of the thermal reduction and oxidation processes. Kinetic models based on experimental rate constants will allow for optimization of transport rates and transit times of ceria based material in the development of solar thermochemical systems. This in turn dictates how quickly the cycles can be completed, and determines the fuel production rate and efficiency of the power plant.

1.3. Background & Literature Review

1.3.1. Thermodynamics of two-step solar thermochemical process.

One path to produce renewable hydrogen is to directly use concentrated solar energy to split water into its molecular components: H₂ and O₂ (thermolysis). However, this approach, the direct thermolysis of water, is thermodynamically very unfavorable and requires temperature above 2500 K to achieve significant degree of decomposition. This extremely high temperature
requirement and the need for gaseous phase O\textsubscript{2}/H\textsubscript{2} separation make direct thermolysis unfeasible. One method to overcome the thermodynamic barrier and eliminate the need for high temperature gas separation is to perform a multi-step thermochemical process, where the water splitting is achieved by two or more steps, as depicted by equations 1.1 – 3 below (for a two-step process).

1.1. \( MO_x \rightarrow MO_{(x-1)} + \frac{1}{2} O_2 \) \hspace{1cm} \( \Delta G_{1}^{o} = \Delta H_{1}^{o} - T \Delta S_{1}^{o} \)

1.2. \( MO_{(x-1)} + H_2O \rightarrow MO_x + H_2 \) \hspace{1cm} \( \Delta G_{2}^{o} = \Delta H_{2}^{o} - T \Delta S_{2}^{o} \)

1.3. \( H_2O \rightarrow \frac{1}{2} O_2 + H_2 \) \hspace{1cm} \( \Delta G_{WS}^{o} = \Delta H_{WS}^{o} - T \Delta S_{WS}^{o} \)

Equation 1.1 represents the thermal reduction process; equation 1.2 represents the water oxidation (fuel production) step; and equation 1.3 is the sum of equations 1.1 and 1.2: the water splitting reaction. MO\textsubscript{x} represents the metal oxide intermediate. The thermochemical cycle proceeds by thermally reducing a metal oxide intermediate at temperatures between 1300 – 1500 °C to produce O\textsubscript{2}, and reoxidizing the reduced metal oxide with steam at \( T < 1000 \) °C to produce H\textsubscript{2}; and thus taking advantage of the redox of the metal cations. Typically, equations 1.1 and 1.2 are performed at two different temperatures where \( \Delta G_{1}^{o} \) and \( \Delta G_{2}^{o} \) are <0. Because the sum of \( \Delta G_{1}^{o} \) and \( \Delta G_{2}^{o} \) is \( \Delta G_{WS}^{o} \) at every temperature, then \( \Delta G_{1}^{o} \) and \( \Delta G_{2}^{o} \) as a function of temperature must have opposite slopes (positive and negative). This is depicted in Figure 1.1. In this manner, each of the steps are more thermodynamically favorable (\( \Delta G_{rxn}^{o} = 0 \) can be achieved at lower T when compared to direct thermolysis), and the water splitting cycle can be accomplished under more reasonable conditions. An analogous thermodynamic argument applies to the carbon dioxide splitting process as well.
Figure 1.1: Thermodynamics of water splitting (WS), thermodynamically not feasible until $T > 2000 \degree C$. The reduction (line A) and oxidation (line B) are hypothetical lines to illustrate the opposite slopes of the two steps. The reduction (A) has a negative slope (positive $\Delta S_{\text{red}}$) and is typically a more endothermic process than water splitting ($\Delta H_{\text{red}} > \Delta H_{\text{ws}}$). Meanwhile the opposite is generally true of the oxidation. An analogous figure can be made for CO$_2$ splitting.

In addition to the two-step process, three or more steps thermochemical cycles can be used to produce H$_2$. Typically, metal oxides that are not thermodynamically favored to be cycled by the two-step process can be cycled with three or more step cycles. For example, Co$_3$O$_4$/CoO and MnO$_2$/MnO redox pairs can be cycled with a three step process involving sodium hydroxide at $T < 700 \degree C$, a thermal reduction temperature range that is much lower than a typical two-step cycle. However, these cycles require the use of stronger oxidizing agent than water, such as NaOH or KOH, to reoxidize the metal oxide. The oxidizing agents are then regenerated by reaction with water.$^{20,21}$ Other multi-step cycles have been proposed throughout the years; such as the Mark 13-V2, UT3, and iodine sulfur (IS) cycle.$^{22-27}$ While these types of multi-step
cycles typically have lower temperature requirement than a two-step process; they typically involve corrosive and toxic chemicals, require expensive separation and recovery process, and present significant safety, environmental, and technical challenges which makes them unfeasible for large scale applications.\textsuperscript{13, 20, 28, 29} This work will therefore focus on the metal oxide intermediate for the two-step cycle.

1.3.2. Chemistries for two-step solar thermochemical water or carbon dioxide splitting.

1.3.2.1. \textit{Ferrite based chemistry}

First proposed by Nakamura in 1977, iron oxide is the prototypical metal oxide for the two-step solar thermochemical process\textsuperscript{19}. The Fe$_3$O$_4$ material is thermally reduced at some high temperature ($T_H$) and subsequently taken off sun to be oxidized by either steam or CO$_2$ at some lower temperature ($T_L$), as described in equations 1.4 – 1.6. Unfortunately, the thermodynamic of reduction is not favorable at low temperature, and, to achieve significant conversion, requires high $T_H$ that is above the melting point of the relevant phases (Figure 1.2.); this leads to rapid surface area loss; and thus, although iron oxide theoretically exhibit large redox potential with favorable water oxidation thermodynamic; in practice, the formation of liquid phase and metal vaporization leads to slow kinetics, irreversible deactivation, and loss of capacity.

\begin{align*}
1.4. \quad & \text{Fe}_3\text{O}_4 \rightarrow 3 \text{FeO} + \frac{1}{2} \text{O}_2 & T_H &= 1400 - 1500 \, ^\circ\text{C} \\
1.5. \quad & \text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 & T_L &= 1000 - 1200 \, ^\circ\text{C} \\
1.6. \quad & \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2
\end{align*}
To reduce thermal reduction temperature, the iron oxide is often doped to form substituted ferrite spinels. The idea is to combine the thermodynamic properties of iron oxide with other metal oxide that has more favorable thermodynamics, such as Co$_3$O$_4$/CoO redox pair, which has more favorable thermal reduction, but worse water oxidation thermodynamics (Figure 1.3.). The goal is to reduce the thermal reduction temperature necessary, while maintaining oxidation activity, by “blending” the two metal oxides to form the ferrite spinel M$_x$Fe$_{3-x}$O$_4$. Here M can be any number of transition metals that form spinel structure with iron, although Ni, Co, and Zn are the most studied. However, further investigation by Miller et al has shown that the spinel redox chemistry is more complex than straightforward mixing. Upon thermal reduction, Co exists almost exclusively in the 2+ state, in Co$_x$Fe$_{3-x}$O$_4$ for $x < 1$. This is in contrast to the reduction of the metal center from 3+ to 2+ oxidation state in the pure Co$_3$O$_4$/CoO chemistry. Furthermore, doping with Ni yields similar results to Co doping; yet Ni exist in only the 3+ state. Calculations performed with the thermodynamic package FactSage database shows that addition of these transition metal dopants induces deeper reduction as the second metal provides alternatives to FeO formation (e.g. CoO or NiO). Thus, improvements in reduction temperature and cycle capacity yielded by these spinels are not due to the presence of easily reducible dopant cations, but suggest more complex solid solution phenomena.
Figure 1.2: Thermodynamics of the two-step solar thermochemical water splitting with iron oxide ($2 \text{Fe}_3\text{O}_4 \rightarrow 6 \text{FeO} + \text{O}_2$ for thermal reduction and $3 \text{FeO} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$ for water oxidation) as calculated with FactSage 6.2®. Although the thermodynamic of the water oxidation step is favorable at moderate temperature, the reduction step is not feasible until temperatures exceeding the melting points of both Fe$_3$O$_4$ and FeO. Adapted from ref.11.

Initially proposed by Kodama et al in an effort to create a high surface area monolith structure to maximize the kinetics of the water oxidation step; these ferrites can be further combined with refractory materials such as zirconia or yttrium stabilized zirconia (YSZ) to improve mechanical integrity and cycle durability.$^6, 18, 30, 33$ In addition to acting as support, it was discovered by Coker et al that, YSZ allows for Fe dissolution into its matrix, creating new free Fe$^{3+}$ species that is more amenable to thermal reduction than the bulk iron oxide, where reduction can be limited by particle size. However, although the dissolved Fe species within YSZ can undergo redox faster than the bulk phase, it has limited contribution towards total fuel
produced since amount of free Fe species is limited by solubility in the YSZ matrix, which was found to be 10.4 mole % at 800 – 1000°C.\textsuperscript{34} Despite these efforts to maximize cycle capacity, lowering the necessary reduction temperature, and maintaining material stability upon repeated cycle, ferrite based metal oxide is still not suitable for large scale thermochemical water (WS) or carbon dioxide splitting (CDS) due to the sintering and deactivation issues.

Figure 1.3: Thermodynamics of the two-step solar thermochemical water splitting with cobalt oxide (\(2 \text{Co}_3\text{O}_4 \rightarrow 6 \text{CoO} + \text{O}_2\) for TR and \(3 \text{CoO} + \text{H}_2\text{O}(g) \rightarrow \text{Co}_3\text{O}_4 + \text{H}_2\) for WO) as calculated with FactSage 6.2\textsuperscript{8}. In contrast to Fe\textsubscript{3}O\textsubscript{4}/FeO redox pair, the thermal reduction of Co\textsubscript{3}O\textsubscript{4}/CoO is more thermodynamically feasible, while the water oxidation step is less favored. Additionally, the melting point of CoO is higher than FeO. Adapted from ref.11.
1.3.2.2. **Displacement type chemistry**

Unlike the aforementioned ferrite chemistry, where the redox active cation is stabilized within a homogenous system where multivalency coexists, (e.g. Fe$^{2+}$/Fe$^{3+}$) in solid solution. The displacement chemistry proceeds by stabilizing the reduced and oxidized moieties in two different compounds. An example of this type of chemistry is the “hercynite cycle”. This cycle was first demonstrated by Scheffe et al., who synthesized a thin film of CoFe$_2$O$_4$ spinel on bulk Al$_2$O$_3$ support and discovered that incorporation of cobalt into a ferrite spinel allows for the formation and decomposition of FeAl$_2$O$_4$ (hercynite) upon reduction and oxidation, respectively. Similar to the ferrite cycle, this chemistry utilizes the oxidation state change of the iron cation (Fe$^{2+}$/Fe$^{3+}$). However, unlike the ferrites, reduction chemistry occurs via a reaction between decomposition products of the CoFe$_2$O$_4$ and Al$_2$O$_3$, forming the corresponding stable aluminates CoAl$_2$O$_4$ and FeAl$_2$O$_4$ according to the following oxygen evolution reaction:

$$1.7. \text{CoFe}_2\text{O}_4 + 3 \text{Al}_2\text{O}_3 \xrightarrow{\text{Heat}} \text{CoAl}_2\text{O}_4 + 2 \text{FeAl}_2\text{O}_4 + \frac{1}{2} \text{O}_2$$

During subsequent oxidation by CO$_2$ (or H$_2$O), the cobalt ferrite spinel and alumina reform and CO (H$_2$) is produced:

$$1.8. \text{CoAl}_2\text{O}_4 + 2 \text{FeAl}_2\text{O}_4 + \text{CO}_2(\text{H}_2\text{O}) \rightarrow \text{CoFe}_2\text{O}_4 + 3 \text{Al}_2\text{O}_3 + \text{CO} (\text{H}_2)$$

The oxygen evolution reaction equation 1.7 occurs to a greater extent at a temperature 150 °C lower than a similarly prepared CoFe$_2$O$_4$-coated m-ZrO$_2$ because compound formation is thermodynamically more favorable than solid solution formation.$^{35}$ While lowering the reduction temperature is an important consideration for solar thermochemical technologies, perhaps more
intriguing is the idea of binding the reduced iron in a compound that is more stable than solid solution and elimination of low melting point phases.

1.3.2.3. Non-stoichiometric chemistry

Similar to the ferrite, in the nonstoichiometric chemistry, multivalency exist within the solid solution of the metal oxide. Cerium dioxide is the prototypical metal oxide for this chemistry and currently the favored material for the two-step solar thermochemical WS and CDS. Ceria has been widely studied in various applications such as: catalyst in vehicle emission system, solid oxide fuel cells, and two-step solar thermochemical H₂O and CO₂ splitting process. The thermochemical cycle of ceria is depicted in Figure 1.4. Heat derived from concentrated solar energy thermally reduces ceria to its sub-stoichiometric oxide (CeO₂₋δ) at temperatures between 1350 °C and 1550 °C, producing O₂. CeO₂₋δ is then taken off sun and oxidized at a lower temperature by exposure to H₂O, thus producing H₂ fuel and completing the cycle. Instead of H₂O, carbon dioxide can also be used as the oxidant to produce CO fuel. This allows for the capture and sequestration of carbon dioxide, which can be used as feedstock to produce CO for synthetic hydrocarbon fuel production. The ability to renewably produce hydrocarbon fuel with this cycle is an important consideration that allows conservation of our natural fossil fuel reserve before a full transition to a hydrogen-based fuel economy becomes a reality. When thermally reduced at these temperatures, ceria maintains its fluorite crystal structure, as the lattice is able to accommodate the strain induced by oxygen vacancy formation. In this temperature range however, thermal reduction of ceria is thermodynamically unfavorable and thus the cycle capacity of ceria, is small compared to other reducible metal oxides.
In addition to ceria based materials, recent work by McDaniel et al introduced a new family of perovskites (ABO$_3$) material for the two-step solar thermochemical process. The authors find that LaAlO$_3$, doped with Mn and Sr will efficiently split water and CO, while maintaining comparable kinetics with ceria, and with cycle capacity that is approximately 9x and 6x (for H$_2$ and CO production respectively) larger than ceria when reduced at 1350 °C and oxidized at 1000 °C. Furthermore, the material exhibit thermal stability that is more robust than ferrite material, and O$_2$ release characteristic that occurs 300 °C lower than ceria. The amenability of the perovskites chemistry opens a vast composition possibility, where even more effective materials can be discovered.$^{40}$

Nonetheless, ceria is currently still the favored metal oxide for this application. The combination of fast kinetics and thermal stability make it a great alternative to the ferrite cycle. It
does not form a molten/slag phase and thus is not plagued by sintering and deactivation issues. The thermochemical cycling aspect of ceria is currently a major area of research. For example, the thermal stability of the ceria cycle has been studied by Chueh et al, up to 500 repeated cycles without significant deactivation.\textsuperscript{16} The thermodynamics,\textsuperscript{41, 42} synthesis method,\textsuperscript{43, 44} and the influence of dopants in the lattice structure on the amount of fuel produced have been studied. Doping and other lattice substitution approaches, to introduce lattice defects and create additional oxygen vacancies, are often used in order to improve the cycle capacity or reduce the necessary thermal reduction temperatures.\textsuperscript{28, 45-49}

Detailed kinetics model and oxidation mechanisms of the thermochemical cycle, on the other hand, have received little attention. None of the work currently published in the literature, as far as the authors are aware of, investigates the intrinsic kinetic of the H\textsubscript{2}O and CO\textsubscript{2} oxidation process of CeO\textsubscript{2} over the complete oxidation reaction domain. Le Gal et-al has studied the H\textsubscript{2}O and CO\textsubscript{2} splitting kinetics of ceria and zirconia doped ceria. They reported that CO\textsubscript{2} oxidation of Zr\textsubscript{0.25}Ce\textsubscript{0.75}O\textsubscript{2} is limited by diffusion and that the activation energy (E\textsubscript{a}) ranges from 83 to 103 kJ/mole, depending on the synthesis method. The authors used the “masterplot analysis” and concluded that the diffusion mechanism fit the CO\textsubscript{2} oxidation data at high extent of reduction. However, no good fit is found for the low extent of oxidation regime. No effort has been made to deconvolute the effects of the experiments, such as detector time lag and gas-phase dispersion, to extract the intrinsic oxidation behavior of the material over the entire reaction domain. Conversely, they have used the same approach to determine that CO\textsubscript{2} oxidation of pure ceria, and concluded that it is surface limited, and that it follows an F2 model; however the quality of the fit and the activation energy of the process are not reported.\textsuperscript{49, 50}
The objective of this research is to contribute towards the development of a hercynite and ceria-based material for thermochemical fuel production, with three specific aims: 1.) Contribute towards a better understanding of the thermochemical aspects of hercynite and CeO$_2$; 2.) Develop a detailed kinetic model of the water and carbon dioxide splitting of CeO$_2$; 3.) Investigate possible physical and chemical changes to CeO$_2$ that can improve cycle capacity.

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CHAPTER 2

CoFe$_2$O$_4$ ON POROUS Al$_2$O$_3$ NANOSTRUCTURE FOR SOLAR THERMOCHEMICAL CO$_2$
SPLITTING

2.1. Abstract

Projected growth in global population and continued industrialization of developing countries will increase total world energy consumption by 50% between 2008 and 2035.\textsuperscript{1} This demand for energy will be largely met by burning more fossil fuels, thereby increasing anthropogenic carbon in the atmosphere and further fuelling geopolitical conflicts over control of dwindling energy resources. Recycling CO$_2$ by splitting it in a solar-based thermochemical process is an attractive solution to both of these 21\textsuperscript{st} century problems. In this communication, we examine a novel chemistry for a two-step, non-volatile metal oxide CO$_2$ splitting cycle that shuttles iron oxidation states (Fe$^{2+/3+}$) between CoFe$_2$O$_4$ and FeAl$_2$O$_4$ spinel compounds within a nano-engineered material. This chemistry is dramatically different than current metal oxide cycles that exploit oxygen non-stoichiometry in ceria or solid solution behavior in ferrites. The engineered material was prepared using atomic layer deposition and maintained structural integrity over 6 heating cycles under conditions that mimic a concentrated solar power application, namely an oxidation temperature of 1000 °C, reduction at 1460 °C, and a heating rate of 16 °C/s from low to high temperature. Oxygen uptake and release behavior was similar to that of ceria. Raman spectroscopy was used to verify cycle chemistry.

