Metal Oxide Catalysts For Renewable Energy Generation And Green Chemistry Purposes

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METAL OXIDE CATALYSTS FOR RENEWABLE ENERGY GENERATION AND GREEN CHEMISTRY PURPOSES

by

CHRISTOPHER LAWRENCE MUHICH

B.A., University of Michigan, 2009

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This thesis entitled:
Metal Oxide Catalysts For Renewable Energy Generation And Green Chemistry Purposes
written by Christopher Lawrence Muhich
has been approved for the Department Chemical and Biological Engineering

________________________________________

Alan Weimer

________________________________________

Charles Musgrave

Date_______

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.
Abstract

Muhich, Christopher, L. (Ph.D. Chemical and Biological Engineering)

Investigations Into Metal Oxide Catalysts For Renewable Energy Generation And Green Chemistry Purposes

Thesis directed by professors Alan W. Weimer and Charles B. Musgrave

Light driven metal oxide catalysts can be used to avert looming energy and environmental challenges by generating hydrogen from water and degrading aqueous organic pollutants. This work reports on investigations of metal oxide catalyzed solar thermal water splitting (STWS) and photocatalytic organic pollutant degradation.

Two-step STWS is a process where solar heat is used to drive the endothermic water splitting process; a metal oxide serves as an O-carrier, where in the first step of the STWS process O\textsubscript{2} is released by the metal oxide at high temperatures and in the second step, the O atoms from H\textsubscript{2}O molecules are re-incorporated into the metal oxide releasing H\textsubscript{2}. The hercynite cycle is a promising STWS material because of its relatively low reduction temperature, high melting point and H\textsubscript{2} production capacity (over 150 μmol of H\textsubscript{2}/g per cycle). Density functional theory (DFT) calculations in combination with high-temperature XRD and EDS analyses show that the hercynite cycle operates via an O-vacancy mechanism, were the O\textsubscript{2} that is released comes from the formation of O vacancies in the doped hercynite according to the reaction: Co\textsubscript{x}Fe\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4} → Co\textsubscript{x}Fe\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4-δ} + 2/δ O\textsubscript{2}.

The hercynite cycle was investigated for use in isothermal solar thermal water splitting where the reduction and oxidation step occur at the same temperature. Isothermal operation was previously thought to not be thermodynamically allowed. Not only does hercynite split water
under isothermal conditions, but the $\text{H}_2$ production yields at 1350°C reduction are, respectively, $>3$ and $>12$ times that of hercynite and ceria on per mass of active material basis when reduced at 1350°C and re-oxidized at 1000°C. A new set of thermodynamic models were developed which more accurately predict STWS behavior, including isothermal modes of operation.

The kinetics of the oxidation step of isothermal hercynite solar thermal CO$_2$ splitting were investigated. Due to complicating reactor and materials behavior, namely CO$_2$ thermolysis on the reactor walls and hence the simultaneous oxidation of hercynite by CO$_2$ and O$_2$, an extended formulation of solid state kinetic theory was developed which enabled the modeling of multiple simultaneous gas solid reactions. A second-order surface reaction model in relation to extent of unreacted material, and a 2.4$^{th}$ order model in relation to CO$_2$ concentration, were found to best describe the CO generation behavior of the doped hercynite.

TiO$_2$ can be used as a photocatalyst for the degradation of organic pollutants. The reaction is relatively slow due to the inability of O$_2$, the electron acceptor, to adsorb to the TiO$_2$ surface. Pt catalysts and material dopants are added to increase the overall rate of reaction. As the content of Pt increase the reaction rates increase and then subsequently decrease. DFT calculations were used to probe the O$_2$ reduction reaction on the TiO$_2$ and Pt decorated TiO$_2$ surface. Pt enables O$_2$ adsorption and reduction by providing high energy electron density which can form an O$_2$-Pt bond, increasing the photocatalytic rate of TiO$_2$. However, Pt also bridges the TiO$_2$ band gap which increases electron/hole recombination, decreasing the photocatalytic rate of TiO$_2$. At low Pt loadings the increased O$_2$ reduction rate is more significant than the electron-hole recombination but at high Pt loadings the increased electron hole recombination is more significant.
Additionally, DFT calculations predict that non-metal near surface TiO$_2$ dopants can serve as a source of high energy electron density to enable O$_2$ adsorption and reduction as long as the energy of the band gap states produced by doping are higher in energy that the empty O$_2$ $\pi^*$ state of the adsorbing O$_2$. B and interstitial C atoms facilitate O$_2$ reduction and adsorption but substitutional C and both interstitial and substitutional N dopants do not. N dopants can even hinder O$_2$ adsorption and the photocatalytic rate by creating electron/hole recombination sites.
This thesis is dedicated to my parents Tony and Martha

who taught me to love knowledge, and be curious about the world
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Chapter 1: Introduction

1.1 Overview

Reduction and oxidation (redox) reactions are some of the most ubiquitous chemical reactions. These reactions include wide ranging processes such as charging and discharging batteries, rusting metal, photosynthesis, combustion, H₂ and CO generation from H₂O and CO₂, respectively, and mineralizing of organic matter. Of these redox reactions, efficient H₂O and CO₂ splitting and mineralization of organic pollutants may help alleviate the looming environmental catastrophes of global warming and water pollution by providing clean fuels and removing organic waste from industrial, agricultural and residential effluents or already contaminated water. However, in order to achieve these goals, catalysts and energy sources to drive these processes must be identified that efficiently, environmentally benignly, and economically facilitate the generation of fuels that do not produce greenhouse gases and pollutant degradation. Due to their ionic nature, and, therefore, the presence of both reduced and oxidized atoms, their potential for maintaining their structures in aqueous environments and at high temperature, and their potential for being semi-conductors, the metal oxide class of materials offers a wide variety of possible redox reaction catalysis. Sunlight is an excellent energy source due to its environmentally benign nature and general availability. Consequently, this thesis reports on the investigation of light driven metal oxide catalysts which are capable of generating H₂ from H₂O and enabling pollutant degradation; specifically, it will address the use of doped hercynite (Co₀.₃₃Fe₀.₆₆Al₂O₄) in solar thermal water splitting (STWS) and the use of TiO₂ in organic pollutant photocatalytic degradation.
1.2 Solar thermal water splitting