2.2. Introduction

Energy security and climate change are linked by the burning of fossil fuels, and as such major research and development efforts around the world are focused on CO$_2$ capture and
sequestration,\textsuperscript{2-4} or re-use by conversion to liquid hydrocarbon fuels.\textsuperscript{5-9} Two-step solar thermochemical processes based on non-volatile metal oxide cycles are an attractive alternative to biomass production and processing, artificial photosynthesis, and photovoltaic-driven electrolysis because they have the potential to operate at higher thermal efficiencies, are technologically less challenging to implement, and require less land and water to operate.\textsuperscript{7, 10}

There are also other two-step cycles based on \textit{volatile} metal oxides, such as the Zn/ZnO cycle, which has been extensively studied and is reviewed elsewhere.\textsuperscript{11} A generic two-step cycle based on ceria is illustrated schematically in Fig. 2.1. Heat derived from concentrated solar energy thermally reduces ceria to a sub-stoichiometric oxide (CeO$_{2-\delta}$) at temperatures between 1350 °C and 1500 °C, producing O$_2$ (step 1). The CeO$_{2-\delta}$ is then taken off sun and oxidized at 1000 °C by exposure to CO$_2$, thus producing CO fuel (step 2) and completing the cycle. Steam can also be used as oxidant to produce H$_2$.

Traditionally, two types of non-volatile metal oxide redox chemistries are utilized in solar thermochemical CO$_2$ splitting. The first is based on the aforementioned non-stoichiometric oxides of which ceria is a representative example. Redox materials of fluorite or perovskite type crystal structures are thermally reduced without undergoing phase change, as the lattice is able to accommodate the strain induced by oxygen vacancy formation. These materials are thermally quite stable, although the extent of reduction, and hence cycle capacity, is small compared to other reducible oxides.\textsuperscript{7, 12, 13} Doping or lattice site substitution strategies are often employed with these oxides in order to introduce crystallographic defects that improve cycle capacity or decrease temperatures required for thermal reduction.\textsuperscript{14-18}
The second prototypical chemistry utilizes materials of the spinel structure that form solid solutions upon reduction. The most common are ferrites where Fe\(^{3+}\) in M\(_x\)Fe\(_{3-x}\)O\(_4\) is partially reduced to Fe\(^{2+}\); here M can be any number of transition metals that form spinel type oxides with iron though Co, Zn, and Ni are the most studied.\(^5\),\(^{19-25}\) In these redox cycles, the ferrite spinel is heated until it decomposes into a mixture of metal oxide solid solutions that are thermodynamically stable at temperatures above which the spinel decomposes.\(^{21}\) Thus, thermal reduction yields a solid solution of oxides with mixed valence (M\(^{2+}\), Fe\(^{2+}\), and Fe\(^{3+}\)). While these materials theoretically exhibit greater redox potential than non-stoichiometric oxides, in practice deactivation induced by irreversible processes such as sintering or the formation of liquid phases and metal vaporization lead to loss of active oxide. One strategy for improving mechanical integrity and cycle durability has been to combine these substituted ferrites with refractory
materials such as zirconia or yttrium stabilized zirconia.\textsuperscript{20,23}

In both the non-stoichiometric oxide and ferrite chemistries, the redox active cation is stabilized within a homogenous system where multivalency coexists, Ce\textsuperscript{3+}/Ce\textsuperscript{4+} in ceria and Fe\textsuperscript{2+}/Fe\textsuperscript{3+} in solid solution. Here we investigate a novel third type of redox chemistry. Similar to the ferrite cycle, this chemistry utilizes the oxidation state change of the iron cation (Fe\textsuperscript{2+}/Fe\textsuperscript{3+}). However, unlike the ferrites this approach proceeds by stabilizing the reduced and oxidized moieties in two different compounds. This cycle was first demonstrated by Scheffe et al.,\textsuperscript{26} who synthesized a thin film of CoFe\textsubscript{2}O\textsubscript{4} spinel on bulk Al\textsubscript{2}O\textsubscript{3} support and discovered that incorporation of cobalt into a ferrite spinel allows for the formation and decomposition of FeAl\textsubscript{2}O\textsubscript{4} (hercynite) upon reduction and oxidation, respectively.

So called the “hercynite cycle”, reduction chemistry occurs via a reaction between decomposition products of the CoFe\textsubscript{2}O\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3}, forming the corresponding stable aluminates CoAl\textsubscript{2}O\textsubscript{4} and FeAl\textsubscript{2}O\textsubscript{4} according to the following oxygen evolution reaction:

1. \textsuperscript{heat}CoFe\textsubscript{2}O\textsubscript{4} + 3 Al\textsubscript{2}O\textsubscript{3} $\rightarrow$ CoAl\textsubscript{2}O\textsubscript{4} + 2 FeAl\textsubscript{2}O\textsubscript{4} + $\frac{1}{2}$O\textsubscript{2}

During subsequent oxidation by CO\textsubscript{2}, the cobalt ferrite spinel and alumina reform and CO is produced:

2. CoAl\textsubscript{2}O\textsubscript{4} + 2FeAl\textsubscript{2}O\textsubscript{4} + CO\textsubscript{2} $\rightarrow$ CoFe\textsubscript{2}O\textsubscript{4} + 3Al\textsubscript{2}O\textsubscript{3} + CO

The oxygen evolution reaction Eq. 2.1 occurs to a greater extent at a temperature 150°C lower than a similarly prepared CoFe\textsubscript{2}O\textsubscript{4}-coated m-ZrO\textsubscript{2} because compound formation is thermodynamically more favourable than solid solution formation.\textsuperscript{26} While lowering the reduction temperature is an important consideration for solar thermochemical technologies, perhaps more intriguing is the idea of binding the reduced iron in a compound that is more stable
than solid solution.

Fig. 2.2. Optical image showing 0.5 mm diameter spheroids of porous Al₂O₃ shells coated in nanometer thick CoFe₂O₄. Colour changes from brown to green when hercynite forms upon thermal reduction (top). FESEM image of the porous Al₂O₃ structure prepared by ALD (bottom left). Schematic illustrating the conceptual layout of the nano-engineered reactive structure, not drawn to scale, and the spinel compound that forms upon calcination (bottom right). A representative FESEM image of the skeletal structure is incorporated into the schematic. The coverage of CoFe₂O₄ on the alumina scaffold is not limited to the outer surface; it coats all gas-accessible surfaces on and within the porous structure (see text).

Inspired by these initial observations, we deposited a nanometer thick film of CoFe₂O₄ on a porous thin-walled (15 nm) skeletal Al₂O₃ support to study the CO₂ splitting capability of this material for use in a concentrated solar power application. The reactive structure is depicted schematically in Fig. 2.2. along with optical images of sample material photographed in the oxidized and reduced states, and an FESEM image of the alumina support before thermal cycling. The cartoon in Fig. 2.2. implies that the CoFe₂O₄ film is located on the exterior surface of the support shell, but the ALD process ensures that the ferrite film covers all gas-accessible
surfaces on and within the porous material. As a result, the cobalt ferrite mass loading is relatively high (20%) and the reactive structure maintains a high effective surface area and low bulk density prior to high-temperature thermal cycling.

The main benefit of this reactive structure that sets it apart from the work by Scheffe et al. is that we can better engineer the spinel-alumina interface. Ideally we would like to irradiate only redox active material, any excess Al₂O₃ would reduce process efficiency by heating of inert carrier. Deposition of CoFe₂O₄ on either high surface area Al₂O₃ powders or monoliths would be undesirable because too much inert material would end up in the structure. Perhaps more important than wasting heat, a large excess of alumina would lead to diffusion of Co and Fe deeply into the bulk and undoubtedly have a detrimental impact on the redox kinetics. The porous Al₂O₃ skeletal support with 15 nm wall thickness addresses both of these concerns.

2.3. O₂ Oxidation and Redox Chemistry

An important measure of a material’s suitability for a thermochemical carbon dioxide splitting cycle is the extent to which oxygen exchange occurs upon heating and cooling. This activity was assessed by exposing the nano-engineered material to a gas flow containing 2000 ppm O₂ in helium and rapidly heating and cooling the material while monitoring the O₂ uptake and release behavior. The results of this experiment are presented in Fig. 2.3. Starting at t = 0 s, a constant background of O₂ is measured by the mass spectrometer. At several time intervals spaced roughly 350 s apart, a laser irradiates the sample raising the temperature from 1000 °C to 1460 °C in 30 s. After a 100 s dwell at 1460 °C, the laser power is turned off and the sample is allowed to cool through conductive, convective, and radiative processes.

According to the data in Fig. 2.3., during the initial part of the heating interval the O₂ signal increases to a peak that is 47% above background, then quickly falls back to baseline
before the 100 s dwell time at high temperature expires. O$_2$ evolution in a gaseous environment where the oxygen activity is relatively high (0.001 atm) indicates favourable thermodynamics for reduction at conditions relevant to solar-driven thermochemistry. Of equal importance is the observation that the material reabsorbs oxygen on cooling, which is evidenced by the O$_2$ signal dropping below the 2000 ppm background level for a short period of time after laser irradiation. To a first approximation, the area under the desorption peak is equal to that of the absorption peak (~100 µmoles O$_2$/g of material). Furthermore, the O$_2$ redox behavior is reproducible over 6 heating cycles indicating that the material remains chemically active and is structurally stable (i.e., no significant irreversible loss of activity, surface area, physical dimension, or metal oxide).

Optical images of the sample taken before and after thermal redox cycling (Fig. 2.2.) show that the material maintains its semi-spherical shape, however, noticeable shrinkage occurs during repeated exposures to 1460 °C. BET analysis on similarly cycled materials confirms internal structural changes that are consistent with loss of porosity and sphere volume as the surface area is reduced from 44 m$^2$/g (as prepared) to 1.6 m$^2$/g (cycled). This is due to collapse of the micropores and mesopores in the alumina material resulting from grain growth at these extreme temperatures.\textsuperscript{27, 28} Nonetheless, after the first cycle, the oxygen capacity did not diminish after 23 thermal reductions, amounting to 20 hours at 1000 °C and 2 hours at 1460 °C, implying that the activity of the material is not affected by loss of internal surface area and that all structural changes occurred during the first cycle. A more rigorous and detailed study investigating the effect of porosity and the thermal stability of the material is currently underway. Also of note is the colour of the material before and after thermal reduction. The brown colour associated with oxidation is indicative of either cobalt ferrite or iron aluminate, while the blue-green hue on the reduced material is due to cobalt aluminate.
Fig. 2.3. Oxygen uptake and release behavior as a function of time and temperature measured in the presence of a constant 2000 ppm $O_2$ background partial pressure indicates thermodynamics for hercynite reduction are favourable for solar-driven thermochemical cycles (see text). The reduction extent as a function of temperature for ceria and hercynite at two different heating rates is shown in the inset.

The graph inset to Fig. 2.3. reveals another important feature of our engineered reactive structure. Here we plot the reduction extent as a function of temperature for two different heating rates. The reduction extent is calculated by taking the ratio of evolved oxygen, integrated as a function of time on a molar basis, to the total amount of oxygen present in the fully oxidized material. There are two pieces of information available in Fig. 2.3.; (1) by comparing a slow heating rate (2 °C/s) to a fast heating rate (16 °C/s) possible kinetic limitations to $O_2$ redox become evident, and (2) the reduction extent for a given temperature provides information on
cycle capacity (i.e., how much fuel can be produced per a mole of material). For comparison, reduction data are also presented for CeO$_2$ particles (nominally 5 $\mu$m diameter) in Fig 3.

Clearly the 2 °C/s heating rate produces more O$_2$ at a given temperature than the 16 °C/s rate, which is likely due to a transport limitation within the reactive structure. However, the nanostructured ferrite performance compares comparably to that of CeO$_2$ which, unlike iron oxide, is known to possess high oxygen ion conductivity and rapid exchange kinetics. Therefore it is conceivable that by reducing the thickness of the Al$_2$O$_3$ skeletal structure, diffusion limitations may be further mitigated allowing greater utilization of the redox active Fe cation and faster redox kinetics.
Fig. 2.4. Surface Raman spectra recorded for ferrite and aluminate reference materials compared to unknown compositions of nano-engineered CoFe$_2$O$_4$-coated Al$_2$O$_3$ material prepared by thermal reduction in helium (a), or oxidation in CO$_2$ (b), or oxidation in O$_2$ (c).

To support our hypothesis that the reactions embodied by Eqs. 2.1 and 2.2 are correct, we analysed the chemical composition of the nanostructured materials using surface Raman spectroscopy. Several representative samples were oxidized in either O$_2$ or CO$_2$, or reduced in pure helium, and then thermally quenched before ex situ examination in a Raman microscope. Presented in Fig. 2.4 are Raman spectra for three of our endpoint compounds, CoFe$_2$O$_4$, CoAl$_2$O$_4$, and FeAl$_2$O$_4$, along with spectra measured from samples taken at various states of oxidation (labeled a-c in the figure). Material fully oxidized in O$_2$ (c) exhibits spectral features indicative of CoFe$_2$O$_4$, with two main excitation peaks observed at 476 and 686 cm$^{-1}$ which
agrees with literature assignments for this compound.\textsuperscript{29-31} Raman spectra for material in the fully reduced state (a) show a mixture of phonon modes that can be attributed to cobalt aluminate\textsuperscript{32} and hercynite.\textsuperscript{33} Furthermore, the strong resonance features of CoFe\textsubscript{2}O\textsubscript{4} are not detectable in (a) indicating that the reduction reaction has gone to completion in the near surface region of the ferrite. Also of note is the relative stability of the reduced compound (FeAl\textsubscript{2}O\textsubscript{4}) in air at room temperature. Samples were removed from the reactor and stored for several days before transport to the Raman microscope without special handling to avoid air exposure.

Fig. 2.5. Production rate of CO as a function of time measured for the nano-engineered CoFe\textsubscript{2}O\textsubscript{4}-coated Al\textsubscript{2}O\textsubscript{3} material oxidized in 50 vol.% CO\textsubscript{2} at 1000 °C, a reactor pressure of 600 Torr, and a thermal reduction temperature (TR) of 1460 °C (top curve) or 1360 °C (bottom curve). The solid curves through the raw data are derived from smoothed interpolating splines. CO production rates are normalized to total mass of material.
2.4. CO₂ Oxidation

The observation that oxygen exchange behavior appears to be thermodynamically favorable and kinetically feasible at conditions typically found in solar thermal reactors is necessary but not sufficient to establish suitability of a reactive structure for use in CO₂ splitting. In fact, additional thermodynamic constraints, kinetic limitations, or undesirable reactions with carbon may preclude use of a particular material chemistry. Presented in Fig. 2.5 is the temporal behavior of the CO production rate measured during CO₂ oxidation at 1000 °C and 600 Torr pressure for two different thermal reduction states. As expected, the amount of CO produced (area under the curves in Fig. 2.5) is dependent on the thermal reduction temperature because this establishes the initial amount of Fe²⁺ (Fe₂Al₂O₄) formed in the first step of the redox cycle (see inset Fig. 2.3). It also appears that the CO₂ oxidation kinetics are somewhat slower than the O₂ oxidation kinetics, as evidenced by the time required to achieve full oxidation. The reaction is not complete after 450 s of CO₂ exposure because the CO signal does not return to baseline. Admittedly a more thorough investigation of this behavior is required because the O₂ oxidation data in Fig. 3 is confounded by a non-isothermal, non-linear temperature profile making a direct comparison more challenging.

Surface Raman spectra presented in Fig. 2.4 supports the notion of incomplete oxidation by CO₂ at reaction times less than 500 s. The curve labelled (b) appears to possess features of all three end point compositions. A detailed principal component analysis is underway to rigorously validate this hypothesis and preclude the possibility that additional compounds are being formed. Our experimental results also suggest that CO₂ splitting may be kinetically limited at the surface; increasing the reactor pressure from 75 to 600 Torr has a similar effect on the CO production rate as increasing the thermal reduction temperature from 1360 °C to 1460 °C (data not shown).
2.5. Conclusion

Currently, we are investigating the role of cobalt and like-type cations in this redox chemistry because hercynite cannot be decomposed into Fe$_3$O$_4$ at these operating conditions.$^{34}$ Furthermore, the effects of CoFe$_2$O$_4$ film thickness and Al$_2$O$_3$ wall thickness are not well understood meaning that a more optimized nano-engineered structure may be accessible because ALD enables atomistic control of the synthesis process. Further lowering the thermal reduction temperature and improving both the oxidation kinetics and iron utilization are possible.

Although there is much more to be learned about this intriguing redox cycle, this paper demonstrates the efficacy of a completely different approach to two-step thermochemical CO$_2$ splitting by blending novel chemistry with a nano-engineered reactive structure. We demonstrate that our CoFe$_2$O$_4$-coated Al$_2$O$_3$ material is capable of producing appreciable amounts of CO after thermal reduction at a temperature as low as 1360 °C, with consistent oxidation behavior up to 23 thermal reductions. This observation is approximately 100 °C to 150 °C lower than values reported for ferrite$^{35}$ or CeO$_2$$^{7,13}$ based systems, respectively. Finally, adding compound-forming redox chemistries to the list of possible candidate material systems opens up new opportunities for discovery of better and more viable metal-oxide based redox cycles for producing fuels from concentrated sunlight.

2.6. Experimental Method

A high surface area support was synthesized by depositing Al$_2$O$_3$ onto a porous poly(styrene-divinylbenzene) (PS-DVB) particle template via atomic layer deposition (ALD). The PS-DVB template was burned away in air during calcination giving rise to a 15 nm thick skeletal Al$_2$O$_3$ structure consisting of a wide distribution of both mesopores and macropores, as described elsewhere.$^{36}$ A nanometer-thick film of stoichiometric cobalt ferrite spinel (CoFe$_2$O$_4$) was applied to the porous Al$_2$O$_3$ support via a similar ALD process$^{37}$, and the structure was
thermally cycled as prepared. The cobalt ferrite loading determined by ICP-AES analysis was 20 % by mass.