Hydrogen, the most abundant element in the universe, has a high specific energy density and forms only water when burned. This makes hydrogen gas (H\textsubscript{2}) an attractive fuel as the world moves away from a carbon based economy.\textsuperscript{3} However, unlike hydrocarbons there is no sizable quantity of free H\textsubscript{2} on Earth to exploit; therefore, H\textsubscript{2} must be produced from other compounds. Steam methane reforming is currently the main H\textsubscript{2} production pathway, but it also generates CO\textsubscript{2} as a by-product.\textsuperscript{4} This means that the majority of the H\textsubscript{2} produced today cannot serve as a carbon-free fuel. Not only are current H\textsubscript{2} production technologies environmentally unfriendly, but as the world transitions to a “H\textsubscript{2} economy” H\textsubscript{2} production capacity must increase to meet the demands of its broadened use.\textsuperscript{5} The renewable methods for H\textsubscript{2} generation that are presently under development are not commercially economical and require further research to achieve the necessary process efficiencies if H\textsubscript{2} is to drive the world economy. This makes the development of a clean and economical H\textsubscript{2} generation process a technological “holy grail” of the 21\textsuperscript{st} century.\textsuperscript{6,7} Generally, renewable H\textsubscript{2} production pathways can be categorized as biologic, including fermentation and photosynthesis; electrolytic, when driven by renewably generated electricity; or solar, including solar photo-electrochemical water splitting and solar thermochemical water splitting.\textsuperscript{8} Solar-based routes are particularly interesting because sunlight has the capacity to provide ample energy to meet human needs. However, the capture and efficient storage of this diffuse resource continues to present technical and economic challenges inhibiting its implementation. Of the current methods proposed for solar energy collection and conversion, solar thermal water splitting (STWS) is particularly promising because it utilizes the entire solar spectrum to split water without the parasitic losses of growing biomass or generating current, enabling high theoretical solar to H\textsubscript{2} efficiencies, as shown in Figure 1.1.\textsuperscript{9-11}
Figure 1.1: Schematic comparing the solar to hydrogen efficiencies of various routes. Produced using data from Ehrhart et al.\textsuperscript{11}

In STWS, sunlight is highly concentrated by mirrors using solar dishes, or power towers, as shown in Figure 1.2a. The collected solar thermal energy then drives the endothermic decomposition of \( \text{H}_2\text{O} \) into \( \text{H}_2 \) and \( \text{O}_2 \). Splitting water in a single step, called direct thermolysis, is impractical both with current technologies and into the foreseeable future because of the ultra-high (>2200°C) reaction temperatures required for even minimal extents of reaction.\textsuperscript{12} Additionally, high temperature \( \text{H}_2/\text{O}_2 \) separation steps would be required to prevent product recombination. However, the reaction can be split into two or more steps in which the net reaction results in water splitting.\textsuperscript{13} In general, two-step water splitting cycles rely on the reduction and subsequent oxidation of metal oxides and require reduction temperatures greater than 1000°C.\textsuperscript{8,10,12,14} Multi-step cycles commonly utilize a metal in conjunction with harsh acids or bases and often include an electrolysis step, but many of these cycles can operate with a maximum temperature below 900°C.\textsuperscript{13,15-21} Because of the hazardous chemicals, design
complications, and the inherent compounding inefficiencies associated with the numerous process steps (reactions and separations), multi-step cycles are unlikely to achieve the high efficiencies required for economical and efficient H\textsubscript{2} generation\textsuperscript{12} and therefore will not be discussed further.

**Figure 1.2:** Methods of solar irradiance concentration using a) power tower and heliostats and b) a parabolic dish concentrator. Reproduced from Roeb et al\textsuperscript{22} c) a schematic of a generic two-step solar thermal water splitting cycle.

In two-step STWS, a metal oxide is heated using concentrated sunlight to high temperatures (T\textsubscript{red}) under low O\textsubscript{2} partial pressures (P\textsubscript{O2}) causing the metal oxide to reduce and generate O\textsubscript{2}, as shown in Equation 1. In the second step, the reduced metal oxide is exposed to steam which re-
oxidizes the material and forms H₂, as shown in Equation 2 and Figure 1.2c. Oxidation has traditionally been carried out at temperatures (T_{ox}) that are at least 500°C lower than T_{red}.\textsuperscript{12} However, it has recently been shown that the oxidation occurs at temperatures up to and including the reduction temperature.\textsuperscript{23}

\begin{align*}
MO_x &\rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \quad (1) \\
MO_{x-\delta} + \delta H_2O &\rightarrow MO_x + \delta H_2 \quad (2)
\end{align*}

In Equations 1 and 2, MOₓ and MOₓ₋δ are the oxidized and reduced states, respectively, of any metal oxide capable of undergoing STWS. The overall reaction is shown schematically in Figure 1.2c. The extent of reduction(δ) can range from 0 to X depending on the material and operating conditions. A similar set of reactions can be written for the reduction of CO₂ to CO in the case of carbon dioxide splitting.

While the above equations indicate that STWS is a simple process, it is much more complicated in practice. There are three main inter-related aspects of STWS that need to be considered and improved upon if STWS is to become an efficient and commercially viable process. These are 1) the optimal active material undergoing the STWS reactions; 2) systems operating conditions and associated efficiencies of these process options; and 3) STWS reactor design, including how the solar thermal energy is delivered to the active materials, how these materials are contained, and how the reactions are controlled. In work will focus on the materials of STWS, particularly the Hercynite cycle, and will also investigate the thermodynamic modes of STWS operation.
The identification of active and robust materials that efficiently undergo STWS redox reactions at practical conditions and rates is an area of substantial research. The ideal STWS material has: 1) high H₂ production capacity, 2) low reduction temperature, 3) fast kinetics, 4) a long lifetime (\(\sim 10^5-10^6\) cycles), 5) compatibility with the reactor containment material, 6) non-toxic composition, and 7) low cost. The first two desirable characteristics are thermodynamic properties of the material, which, together with fast kinetics, are the major materials attributes that determine the overall efficiency of the system. The other desirable qualities affect the costs and potential hazards of operating a STWS system based on a particular redox material.

Two-step water splitting cycles can be categorized by their reaction mechanisms, which are oxygen vacancy based chemistries, volatile displacement chemistries, or non-volatile displacement chemistries. In vacancy based chemistries, O₂ is released by the formation of O vacancies in the metal oxide lattice without a phase change (e.g., \(\text{CeO}_2 \rightarrow \text{CeO}_{2-\delta} + \delta/2 \text{O}_2\)). Both of the displacement chemistry mechanisms involve phase transitions of the active material as it undergoes reduction or oxidization. For volatile displacement chemistries (e.g., \(\text{ZnO} \rightarrow \text{Zn}_{(g)} + 1/2\text{O}_2\)) the phase transition is sublimation (solid to gas phase transition) whereas for non-volatile displacement chemistries (e.g., \(\text{Fe}_3\text{O}_4 \rightarrow 3\text{FeO} + 1/2\text{O}_2\)) the transition is to a different crystal structure or melting.

1.2.1 O-Vacancy Mechanism STWS Cycles

The O-vacancy mechanism materials maintain the same phase throughout reduction and oxidation and the O₂ released during the reduction results from the formation of vacancies within the material. Therefore, many of these cycles represent incomplete reduction of a displacement type chemistry, where, due to a “low” reduction temperature, the amount of O that is liberated is insufficient to drive a complete collapse of the reduced phase into a different structure but is
sufficient to produce practical amounts of H₂O on oxidation. This is exemplified by the Fe₃O₄ system where Fe₃O₄ forms O vacancies before phase transitioning to FeO. The materials involved in these redox cycles, in general, do not suffer the problems of melting or formation of gaseous reduced products. However, the H₂ production capacities of O-vacancies mechanism materials are generally lower than those of displacement chemistries because only a fraction of the metal cations participate in the redox process by changing oxidation state, while others provide the structural stability required to avoid a phase transition.