Samples were reduced and oxidized in a stagnation flow reactor (SFR) equipped with a modulated effusive beam mass spectrometer and laser-based sample heater. In stagnation flow, the gas-phase region above the sample between centerline and reactor wall can be considered an ideal one-dimensional stagnation plane governed by diffusive transport. Samples were placed in a loosely-packed shallow bed within the stagnation plane allowing gases to access all exposed surfaces within a well-mixed control volume.

Approximately 80 mg of CoFe$_2$O$_4$-coated Al$_2$O$_3$ were placed in the SFR. Typical operating conditions were either 75 or 600 Torr total pressure, a gas flow rate of 500 sccm consisting of either pure helium, a mixture of 0.2 vol.% O$_2$ in helium, or a mixture of 50 vol.% CO$_2$ in helium depending on the experiment. During thermal reduction samples were held at a baseline temperature of 1000 °C, maintained by a laboratory furnace, and heated to a temperature between 1300 and 1460 °C using a 500W CW near-IR diode laser in a pure helium flow. The laser was focused onto a 2.9 cm$^2$ area providing an equivalent solar concentration of approximately 1700 suns at full power, albeit at discrete wavelengths as opposed to a solar spectrum. Typical heating rates were 16 °C/s, which closely mimic the thermal environment expected in a concentrated solar power application. Samples were oxidized with either CO$_2$ or O$_2$ at 1000 °C. Temperature was measured with an optical pyrometer that is accurate to ±25 °C. Gas composition of the reactor effluent was determined by measuring the partial pressure of O$_2$, CO, and CO$_2$ using a mass spectrometer.
2.7. Characterization Method

Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES) was used to determine cobalt and iron mass loading of the material. A Raman microscope was used to interrogate phonon modes in the films to fingerprint the chemical structure of the deposits after heat treatment in helium, oxygen, or carbon dioxide. Spectra were acquired ex situ in a 180° backscattering geometry using a 100× objective lens and 532-nm excitation from a frequency-doubled Nd:YAG laser. A Semrock edge filter was used to reject the elastically scattered light. A spectrograph with a single 1200 groove/mm grating dispersed the light onto a CCD detector cooled by liquid nitrogen. The laser has a spot size of approximately 1 μm and the spectrometer was calibrated with a neon lamp.

2.8. Acknowledgements

This work was supported by the National Science Foundation via Grant CBET 0966201, by the U.S. Department of Energy Fuel Cell Technologies Program via the Solar Thermochemical Hydrogen (STCH) directive, and by Laboratory Directed Research and Development at Sandia National Laboratories. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.
2.9. References


CHAPTER 3

KINETICS AND MECHANISM OF SOLAR-THERMOCHEMICAL H\textsubscript{2} AND CO PRODUCTION BY OXIDATION OF CeO\textsubscript{2}

3.1. Abstract

The combination of high thermal stability and fast reduction/oxidation kinetics has drawn attention to CeO\textsubscript{2} for use in solar-driven, two-step thermochemical cycles for water and/or carbon dioxide splitting. In accordance with this renewed interest in CeO\textsubscript{2}, there is a need to better understand the gas splitting chemistry on the reduced oxide at the extreme thermal conditions encountered in such solar-driven processes. Here we measured the H\textsubscript{2} and CO production rates over ceria powder, thermally reduced by laser irradiation, during oxidation by H\textsubscript{2}O and CO\textsubscript{2} in a stagnation flow reactor. The reaction kinetics intrinsic to the material were extracted using a model-based analytical approach to account for the effects of mixing and dispersion in the reactor. We find the rigor of this approach necessary in order to identify the rate controlling mechanism and assign parameters to the kinetic model. The water splitting reaction, in the range of 750 – 950 °C and 20 – 40 vol.% H\textsubscript{2}O, can best be described by a first-order kinetic model with low apparent activation energy (29 kJ/mol). The carbon dioxide splitting reaction, in the range of 650 – 875 °C and 10 – 40 vol.% CO\textsubscript{2}, is a more complex surface-mediated phenomena that we propose is controlled by a temperature-dependent surface site blocking mechanism involving adsorbed carbon.
3.2. Introduction

The development of carbon-neutral, environmentally-sustainable energy carriers is a technological imperative necessary to mitigate the impact of anthropogenic carbon dioxide on earth’s climate.\(^1\) Solar energy can fulfill this need given its accessibility and abundance. However, harvesting and storing solar energy continues to be a challenging endeavor, especially energy stored in the form of fungible fuels.\(^2, 3\) One compelling approach rapidly gaining international attention is the conversion of solar energy into H\(_2\) or CO via a two-step thermochemical cycle driven by concentrated solar power.\(^4, 5\) In this process, described by reactions (1) and (2) for water splitting (WS) on ceria,\(^6-8\)

\[
\frac{1}{\delta}\text{CeO}_2 \rightarrow \frac{1}{\delta}\text{CeO}_2 - \delta + \frac{1}{2} \text{O}_2 \quad (3.1)
\]

\[
\frac{1}{\delta}\text{CeO}_2 - \delta + \text{H}_2\text{O} \rightarrow \frac{1}{\delta}\text{CeO}_2 + \text{H}_2 \quad (3.2)
\]

heat derived from concentrated solar energy reduces ceria to its sub-stoichiometric oxide (\(\text{CeO}_2 - \delta\)) at temperatures above 1500 °C, producing \(\text{O}_2\). \(\text{CeO}_2 - \delta\) is then taken off sun and oxidized at a lower temperature by exposure to \(\text{H}_2\text{O}\), thus producing \(\text{H}_2\) and completing the cycle. The carbon dioxide splitting (CDS) reaction is completely analogous. Both \(\text{H}_2\) and \(\text{CO}\) can be produced continuously during daylight hours, and can be further processed into synthetic hydrocarbon fuels.\(^5, 9\)

Currently ceria is a favored material within the concentrated solar power fuels community because of its high thermal stability (i.e., does not deactivate or sinter appreciably), high surface reactivity,\(^10\) high oxygen ion conductivity,\(^11, 12\) and because it is relatively earth abundant.\(^13\) Active areas of research are focused on improving ceria’s cycle capacity, essentially the amount of \(\text{H}_2\) or \(\text{CO}\) produced per mass of irradiated material, through manipulation of the lattice structure by cation doping and substitution.\(^8, 14-18\) In effect, borrowing ideas from the
solid-oxide fuel cell community\textsuperscript{11, 19} for destabilizing the fluorite lattice by introducing oxygen vacancies that in turn create a higher degree of oxygen non-stoichiometry relative to the undoped material. This has been shown to lower the temperature required for reduction.\textsuperscript{18} These efforts have resulted in a number of studies investigating the effects of dopant choice (e.g., alkaline-earth, transition, or rare-earth metals) and dopant concentration on three key thermodynamic properties; oxygen non-stoichiometry ($\delta$), $O_2$ activity, and temperature.\textsuperscript{20-22} While the aforementioned work does provide a useful basis for understanding gas splitting thermochemistry, little or no attention has been given to the kinetics of oxidation. It is well known that the design and operation of efficient solar receiver/reactors is critically linked to kinetic behavior.\textsuperscript{23}

The kinetic mechanisms that govern ceria’s catalytic activity have been studied in great detail at temperatures below 800 °C, and under a myriad of chemical environments, principally due to its use in catalytic converters,\textsuperscript{24} carbon-soot particulate traps,\textsuperscript{25, 26} and solid-oxide fuel cells.\textsuperscript{27} However, insights gained from these studies are not directly transferrable to the high temperatures encountered in the concentrated solar power application. Specifically, the stoichiometric oxidation reaction does not behave in a manner consistent with a catalytic process because oxygen vacancies are consumed, though we do recognize surface-mediated reactions play an important role. The results of two recent kinetic studies within the context of solar-fuel chemistry by Le Gal et al\textsuperscript{18, 28} fall short due to complications of using a thermogravimetric analyzer (TGA) for extracting kinetic data, as we describe next.

Le Gal et al. investigated the $H_2O$ and $CO_2$ splitting kinetics of undoped ceria and zirconia-doped ceria using a TGA.\textsuperscript{18, 28} On undoped ceria, they identified a surface-limited reaction mechanism described empirically by a second-order power law model for $CO_2$
oxidation. This interpretation was a consequence of using the so-called “Master Plot” approach to analyzing the mass gain measured by the TGA during oxidation. However, kinetic parameters were not reported for this model and identification of the governing mechanism is suspect due to fitting errors. These authors also used the same approach to investigate CO oxidation of a zirconia-doped ceria (Zr0.25Ce0.75O2) material. In this case they ascribed a diffusion limited process to the oxidation reaction, and reported activation energies in the range 83 – 103 kJ/mole depending on the material synthesis method. Here again, their conclusions are questionable because the proposed diffusion model poorly fits the entirety of the mass gain signal. In addition, no effort was made to critically assess the effects of heat and mass transfer limitations within the TGA on the recorded mass signal, which we know to be important. More importantly, the production of CO was not measured in either case during the TGA runs, but inferred from mass changes in the solid.

In this work we use an idealized flow reactor, and a rigorous model-based analytical methodology, to reveal the kinetic behavior intrinsic to CeO2 during oxidation by measuring the production rates H2 and CO. We present parameterized kinetic models that show the WS reaction is limited by a process best described using a power-law model consistent with an activated surface-mediated reaction; and that the CDS reaction is a complex process subject to temperature-dependent site blocking and a mechanism transition that occurs over a narrow range of oxidation temperatures. Our results provide new insights into ceria reactivity that fill a critical gap in the knowledge base required to develop high-fidelity computational models for the design of concentrated solar receiver reactors.
3.3. **Experimental Methods**

Commercial ceria powder (Alfa Aesar, 99.9% purity, 5 µm nominal diameter) was used without modification for this study. Kinetic measurements were conducted in an idealized stagnation flow reactor (SFR) which has been described previously.\textsuperscript{31-33} Key features of this apparatus are: (1) the flow field is well characterized and easily modeled, (2) during thermal reduction, samples are heated by irradiation from a 500 W continuous wave near-IR laser (Apollo Instruments model F500-NIR600), otherwise the SFR temperature is maintained by a SiC furnace (Carbolite STF16/180), and (3) gas composition is measured by a modulated molecular beam mass spectrometer (Extrel C50). In addition, mass flow controllers are used to meter all gas flow rates and the reactor pressure is under closed-loop control.

Between 150 – 200 mg of CeO\textsubscript{2} was placed in the SFR in a loosely packed, shallow particle bed where all exposed surfaces experience a well-mixed gaseous environment within the stagnation plane. Prior to data collection, the powder was cycled several times at 1000 °C, until H\textsubscript{2} and CO production curves no longer changed, to ensure that the material is crystallographically and morphologically stable. A typical redox cycle consisted of holding the base temperature of the SFR at the oxidation temperature while flowing 500 sccm of ultra-high purity He over the sample (O\textsubscript{2} partial pressure < 10 ppm). During *reduction*, the ceria powder was heated from the oxidation temperature to 1500 °C at 17 °C per s, and then held at this temperature for 240 s while the O\textsubscript{2} flow rate was recorded at approximately 1 s intervals. The laser was then turned off and the powder allowed to return to the oxidation temperature by convective and radiative forces. Temperatures were measured by optical pyrometry and a thermocouple embedded in the SiC furnace. During *oxidation*, the ceria powder was exposed to various partial pressures of H\textsubscript{2}O or CO\textsubscript{2} added to the He flow for a period of either 600 s or 1800
s, respectively. The total flow rate again was held constant at 500 sccm and the H₂ or CO flow rate measured at approximately 1 s intervals.

WS experiments were conducted isothermally at temperatures between 750 – 950 °C, H₂O concentrations between 20 – 40 vol.% in He, and a reactor pressure of 75 torr. CDS experiments were also performed isothermally at temperatures between 650 – 875 °C, CO₂ concentrations between 10 – 40 vol.% in He, and at reactor pressures in the range 75 – 600 torr. The concentration of molecular species, such as H₂ (m/e = 2), CO (m/e = 28), O₂ (m/e = 32), and CO₂ (m/e = 44), in the reactor effluent was recorded during both thermal reduction and WS or CDS. A liquid-nitrogen cooled cryogenic trap was used to condense the H₂O or CO₂ before gases in the reactor effluent were sampled by the mass spectrometer. Analytical standards for O₂, H₂, and CO were used to calibrate the mass spectrometer signal.

3.4. Computational Methods

Analytical approach using a solid state (SS) kinetic model. Unlike a strictly catalytic reaction, the production of H₂ or CO during oxidation of bulk CeO₂ is limited by stoichiometry and governed by transient, surface- and/or bulk-mediated phenomena. In addition, physical processes inherent to the SFR apparatus, such as gas-phase dispersion, oxidant mixing, and detector time lag, impose a temporal imprint on the H₂ and CO production rate curves. Therefore, to correctly extract the intrinsic kinetic behavior of the WS or CDS process, it is necessary to strip these experimental effects from the as-recorded ion signals.

Separating the temporal imprint of the SFR apparatus from the kinetic signature of the material was accomplished using a model-based data reduction algorithm that combines a validated mixing model of the SFR with a material-specific SS kinetic model to predict the H₂ or CO flow rate. Then, the simulated flow rate is best-fit to the experimental data and the kinetic
mechanism and associated kinetic parameters recovered. Conceptually, the numerical analysis assumes the WS or CDS reaction can be described using empirical models taken from solid state kinetic theory. In both the actual SFR experiment and simulation, the oxidation chemistry is initiated by a step-change in the \( \text{H}_2\text{O} \) or \( \text{CO}_2 \) concentration. In response to this, a waveform representative of the transient production of \( \text{H}_2 \) or \( \text{CO} \) is created and subsequently propagated through a series of continuously-stirred tank reactors. This alters the temporal characteristic of the kinetic waveform, thus simulating the effects of mixing and dispersion inherent to the experimental apparatus.

A least-squares residual value formulated from the difference between simulation and experimental data at each time step is used as an objective function within a Differential Evolution (DE) minimization routine. The DE algorithm stochastically solves a constrained, mixed-integer optimization problem that searches for the best-fit SS kinetic model and its associated kinetic parameters. Preferential weighting is applied on the objective function by applying a penalty function to emphasize the fit in the first 300 s of the oxidation process, where typically more than 90 % of the fuel is produced.

The material-specific oxidation rate equation used to generate the aforementioned waveforms takes the following Arrhenius form:

\[
\text{rate} \left[ \frac{1}{s} \right] = A_0 e^{\left( \frac{E_0}{RT} \right)} \left[ Y_{\text{oxid}}(t) \right]^{\gamma} f(\alpha) \tag{3.3}
\]

where \( A_0 \) and \( E_0 \) are the respective pre-exponential factor and apparent activation energy, \( Y_{\text{oxid}} \) is the time-dependent mole fraction of \( \text{H}_2\text{O} \) or \( \text{CO}_2 \), \( \gamma \) is the reaction order of the oxidant mole fraction, \( \alpha \) is the normalized extent of reaction, and \( f(\alpha) \) is a functional taken from SS kinetic theory that describes the rate of progress of the oxidation. The normalized extent of reaction (\( \alpha \)), employed here is described in Equation 3.4, and is assumed to always go from 0 \( \rightarrow \) 1, which
implies complete reoxidation is achieved after every WS or CDS. There are two possible limitations that could prevent complete reoxidation of ceria: the first is thermodynamic limitation, where at the $P_{\text{H}_2\text{O}}/P_{\text{CO}_2}$ and temperature used, $\delta_T \neq 0$. However, based on thermodynamic data published by Panlener et al.$^{35}$, all the WS and CDS conditions used in this study has enough oxygen activity to reoxidize the material fully and achieve $\delta_T = 0$. The second is kinetic limitation, where the WS and CDS are not allowed to proceed to completion. The oxidation times employed here, 600 s and 1800 s for WS and CDS respectively, are sufficient to allow fuel production to return to baseline, an indication that the oxidation reaction is kinetically completed.

$$\alpha = \int_0^t \frac{H_{2(t)}}{H_{2\text{total}}} \text{ or } \int_0^t \frac{CO(t)}{CO_{\text{total}}}$$

(3.4)

Our analysis searches through 14 different functional forms for $f(\alpha)$, representative of various rate-limiting reaction phenomena, thereby identifying the governing mechanism within the context of SS kinetic theory. The kinetic parameters unique to this mechanism (i.e., $A_0$, $E_0$, and $\gamma$) are also solved for. A more detailed description of this numerical approach can be found elsewhere.$^{31}$

**Analytical approach using a microkinetic (MK) model.** The empirical equation adopted from SS kinetic theory that describes oxidation is essentially a lumped parameter model, and does not provide sufficient fidelity to understand the reaction pathway. And while this course level of detail can be used effectively to simulate H$_2$ fuel production from H$_2$O oxidation of undoped ceria, it is not adequate to comprehensively describe the transient CO production rates we observe over the entire range of oxidation conditions (i.e., temperature and CO$_2$ partial pressure). The CDS reaction is a more complex process that requires a different approach in order to gain a phenomenological understanding of the surface chemistry. Therefore, a
microkinetic (MK) analysis was conducted to derive a plausible surface reaction network able to describe the experimental data.