In the case of O-vacancy mechanism STWS cycles, the relevant measure of the activity of the material is the change in the extent of O non-stoichiometry between the oxidation and reduction step, or the Δδ of a material as shown in Equations 3-5.

\[ MO_{x-δ_{ox}} \rightarrow MO_{x-δ_{red}} + \frac{Δδ}{2} O_2 \quad (3) \]

\[ MO_{x-δ_{red}} + Δδ H_2 O \rightarrow MO_{x-δ_{ox}} + Δδ H_2 \quad (4) \]

\[ Δδ = δ_{red} - δ_{ox} \quad (5) \]

The Δδ achieved for a given process is the H₂ production per redox cycle. Specifically, the quantity of H₂ produced, or Δδ, is determined both by the temperature, and oxygen partial pressure operating conditions of the individual reaction steps as well as the degree to which the thermodynamic equilibrium is achieved in each step. This can be seen graphically in Figure 1.3, which shows the O non-stoichiometry for CeO₂ at various temperatures and O₂ partial pressures. The amount of non-stoichiometry at a set of operating conditions depends on the material undergoing STWS.
Since its identification by Adanades et al., the use of ceria in STWS has attracted substantial interest. The originally proposed cycle was the reduction of CeO$_2$ to Ce$_2$O$_3$; however, this reaction required a reduction temperature of over 2000°C, which is near the melting temperature of the reduced product leading to sintering of the materials and was accompanied by substantial evolution of gaseous Ce. In 2007, Kaneko et al. suggested that ceria could function as an O-vacancy mechanism STWS material after testing various mixed metal cerium oxides. They found that Mn, Fe, and Ni doped ceria were capable of producing more H$_2$ than Fe$_3$O$_4$-YSZ when reduced at or above 1500°C, but produced less H$_2$ at lower reduction temperatures. Chueh et al. were the first to use un-doped ceria as an O-vacancy mechanism STWS material and found that ceria produced ~379 μmol H$_2$/g when reduced at 1500°C and oxidized at 800°C. The H$_2$ production capacity increases as the reduction temperature increases the extent of reduction, as demonstrated by the 527 μmol H$_2$/g produced after a 1600°C reduction.
H₂ production capacities were accompanied by rapid reduction kinetics, which were limited by the heating rates of the reactor. The kinetics of the ceria oxidation reaction can be increased by depositing Rh on the surface, which suggests that ceria oxidation is a surface limited process. The surface limited oxidation hypothesis was also supported by the work of Furler et al. that showed that increasing the porosity of a ceria foam increased the rate of hydrogen production by an order of magnitude. Not only does ceria reduce and oxidize quickly, but ceria is stable over hundreds of cycles as shown in Figure 1.4, and is capable of undergoing isothermal water splitting. However, the practicality of pure ceria in STWS applications is limited by the high reduction temperature required to produce substantial quantities of H₂.

![Figure 1.4](image-url)
Many elements have been doped into ceria in an attempt to increase the H₂ production and lower the required reduction temperature. The divalent (Li, Mg, Cu, Zn, Sr)\(^{35-37}\) and trivalent (Al, Sc, Cr, Mn, Fe, Co, Ni, Y, La, Pr, Sm, Gd, Ta)\(^{24,34,35,38-43}\) elements have not been successful at achieving these goals. Some of the elements which take on a 4\(^+\) oxidation state have proven to be more successful at increasing the H₂ production of ceria, as shown in Figure 1.4. While Sn and Ti dopants increase the degree of reduction, they form Ce₂MO₇ phases which are not oxidized by steam.\(^{40}\) However, Zr and Hf dopants increase the STWS capacity of ceria at the cost of lowering the oxidation rate.\(^{34,44}\) In the case of Zr doping, the H₂ production increases with Zr content up to a molar concentration of roughly 25%.\(^{45}\) Hf, due to its similarity to Zn, behaves similarly. Additional dopants, namely Mg, Ca, Ni, Fe, and rare earth elements, have been doped into Ce\(_{1-x}\)Zr\(_x\)O₂ in attempts to further increase H₂ yields.\(^{43,46-48}\) Of these elements, Ni and Fe had no effect on H₂ production,\(^{46}\) while Ca and Mg both increased the H₂ yields. Co-doping Ce\(_{1-x}\)Zr\(_x\)O₂ with rare earth elements produced 205, 178, and 165 μmol of H₂/g for Pr, La, and Tb doping, respectively, while single-doped Ce₀.₇₅Zr₀.₂₅O₂ produced 134 μmol/g.\(^{48}\) Additionally, La and Gd were found to increase cycling stability of the doped ceria.\(^{43}\)

Hf doping of ceria, although not as widely studied as Zr doping, was found by Scheffe \textit{et al.} to produce 35% more CO than un-doped ceria in CO\(_2\) reduction, and outperforms Zr-doped ceria as shown in Figure 1.4.\(^{34}\) However, just as in the case of Zr-doped ceria, Hf-doped ceria exhibits longer oxidation times than un-doped ceria, which is likely attributable to a lower thermodynamic driving force for the oxidation reaction.\(^{34,36}\) The ability of the tetravalent ions to facilitate STWS likely arises from their ability to induce lattice strain rather than their ability to take on varying reduction states. When Zr\(^{4+}\) and Hf\(^{4+}\) are doped into ceria, their small size (72 pm and 71 pm, respectively, as compared to 101 pm for Ce\(^{4+}\)) induces tensile strain in the...
material due to a local lattice contraction. Conversely, when oxygen vacancies form they normally produce compressive lattice strain. Consequently, the tensile strain field surrounding Zr$^{4+}$ and Hf$^{4+}$ dopants lowers the O vacancy enthalpy of formation for O vacancies near the dopant as the superimposed strain fields of the dopant and O vacancy cancel, thus compensating for the energy required to break the O-Ce bonds to form the vacancy. However, the decrease in O vacancy formation energy is sufficient to facilitate reduction but not so large as to hinder water splitting (oxidation).

Of the other ceria dopants examined, W was found to not facilitate STWS\textsuperscript{41}. However, U was found to increase STWS, either due to its ability to enable over-oxidation, i.e. Ce$_{1-x}$U$_x$O$_{2+y}$,\textsuperscript{49} or its ability to take on multiple oxidation states which then aid Ce$^{4+}$ reduction.\textsuperscript{50} While U is unlikely to be used in commercial processes due to its radioactive nature, it may serve as a useful tool for identifying other dopants. Despite the extensive effort to dope ceria to achieve a better STWS material, the relatively low H$_2$ production capacity at reasonable reduction temperatures ($\leq 1500^\circ$C) still limits its potential application in commercial STWS processes; therefore other materials are needed for if STWS is to become a viable H$_2$ production process.

### 1.2.2 Volatile Displacement Chemistries

As the name suggests, the STWS volatile displacement chemistry cycle materials produce a metallic or metal oxide gas upon reduction and generation of O$_2$. This category of STWS reactions is attractive because it offers high specific H$_2$ producing capacities. For example BeO, which is not a STWS material but serves as a good illustration, could theoretically produce 40,000 µmol of H$_2$/g of BeO, the highest theoretical H$_2$ production capacity of any material. All of the material in these cycles is active and participates in the redox cycle and there is no inactive
material, and therefore no excess mass which stabilizes the reduced material as a condensed phase, resulting in complete sublimation of the active material. This necessitates difficult gas handling steps that are not required in other STWS cycles, namely quenching of the product gases to separate the reduced material from the liberated $\text{O}_2$ and preventing the reverse re-oxidation reaction with $\text{O}_2$.\textsuperscript{22} Furthermore after the reduced material desublimizes, complicated transport and processing steps are required to move transport the reduced solid material out of the quenching zone and into the oxidation reactor. Despite these challenges, two volatile displacement chemistry cycles are under development, the ZnO and the SnO\textsubscript{2} cycles.\textsuperscript{25,51}

1.2.2.1 The ZnO/Zn Cycle

The ZnO/Zn system was an early promising redox cycle for splitting water.\textsuperscript{25} Initially, the reduction of ZnO was investigated at atmospheric pressures and without an inert sweep gas to remove the generated $\text{O}_2$; this required a high reduction temperature, on the order of 1700-2000 °C, for thermal reduction.\textsuperscript{52} However, by lowering the $\text{O}_2$ partial pressure in the reactor via pumping or the use of an inert sweep gas, the onset temperature of thermal reduction was lowered to ~1300°C, although at these temperatures the overall reaction is slow.\textsuperscript{53,54} More recently, researchers have focused on the lower temperature, low $\text{O}_2$ partial pressure reduction conditions. The activation energy of the thermal reduction of ZnO has been found to be 312-380 kJ/mol, depending on the experimental and sample preparation methods, and was found to be a surface reaction limited process.\textsuperscript{53,55,56} ZnO reduction conducted at ~1450-1650 °C using a 10 kW lab scale rotary reactor was capable of producing 5-10 g of Zn/min.\textsuperscript{57,58}

While high reduction temperatures and a slow reduction rate are detrimental to efficient STWS, the most challenging impediment to efficient hydrogen generation is the re-oxidation of Zn\textsubscript{(g)} to ZnO by reaction with the released $\text{O}_2$ on cooling of the product stream. This reaction is
not only thermodynamically favored, but it has a low activation energy of 35±5kJ/mol;\textsuperscript{59} therefore the produced gases must be separated rapidly, which is usually done by quenching the Zn. Weidenkaff et al. found that while Zn\(_{(g)}\) and O\(_2\)(g) do not react rapidly when nucleation is suppressed, liquid Zn is particularly susceptible to oxidation by O\(_2\).\textsuperscript{60} However, if large solid Zn particles form, further oxidation of the reduced Zn is limited by the formation of a thin ZnO shell.\textsuperscript{60} Depending on the method and rate of cooling, reduced Zn recovery can range from 20-94\%.\textsuperscript{55,61} With this in mind, Gstoehl et al. developed a three step quenching system where the injection of cold inert gas both cools the produced Zn at rates of 20,000-120,000 K/s and dilutes the Zn and O\(_2\) concentrations, further lowering the re-oxidation rate.\textsuperscript{61} The first stage of this quenching system involves transport of the produced gases to a transition zone; throughout this first stage the temperature is maintained at the reduction temperature. The second stage of the quenching system is the transition zone where the temperature is reduced to below the ZnO reduction temperature, but above the Zn condensation temperature. An annular flow of inert gas prevents Zn from contacting the walls and nucleating ZnO. In the final step, massive injection of cold Ar inert rapidly cools the Zn driving desublimation and the formation of sizable Zn particles and thus preventing re-oxidation of the Zn by O\(_2\).\textsuperscript{62} This last step can require a dilution ratio of inert to Zn to be on the order of several hundred or several thousand. Although this requires a large quantity of inert gas, Zn recovery of up to 94% can be achieved using a dilution ratio of on the order 530.\textsuperscript{61} The quenching requirements necessary to achieve this level of Zn recovery lowers the overall solar to hydrogen efficiencies substantially because rapid quenching engenders irreversible heat losses, and requires significant gas pumping and inert gas processing to remove the generated O\(_2\).
In addition to the reduction reaction, the oxidation reaction must also be efficient and effective if the ZnO/Zn cycle is to be utilized in commercial STWS. The oxidation half-cycle involves reoxidation of Zn by hydrolysis. Hydrolysis of solid, liquid,\textsuperscript{53,63} or gaseous\textsuperscript{64-66} Zn are all observed, although reaction of H\textsubscript{2}O with either liquid or gaseous Zn is significantly faster than with solid Zn. Hydrolysis of solid Zn is slow because the ZnO film that forms on solid Zn upon oxidation acts as a diffusion barrier that limits Zn\textsuperscript{2+} and O\textsuperscript{2-} diffusion and thus makes Zn\textsubscript{(s)} oxidation transport limited by solid state diffusion.\textsuperscript{53,67} This is demonstrated by a set of experiments on the re-oxidation of Zn produced by the volatilization of metallic Zn. For gas phase Zn, a 100% reaction yield of ZnO was observed, however only an 83% conversion was obtained when the same Zn had been allowed to solidify before re-oxidation.\textsuperscript{68} Unfortunately, while the kinetics of gas phase reaction is rapid, it produces small particles that thermophoretically deposit on cold walls, limiting its collection efficiency.\textsuperscript{65} The study of the H\textsubscript{2} generating Zn oxidation step is complicated by the method of producing the reduced Zn. Zn oxidization studies have used Zn nano-powders, evaporation and re-condensation of pure Zn, and thermal reduction of ZnO. When a Zn nanopowder was used as the reactant, researchers see almost complete oxidation when the material was allowed time (>1s) to react;\textsuperscript{69,47}\textsuperscript{70} however, short reduction times (<1 s) resulted in lower overall conversion.\textsuperscript{71} Zn materials which were produced by the thermal decomposition of ZnO are more varied in their extents of oxidation, ranging from 55% to full conversion.\textsuperscript{72,73} The differences in re-oxidation behavior arise from the various morphologies of the condensed Zn produced by ZnO decomposition, where smaller particles, and rod-shaped particles result in higher extents of re-oxidation.\textsuperscript{72,74} This is likely due to the formation of protective ZnO coatings, which do not protect the reduced Zn at small length scales. The importance of Zn morphology on the re-oxidation behavior and the dependence of
morphology on the quenching approach suggest that in future studies of Zn oxidation, it is important to use Zn produced by the thermal decomposition of ZnO so as to more accurately represent realistic Zn morphologies which will be produced under STWS conditions.

While the reduction, quenching, and hydrolysis steps of Zn/ZnO STWS has been the focus of various research efforts, little attention has been paid to the challenges of transporting the quenched Zn to the hydrolysis zone, nor to the transport of the oxidized ZnO to the solar reactor feeder. In addition to the significant improvements needed to the quenching step, transport of the reduced and oxidize materials (which often deposit on the walls of the quenching or oxidization reactors) will have to be considered if the ZnO/Zn process is to become viable STWS system.