In the MK analysis, the network of four reversible elementary reactions listed here are used to describe surface reactions involving CO$_2$ and CO with CeO$_2$;

$CO_2 + 2\theta_v \xleftrightarrow{K_1} \theta_{CO} + \theta_O$ (3.5)

$\theta_{CO} \xleftrightarrow{K_2} CO + \theta_v$ (3.6)

$\theta_{CO} + \theta_v \xleftrightarrow{K_3} \theta_C + \theta_O$ (3.7)

$\theta_C + \theta_O \xleftrightarrow{K_4} CO + 2\theta_v$ (3.8)

Equation (3.5) in the forward direction is the dissociative adsorption of a CO$_2$ molecule on two vacant oxygen sites ($\theta_v$), creating an adsorbed CO intermediate ($\theta_{CO}$) and filling one oxygen vacancy with an O atom ($\theta_O$). Equation (3.6) describes unimolecular desorption of CO from the surface-bound intermediate resulting in the creation of an oxygen vacancy. The reverse of Equation (3.6) is the associative adsorption of CO. Equation (3.7) is the atomization of surface-bound CO ($\theta_{CO}$), which produces adsorbed carbon ($\theta_C$) and fills an oxygen vacancy. And Equation (3.8) describes the recombination of surface-bound carbon and oxygen atoms thus providing an alternate pathway for CO evolution into the gas. The reverse of Equation (3.8) represents the dissociative adsorption of CO. $K_i$ ($i = 1 – 4$) in these equations is the equilibrium constant for each reaction taken from the standard definition ($K_i = R_{i,f} / R_{i,r}$), where $R_{i,f}$ is the forward rate and $R_{i,r}$ the reverse rate of the $i^{th}$ reaction.

These reactions, comprised of two gas-phase species (CO$_2$ and CO) and four adsorbed species ($\theta_O$, $\theta_v$, $\theta_C$, and $\theta_{CO}$), are commonly proposed for the catalytic reduction of CO$_2$ on surfaces and are a list of the fewest possible steps needed to simulate CO production. Noticeably
absent from this network are reactions that involve O\textsubscript{2} molecules with the CeO\textsubscript{2} surface. This is a reasonable omission because O\textsubscript{2} was not detected above baseline levels during CDS. For the sake of simplicity, this reaction scheme also excludes surface carbonate and carboxylate intermediates because these species are known to decompose below 300 °C.\textsuperscript{36,37}

In addition to Equations (3.5 – 3.8), we include a conservation equation of the form:

$$\theta_O + X_v \leftrightarrow X_O + \theta_v$$

(3.9)

where $X_v$ is the bulk-phase mole fraction of oxygen vacancies and $X_O$ is the bulk-phase mole fraction of O atoms in CeO\textsubscript{2-δ}. Equation (3.9) must obey constraints imposed by the solid-phase stoichiometry (i.e., the mole fractions $X_{Ce}$, $X_v$, and $X_O$ in the lattice sum to unity, $X_{Ce} = 1/3$, $X_v = 0$, and $X_O = 2/3$ for fully oxidized CeO\textsubscript{2}). Equation (3.9) is also considered to be equilibrated at all times and represents the instantaneous transport of surface oxygen into an open lattice site thereby producing a surface oxygen vacancy. Thus, unlike a catalytic process, surface reactivity is limited by the availability of bulk oxygen vacancies ($X_v$) and once CeO\textsubscript{2-δ} is fully oxidized ($\delta = 0$) CO production stops.

The MK model for CO\textsubscript{2} oxidation of CeO\textsubscript{2} was formulated from the system of ordinary differential equations that result from deriving mass balances for each of the six independent species, according to the reactions proposed by Equations (3.5 – 3.9) (see supplemental information section). Currently, the elementary rate constants ($R_{i,f}$ and $R_{i,r}$) in the MK model are unknown for thermochemical CO\textsubscript{2} splitting on ceria. However, this does not compromise the main objective of the MK analysis, which is to determine plausible pathways for CO formation on the CeO\textsubscript{2} surface under conditions appropriate to thermochemical cycles. By solving the system of ordinary differential equations and reconciling the solution to our experimental observations, we can map the carbon flux through the reaction network and determine the rate
governing mechanism. We minimize a least-squares residual value formulated from the difference between the MK model (CO_{MK}) and experimentally derived solid state model (CO_{SS}) data at each time step to reconcile our experimental observations with the MK model.

3.5. Results

**Oxidation of thermally-reduced cerium oxide by water.** In this work thermally reduced CeO$_2$, in the form of undoped commercial powder, was re-oxidized by exposure to steam. The oxidation reaction is a transient process where oxygen atoms are taken from a water molecule and transferred to the ceria via various surface- and bulk-mediated processes. The net result is the production of H$_2$. As bulk oxygen vacancies are depleted in the ceria, the H$_2$ production rate decreases and eventually stops. Shown in Figure 3.1 is the mole fraction of H$_2$ measured in the SFR effluent as a function of time for several WS conditions. The curves are representative of the transient temporal behavior often observed in this type of experiment and show a clear dependence on oxidation temperature and vol.% H$_2$O.

It is easily seen in Figure 3.1 that the peak in H$_2$ mole fraction, which correlates to the reaction rate, increases with temperature and oxidant concentration. What is less obvious from this figure is that the total area under each curve, essentially the net amount of H$_2$ produced per gram of ceria, remains constant under first approximation. Under all experimental conditions, H$_2$ production initiates from a rapid step-change (~0.5 s) in the SFR inlet H$_2$O concentration at time = 0 s (not shown in Figure 3.1). The H$_2$ mole fraction peaks at approximately 100 s, and then decreases back to the original baseline in less than 600 s with 90% of the H$_2$ produced in less than 300 s. We note that the same sample of ceria was continuously cycled to generate the data in Figure 3.1. The delay in the onset of the H$_2$ signal, and subsequent shape of the entire envelope, is due to dispersion, mixing, and detector time lag inherent to the SFR apparatus and
not WS chemistry. Therefore, it is essential to remove these temporal imprints in order to resolve the WS kinetics of the material.

![Figure 3.1](image)

Figure 3.1. The mole fraction of H₂ as a function of time measured in the SFR during oxidation of thermally reduced CeO₂ by water at temperatures between 750 – 950 °C, 20 – 40 vol.% H₂O, and 75 torr reactor pressure. CeO₂ was reduced in helium at 1500 °C for 240 s. The open symbols are data points, the solid lines are simulations using a single best-fit kinetic model (see text). Note: x-axis is in log time.

**Analysis of water oxidation kinetics.** Due to the confounding effects of the SFR experimental apparatus, we use a model-based approach to analyzing the H₂ production rate curves. Identification of the rate limiting mechanism(s) and/or values for the kinetic parameters
may be in error if experimental effects are not adequately taken into account.31 Here we identify the rate governing mechanism without a priori assumptions, other than the belief that models taken from solid state kinetic theory can explain the observed oxidation behavior.

Applying the aforementioned SS analytical approach to all of the H₂ production rate curves shown in Figure 3.1 for WS resulted in a single kinetic model that adequately describes the entirety of our experimental observations (solid lines in Figure 3.1). In total, fourteen different SS reaction mechanism spanning four distinct reaction phenomena were tested against the experimental data using a least-squares objective function evaluated at every time step. Over 8400 data points were considered during each iteration of the DE optimizer, spanning the entire experimental campaign (WS temperatures between 750 – 950 °C, and concentrations between 20 – 40 vol.% H₂O). The unique solution to the SS kinetic model for WS is summarized in Table 3.1.

Tables 3.1. The best-fit solid state reaction model and associated kinetic parameters derived from the SS analysis for WS and CDS at 75 torr reactor pressure.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A_0 ) (1/s)</th>
<th>( E_0 ) (kJ/mole)</th>
<th>( \gamma )</th>
<th>( f(\alpha) = (1-\alpha)^n )</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS</td>
<td>1.0</td>
<td>29</td>
<td>0.89</td>
<td>( n = 1.0 )</td>
<td>750 – 950</td>
</tr>
<tr>
<td>CDS</td>
<td>4.2</td>
<td>47</td>
<td>0.53</td>
<td>( n = 1.0 )</td>
<td>650 – 725</td>
</tr>
<tr>
<td>CDS</td>
<td>3.4</td>
<td>45</td>
<td>0.65</td>
<td>( n = 1.2 )</td>
<td>750 – 800</td>
</tr>
<tr>
<td>CDS</td>
<td>2.5</td>
<td>41</td>
<td>0.70</td>
<td>( n = 1.7 )</td>
<td>825 – 875</td>
</tr>
</tbody>
</table>

We find that a first-order deceleratory mechanism of the form \( f(\alpha) = (1-\alpha) \) best describes the WS kinetics on undoped ceria. This suggests that oxidation is likely governed by a process analogous to a homogenous reaction. We will discuss the mechanistic implications later. To illustrate uniqueness of this solution, three other \( f(\alpha) \) functions are plotted in Figure 3.2 against
the best-fit SS model simulating H₂ mole fraction measured during WS at 900 °C and 40 vol.% H₂O. These functions represent rate-limiting phenomena such as geometric contraction (R3 in Figure 3.2), solid diffusion (D3 in Figure 3.2), and nucleation and growth (A2 in Figure 3.2). A complete description of all the SS models we tested against and their physical interpretation can be found elsewhere. The first-order process is labeled F1 in the figure.

Figure 3.2. The mole fraction of H₂ as a function of time measured in the SFR during oxidation of thermally reduced CeO₂ by water at 900 °C, 40 vol.% H₂O, and 75 torr reactor pressure. CeO₂ was reduced in helium at 1500 °C for 240 s. The open symbols are data points, the solid and dashed lines are simulations showing the quality of fit to four kinetic models that have different functional forms for \( f(\alpha) \) (see text). It is clear that the model labeled F1 is the best-fit. Note: x-axis is in log time.
The diffusion family of models (D), regardless of the characteristic dimensions over which they act, always over-predict the H\textsubscript{2} mole fraction at early times and under-predict at later times. Both the Avrami-Erofeyev (A) and geometric contraction (R) models, again regardless of dimension, under-predict at early times and over-predict at later times. Only the first-order F1 model fits the data throughout the entire time domain. The complete kinetic model for WS is expressed by applying the F1 function to Equation (3.3) using the fitted results from Table 3.1.

**Oxidation of thermally-reduced cerium oxide by carbon dioxide.** The CDS reaction on ceria behaves analogously to WS. Upon exposure to CO\textsubscript{2}, surface- and bulk-mediated processes govern the formation of CO and the re-oxidation of the CeO\textsubscript{2}. In this series of experiments, a freshly prepared sample of ceria powder was continuously cycled to generate the 27 time-dependent CO mole fraction curves shown in Figure 3.3. Production of carbon monoxide is characterized by a rapid increase in the CO mole fraction, followed by a slower decline back to baseline levels completing the oxidation in less than 1800 s. Similar to the transient H\textsubscript{2} signal, CO production decreases as oxidation goes to completion (i.e., no extraneous catalytic CO\textsubscript{2} splitting at temperatures below 875 °C).

We find that the rate of CO\textsubscript{2} oxidation, and the total amount of CO produced per gram of CeO\textsubscript{2}, is dependent on both the CDS temperature and volume fraction of CO\textsubscript{2} in the SFR. Apart from the obvious trends, the CDS reaction does behave differently than the WS reaction. The CDS process appears to be slower than WS; peak CO mole fractions are consistently half those of H\textsubscript{2} and the time required to achieve complete oxidation is markedly longer (1800 s as opposed to 600 s). A detailed kinetic analysis of the CDS reaction follows.
Figure 3.3. The mole fraction of CO as a function of time measured in the SFR during oxidation of thermally reduced CeO$_2$ by carbon dioxide at temperatures between 650 – 875 °C, 10 – 40 vol.% CO$_2$, and 75 torr reactor pressure. CeO$_2$ was reduced in helium at 1500 °C for 240 s. The open symbols are data points, the solid lines are simulations using a series of best-fit kinetic models (see text). Note: x-axis is in log time.

**Analysis of carbon dioxide oxidation kinetics using the SS model.** Unlike the WS chemistry, we found it difficult to converge on a single kinetic model that adequately predicts the CO production behavior over the entire temperature range using the SS analytical approach. An attempt to fit all 27 time-dependent CO mole fraction measurements to a single SS model yielded unsatisfactory results. In order to achieve a high quality fit to the data, three separate temperature ranges (650 – 725, 750 – 800, and 825 – 875 °C) had to be used. And while the F
family of models continued to give best-fits to the transient CO signal, the kinetic parameters changed over these temperature ranges.

The power law governing CO production by \( f(\alpha) = (1-\alpha)^n \) functionality means CDS is not diffusion limited, or limited by the other previously mentioned solid state processes, and therefore is in agreement with calculations made by Chueh et al.\(^7\) However, the apparent activation energy \( (E_0) \), pre-exponential factor \( (A_0) \), dependence on CO\(_2\) concentration \( (\gamma) \), and order \( (n) \) of the CDS reaction are dissimilar to WS implying these two chemistries do not share a common rate limiting step. The results of the SS analysis for CDS are also summarized in Table 3.1.

According to the data presented in this Table, the order of the power law model \( (n) \) increases from 1.0 to 1.7 as the temperature increases from 685 °C to 875 °C. In addition, the dependence on vol.% CO\(_2\) \( (\gamma) \) increases from 0.53 to 0.70. These changes signify that the rate governing mechanism is evolving over the narrow range of temperatures we investigated. In fact, this trend is typical of catalytic reactions where temperature-dependent site blocking occurs on the surface.\(^{36, 38-40}\) Since the empirical nature of the SS analytic approach, which is essentially a lumped-parameter model, cannot provide detailed insight into more complicated surface-mediated phenomena like site blocking, we next attempt to understand this chemistry using a different kinetic model.
Figure 3.4. The mole fraction of CO as a function of time simulated by the best-fit SS kinetic models (solid lines) derived from the experimental data for oxidation of thermally reduced CeO$_2$ by carbon dioxide at temperatures between 650 – 875 °C, 40 vol.-% CO$_2$, and 75 torr total pressure. CeO$_2$ was reduced in helium at 1500 °C for 240 s. The dashed lines are the result of fitting the MK kinetic model to the SS kinetic model (see text). Note: x-axis is in log time.

**Analysis of carbon dioxide oxidation kinetics using the MK model.** We propose that the reaction network outlined in Equations (3.5 – 3.9) provides a basis from which further insight into the CDS reaction on ceria can be gained. Unfortunately the CO$_x$ chemistry on ceria is poorly understood at the CDS conditions we investigated, meaning that we are not aware of any elementary kinetic or thermodynamic data available to describe Equations (3.5 – 3.9). Thus, the flux of carbon on the surface of ceria is determined by solving the necessary rate of each of the reactions in the network, both in the forward and reverse directions ($R_i$) to give the best fit between CO$_{MK}$ and CO$_{SS}$. The result of the fit is summarized in Figure 3.4 for CDS between 685
– 875 °C and at 75 torr total pressure. Quality fit can be obtained over the entire CO envelope at the different oxidation temperatures. The agreement between \( \text{CO}_{\text{MK}} \) and \( \text{CO}_{\text{SS}} \) is the basis for the CO\(_x\) flux map shown in Figure 3.5. We note that the \( \text{CO}_{\text{SS}} \) value is tied to the experimental observation and serves as the ground truth in this analysis. The analysis reveals that at the low temperature range, the rate governing step is surface recombination of carbon to gaseous CO. And at the high temperature range, the rate determining step is the dissociative adsorption of CO\(_2\) on the surface.

Figure 3.5. Analysis of the reaction pathways, derived from the MK model, that consume CO\(_2\) and produce/consume CO during oxidation of thermally reduced CeO\(_2\) by carbon dioxide. The width, direction, and shading of the arrows are proportional to the flux of carbon through the reaction network. Darker shades and larger line widths mean more carbon passes through that particular pathway. “R.D.S” is the rate determining step. (a) At 685 °C, the R.D.S. is the surface recombination of \( \theta_C \) and \( \theta_O \) to form CO. (b) At 875 °C, the R.D.S. is dissociative adsorption of CO\(_2\).
In accordance with equations (3.5 – 3.9), and as can be seen in the carbon flux map in Figure 3.5, there are two major pathways to produce CO: the *direct desorption of surface CO* (Equation (3.6)), and the *recombination of surface carbon with surface oxygen* (Equation (3.8)). According to the MK analysis, the prevailing pathway changes with oxidation temperature. *At the low temperature range*, both pathways are active in forming CO. However, the pathway involving direct desorption of surface CO occurs at a faster rate than the surface recombination process. Thus, the rate governing mechanism is the surface recombination of carbon and oxygen. This agrees with the SS results, where $\gamma$ is 0.53 and power law model ($n$) is 1.0. The SS model extracts a lumped parameter from the surface reaction network, yet still probes the slowest elementary reaction within the network. Due to the slow recombination of surface carbon with surface oxygen, carbon can act as a site blocker. This is why $\gamma$ extracted by the SS model is 0.53. Furthermore, although this recombination is a bimolecular process, the power law model ($n$) exhibits a first order dependence. This is because surface coverage of carbon is two orders of magnitude lower than coverage of oxygen, as calculated by the MK analysis (Figure 3.9), and therefore the recombination behaves in a first order manner.

*At the high temperature range*, only the direct desorption of surface CO pathway is active. The pathway involving surface recombination of carbon terminates. According to our MK analysis, the rate of surface carbon formation decreases to zero at 875 °C (see Figure 3.8 in the supplemental section for complete list of $R_i$ at the different temperatures). Surface carbon is no longer produced, and thus site blocking is ceased. This is why $\gamma$ increases from 0.53 to 0.70. This termination is in agreement with literature reports: that surface atomization of gaseous carbonaceous species to form carbon on the catalyst surface is not thermodynamically favorable at higher temperatures. Thus, at the high temperature range, the CO production pathway
involves only dissociative adsorption of CO$_2$ (Equation (3.5)), followed by direct desorption of surface CO (Equation (3.6)). In accordance with the MK analysis, the desorption process becomes very fast, and the dissociative adsorption of CO$_2$ becomes rate limiting. This adsorption involves two surface oxygen vacancy sites and therefore the power law model ($n$) is 1.7 at this temperature range. In short, if the MK analysis is correct, there should be a difference in CO rate sensitivity towards CO$_2$ flux at the different oxidation temperatures.