1.2.2.2 The SnO$_2$/SnO Cycle

SnO$_2$ dissociates to form the reduced species SnO at reduction temperatures of ~1200°C and at low P$_{O_2}$, which is more practical than ZnO reduction. However, unlike ZnO which forms metallic Zn, SnO$_2$ decomposition produces gaseous SnO. Further reduction to form Sn metal requires higher reduction temperatures or a low temperature self-reduction reaction, for example by SnO disproportionation ($2\text{SnO} \rightarrow \text{SnO}_2 + \text{Sn}$). $^{75}$ Forming SnO rather that the more reduced Sn metal decreases the theoretical H$_2$ production capacity of SnO$_2$ by half, but simplifies the H$_2$ production step by eliminating the need to carry out the self-reduction reaction. Additionally, H$_2$ reduction of SnO competes with H$_2$O oxidation of Sn while H$_2$ reduction of SnO$_2$ is not competitive with H$_2$O oxidation of SnO. Consequently, Sn re-oxidation is complicated by the competing back reaction between H$_2$ and SnO, while SnO reoxidation is not affected by this problem. $^{76}$ Furthermore, SnO oxidation is feasible at higher oxidation temperatures, and therefore achieves faster oxidation rates than Sn oxidation. $^{76}$ These advantages of SnO oxidation
over SnO₂ oxidation suggest that commercial H₂ production using SnO₂ would likely utilize the SnO₂/SnO cycle over the SnO₂/Sn cycle.

The thermal reduction of SnO₂ to SnO has a reported experimental reaction energy of 557 kJ/mol²⁵,⁵¹ and an activation energy of 334 kJ/mol.⁵⁴ Similar to the ZnO/Zn cycle, it is imperative to suppress the re-oxidation of the reduced SnO by the produced O₂, and to achieve nearly complete re-oxidation of SnO by H₂O if the SnO₂/SnO STWS cycle is to be sufficiently efficient to be practical. In these respects, the SnO₂ cycle is more promising than the ZnO cycle. First, SnO condenses at 1527 °C while Zn condenses at 907°C. Consequently, a slower quench rate can be employed to limit gas phase re-oxidation during SnO/O₂ separation.⁵¹ Additionally, the undesirable re-oxidation of SnO(s) by O₂ is slower than the re-oxidation of Zn(s), as evidenced by their oxidation activation energies of 42±4 kJ/mol and 35±5 kJ/mol respectively; this corresponds to a Zn re-oxidation reaction which is roughly twice as fast as the SnO re-oxidation reaction.⁵⁹ Slower re-oxidation of SnO enabled Charvin et al. to recover 34% of the produced SnO as compared to only 29% recovery of Zn using the same experimental apparatus, as shown in Figure 1.⁵⁵ Additionally, while both Zn and SnO were deposited during quenching as high surface area nano powders, SnO produced a higher surface area powder with a specific surface area of roughly 41-64 m²/g, depending on condensing temperature; the specific surface area of the deposited Zn was roughly of 17-50 m²/g which was lower than that of SnO at all conditions.⁵⁵ Furthermore, not only are the recovery yields of reduced SnO high for a volatile displacement reaction material, but water almost completely re-oxidizes SnO back to SnO₂, with observed conversions of ~90%,⁵¹,⁷³,⁷⁷ significantly higher than the observed 55% extent of re-oxidation of Zn using the same apparatus and conditions.⁷³ However, the oxidation of SnO is slower than the oxidation of Zn, having an activation energy of 122±13 kJ/mol while Zn oxidation has an
activation energy of 87 kJ/mol. \textsuperscript{73} While the SnO\textsubscript{2}/SnO STWS cycle appears to be more promising than the ZnO/Zn cycle, the SnO\textsubscript{2}/SnO cycle is still plagued by low recovery of the reduced material and the difficulties inherent in quenching the reduction product and handling the resulting reduced solids. Without significant improvements to address these issues, volatile displacement STWS cycles will likely be impractical for commercial water splitting.

![Graph](image)

**Figure 1.5:** A comparison of the reduced Zn and SnO recovery after thermal ZnO and SnO\textsubscript{2} decomposition using the same experimental apparatus and conditions. Reproduced from Chambon et al.\textsuperscript{59}

### 1.2.3 Non-volatile Displacement Reactions

Nakamura developed the first two-step non-volatile metal oxide redox cycle based on the oxidation and reduction of Fe\textsuperscript{2+/3+} as it transitions from the magnetite (Fe\textsubscript{3}O\textsubscript{4}) spinel to wüsite (FeO) with the rock salt structure. \textsuperscript{26} Ferrite is an attractive material for STWS because of its relatively high theoretical H\textsubscript{2} production capacity (roughly 4,300 \(\mu\text{mol/g}\)) and the absence of a volatile reduced metal oxide product. Originally researchers suggested that the reduction step would operate at \(\sim2,200\) °C where Fe\textsubscript{3}O\textsubscript{4} reduces under atmospheric conditions, however the reduction temperature can be lowered significantly by lowering the oxygen partial pressure. For
example, Fe$_3$O$_4$ reduces at 1300 °C at a O$_2$ partial pressure of 10$^{-11}$ atm.$^{14}$ However, Fe$_3$O$_4$ reduction is complicated by the low melting temperature of Fe$_3$O$_4$ (~1700 °C) and the even lower melting temperature of the reduction product, FeO (~1350 °C).$^{14,26,78}$ Low melting temperatures of active materials used in STWS cycles leads to extensive sintering of the active materials. Sintering of the active materials deactivates them by decreasing the surface area available for O$_2$ evolution, which lengthens the distances over which the O$^{2-}$ ions must diffuse to reach the surface.$^{79}$ Additionally, at the temperatures required to reduce Fe$_3$O$_4$, the reduced FeO product is a liquid, which on solidification produces a low surface area FeO mass, thus limiting the surface reactions with H$_2$O that re-oxidize the material and generate H$_2$.$^{79}$ This exacerbates issues associated with slow solid state diffusion of Fe$^{2+}$ within the oxidizing FeO or the produced Fe$_3$O$_4$. This is corroborated by the low yields of Fe$_3$O$_4$ obtained from the steam oxidation of FeO, which is transport limited.$^{80,81}$ These factors complicate the design and operation of STWS reactors based on the Fe$_3$O$_4$/FeO redox material.