Figure 3.6. The mole fraction of CO as a function of time simulated by the best-fit SS kinetic models (solid lines) derived from the experimental data for oxidation of thermally reduced CeO$_2$ by carbon dioxide at 685°C and 875 °C, 40 vol.% CO$_2$, and reactor pressures between 150 – 600 torr. CeO$_2$ was reduced in helium at 1500 °C for 240 s. The dashed lines are the result of fitting the MK kinetic model to the SS kinetic model (see text). Note: x-axis is in log time.
Therefore, in addition to MK analysis at 75 torr, further MK and SS analysis were performed on CDS experiments performed at various flux of CO$_2$ (150 – 600 torr total pressure with 40 vol.% CO$_2$), at the two temperatures regimes: 685 and 875 °C. The resulting CO$_{MK}$ fit is shown in Figure 3.6. Increasing total pressure from 150 to 600 torr, increases the flux of CO$_2$ onto the surface of ceria four-fold. As expected, the rate of CO production increases accordingly. However, there is a clear CO rate increase difference towards change of CO$_2$ flux at the two temperatures: increase in CO peak rate is much higher at 875 °C than at 685 °C. Figure 3.7 shows the calculated reaction rate constant ($k_0$) as calculated by our model-based algorithm. At 685 °C, increasing the flux of CO$_2$ four-fold increases $k_0$ only by approximately 70 %. This is consistent with the aforementioned MK analysis, where at the low temperature range, site blocking by surface carbon is prevalent, and that the rate governing step is the recombination of surface carbon with surface oxygen. In contrast, at 875 °C, increasing the CO$_2$ flux by the same amount yields a seven-fold increase in $k_0$. This again is consistent with our MK analysis. At this high temperature range, direct desorption of surface CO becomes very rapid, dissociative adsorption of CO$_2$ becomes rate limiting, and thus the CDS process becomes very sensitive to the total flux of CO$_2$. 
3.6. Discussion and Conclusions

Mechanism of water oxidation. The experimental methods and numerical solid state approach applied in this work to extract the WS kinetic parameters is distinct compared to other works reported in the literature. Unlike a simple peak rate analysis or the “master-plot” analysis, our method separates experimental effects from material specific H₂ and CO curve rates, and makes use of the entire envelope of the fuel curve to analytically determine the rate governing mechanism. This analysis results in the first order based model, F1, which is an activated process, with $E_0 = 29$ kJ/mole and a reaction order for the water mole fraction, $\gamma = 0.89$. This suggests that WS will scale with surface area, as has been experimentally shown elsewhere. The $E_0$ reported here is much lower than the 51 kJ/mole for Ce₀.₇₅Zr₀.₂₅O₂ reported by Le Gal et al. This large discrepancy is most likely due to errors in their analytical methods.
and not effects of the dopant. The authors rely on analysis only at early reaction times, and effects of experimental effects such as dispersion in their thermogravimetric analyzer were not separated from their observed rate curves.31

\[ H_2O(g) + (V_0 + 2e') \rightarrow 2OH + O_0^x \]  \hspace{1cm} (3.10)

\[ 2OH \rightarrow H_2(g) \]  \hspace{1cm} (3.11)

\[ 2Ce^{l'}_Ce \rightarrow 2Ce^{x}_Ce + 2e' \]  \hspace{1cm} (3.12)

\[ H_2O(g) + V_0 + 2Ce^{l'}_Ce \rightarrow H_2(g) + O_0^x + 2Ce^{x}_Ce \]  \hspace{1cm} (3.13)

The kinetic parameters reported in this work represent surface and bulk processes, represented in Equations 3.10 – 3.13 (written in the Kröger – Vink notation). Equation (3.10) represents dissociative adsorption on the external surface of ceria converting oxygen vacancies to bulk oxygen. Equation (3.11) represents surface hydroxyl recombination and H₂ desorption. Equation (3.12) is oxidation of Ce³⁺ cations to Ce⁴⁺. Equation (3.13) is the sum of Equations 3.10 – 12 to give the net result of oxygen vacancies consumption and reoxidation of ceria cations by steam. This network of reactions provides several possible candidates for the rate determining step, among them are: dissociative adsorption of water on the surface, ambipolar diffusion of neutral oxygen from bulk to the surface, or surface mediated recombination/desorption yielding the gaseous product, H₂.

The F1-model is reflective of the global surface reaction network and may not be attributed to a single elementary process. It can however discriminate against other non-surface reaction order mechanisms, as all other \( f(\alpha) \), such as geometric contraction, nucleation and growth, and diffusion models, do not adequately describe the H₂ rate curves, as has been shown in Figure 3.2. Therefore, our analysis suggests that the WS reaction is controlled by surface processes with apparent first order dependence towards steam. These surface processes can be
either dissociative adsorption of water (Equation (3.9)) or desorption of H₂ (Equation (3.10)).

One possible method to elucidate the elementary rate controlling surface reaction is by increasing the flux of steam (P_{H2O}) onto the surface of ceria. If the rate controlling step is desorption of H₂, then H₂ rates will have less sensitivity towards increasing P_{H2O} than if the rate controlling step is dissociative adsorption. Unfortunately, at this time we are unable to perform this experiment due to the limitation of our experimental set up, e.g. preventing condensation of steam at higher levels of P_{H2O}.

**Mechanism of carbon dioxide oxidation.** To our knowledge, no rigorous analysis of the CO₂ splitting phenomena has been reported in the literature, with the exception of work by Le Gal et al. Previous investigation of CDS on undoped ceria by Le Gal et al with the “Master Plot Analysis”, performed between 1000 – 1200 °C, has yielded the F2 model (n = 2); however experimental effects such as dispersion were not resolved, and hence, as has been discussed by Scheffe et al, misinterpretation of the results occurred. Pertinent information such as quality of fit, energetics, and CO₂ concentration dependence were not discussed; therefore, meaningful comparison with our results cannot be performed and similarity to this work in the F-model dependence may be purely coincidental.

Our SS analysis suggests that the CDS process is a more complex surface phenomenon than the WS reaction. In contrast to WS, where H₂ production can be predicted by one F1 model over the temperature range examined, CDS necessitates incorporation of various F-models where the power law order (n) evolves from unity to approaching two at higher oxidation temperature; with apparent energy of activation that decreases from 47 – 41 kJ/mole; and γ that increases from 0.53 to 0.70., a trend that is characteristic of diminishing temperature-dependent site blocking.
To understand this trend, we have applied an MK analysis and derived a surface carbon flux, as shown in Figure 3.5. It is to be noted that the width and darkness of the arrows representing the flux are proportional to the magnitude of the reaction rate (i.e. darker and wider indicates larger \( R_i \) value). At lower temperatures, CO can be produced by two pathways: 1.) direct desorption of surface CO; 2.) or alternatively, surface CO can atomize to form surface carbon, which then recombines with surface oxygen to form gaseous CO. Results of the MK analysis, suggests that at the lower temperature regime, both pathways are active, but the rate governing step is the recombination of surface oxygen and surface carbon; and thus rate of CO production is not very sensitive to flux of CO\(_2\). Indeed, carbon deposition on ceria at this temperature range, by exposure to hydrocarbons or alcohols, has been reported by others.\(^{39, 44, 45}\) And temperature dependent site blocking by carbon has been observed in other surface mediated processes involving hydrocarbons as well, such as in steam-methane reforming.\(^{40}\)

On the other hand, at the higher temperatures, the propensity for surface carbon formation and thus site blocking is diminished. Therefore \( \gamma \), as derived by the SS model, increases to approach unity. Direct desorption of surface CO to the gaseous phase becomes very rapid, so the dissociative adsorption becomes rate limiting. Therefore, CDS experiments performed at this temperature regime have much higher sensitivity to the flux of CO\(_2\).

In addition to the evolving \( n \) and \( \gamma \), the CDS energetics found here varied from 47 – 41 kJ/mole as oxidation temperature is increased (Table 3.1). These values are much less than the aforementioned 83 – 103 kJ/mole for \( \text{Zr}_{0.25}\text{Ce}_{0.75}\text{O}_2 \) reported by Le Gal et al\(^{28}\) or the 77 kJ/mole reported for \( \text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{0.1925} \).\(^{46}\) As previously discussed; the “master plot” and peak rate analysis used in the respective works is questionable due to its failure to describe the CO rates
over the entire time domain of the reaction and to critically assess the effects of experimental effects on the CO rates.

In summary, the transition of the dominant surface mediated CO production pathway is responsible for the apparent governing mechanism shift in the F-model in the CDS. This is expressed in the evolution of $E_0$, $n$, and $\gamma$ values as the CDS temperature is increased. At the lower temperature region, CO can be produced by two parallel pathways. At the higher temperature, the dominant pathway is the direct desorption of surface CO, which occurs very rapidly and becomes limited by dissociative adsorption of CO$_2$; hence reaction rate increases greatly with increase in flux of CO$_2$.

In closing, we have evaluated the kinetics of ceria as a medium for solar thermochemical fuel production. Employing experimental protocols in an ideal reactor, with rigorous solid state model-based analytical methodology, coupled with a microkinetic analysis, we have obtained parameterized kinetic models that can describe the transient H$_2$ and CO production over the entire time domain of the process. We have illustrated the importance of this rigorous analytical approach to account for the effects of mixing and dispersion in the reactor when identifying the rate controlling mechanism of both WS and CDS. For the WS, the F1 model represents a classic surface mediated process with activation energy of 29 kJ/mole. On the other hand, we discover that the CDS process is a more complex surface mediated reaction that is convoluted by temperature dependent site blocking and mechanism transition at different oxidation temperatures. Nonetheless, both WS and CDS processes occur rapidly and can benefit by optimization of the gas/solid interface, such as the creation of a high surface area ceria structure, as has been demonstrated by Venstrom et al.$^{43}$
The combination of high thermal stability and fast kinetics has established ceria as a good candidate for the solar thermochemical process. Understanding the oxidation kinetics of ceria is vital to the development of detailed engineering models of ceria based solar receiver reactors. Due to limited solar availability in a day; it is important to maximize the solar to fuel conversion efficiency, and that requires optimization of the thermal reduction and oxidation process. Models based on experimental kinetic rate constants and insight into the oxidation mechanism will allow for optimization of transport rates and transit times of ceria in the solar receiver/reactor. This in turn allows for maximization of the number of thermochemical cycles that can be completed, and determines the fuel production rate and efficiency of the power plant.

3.7. Supplemental Information

MK Analysis. The system of equations representing the time dependent mass balance of surface and gaseous species used to simulate the microkinetic CO\textsubscript{MK} rate curves are as follows:

\[ S_k \text{ or } \frac{d\theta_j}{dt} = \Sigma (R_{i,f} * \theta_j^n * Y_k) - \Sigma (R_{i,r} * \theta_j^n * Y_k) \]  \hspace{1cm} (3.14)

\[ \frac{dy_k}{dt} = -\frac{1}{r} * (Y_k - Y_k^o) + \frac{\gamma}{\rho_{gas}} * S_k * W_k \]  \hspace{1cm} (3.15)

\[ \frac{dx_O}{dt} = \frac{\theta_o}{dt} \]  \hspace{1cm} (3.16)

\[ \frac{dx_V}{dt} = \frac{\theta_V}{dt} \]  \hspace{1cm} (3.17)

\[ X_{Ce} = 1 - X_O - X_V \]  \hspace{1cm} (3.18)

\[ 1 = \Sigma Y_k + Y_{He} \text{ and } 1 = \Sigma \theta_j \]  \hspace{1cm} (3.19)

In order to solve for the transient CO\textsubscript{MK} curves, elementary surface reactions listed in Table 3.2 were incorporated into a CSTR model; whereby a system of ordinary differential equations (ODEs) describing time-dependent mass balances of surface and gaseous species.
(Equations 3.14 – 3.19) were solved. Equation 3.14 represents the rate of generation/consumption of surface $i$ species ($\theta_i$) or gaseous $k$ species ($S_k$). Equation 3.15 represents the transient conservation equation of gaseous species occurring within the CSTR model. Equations 3.16 and 3.17 represent instantaneous equilibrium between surface and bulk oxygen and vacancy, respectively. And, Equations 3.18 and 3.19 describe the mass conservation equations, where mole fraction of both bulk species and surface sites must be equal to unity. Equation 3.18 must obey constraints imposed by the solid-phase stoichiometry (i.e., the mole fractions $X_{Ce}$, $X_v$, and $X_O$ in the lattice sum to unity, $X_{Ce} = 1/3$, $X_v = 0$, and $X_O = 2/3$ for fully oxidized CeO$_2$). Thus, unlike a catalytic process, surface reactivity is limited by the availability of bulk oxygen vacancies ($X_v$) and once CeO$_{2-\delta}$ is fully oxidized ($\delta = 0$), CO production stops.

The system of ODEs was numerically solved using the built-in computational tool in Mathematica 8® (NDSolve) to give $R_i,f/r$ pair in the MK ensemble that were scaled accordingly to reflect the influence of the rate determining step and achieve a best fit to the experimentally derived CO production rate ($CO_{SS}$).

Initial conditions used were as follow: $\theta_V = 0.1$, $\theta_O = 0.9$, and $X_{Ce} = 1/2.974$. Initial bulk mole fraction of reduced ceria, $X_{Ce}$, was calculated based on the average O$_2$ released during thermal reductions, which correspond to $\delta_{avg} = 0.026$, or $[V_{O}]_{bulk} = 0.013$. This gave a $\theta_V$ to $[V_{O}]_{bulk}$ ratio of approximately 1:10. These initial conditions were reasonable approximations and were based on recent experimental work done by Chueh et al., where they have experimentally shown that due to large differences between surface and bulk entropic contributions, concentration of surface defects of ceria can be one to two orders of magnitude higher than bulk, especially at low oxygen non-stoichiometry, such as in our case.$^{47}$
Tables 3.2. Model Nomenclature for micro-kinetic parametric study.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_k$</td>
<td>Mole fraction of gaseous species $k$, $k = \text{CO}_\text{g}, \text{CO}_2\text{(g)}$</td>
<td>none</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Fractional surface coverage of species $i$ ($i = \bar{V}_\text{O}, \text{O}, \text{C}, \text{CO}$)</td>
<td>none</td>
</tr>
<tr>
<td>$\dot{S}_k$</td>
<td>Rate of generation/consumption of gaseous species $k$</td>
<td>1/s</td>
</tr>
<tr>
<td>$n$</td>
<td>Stoichiometric constant of species $i$ or $k$</td>
<td>none</td>
</tr>
<tr>
<td>$R_{s,f}$</td>
<td>Reaction rate forward for equation $s$, where $s$ represents elementary reaction # from Equations 3.4 – 7, $s = 1 – 4$.</td>
<td>1/s</td>
</tr>
<tr>
<td>$R_{s,r}$</td>
<td>Reaction rate reverse for reaction $i$</td>
<td>1/s</td>
</tr>
<tr>
<td>$X_{\text{Ce}}, X_{\text{O}}, X_{\text{v}}$</td>
<td>Bulk mole fraction of Ce, O, or oxygen vacancies.</td>
<td>none</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Geometric factor for bed of particle.</td>
<td>mole/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{\text{gas}}$</td>
<td>Average density of gas within CSTR at time $t$ at temperature $T$.</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td>$W_k$</td>
<td>Molar mass of gaseous species $k$</td>
<td>g/mole</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Space velocity for CSTR</td>
<td>1/s</td>
</tr>
</tbody>
</table>
Figure 3.8. Fractional Surface Coverage of $\theta_{\text{CO}}$ (left) and $\theta_{\text{V}}$ (right) as calculated by MK analysis. Note that the surface coverage of carbon is approximately two orders of magnitude smaller than surface oxygen at 685 °C.
As temperature of oxidation is increased, all $R_{f}$ increase. At the highest temperature of 875 °C however, $R_{3,f}$ and $R_{4,f}$ decreases to zero while at this temperature $R_{2,f}$ is at its maximum. Reaction 3 (Equation(3.7)) is the atomization of surface CO that contributes to the formation of surface carbon on the surface. In accordance to the MK analysis, this leads to site blocking and inhibits dissociative adsorption. It has been well documented that surface atomization to form carbon on a catalyst surface is not thermodynamically favorable at higher temperatures and thus the decreasing trend of $R_{3,f}$ at the higher temperature regime agrees with this.\textsuperscript{36, 41, 42} This behavior is in agreement with the trend in $\gamma$, within our solid state kinetic model, where at low
oxidation temperature site blocking phenomena is prevalent and is diminished at the high temperature region.

3.8. Acknowledgements

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3.9. References


CHAPTER 4

INVESTIGATION OF Zr, Gd/Zr, AND Pr/Zr – DOPED CERIA FOR THE REDOX SPLITTING OF WATER

4.1. Abstract

Currently, there is a renewed interest in CeO$_2$ for the use in solar-driven, two-step thermochemical cycles for water splitting. However, despite its fast reduction/oxidation kinetics and high thermal stability, the cycle capacity of CeO$_2$ is low due to thermodynamic limitations. Thus, in an effort to increase cycle capacity and reduce thermal reduction temperature, we have studied binary zirconium-doped ceria ($\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$, $x = 0.1, 0.15, 0.25$) and ternary praseodymium/gadolinium doped zirconium-ceria ($\text{M}_{0.1}\text{Zr}_{0.25}\text{Ce}_{0.65}\text{O}_2$, $\text{M} = \text{Pr}, \text{Gd}$). Here, we evaluate the oxygen cycle capacity and water splitting performance of crystallographically and morphologically stable powders that are thermally reduced by laser irradiation in a stagnation flow reactor. We find that the addition of zirconium dopant into the ceria lattice improves O$_2$ cycle capacity and H$_2$ production by approximately 30 % and 11 %, respectively. This improvement is independent of the zirconium dopant level, suggesting that zirconium might be coming out of solid solution. On the other hand, the addition of Pr and Gd to the binary zirconium-ceria mixed oxide is detrimental to H$_2$ production. Moreover, a kinetic analysis is performed using a model-based analytical approach to account for effects of mixing and dispersion, to identify the rate controlling mechanism of the water splitting process. We find that, despite the lattice modifications, the water splitting reaction, at 1000 °C and with 30 vol.% H$_2$O for all the doped ceria, is surface limited and best described by a deceleratory power law model (F-model), similar to undoped CeO$_2$. 
4.2. Introduction

One of the most difficult challenges that we face in the 21st century is building a sustainable energy economy that can ensure our energy security and mitigate anthropogenic climate change. Our over reliance on fossil fuel, a non-renewable energy source that is geographically distributed inhomogenously, often fuels geopolitical conflicts and contributes towards global climate instabilities. Despite these issues, the usage of a liquid chemical energy carrier such as petroleum will persist. Hydrogen is a very promising alternative to petroleum. It has high energy density, and similar to electricity, is a supple energy carrier that can be used in many different forms while giving out zero emission. Unfortunately, natural abundance of hydrogen in the atmosphere is less than 6 ppm due to its reactivity and low molecular weight. To support a hydrogen based energy economy, a sustainable hydrogen production method is necessary. Currently, steam methane reforming with natural gas is the main technique to produce hydrogen. However, this process offers only modest reduction in the net carbon emission. Fortunately, hydrogen can potentially be produced in large quantities using abundant and renewable resources. Two-step solar thermochemical processes utilizing non-volatile metal oxide cycling is a promising method to capture and utilize solar energy to produce hydrogen: the process can be carbon neutral and does not require a difficult or expensive separation process. When compared to other processes, such as biomass production and processing, artificial photosynthesis, and photovoltaic-driven electrolysis, two-step solar thermochemical processing can operate at higher thermal efficiencies, and requires less land and water to operate.

A generic two-step cycle based on ceria is described by reactions (4.1) and (4.2). Heat from concentrated solar energy thermally reduces the metal oxide (CeO₂) to a sub-stoichiometric oxide (CeO₂₋δ, where δ represents the extent of oxygen non-stoichiometry in the solid) at
temperatures ($T_H$) between 1350 - 1500 °C, producing $O_2$. The sub-stoichiometric ceria is then taken off sun and oxidized by exposure to steam at some lower temperature ($T_L \leq 1100$ °C); thus producing $H_2$ and completing the cycle.

\[
\frac{1}{\delta}CeO_2 \xrightarrow{+\Delta} \frac{1}{\delta}CeO_{2-\delta} + \frac{1}{2}O_2 \quad (4.1)
\]

\[
\frac{1}{\delta}CeO_{2-\delta} + H_2O \xrightarrow{-\Delta} \frac{1}{\delta}CeO_2 + H_2 \quad (4.2)
\]

This same cycle can be used to perform carbon dioxide splitting to produce CO, which can be used as feedstock for synthetic fuel production.$^{3,4,6}$

There are numerous types of metal oxide chemistries for two-step solar thermochemical cycling reported in the literature. The volatile Zn/ZnO cycle, for example, has been studied and reviewed; the chemistry has the potential to produce a large amount of $H_2$; however process complexities and gaseous phase recombination limit the feasibility of this cycle.$^8$ Another metal oxide cycle is the prototypical non-volatile ferrite cycle, where thermal reduction of ferrite spinels ($M_xFe_{3-x}O_4$, where $M$ is typically Mn, Co, Ni) form solid solutions with mixed valencies ($M^{2+}$, $Fe^{2+}$, and $Fe^{3+}$).$^9$ While this chemistry also has the potential for large cycle capacity, in reality, sintering and formation of a molten phase leads to irreversible deactivation. Often, to improve cyclability and mechanical integrity, these ferrites are combined with refractory materials such as ZrO$_2$, YSZ,$^{10-12}$ or Al$_2$O$_3$.$^{13-15}$

The final type of chemistry for solar thermochemical processing is the non-stoichiometric oxide cycle. The aforementioned ceria is the prototypical non-stoichiometric oxide that has fast redox kinetics,$^{35}$ however, very high temperatures ($T_H = 1500$ °C) are necessary to achieve a high extent of oxygen deficiency for efficient fuel production.$^{16}$ This non-stoichiometric ceria cycle is in contrast to the stoichiometric reduction of ceria to $Ce_2O_3$ that requires temperatures in
excess of 2000 °C and is plagued with sublimation of the oxide. Another type of non-stoichiometric oxide is the perovskites compounds (ABO$_3$) that have recently been shown to achieve higher oxygen deficiencies than reduced ceria at lower T$_{H}$. Nonetheless, cerium oxide is still a favored material for the two-step solar thermochemical water splitting because of its high ion conductivity, rapid exchange kinetics, and excellent thermal stability.

In an effort to increase cycle capacity and reduce the necessary thermal reduction temperature, lattice substitution and doping of ceria are often employed to introduce lattice defects and create additional oxygen vacancies. Kaneko et al performed lattice substitution with reducible transition metal dopants, specifically: Fe, Mn, Ni, Cu. Higher O$_2$ and H$_2$ production was reported despite experimental issues such as air leaks that occurred prior to the water splitting step. On the other hand, Abanades et al investigated the effects of doping ceria with tantalum and trivalent lanthanum dopants, and observed enhancement in thermal stability of the mixed metal oxides; but no improvement on the cycle capacity was observed. Taking a page from three way catalysts (TWCs) and heterogeneous catalysis, these authors also examined the effect of incorporating non-reducible isovalent dopants such as Zr$^{4+}$ into the lattice. Substitution of Ce$^{4+}$ by isovalent Zr$^{4+}$ enhances the reducibility of ceria by a significant reduction of reduction enthalpy; and has been shown to result in higher redox performance. In addition to zirconium, the addition of reducible dopants such as praseodymium (Pr) and trivalent cations such as gadolinium (Gd$^{3+}$) have been reported to increase oxygen storage capacity (OSC) and enhance reducibility of ceria based materials.

In addition to the redox cycle evaluation, Abanades et al has also studied the kinetics of water and carbon dioxide splitting of zirconium doped ceria. They reported that carbon dioxide splitting (CDS) of Zr$_{0.25}$Ce$_{0.75}$O$_2$ is limited by diffusion, with activation energies ranging from 83
– 103 kJ/mole depending on the synthesis method.\(^{29}\) In a different report, the authors used a similar approach to evaluate the kinetics of water splitting (WS) of Zr\(_{0.25}\)Ce\(_{0.75}\)O\(_2\), yielding 51 kJ/mole activation energy. Again, in this work, the authors attributed surface reaction followed by *diffusion* to be the rate controlling mechanism.\(^{28}\) In these studies, thermochemical cycles were only repeated two or three times, and their fuel production data suggests that the materials examined are not morphologically stable. Moreover, the diffusion model only fits the TGA data collected at later times in the oxidation process: error between experimental data and the model is apparent, and no effort was made to critically assess the effect of experimental effects such as gas-phase dispersion and mixing on the fuel production curve.\(^{33}\)

In light of these reports, we evaluate the thermochemical water splitting (WS) of binary (Zr\(_{0.1}\)Ce\(_{0.9}\)O\(_2\), Zr\(_{0.15}\)Ce\(_{0.85}\)O\(_2\), and Zr\(_{0.25}\)Ce\(_{0.75}\)O\(_2\)) and ternary oxides (Pr\(_{0.1}\)Zr\(_{0.15}\)Ce\(_{0.75}\)O\(_2\), Pr\(_{0.1}\)Zr\(_{0.25}\)Ce\(_{0.65}\)O\(_2\), and Gd\(_{0.1}\)Zr\(_{0.25}\)Ce\(_{0.65}\)O\(_{1.95}\)). Distinct to the aforementioned work by Le Gal *et al.*, we evaluate the capacity of well cycled materials that are compositionally and crystallographically stable. We observe an increase of approximately 11% of H\(_2\) production upon addition of Zr dopant, regardless of the Zr level. Furthermore, we observe that addition of praseodymium (Pr) and gadolinium (Gd) to the binary Zr/Ce oxides offers no improvement in the total H\(_2\) produced. In fact, addition of Gd is detrimental to H\(_2\) production. Additionally, we have applied a rigorous model-based analytical methodology to reveal intrinsic kinetic behavior of the H\(_2\) production of zirconium doped ceria. We find that, analogous to undoped ceria, the water splitting (WS) kinetics of the binary and ternary doped ceria system is governed by a power-law model consistent with an activated surface mediated process, and not diffusion controlled chemistry as has been previously suggested.
4.3. Experimental

The materials were synthesized by co-precipitation of the requisite metallic nitrates, using a similar procedure reported by Higashi et al.\textsuperscript{34} Appropriate amounts of the different metal (Ce, Gd, Pr, and Zr) nitrates (Alfa Aesar, Ward Hill, MA) were dissolved in distilled water. The nitrate solution was then mixed to give a mixture with the desired cation molar ratio. The pH of the mixture was then adjusted by drop wise addition of 1 M oxalic acid until precipitation is complete. The supernatant liquid was analyzed by induced coupled plasma-atomic emission spectroscopy (ICP-AES) to ensure complete precipitation of the metal cations. The precipitate was filtered, washed with distilled water, and dried in air overnight. The resulting powder was then calcined in air at 700 °C for 12 hours, and further calcined in air at 1500 °C for 16 hours. The following materials were made and thermochemically cycled: CeO\textsubscript{2}, Zr\textsubscript{0.1}Ce\textsubscript{0.9}O\textsubscript{2} (10ZrCe), Zr\textsubscript{0.15}Ce\textsubscript{0.85}O\textsubscript{2} (15ZrCe), Zr\textsubscript{0.25}Ce\textsubscript{0.75}O\textsubscript{2} (25ZrCe), Pr\textsubscript{0.1}Zr\textsubscript{0.15}Ce\textsubscript{0.75}O\textsubscript{2} (10Pr15ZrCe), Pr\textsubscript{0.1}Zr\textsubscript{0.25}Ce\textsubscript{0.65}O\textsubscript{2} (10Pr25ZrCe), and Gd\textsubscript{0.1}Zr\textsubscript{0.25}Ce\textsubscript{0.65}O\textsubscript{1.95} (10Gd25ZrCe).

X-ray diffraction (XRD, Scintag PAD5 Powder Diffractometer, CuKα radiation, λ = 1.5406 Å) analysis was performed using a scan rate of 2°/minute and step size of 0.02°, over the range of 20 – 70° to determine phase purity and to evaluate lattice size changes due to incorporation of dopants with different ionic radii. A JEOL JSM-6480 scanning electron microscope (SEM) operating at 15 and 20 kV was used to examine the microstructure and local chemical composition for both the as-calcined and post heat-cycled materials. Elemental composition was determined via energy dispersive X-ray spectroscopy (EDS).

Reduction and oxidation cycles of the ceria and doped ceria oxides were performed in an idealized stagnation flow reactor (SFR) under thermal conditions that resembles a solar reactor, i.e. high heating rates (17 °C s\textsuperscript{-1}), isothermal oxidation conditions, and low P\textsubscript{O\textsubscript{2}}. The SFR has
been described in more detail elsewhere;\textsuperscript{14, 33, 35} but the important features of the SFR are: (1) the flow field is well characterized and easily modeled, (2) during thermal reduction, samples are heated by irradiation from a 500 W continuous wave near-IR laser (Apollo Instruments model F500-NIR600), otherwise the SFR temperature is maintained by a SiC furnace (Carbolite STF16/180), (3) gas composition is measured by a modulated molecular beam mass spectrometer (Extrel C50), and (4) pressure and flow within the reactor were feedback controlled to give 75 torr and 500 sccm total flow rate, respectively.

Between 150 – 200 mg of material were placed in the SFR as a loosely packed bed where all exposed surfaces experience a well mixed gaseous environment within the stagnation flow. \textit{Thermal reductions} were performed by heating the powder to 1500 °C, at a rate of 17 °C s\textsuperscript{-1}, and holding at this temperature for 240 seconds under a flow of 500 sccm of ultra high purity helium (P\textsubscript{O2} < 10\textsuperscript{-3} mbar). The powder was then allowed to cool down to the SiC furnace temperature that was set at the oxidation temperature. \textit{Water splitting} experiments (WS) were performed isothermally by exposing the reduced material to 30 vol.\% steam in helium flow, at 1100 or 1000 °C, over a 600 s time interval.

Steam was delivered via a research grade humidifier system (RASIRC Rainmaker Humidification System). The concentration of molecular species, such as H\textsubscript{2} (m/e = 2) and O\textsubscript{2} (m/e = 32), in the reactor effluent was recorded during both thermal reduction and WS. A liquid-nitrogen cooled cryogenic trap was used to condense the H\textsubscript{2}O before gases in the reactor effluent were sampled by the mass spectrometer. Analytical standards of O\textsubscript{2} and H\textsubscript{2} were used to calibrate the mass spectrometer. In the post-experimental data analysis, a rigorous numerical procedure was applied to separate material specific H\textsubscript{2} production from experimental effects such as detector time lag, gas phase dispersion, and mixing.
4.4. Computational Methods

The heterogeneous nature of the oxidation reaction allows physical processes inherent to the experimental apparatus, such as finite detector time lag and gas phase dispersion/mixing, to impose their temporal imprint on the rate curves of H$_2$ production. Therefore, before any assessment of the kinetics can be performed, these experimental effects have to be separated from the as recorded H$_2$ rates. This was done by the application of a model based algorithm that assumes that the WS reaction can be described using an empirical model taken from the solid state (SS) kinetic theory,$^{36-38}$ and that combines the solid state model with a validated mixing model of the SFR in the post experimental data analysis.

In both the SFR experiments and simulation, the WS is initiated by a step-change in H$_2$O concentration, occurring in less than 0.5 s in the inlet of the SFR. This step change initiates the transient H$_2$ production (as governed by equation (4.3)) that is then propagated through a series of continuously-stirred tank reactors (CSTRs). The series of CSTRs simulates the downstream gas phase dispersion and mixing inherent to the experimental apparatus which alters the temporal characteristics of the rate curve. The dispersed simulated waveform is then compared to the experimentally observed H$_2$ curve. Kinetic rate constants and governing solid state model are then extracted by minimizing a weighted least square objective function that compares simulated rates to experimental values at each time step. This optimization process uses a Differential Evolution (DE) algorithm routine to stochastically determine the best-fit SS model and the accompanying kinetic parameters that are unique to the SS model. The governing rate equation used in this analysis is as follows:

$$\text{rate} \left[ \frac{1}{s} \right] = k_0 \left[ Y_{\text{oxid}}(t) \right]^n f(\alpha)$$  \hspace{1cm} (4.3)
where $k_0$ is the rate constant of the WS, $Y_{oxid}$ is the time-dependent mole fraction of H$_2$O, $\gamma$ is the reaction order of the H$_2$O mole fraction, $\alpha$ is the normalized extent of reaction, and $f(\alpha)$ is the functional taken from SS kinetic theory; it describes the transient H$_2$ rates as WS progresses. The algorithm samples one of fourteen possible functional forms $f(\alpha)$, representing different rate-limiting phenomena that allows the identification of the governing mechanism within the context of SS kinetic theory. A more detailed description of the numerical approach can be found elsewhere.$^{33,35}$

4.5. Results and Discussions

4.5.1. Structural Characterization

Figure 4.1. SEM micrographs of co-precipitated 25ZrCe: as calcined (a) and after thermochemical cycling (d). EDS maps of Ce($L_{\alpha 1}$) absorption edge (light areas) of as calcined material (b) and after thermochemical cycling (e). EDS maps of Zr($L_{\alpha 1}$) absorption edge (light areas) of as calcined material (c) and after thermochemical cycling (f).

A representative SEM image of the as calcined 25ZrCe material is presented in Figure 4.1 (panel (a)), where primary particles of diameter 1 – 5 $\mu$m are easily visible. Additionally, an X-ray fluorescence map of Ce($L\alpha 1$) and Zr($L\alpha 1$) absorption edges, shown in panel (b) and (c),
indicates that a homogenous dispersion of the cerium and zirconium elements within the solid is maintained, even after the prolonged air calcination at 1500 °C. The SEM image of the cycled material is shown in Figure 4.1, panel (d). After more than thirty repeated thermochemical cycles at 1500 °C (with both O₂ and H₂O oxidations), the image shows that minimal grain growth/sintering occurs; primary particles of similar size are still visible. This suggests that evaluation of O₂ and H₂ cycle capacity performed on this study is conducted with material that is morphologically and crystallographically stable. Panels (e) and (f) shows the Ce(Lα1) and Zr(Lα1) absorption edges of the cycled material. Similar to the as calcined powder, the cycled material still exhibits homogenous phase distribution of cerium and zirconium elements. A similar observation was made on the other binary and ternary materials, but micrographs are not shown here.

In addition to SEM analysis, phase analysis of the thermochemically cycled mixed oxide is performed with X-ray diffraction, and the resulting spectra is presented in Figure 4.2. A homogenous cubic fluorite structure, without any evidence of a secondary crystalline phase is observed for both the pure and doped ceria materials, consistent with our SEM-EDS fluorescence map. We also note that the X-ray patterns of the cycled materials are identical to the as calcined materials (not shown); further evidence that the thermochemical cycles are performed on a crystallographically stable compound. A small shift in 2θ to a higher angle is evident for the doped ceria. Specifically, the Zr doped ceria, since the substitution of Ce cation (Ce⁴⁺ = 0.97 Å) with the smaller Zr cation (Zr⁴⁺ = 0.84 Å) in the lattice leads to lattice contraction. Interestingly, the 2θ shift appears to be the same for the 10ZrCe, 15ZrCe, and 25ZrCe materials. The constant 2θ shift that is independent of the zirconium content can be caused by either phase segregation/enrichment that cannot be detected with XRD, due to lack of long range ordering, as
has been reported elsewhere, or due to zirconium ions coming out of solid solution and thus reducing the effective zirconium substitution in the lattice. Since our aforementioned SEM-EDS analysis of the primary particles does not show any phase segregation; it is likely that the latter phenomenon is occurring within the lattice. The implication of this phenomenon on oxygen capacity and H₂ production will be discussed later.

Figure 4.2. XRD Patterns of thermochemically cycled binary and mixed oxides. We note that the spectra for the as calcined material (1500 °C for 16 hours) is identical to the thermochemically cycled material. (a) complete spectra of the undoped, binary and ternary ceria material. No secondary phase is observed. (b) a closer look at the 2θ shift due to dopant incorporation.
4.5.2. Oxygen Activity of Doped Ceria.