Two potential modifications have been suggested to overcome the deficiencies of the Fe$_3$O$_4$/FeO redox cycle: 1) introduction of an inert carrier or buffer to prevent sintering and 2) doping Fe$_3$O$_4$ to lower the reduction temperature of the oxidized phase and to raise the melting temperature of the reduced phase. In an attempt to avoid melting and sintering, Allen et al. fabricated a support system using magnetic stabilization consisting of silica particles embedded between thin layers of Fe$_3$O$_4$. $^{82}$ While this prevented the formation of a monolithic solid mass of reduced FeO, the melting and re-solidification within the layer resulted in low surface area FeO and, therefore severe diffusional limitations resulting in slow oxidation kinetics. These factors resulted in only a 50% re-oxidation of the FeO after roughly three hours of exposure to steam.$^{82}$ Kodama, on the other hand, deposited Fe$_3$O$_4$ directly onto a yttrium stabilized zirconia (YSZ)
support which prevented sintering of the Fe$_3$O$_4$ and maintained activity over several cycles.$^{83}$ The chemical mechanism did change, however. Rather than merely forming FeO by the release of O$_2$ during reduction, some of the reduced Fe$^{2+}$ cations dissolved into the YSZ substrate and subsequently came out of solution to form Fe$_3$O$_4$ upon re-oxidation.$^{83}$ Not only does this prevent sintering and loss of STWS activity, but the oxidation reaction kinetics of Fe$_3$O$_4$ on YSZ materials are improved over pure Fe$_3$O$_4$ materials. While the rate-limiting step for FeO oxidation is the relatively slow diffusion of Fe$^{2+}$ ions, the significantly faster diffusion of O$^{2-}$ ions in YSZ limits the Fe oxidation in Fe$_3$O$_4$ on YSZ materials.$^{80}$ However, the utility of Fe$_3$O$_4$ on YSZ is limited by the only 9.4 mol% solubility of Fe in YSZ,$^{80}$ which leads to a low overall H$_2$ production capacity. Furthermore, employing the YSZ support decreases the specific H$_2$ production capacity as the additional inactive material both does not produce H$_2$ but adds to the thermal mass of the system.

In the second suggested approach, Fe$_3$O$_4$ is doped with other metals in an attempt to lower the reduction temperature and to prevent the sintering and melting of the reduced species. A broad spectrum of mixed metal ferrites (M$_x$Fe$_{3-x}$O$_4$ where M= Zn, Sn, Mn, Co, Ni, and combinations thereof) have been examined for STWS capabilities.$^{2,84-88}$ The use of Zn and Sn as dopants in mixed metal ferrites is impractical due to phase separation; where doping with Sn results in the formation of a SnO$_2$ phase and doping with Zn results in substantial Zn sublimation as shown in Figure 1.$^6$ and deposition of ZnO on the reactor walls.$^{22,84,86}$ Mn doping does not change the hydrogen capacity of Fe$_3$O$_4$, but lowers the oxidation rate.$^{85}$ However, Co and Ni doping of Fe$_3$O$_4$ show promise as STWS materials as the reduction products of both CoFe$_2$O$_4$ and NiFe$_2$O$_4$ melt at temperatures roughly 125°C higher than pure Fe$_3$O$_4$, as seen in Figure 1.$^6.$$^2$ Kodama et al. showed that CoFe$_2$O$_4$ facilitates STWS and that increasing the Co content
increases the H₂ generating capacity up to a maximum production capacity of 536 μmol/g using Co₀.₇⁵Fe₂.₂₅O₄ deposited on ZrO₂ using a 1400 °C reduction temperature.⁸⁷ Scheffe et al., who studied the kinetics of the CoFe₂O₄/YSZ STWS oxidation step, found that similar to Fe₃O₄ deposited on YSZ, some of the reduced Fe²⁺ dissolves into the YSZ support.⁸⁹ The oxidation of both the surface CoOFeO and dissolved Fe²⁺ lead to a complicated oxidation behavior modeled by a combination of reaction order and diffusion models. The oxidation of the dissolved Fe²⁺ is modeled by the F2 mechanism with an activation energy of 53.9 kJ/mol, where an F2 mechanism indicates either a reaction controlled by surface processes or O vacancy filling processes. The oxidation of the surface solid solution of CoOFeO is limited by diffusion with an activation energy of 141 kJ/mol.⁸⁹

Figure 1.6: Thermodynamic predictions of the reduction of MFe₂O₄ where M= Fe, Co, Ni or Zn. a) shows the simulated MFe₂O₄ (blue) and O content (red) while b) shows the reduced metal oxide content in a solid (orange), liquid (black), or gas (green) phase. Reprinted from Allendorf et al.⁴
Thermodynamic modeling predicts that NiFe$_2$O$_4$ should behave similarly to CoFe$_2$O$_4$. Indeed NiFe$_2$O$_4$ splits water repeatedly with a high H$_2$ production capacity, producing roughly 179 μmol H$_2$/g, a theoretical yield of 42%, when deposited on YSZ and reduced at under 1500°C. Analogous to the cases of CoFe$_2$O$_4$ and Fe$_3$O$_4$ deposited on YSZ, Fe$^{2+}$ ions from the reduction of NiFe$_2$O$_4$ dissolve into the YSZ support and the NiFe$_2$O$_4$ is stable over multiple cycles. However, when no support material is used, NiFe$_2$O$_4$ sinters and requires grinding between cycles to produce a high surface area powder. This is due to operating at conditions near the melting temperature of the products.

Overall, Co and Ni mixed metal ferrites are more promising STWS materials than the volatile oxide cycles because the challenges associated with handling gaseous reduced products can be avoided. However, techniques to avoid sintering of the reduced product, such as deposition of the active material on supports, are required because reduction of the mixed metal ferrites is carried out at conditions near their melting temperatures. This lowers the specific hydrogen production capacity of the mixed metal ferrites and adds to the thermal mass of the system. Additionally, ferrite cycles suffer from slow oxidation kinetics because of the slow rate of diffusion through the iron spinel phases.

### 1.2.4 The Hercynite Cycle

In 2010, Scheffe et al. discovered that when cobalt ferrite was deposited on alumina it would produce H$_2$ after reduction at 1200°C, which is 200-300°C lower than when cobalt ferrite was deposited on a zirconia support, as shown in Figure 1.7. Scheffe proposed that this reaction operates through a displacement mechanism where the CoFe$_2$O$_4$ reacted with the Al$_2$O$_3$ support during reduction to produce a solid solution of FeAl$_2$O$_4$ (hercynite) and CoAl$_2$O$_4$ as shown in
Equation 6. It was also suggested that this solution would revert back to two separate phases upon oxidation by steam, as shown in Equation 7.\textsuperscript{92}

\begin{equation}
\text{CoFe}_2\text{O}_4 \text{ + } 3\text{Al}_2\text{O}_3 \rightarrow \text{CoAl}_2\text{O}_4 \text{ + } 2\text{FeAl}_2\text{O}_4 + \frac{1}{2} O_2 \quad (6)
\end{equation}

\begin{equation}
\text{CoAl}_2\text{O}_4 + 2\text{FeAl}_2\text{O}_4 + H_2O \rightarrow \text{CoFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 + H_2 \quad (7)
\end{equation}

However, while Scheffe et al made the suggestion for this mechanism based on the fact that traditional ferrite materials operate via a displacement reaction mechanism, and the formation of the hercynite phase (FeAl\textsubscript{2}O\textsubscript{4}) after initial reduction, the validity of the Equation 7 was never examined.\textsuperscript{92}

\textbf{Figure 1.7:} a) The doped-hercynite cycle H\textsubscript{2} production rates after reduction at various temperatures and oxidation at 1000°C. b) the doped-hercynite cycle H\textsubscript{2} production rates of CoFe\textsubscript{2}O\textsubscript{4} on ZrO\textsubscript{2} after reduction and oxidation under the same conditions as a). Reproduced from Scheffe \textit{et al.}\textsuperscript{92}
In addition to producing H\textsubscript{2} at relatively low reduction temperatures\textsuperscript{92,93}, the hercynite materials are less prone to sintering than traditional ferrite material because the doped hercynite phase does not melt below 1600°C\textsuperscript{92}, which is high than STWS operations are likely to occur. On-sun experiments have shown that the doped-hercynite material produces roughly 10 times the H\textsubscript{2} produced by the traditional Fe\textsubscript{3}O\textsubscript{4} material, and that the doped-hercynite materials do not sinter as badly as the Fe\textsubscript{3}O\textsubscript{4} materials.\textsuperscript{79} However, at reduction temperatures above 1500°C CoFe\textsubscript{2}O\textsubscript{4} produces more H\textsubscript{2} per gram of active material than doped-hercynite\textsuperscript{92} because a larger portion of the material undergoes active reduction and oxidation. The hercynite cycle materials appear to be promising for STWS, however they have not been examined in as much detail as the other STWS materials. Therefore more in depth knowledge should be developed about the hercynite mechanism, H\textsubscript{2} production capacities and kinetics. This work will attempt to fill in these knowledge gaps.