Figure 4.3. Rate of $O_2$ release and uptake of CeO$_2$ and 25ZrCe with constant background $O_2$ of 0.2 mbar. Samples heated at 17 °C s$^{-1}$ from 1000 – 1500 °C, and held at that temperature for 100 s, before being cooled back to 1000 °C at the same rate. Positive rates indicates $O_2$ release during heating, negative rates indicate $O_2$ uptake of background $O_2$ during cooling. Averages of ten total $O_2$ release and uptake are summarized in the inset.

Evaluation of $O_2$ capacity. An important first step in evaluating the redox capacity of metal oxides for solar thermochemical water splitting is the assessment of the materials’ oxygen capacity. This can be done by exposing the materials to rapid heating/cooling under a constant oxygen partial pressure, while monitoring the oxygen release and uptake behavior. All materials were heated and cooled between 1000 – 1500 °C at a rate of 17 °C s$^{-1}$ under constant $P_{O_2}$ of 0.2 mbar $O_2$ with helium flow. Presented in Figure 4.3 is the representative $O_2$ uptake and release characteristic for CeO$_2$ and 25ZrCe. Upon heating, the powder undergoes thermal reduction, yielding positive $O_2$ production rates. And upon cooling, it undergoes reoxidation by background...
O₂, yielding negative rates. The O₂ uptake and release characteristics are rapid: the release peaks and reoxidation valleys are almost symmetrical, which imply that the reoxidation by O₂ is as rapid as the thermal reduction under these experimental conditions. The transient uptake and release behavior are similarly rapid for all the other doped materials, therefore only CeO₂ and 25ZrCe are shown in Figure 4.3. The total amount of O₂ released and reabsorbed by the material represents the total amount of O₂ capacity at 0.2 mbar P₀₂ (inset Figure 4.3). The average of ten repeated uptake/release is summarized in the inset of Figure 4.3. We observe a ca. 30 % increase in O₂ capacity that is independent of Zr content.

Additionally, the addition of 10 % Pr and Gd to form ternary oxides does not seem to improve O₂ capacity. In fact, the ternary compound, 10Pr15ZrCe, evaluated here appears to have diminished O₂ capacity compared to the Zr doped material. This is unexpected since others have reported that solid solution of praseodymium in ceria reduces energy for oxygen vacancy formation and increase the oxygen nonstoichiometric of ceria at more accessible P₀₂ levels.³¹,⁴⁰-

⁴² We will discuss the implication of this diminished OSC on WS reaction later. We note that during ten repeated cycles, the materials maintain its rapid kinetics and its cycle capacity.
Figure 4.4. Rate of O\textsubscript{2} evolution of under slow heating rate. Samples heated at 10 °C min\textsuperscript{-1} under helium flow at 75 torr. Ternary materials doped with praseodymium exhibits low temperature O\textsubscript{2} peaks that are dependent on the concentration of Zr. Onset of O\textsubscript{2} evolution appears to be constant regardless of the dopants.

**Onset of O\textsubscript{2} evolution.** Another goal of lattice substitution in ceria is to incorporate additional defects in the lattice and weaken the cation-oxygen bonds in order to reduce the necessary temperature for thermal reduction. Thus, we evaluated the onset of O\textsubscript{2} evolution (T\textsubscript{onset}) exhibited during thermal reduction of the various doped ceria materials, by heating the material at a rate of 10 °C min\textsuperscript{-1} under helium ambient (with P\textsubscript{O2} < 10\textsuperscript{-3} mbar). Under this slow heating condition, the materials are presumed to be in thermal equilibrium. Figure 4.4 presents the rate of O\textsubscript{2} evolution as a function of temperature. It is evident that our co-precipitated CeO\textsubscript{2} begins to evolve O\textsubscript{2} at ca. 1000 °C (Figure 4.4 (a)). And addition of 10 – 25 % Zr and 10 % Gd to 25ZrCe do not affect the onset of O\textsubscript{2} evolution (Figure 4.4 (b) and (c)). Again, here we observe that the O\textsubscript{2} evolution behavior of Zr doped material is independent of the dopant level. This is in agreement with the aforementioned O\textsubscript{2} uptake and release results.
In contrast to the ZrCe and GdZrCe materials, the tertiary PrZrCe materials exhibit low temperature O\(_2\) evolution peaks, between 600 – 900 °C (Figure 4.4 (c)). The T\(_{\text{onset}}\) where these low energy peaks occur appears to depend on Zr concentration. The evolution of the lower energy oxygen can be attributed to the reduction of Pr\(^{4+}\) to Pr\(^{3+}\) that is accompanied by formation of oxygen vacancies and release of O\(_2\) from the bulk. In a PrCe system, Pr\(^{4+}\) cations are more amenable to reduction to form Pr\(^{3+}\), than Ce\(^{4+}\) to Ce\(^{3+}\) reduction.\(^{31}\) In fact, according to XPS analysis by Reddy et al, mixed Pr\(^{4+}\)/Pr\(^{3+}\) can coexist in ceria solid solution at temperatures as low as 500 °C under air.\(^{32}\) Therefore, unlike Gd, which is a fixed acceptor dopant, incorporation of reducible Pr cations produce additional oxygen vacancies that, if can be refilled with H\(_2\)O or CO\(_2\), can increase thermochemical fuel production.

To evaluate if the Pr redox pair contributes towards thermochemical H\(_2\) production, we performed two subsequent thermal reductions on 10Pr15ZrCe: The first thermal reduction was performed subsequent to O\(_2\) reoxidation (yielding a fully oxidized material), and the second thermal reduction was conducted subsequent to WS with 30 vol.% H\(_2\)O at 650 °C. In short, we are evaluating if the oxygen vacancies that are produced at the lower temperature can be refilled with oxygen from water. Figure 4.5 presents the O\(_2\) release during these two thermal reductions. The first thermal reduction exhibits two O\(_2\) release peaks, similar to the O\(_2\) release characteristic shown in Figure 4.4, where a low temperature O\(_2\) release, due to the reduction of Pr\(^{4+}\) to Pr\(^{3+}\), occurs between 700 – 900 °C, followed by a high temperature O\(_2\) release, which can be attributed to the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) cations. In contrast, the second thermal reduction only exhibits the high temperature O\(_2\) release. Therefore, addition of Pr\(^{4+}\)/Pr\(^{3+}\) redox pair to into ceria based oxide will most likely not increase H\(_2\) production as the low energy oxygen vacancies are not
thermodynamically accessible by oxidation with H$_2$O. Further discussion of WS experiments on these ternary compounds will be continued in the subsequent section.

Figure 4.5. Rapid thermal reduction of 10Pr15ZrCe ($\text{Pr}_0.1\text{Zr}_{0.15}\text{Ce}0.75\text{O}_2$) from 650 to 1500 °C, with a heating rate of 10 °C s$^{-1}$, at 75 torr, and under helium flow. Grey line: thermal reduction after material was oxidized with 0.2 mbar O$_2$. Black line: thermal reduction after material was oxidized with 30 vol.% H$_2$O at 650 °C and 75 torr. The total amount of O$_2$ is shown in parentheses (µmoles/g of material). Low temperature O$_2$ peak can only be reclaimed if the material is oxidized with O$_2$ and not H$_2$O.

4.5.3. WS Activity of Doped Ceria.

**Evaluation of total H$_2$ produced.** Having high oxygen activity is necessary, but doesn’t guarantee the ability to split water to produce H$_2$. In order to evaluate the H$_2$ cycle capacity of the various mixed metal oxides, a series of isothermal WS experiments was conducted with 30 vol.% H$_2$O at both 1000 and 1100 °C. We note that the same powders used for the O$_2$ uptake/release experiments are used for the WS evaluation. The total H$_2$ produced is summarized in Figure 4.6. The 10ZrCe, 15ZrCe, and 25ZrCe produced approximately 11 % more H$_2$ than
undoped CeO$_2$ at both 1000 and 1100 °C. This is much less than the 48 % increase afforded by co-precipitated 25ZrCe that was reported by Le Gal et al. This 48 % gain may not be the final, stable H$_2$ productivity gain however, since H$_2$ productivity can be seen to decrease by ~20 % from cycle #1 to #3 due to morphological/crystallographical changes taking place during their repeated WS (note: only three cycles are shown in their work).

On the other hand, the ternary oxides PrZrCe and GdZrCe, produces less H$_2$ than the binary ZrCe. We have shown in the previous section that the Pr$^{4+}$/Pr$^{3+}$ redox pair most likely does not participate in the water splitting, and consequently does not improve H$_2$ production. In fact, we observe that addition of a ternary dopant such as Pr and Gd to zirconium doped ceria decreases H$_2$ production; especially addition of Gd to the binary oxide, which further suppress H$_2$ production to below that of undoped ceria (Figure 4.6), which is consistent with our aforementioned O$_2$ activity observations. This is in agreement with recent work by Kuhn et al, where they reported that due to thermodynamic and crystallographic effects, addition of trivalent dopant into the ceria lattice can be detrimental to the gain afforded by Zr dopants.
Figure 4.6. Total amount of H\textsubscript{2} (µmoles/g of material) produced during isothermal WS with 30 vol.% H\textsubscript{2}O at 1000 and 1100 °C for 600 s. WS was carried out after 240 seconds thermal reduction at 1500 °C.

**WS Kinetics.** The observation of the progress of the water splitting reaction is limited by indirect measurements of H\textsubscript{2} produced, such in our SFR experiments, or mass gain of the metal oxide during steam exposure, such as in thermogravimetric studies. Both types of observations are susceptible to experimental effects, such as detector time lag and gaseous phase dispersion that leaves a temporal imprint on the rate curve of the reaction.\textsuperscript{33} To correctly assess the intrinsic kinetics of the WS reaction, these experimental effects have to be separated from the material specific transient H\textsubscript{2} production. Failure to do so can lead to an erroneous conclusion on the rate governing mechanism. For example, Le Gal et al, via the “master plot analysis”,\textsuperscript{38} had identified
the CO$_2$ splitting kinetic of Zr$_{0.25}$Ce$_{0.75}$O$_2$ as a diffusion controlled reaction with an activation energy value ranging from 83 – 103 kJ/mole, depending on the synthesis method. They argue that, due to increased bulk participation in these ceria zirconia materials, oxygen mobility in the bulk limits the oxidation reaction. However, their thermogravimetric data fit the diffusion model only at later times (conversion values ($\alpha$) ≥ 0.15); and no effort to deconvolute experimental effects from the intrinsic fuel production rates was made. The same authors studied the WS kinetics Zr$_{0.25}$Ce$_{0.75}$O$_2$ and employed the peak rate analysis, which was a similarly flawed approach, as has been shown by Scheffe et al.

This work is distinct from that of previous zirconium-ceria system studies reported in the literature. Here, we employ an idealized flow reactor that is coupled with a post experimental data reduction algorithm to separate the material specific transient H$_2$ production from the experimental effects. The WS is a transient process where oxygen is separated from water, via surface and bulk mediated processes, and transported into the sub-stoichiometric ceria. And unlike a purely catalytic process, the WS reaction goes into completion as the oxygen vacancies within the solid are depleted. Figure 4.7 presents the time dependent H$_2$ production curve of ZrCe materials at 1000 °C: upon exposure to 30 vol.% steam, H$_2$ production increases to some maximum peak rate, which then decreases back to baseline as vacancies are depleted and reaction progresses to completion. This H$_2$ production rate curve is typical of a WS process often observed for this type of experiment. Similar to undoped ceria, the rate of H$_2$ production is rapid, with more than 90 % of the H$_2$ produced within the first 300 s.

Applying the aforementioned analytical model-based analysis yields a single kinetic model for the WS that describes the H$_2$ rates over the entire time domain (solid lines shown in Figure 4.7 (left)). A total of fourteen different SS mechanisms, representing different rate
governing processes, was tested against experimental data using a least square objective function evaluated at every time step. We find that the F-model, a power-law deceleratory model, is best to describe the H₂ production. This suggests that the WS kinetics of zirconium doped ceria is analogous to undoped ceria, and that the WS is still governed by a surface mediated process which is comparable to a homogenous reaction, contrary to Le Gal’s et al aforementioned results.⁴⁵ A complete list of the kinetic parameters associated with the SS models that are used in conjunction with equation (3) to generate these fits is listed in Table 4.1.

Table 4.1. Oxidation reaction rate constants (k₀) extracted from fits to experimental data, shown in Fig. 6 and 7, using a coupled kinetic and dispersion model.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>log k₀ (s⁻¹)</th>
<th>RateH₂αk₀YH₂O(1−α)ⁿ</th>
<th>n</th>
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<td>CeO₂</td>
<td>-1.10</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>10ZrCe</td>
<td>-1.03</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>15ZrCe</td>
<td>-0.94</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>25ZrCe</td>
<td>-0.90</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>10Pr25ZrCe</td>
<td>-1.31</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>10Gd25ZrCe</td>
<td>-1.30</td>
<td>1.72</td>
<td></td>
</tr>
</tbody>
</table>

To illustrate that the diffusion model cannot sufficiently describe the H₂ production, three diffusion models are plotted against the H₂ production by 15ZrCe at 1000 °C (Figure 4.7 (right)). We show that the diffusion models, regardless of the characteristic dimensions (D₁ – 3), cannot adequately describe the H₂ produced by 15ZrCe (similar observations are true for the other ZrCe materials, but not shown here). Since the majority of H₂ is produced in the first 300 s of the reaction, preferential weighting of the objective function is used to emphasize fit of all the diffusion models early in the reaction. However, in doing so, mass conservation is violated for D₁ and D₂; the total H₂ produced by the two diffusion models exceed what is experimentally observed. This is caused by over-prediction of H₂ at later times; the D₁ and D₂ models have
decay characteristics that are slower than the experimentally observed phenomenon. Similarly, the D3 model cannot adequately describe the transient H\textsubscript{2} production: it over-predicts the rates at early times, and under-predict at later times.

![Figure 4.7](image)

Figure 4.7. (left) H\textsubscript{2} production rates as a function of time measured during oxidation in 30 vol.% H\textsubscript{2}O at 1000 °C (open symbols). Oxidation performed after thermal reduction at 1500 °C for 240 s. The F-model can adequately describe H\textsubscript{2} production over the entire time domain. (right) Comparison of actual H\textsubscript{2} production rates by 15ZrCe to three different diffusion models acquired by the model-based analysis. Solid and dashed lines are the result of diffusion governed kinetic modeling (see text). A complete list of the kinetic parameters associated with the SS models that are used to generate these fits is listed in Table 4.1. Note: x-axis is in log scale.

The same numerical procedure is applied to the H\textsubscript{2} production of the ternary metal oxides, specifically 10Pr25ZrCe and 10Gd25ZrCe. Figure 4.8 summarizes the H\textsubscript{2} production rates of these oxides. Open symbols represent the experimentally recorded H\textsubscript{2} production rates, whereas the solid lines represent the results of the SS model. Similar to the binary ZrCe system,
the H₂ production is still best described by the F-model. Even-though, we have shown that addition of Pr and Gd to the binary ZrCe system alters the local oxygen environment within the lattice, affecting the O₂ and H₂ cycle capacity; our kinetic model suggests that these bulk perturbations have no effect on the rate governing mechanism of the WS reaction, which remains the order based deceleratory model. These results imply that the WS process of the doped ceria material studied here is surface mediated and not bulk diffusion limited, the same as the rate governing mechanism of undoped CeO₂.³⁵,⁴⁴

Figure 4.8.  H₂ production rates as a function of time measured during 30 vol.% WS at 1000 °C (open symbols). Solid lines are the results of kinetic modeling (see text). Total H₂ produced is shown in parentheses (µmoles/g of material). A complete list of the kinetic parameters associated with the SS models that are used to generate these fits is listed in Table 4.1.
4.6. Discussion and Conclusions

It has been well documented that the incorporation of Zr\textsuperscript{4+} dopant into the ceria lattice improves ceria’s oxygen capacity, whether for low temperature\textsuperscript{45-47} or high temperature solar thermal applications.\textsuperscript{29,48} Indeed, calculated values of $\Delta H_{\text{red}}$ for the Ce/Zr system are typically lower than those of undoped ceria, as much as a 30 % decrease can be achieved by 10 % Zr addition.\textsuperscript{49} It is theorized that Zr\textsuperscript{4+} is smaller and thus relieves additional strain associated with formation of Ce\textsuperscript{3+}.\textsuperscript{46,49} Others have hypothesized that the much smaller Zr\textsuperscript{4+} prefers the 7-fold coordination, in contrast to the 8-fold coordination in the fluorite system, which can drive formation of additional oxygen vacancies through the reduction of ceria cations.\textsuperscript{27} Furthermore, for Zr $\geq$ 20 %, the Ce/Zr system can undergo phase enrichment that forms a mixture of fluorite and pyrochlore structures, where the pyrochlore could be more amenable to reduction.\textsuperscript{50}

Several implementation of zirconium doped ceria has been reported in the literature and shown to improve cycle capacity for the solar thermochemical application space. For example, Petkovich et al created a three dimensional ordered macroporous structure of 20 % Zr doped ceria and have shown that H\textsubscript{2} production and peak production rates are improved compared to similarly prepared undoped CeO\textsubscript{2}.\textsuperscript{48} Similarly, Le Gal et al has studied the viability of using Zr dopants to improve thermochemical cycle capacity of ceria, reporting a higher fuel production of Zr doped ceria,\textsuperscript{28} over Fe and Ni doped ceria previously reported by others;\textsuperscript{51,52} They observed that the amount of fuel produced is dependent on zirconium content, which does not agree with our results.