1.2.5 The spinel crystal structure

The hercynite cycle is proposed to operate via a displacement reaction between CoFe\textsubscript{2}O\textsubscript{4} and Co\textsubscript{2}Fe\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{4} spinels.\textsuperscript{92} A spinel is a material with an AB\textsubscript{2}O\textsubscript{4} formula where the A ions usually take on a 2+ oxidation state and the B ions take on a 3+ oxidation state.\textsuperscript{94} The O atoms in the spinel structure are coordinated to three octahedrally coordinated cations and one tetrahedrally coordinated cation. In “normal” spinels the A\textsuperscript{2+} ions occupy the tetrahedral sites while the B\textsuperscript{3+} ions occupy the octahedral sites, as shown in Figure 1.8a. “Inverse” spinels, however, are disordered, where the B\textsuperscript{3+} ions occupy all the tetrahedral sites and half of the octahedral sites and the A\textsuperscript{2+} ions occupy the other half of the octahedral sites, as shown in Figure 1.8b. Spinels are not found with just a normal or inverse structure, but rather fall somewhere in between, the extent of which is usually reported using the inversion parameter, x, where x=0.
indicates a completely normal spinel and \( x=1 \) indicates a completely inverse spinel. The inversion parameter can be thought of as the percent of the material which is in an inverse structure. Under relevant conditions \( \text{CoFe}_2\text{O}_4 \), \( \text{CoAl}_2\text{O}_4 \) and \( \text{FeAl}_2\text{O}_4 \) are majority inverse, normal and normal spinels, respectively.\(^95\)

**Figure 1.8:** Schematic of the spinel structure where a) shows the "normal" and b) shows the "inverse" cation arrangement. The gray and white squares indicate repeated substructures.

1.3 Photocatalytic organic pollutant degradation

Organic water pollutants, stemming from surface run-off, agricultural waste, illegal dumping and incomplete waste treatment have large negative effects on aquatic ecosystems, nations where water treatment is insufficient and developed locations where people come in contact with untreated water. Organic pollutants (OPs) can cause a myriad of health problems including cancer,\(^96-99\) endocrine and reproduction disruption,\(^96,99,100\) disruption of DNA
transcription,\textsuperscript{97} and poisoning\textsuperscript{99} among others. Currently, the main mechanisms for OP’s remediation are microbial oxidation, phytoremediation, adsorption onto activation carbon or chemical oxidation often using O\textsubscript{3}.\textsuperscript{101-104} While effective these methods require input of mechanical work, such as aeration of microbial ponds, or consumables, such as sorbents or oxidizing agents. Additionally, these systems are generally un-economical at small scales, and not easily implementable. Therefore a simpler, more economical, and down-scalable method of OP degradation could minimize the contamination of water by OP. A photocatalytic route could be used for multi-scale, wide spread OP degradation (OPD) because it is relatively simple to operate, and the process is driven by light which could come either come from sunlight or lamps where electricity is bountiful or higher through put is needed.

Due to their high photoactivity, chemical stability and low cost, TiO\textsubscript{2} photocatalysts have been widely applied since their discovery in the 1970’s. TiO\textsubscript{2} is a widely-used and studied photocatalyst due to its remarkable ability to harness the energy of photons to drive oxidation/reduction reactions.\textsuperscript{105} In addition to being photochemically active, TiO\textsubscript{2} is inexpensive, generally stable in solution, and its band edges straddle the reduction-oxidation potentials of many valuable chemical processes. These reactions include water\textsuperscript{106,107} and carbon dioxide splitting,\textsuperscript{108-110} NO\textsubscript{x} oxidation and reduction,\textsuperscript{111} and OPD, which is currently the most common application.\textsuperscript{112-114} However, TiO\textsubscript{2}’s effectiveness as a photocatalyst is constrained both by its inefficient use of solar energy that results from the small fraction of incident solar radiation that possess energies exceeding its 3.2 eV band gap, and the slow reaction kinetics of the photochemical processes that occur on TiO\textsubscript{2}’s surface. Despite these limitations, TiO\textsubscript{2} is nevertheless widely used as a photocatalyst where efficiency and rapid reactions are not critical,
such as in self-cleaning and antibacterial surfaces.\textsuperscript{115,116} This work will investigate the use of TiO\textsubscript{2} for OPD.

1.3.1 Mechanism of photocatalysis

Photocatalytic reactions take place when photons with energies in excess of the band gap excite electrons from the semiconductor valence band into the conduction band producing an electron-hole (e-h) pair. The e-h quasiparticle can separate into free carriers which then migrate to the surface where the photoinduced excited electron reduces an acceptor molecule and the hole oxidizes a donor molecule, as shown in Figure 1.9. Because reduction or oxidation by the photoinduced charges of the reacting species involves electron transfer, these redox processes usually occur with species adsorbed to, or very close to the surface. If no acceptor or donor species are present, the photoexcited particles can recombine generating light or heat, which lowers the photocatalytic efficiency of the process.

![Figure 1.9: Schematic of a photocatalytic process. e- and h+ represent electrons and holes respectively and A and D represent acceptor and donor species respectively.](image)
In TiO$_2$ photocatalytic OPD where O$_2$ is available, which is shown schematically in Figure 1.10, O$_2$ acts as an electron scavenger, where it forms highly oxidative species and by removing electrons reduces e-h pair recombination. The reactive oxygen contributes to the oxidation of organic compounds by either directly attacking the organic or by producing hydrogen peroxide, which is a source of hydroxyl radicals that act as a strong oxidizer as shown in Equation 8:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \rightarrow 2 HO^{ullet}$$ (8)

In aqueous solutions, several different pathways have been suggested for O$_2$ reduction and oxidative species formation. For example, Hoffman suggested that O$_2$ first adsorbs to the TiO$_2$ surface before gaining an electron and then combines with two protons to form H$_2$O$_2$, which subsequently converts to hydroxy species that degrade organic compounds.$^{117}$ Nakamura suggested two mechanisms for this process; one where an O$^-$ on the TiO$_2$ surface transfers an electron to an O$_2$ in solution that then reacts with H$^+$ to form HO$_2^-$ and eventually H$_2$O$_2$; and a second mechanism involving an O$_2$ in solution that adsorbs to a surface Ti$^{4+}$ site by sequentially accepting two electrons and subsequently reacting with two protons to form H$_2$O$_2$, which is released into solution upon addition of the second H$^+$.\textsuperscript{118} Mattioli \textit{et al.} and Filippone \textit{et al.} both suggested that O$_2$ accepts two electrons as it adsorbs on the TiO$_2$ surface and subsequently accepts two protons to form adsorbed H$_2$O$_2$, which then desorbs.$^{119,120}$ When O$_2$ is not present, some organic molecule can behave as an electron accepter, but at slower rates because O must be extracted from the bulk TiO$_2$.\textsuperscript{121} As most processes will be carried out in an environment with O$_2$ present, anaerobic photocatalytic OPD will not be discussed further.
Figure 1.10: Schematic of the TiO$_2$ based photocatalytic OPD process. The O$_2$ reduction step, shown on the right side of the figure, is the rate limiting step.