In our aforementioned O\textsubscript{2} release and uptake (Figure 4.2), we observe an increase in O\textsubscript{2} capacity afforded by the Zr dopants as well. However, in contrast to what was observed by Le Gal et al,\textsuperscript{28} we observe a ca. 30 % increase in O\textsubscript{2} capacity that is independent of Zr content.
Likewise, our evaluation of the H\textsubscript{2} production is *independent* of the zirconium content. These results are in agreement with our SEM-EDS and X-ray analysis results that suggest that zirconium is coming out of solid solution, which in turn leads to a decrease in the effective zirconium dopant level within the fluorite lattice. Similar observations regarding redox performance and zirconium composition have been made by others. For example, Atribak *et al* reported that after 1000 °C calcination, catalytic activity of ceria zirconia mixed oxides have little dependence on zirconium molar content (Zr molar content from 0.11 to 0.5).\textsuperscript{53} And recently, Call *et al* has published a report on carbon dioxide splitting of Ce\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} (with 0 ≤ x ≤ 0.4), and found that CO\textsubscript{2} splitting performance is increased by ~50 % for 0.15 ≤ x ≤ 0.225. However, after four thermochemical cycles, their results show that the redox performance difference for the different zirconium levels, within this composition range, is not statistically significant.\textsuperscript{54}

We believe one primary difference between the results reported here, and the aforementioned work by Le Gal *et al*, is that the O\textsubscript{2} and H\textsubscript{2} cycle capacity reported here are of materials that are compositionally and morphologically stable. In their WS and CDS studies, oxidation experiments were only repeated twice, and fuel production, within the two cycles, continues to decline.\textsuperscript{28, 29} Furthermore, in the preparation of these mixed metal oxides, the authors used a relatively low calcination temperature (between 600 – 800 °C); and therefore the material tested may not be cycle-stable, and morphological and chemical changes could be occurring during thermochemical cycling. In our experimental campaign on the other hand, the material is not only calcined at higher temperature for a longer time (1500 °C for 16 hours), but is cycled much more extensively. And thus, it is conceivable that after prolonged heat treatment, some zirconium comes out of solid solution (see section 4.7). This in effect reduces the effective
zirconium dopant level within the fluorite lattice, yielding the same effective dopant level for the 10, 15, and 25ZrCe studied here; and therefore, addition of Zr above 10 mole % does not yield additional cycle capacity.

The consequence of this phenomenon is that the improved H₂ production is less than what has been reported by others. The improved yield we observe can be considered marginal, and not as extreme as has been previously demonstrated for non-aged materials, and certainly, much less than has been reported for lower temperature catalysis applications. It has been documented by others that that phase homogeneity and the degree of mixing of cerium and zirconium cations is important; it affects the perturbation in the local oxygen environment and affects the level of oxygen storage capacity (OSC) enhancement.²⁷, ⁵⁰, ⁵⁵

In addition to the cycle capacity evaluation, we have performed a detailed numerical analysis on the H₂ production rates of the doped ceria materials. This resulted in the high quality fits to our kinetic models that are evident from the solid lines shown in Figure 4.7 and 4.8. Regardless of the dopant, all of the mixed cerium oxides evaluated in this work still exhibits an order dependence model, which imply surface limited H₂ production kinetics. Furthermore, we have shown that the diffusion model, regardless of the dimension over which they act, cannot describe the H₂ rate curve over the entire time domain. Our previous work has shown that the WS kinetics of ceria is surface limited, and this still holds true despite crystallographic modifications of the binary (ZrCe) or ternary (PrZrCe and GdZrCe) oxides.

The results presented in this work prompt us to reevaluate if lattice modification of ceria is a worthwhile endeavor in the search for new materials that can significantly improve the yield of solar thermal H₂ production. Recent work by McDaniel et al has shown that perovskites type
materials appear to be a much more promising new class of metal oxide for solar thermochemical applications. The authors discovered that LaAlO$_3$ doped with Mn and Sr not only has high thermal stability, but also exhibits higher cycle capacity than ceria, up to 9 x greater, at a thermal reduction temperature that is 150 °C lower. The discovery of these perovskites materials for solar thermochemical redox opens up a new class of possible materials that has the potential to achieve higher process efficiency.

4.7. Supplemental Characterization

Evaluations of the zirconium content within the binary zirconium doped ceria (ZrCe) materials were performed by two methods: (1) lattice parameter calculations based on the XRD spectra, and (2) elemental analysis from SEM-EDS.

Incorporation of the smaller zirconium cations into ceria lattice causes a decrease in lattice parameter, which according to Vegard’s law, the decreases linearly with increasing zirconium content. Therefore the amount of zirconium within the cubic solid solution can be approximated based on the lattice parameters of the ZrCe materials. In this study, we have employed rietveld refinement on the XRD spectra shown in Figure 4.2 and calculated the lattice parameters of the zirconium doped ceria. The calculated parameters are fitted on the vegard’s line, as shown in Figure 4.9. We note that lattice contraction of the cubic structure can be influenced by not only zirconium cations, but also oxygen vacancies. However, with approach outlined by Kuhn et al, we estimate that lattice contraction due to oxygen vacancies to be relatively small compared zirconium dopant influence. Estimation of the zirconium content by this method is presented in Figure 4.9. For all of the as-calcined and cycled materials, the zirconium content is estimated to be less than 6 mole % Zr.
Figure 4.9. Lattice parameters of zirconium doped ceria fitted on the Vegard’s line

A second zirconium content analysis is performed with the SEM – EDS on the as-calcined and cycled material. Figure 4.10 presents the zirconium content summary. Consistent with the aforementioned XRD analysis, zirconium content is less than 5 mole % for all the materials evaluated.
Figure 4.10. Qualitative elemental analysis with SEM – EDS. All materials are approximately 3 – 5 mole % zirconium.

The two methods outlined here are in agreement: the zirconium content of the as-calcined and cycled materials are in the range of ~5 mole %, which suggests that zirconium might be coming out of cubic solid solution, and that the nominal 10, 15 and 25 mole % zirconium initially synthesized are not maintained after extended high temperature treatment. These results are consistent with the O$_2$ and H$_2$ cycle capacity evaluations discussed in the main text. As further evidence that zirconium might be coming out of cubic solid solution (CSS), we have mapped our experimental conditions in the ceria-zirconia phase diagram. Presented in Figure 4.11 is the ceria-zirconia phase diagram as calculated by Li et al.$^{56}$ In this Figure, we illustrate that when the temperature of the material is varied between 1000 and 1500 °C, materials with nominal zirconium content of 25 mole % will result in zirconium coming out of the CSS. Only when zirconium mole content is below approximately 10 % will CSS be maintained. Consistent
with our aforementioned analyses, we illustrate that nominal zirconium mole content of approximately 5% will remain in the CSS phase.

Figure 4.11. Cerium and zirconium phase diagram adapted from work by Li et al.\textsuperscript{56} (a) Thermochemical cycling between 1500 - 1000°C, of cerium-zirconium oxide with Zr content of 25 mole %, most likely results in zirconium coming out of cubic solid solution (CSS); (b) on the other hand, zirconium content in the range of ~5 mole % most likely remains in cubic solid solution during repeated thermochemical cycling. Note: TSS: tetragonal solid solution, MSS: monoclinic solid solution.

4.8. Acknowledgements

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4.9. References


CHAPTER 5
CONCLUSION AND FUTURE DIRECTIONS

5.1. Summary and Conclusions

The work presented here evaluates two types of metal oxide chemistries for water splitting (WS) and CO\textsubscript{2} splitting (CDS) for the production of H\textsubscript{2} and CO; namely the “hercynite” chemistry and the ceria based redox cycle. We first investigate the role of cobalt cations in the redox chemistry of the “hercynite” cycle, because hercynite, in the absence of cobalt, cannot be decomposed into Fe\textsubscript{3}O\textsubscript{4} at these operating conditions. The evaluation of the “hercynite” chemistry was conducted by the study of a nano-engineered material, synthesized with atomic layer deposition (ALD). We note that currently the effects of CoFe\textsubscript{2}O\textsubscript{4} film thickness and Al\textsubscript{2}O\textsubscript{3} wall thickness comprising the nano materials are not well understood, meaning that a more optimized nano-engineered structure may be accessible because ALD enables atomistic control of the synthesis process. Further lowering the thermal reduction temperature and improving both the oxidation kinetics and iron utilization are possible.

Although there is much more to be learned about the “hercynite” redox cycle, the work performed here demonstrates the efficacy of a completely different approach to two-step thermochemical CO\textsubscript{2} splitting by blending novel chemistry with a nano-engineered reactive structure. We demonstrate that our CoFe\textsubscript{2}O\textsubscript{4}-coated Al\textsubscript{2}O\textsubscript{3} material is capable of producing appreciable amounts of CO after thermal reduction at a temperature as low as 1360 °C, with consistent oxidation behavior up to 23 thermal reductions. This observation is approximately 100 °C to 150 °C lower than values reported for ferrite or CeO\textsubscript{2} based systems, respectively. Furthermore, with Raman spectroscopy, we have identified that, at the near surface region, compound formation occurs. And, therefore, adding compound-forming redox chemistries to the
list of possible candidate systems opens up new opportunities for discovery of better and more viable metal-oxide based redox cycles for producing fuels from concentrated sunlight.

The second material studied in this work is the ceria based compounds that undergoes sub-stoichiometric redox upon exposure to extreme thermal conditions. The combination of high thermal stability and fast reduction/oxidation kinetics has drawn attention to CeO$_2$ for use in solar-driven, two-step thermochemical cycles for water and/or carbon dioxide splitting. In accordance with this renewed interest in CeO$_2$, there is a need to better understand the gas splitting chemistry on the reduced oxide at the extreme thermal conditions encountered in such solar-driven processes. In this work, we have measured the H$_2$ and CO production rates over ceria powder, thermally reduced by laser irradiation, during oxidation by H$_2$O and CO$_2$ in a stagnation flow reactor. The reaction kinetics intrinsic to the material were extracted using a model-based analytical approach to account for the effects of mixing and dispersion in the reactor. We find the rigor of this approach necessary in order to identify the rate controlling mechanism and assign parameters to the kinetic model.

From this analytical approach, we learned that the water splitting of ceria powder to produce H$_2$, in the range of 750 – 950 °C and 20 – 40 vol.% H$_2$O, can best be described by a first-order kinetic model with low apparent activation energy (29 kJ/mol). This first order kinetic model is analogous to the homogenous reaction kinetics, which implies that the WS process is surface limited. On the other hand, the carbon dioxide splitting reaction, in the range of 650 – 875 °C and 10 – 40 vol.% CO$_2$, is a more complex surface-mediated process that we believe to be controlled by a temperature-dependent surface site blocking mechanism involving adsorbed carbon. Unlike the WS reaction, one set of kinetic parameter is not sufficient in generating high quality fit for the CO production curve. Instead, a set of temperature dependent kinetic
parameters that governs the F-model is necessary.

Our results indicate that path transition within the surface mediated CO production network is responsible for the apparent governing mechanism shift in the F-model in the CDS. This is expressed in the evolution of $E_0$, $n$, and $\gamma$ values as the CDS temperature is increased. At the lower temperature region, CO can be produced by two parallel pathways that involve temperature dependent site blocking. At the higher temperature, the dominant pathway is the direct desorption of surface CO, which occurs very rapidly and becomes limited by dissociative adsorption of CO$_2$; hence at higher temperature, reaction rate increases greatly with increase in flux of CO$_2$. Although there are significant differences in fundamental kinetics between the WS and CDS process, both are still surface mediated and occur rapidly. Thus both processes can benefit by optimization of the gas/solid interface, such as the creation of a high surface area ceria structure.

The combination of high thermal stability and fast kinetics have established ceria as a good candidate for the solar thermochemical process. However, despite these characteristics, the cycle capacity of CeO$_2$ is low due to thermodynamic limitations. Thus, in an effort to increase cycle capacity and reduce thermal reduction temperature, we have studied binary zirconium-doped ceria ($\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$, $x = 0.1$, 0.15, 0.25) and ternary praseodymium/gadolinium doped zirconium-ceria ($\text{M}_{0.1}\text{Zr}_{0.25}\text{Ce}_{0.65}\text{O}_2$, $\text{M} = \text{Pr, Gd}$). Here, we evaluate the oxygen cycle capacity and water splitting performance of crystallographically and morphologically stable powders that are thermally reduced by laser irradiation in a stagnation flow reactor.

We find that the addition of zirconium dopant into the ceria lattice improves O$_2$ cycle capacity and H$_2$ production by approximately 30 % and 11 %, respectively. This improvement is independent of the zirconium dopant level, suggesting that zirconium might be coming out of
cubic solid solution. These observations are corroborated by X-ray diffraction and SEM-EDS analysis. The consequence of this is that the improved H₂ production is less than what has been reported by others. On the other hand, the addition of Pr and Gd to the binary zirconium-ceria mixed oxide is found to be detrimental to O₂ and H₂ cycle capacity. We have shown that the Pr⁴⁺/Pr³⁺ redox pair most likely does not participate in the water splitting, and consequently does not improve H₂ production. In fact, we discovered that addition of a ternary dopant such as Pr and Gd to zirconium doped ceria decreases H₂ production; especially addition of Gd to the binary oxide, which further suppress H₂ production to below that of undoped ceria.

The improved H₂ production we observe with the zirconium dopants can be considered marginal, and not as extreme as has been previously demonstrated for non-aged materials, and certainly, much less than has been reported for lower temperature catalysis applications. We believe one primary difference between our results and the aforementioned work by others is that the O₂ and H₂ cycle capacity reported here are of materials that are compositionally and morphologically stable. Once the zirconium doped ceria materials are stable, some zirconium cation comes out of cubic solid solution, and this effectively reduces the effective dopant level.

In addition to the cycle capacity evaluation, we have performed a detailed numerical analysis on the H₂ production rates of the doped ceria materials. The aforementioned numerical algorithm is applied on the WS of doped ceria materials, specifically the binary zirconium-ceria, and the ternary Pr or Gd doped zirconium-ceria. The result of the kinetic analysis provides high quality fits to experimentally observed H₂ productions. Regardless of the dopant used, all of the mixed cerium oxides evaluated in this work still exhibit an order dependence model. Furthermore, we have shown that the diffusion model, regardless of the dimension over which they act, cannot describe the H₂ rate curve over the entire time domain. Thus, despite the
crystallographic modifications of the binary (ZrCe) or ternary (PrZrCe and GdZrCe) oxides, WS kinetics is surface limited similar to undoped ceria.

Understanding the oxidation kinetics of ceria and doped ceria materials is vital to the development of detailed engineering models of ceria-based solar receiver reactors. Due to the diurnal nature of solar availability; it is important to maximize the solar to fuel conversion efficiency, and that requires optimization of the thermal reduction and oxidation process. Models based on experimental kinetic rate constants and insight into the oxidation mechanism will allow for optimization of transport rates and transit times of ceria in the solar receiver/reactor. This in turn allows for maximization of the number of thermochemical cycles that can be completed, and determines the fuel production rate and overall efficiency of the process.

5.2. Future Research Directions

The two-step solar thermochemical process, although it has the ability to achieve the highest theoretical efficiency in renewable H₂ production when compared to traditional methods such as solar panel–electrolysis systems and traditional concentrated solar power applications (CSP), faces significant technical hurdles before industrial scale deployment is achievable. Chief among them are: (1) the typical temperatures for the thermal reduction are between 1350 – 1500 °C, a very high temperature range that poses significant engineering challenge and (2) the metal oxide intermediates that are considered for the cycle require high thermal stability and fast redox kinetics. The overall objective of this study is to evaluate various chemistries that can address both concerns. The current work focuses on two things: first, to evaluate efficacy of various metal oxide materials for the two-step solar thermochemical water and CO₂ splitting. Second is to develop a theoretical framework to study the heterogeneous WS and CDS chemistry; in order to gain fundamental mechanistic understanding, and to generate predictive models that can
simulate the H\textsubscript{2} and CO production for the development of a solar receiver/reactor. In regards to the evaluation of metal oxides chemistry, the current study focuses on two types of chemistry: the displacement chemistry of "hercynite" and the sub-stoichiometric ceria based redox cycle.

The "hercynite" cycle has the advantage that it can be thermally reduced to a more significant extent at \( \sim 150 \, ^\circ\text{C} \) lower than ceria, or other Fe based chemistry. The cycle has also shown consistent fuel production behavior over 23 thermal reductions, with no evidence of sintering/formation of molten phase. Despite these desirable redox traits, however, the oxidation kinetics, even with the formation of nano-engineered novel structure, are still slow. The oxidation process exhibits high temperature dependence, and higher oxidation temperature is necessary to achieve practical cycling times.

On the other hand, in spite of its fast kinetics and thermal stability, ceria has low cycle capacity and thus a large amount of metal oxide is necessary for efficient fuel production. One favored approach to improve ceria’s cycle capacity is by incorporating dopants into the lattice to weaken the ceria-oxygen bond and induce higher extent of thermal reduction at more accessible temperatures and P\textsubscript{O2}. However, this work has shown that the potential improvement on H\textsubscript{2} production that can be achieved with this approach is marginal. The results presented here prompt us to reevaluate if lattice modification of ceria is a worthwhile endeavor in the search for new materials that can significantly improve the yield of solar thermal H\textsubscript{2} and CO production.

A new material that has the capability to achieve higher extents of reduction at more moderate reduction temperatures, and less stringent P\textsubscript{O2} requirement, is necessary for the process to achieve the efficiency that would allow it to be competitive with fossil fuel. One early example of such a material is the perovskite chemistry. Recent work by McDaniel \textit{et al} has shown that perovskite type materials appear to be a much more promising new class of metal
oxide for solar thermochemical applications. The authors discovered that LaAlO$_3$ doped with Mn and Sr not only has high thermal stability and comparable oxidation kinetics to ceria, but also exhibits higher cycle capacity than ceria, up to 9 x greater, at a thermal reduction temperature that is 150 °C lower. The discovery of these perovskite materials for solar thermochemical redox opens up a new class of possible materials that has the potential to achieve high process efficiency and, therefore, may accelerate the realization of fuel production based on thermochemical cycles. Studies on these materials have just begun and much more needs to be learned about them.

And finally, assessment of process efficiency is a complex proposition that needs to take into account the specific reactor design and method of operation. Typically, the development of a solar receiver/reactor is an iterative process that comes hand in hand with material development. Therefore, models based on experimental kinetic rate constants and insight into the oxidation mechanism are crucial for optimization of transport rates and cycle times of metal oxides in the solar receiver/reactor. We note that accurate fuel production models can be achieved only when the material specific behavior is separated from experimental effects such as detector time lag and gas phase dispersion/mixing.
BIBLIOGRAPHY