Surface adsorbed water or hydroxide anions act as the main hole acceptors in aqueous TiO$_2$ photocatalytic OPD, although it has been suggested that certain organic materials may directly accept holes from TiO$_2$ and decompose.$^{117,122}$ When an H$_2$O accepts a hole from TiO$_2$ either hydroxyl radicals or O$_2$ are produced:

$$2 \text{H}_2\text{O} + 2 \text{h}^+ \rightarrow 2 \text{HO}^\bullet + 2 \text{H}^+ \quad (9)$$

$$2 \text{H}_2\text{O} + 4 \text{h}^+ \rightarrow \text{O}_2 + 4 \text{H}^+ \quad (10)$$

However, Li et al. suggested that as H$_2$O proceeds along its oxidation path on anatase TiO$_2$ in an aqueous solution no H$_2$O$_2$, or similar species are produced$^{123}$ indicating that O$_2$ is likely to be the only product of H$_2$O oxidation unless the solution is acidic. Therefore, it can be concluded that the main source of H$_2$O$_2$, and hydroxyl radicals, and hence the pollutant degrading agent, arises from O$_2$ reduction and that H$_2$O mainly serves as a hole acceptor.
In the case of OPD where O\textsubscript{2} is present, the reduction of O\textsubscript{2} is the rate-limiting step in semiconductor base organic pollutant degradation.\textsuperscript{117,124} The slow kinetics of oxygen reduction stem from O\textsubscript{2}’s inability to adsorb to the perfect anatase (101) surface, which is the most stable surface of TiO\textsubscript{2}’s most photocatalytically active phase.\textsuperscript{119,120,125} The rate of electron transfer to O\textsubscript{2} that is in solution and not adsorbed to the TiO\textsubscript{2} surface is insignificant. These two factors result in a slow rate of oxygen reduction by photoexcited electrons on the perfect (101) anatase surface. Additionally, because O\textsubscript{2} scavenges excited electrons slowly, significant electron-hole recombination likely occurs within photoexcited TiO\textsubscript{2}. Two previous approaches to increase the rate and efficiency of OP photodegradation include deposition of Pt clusters onto the TiO\textsubscript{2} surface to increase UV activity\textsuperscript{126-135} and doping TiO\textsubscript{2} in an attempt to induce visible light photoactivity\textsuperscript{134,136-145} and thereby increase the fraction of absorbed solar photons. Although neither of these approaches was intended to increase the adsorption of oxygen and the rate of the ORR, they both resulted in improved photocatalytic activity towards OPD.

1.3.2 Pt on TiO\textsubscript{2}

The photoactivity of TiO\textsubscript{2} is enhanced by doping the surface with Pt as reported by numerous researchers.\textsuperscript{122,127-130,146-148} However, the mechanism for the improved photoactivity is still not clearly understood. In addition, photoactivity is sensitive to the level of Pt loading, as shown in Figure 1.11. Numerous reports have indicated the existence of an optimal weight loading of Pt for photo oxidation of pollutants.\textsuperscript{127-133} For example, Kennedy \textit{et al.} report that the optimum loading of Pt is 1.0 wt% for photo oxidation of liquid phase alcohols.\textsuperscript{128} Lam \textit{et al.} suggested that Pt/TiO\textsubscript{2} exhibits a maximum photoactivity at a Pt loading of 2 wt% for resorcinol degradation.\textsuperscript{129} Cho \textit{et al.} observed that Pt deposited on TiO\textsubscript{2} increased the overall photocatalytic decomposition of O\textsubscript{3} for Pt loadings up to 1.0 wt%.\textsuperscript{127} It has also observed that the photocatalytic
activity of Pt/TiO$_2$ first increases and then decreases with increasing Pt loading, reaching a maximum at an optimum weight loading for methylene blue decomposition.$^{12}$ When Pt nanoparticles are deposited on Degussa P25 TiO$_2$ powders by atomic layer deposition (ALD), the photoactivity of TiO$_2$ rose with increasing Pt ALD cycles to a maximum of a three-fold increase after three cycles, followed by a drop in photoactivity with additional Pt ALD cycles corresponding to higher Pt loadings.$^{126}$ To explain the effect of Pt loading on photoactivity some reports have suggested that Pt clusters act as an electron-hole (e-h) separation center and therefore inhibit e-h recombination at low Pt loadings, but that at high loadings Pt acts as an e-h recombination center.$^{131,132,146,149,150}$ Unfortunately, this suggestion has not been verified or explained mechanistically, leaving the field with no proven, fundamental explanation for the mechanism by which Pt affects the photoactivity of TiO$_2$.

**Figure 1.11:** The effect of Pt deposition on the photocatalytic activity of TiO$_2$ as measured by methylene blue conversion after 30 min. The Pt was deposited on Degussa P25 TiO$_2$ by atomic layer deposition (ALD). The Pt loading increases with each additional ALD cycle. Reproduced from Zhou et al.$^{126}$
1.3.3 Doping TiO$_2$

TiO$_2$ can also be modified by inducing defects by doping TiO$_2$ with either non-metals, such as B, C, N, S and P$^{151-162}$ or other transition metals such as V, Fe, Cr, Nb, and Mn.$^{143,163-166}$ Although modified TiO$_2$ materials are often fabricated in an attempt to enable visible light photoactivity, B doped TiO$_2$ outperforms undoped TiO$_2$ even under UV illumination and specific reaction and preparation conditions,$^{167,168}$ in contrast, N doping was shown to have a detrimental effect on UV light photoactivity,$^{136,167,169}$ as shown in Figure 1.12. In addition to altering the OPD rates, doping TiO$_2$ may also alter electron-hole recombination, which is likely a non-radiative process, by decreasing the bandgap or by altering the phonon modes. However, the specific effect of doping on recombination is not yet determined and likely depends on the particular dopants and preparation methods used.$^{106,170-172}$ While many theoretical studies have examined the effect of doping on the band structure of TiO$_2$, from which O$_2$ reduction and photocatalytic behavior has been hypothesized (where high energy states and band gap lowering dopants are associated with increasing the catalytic rates), no study has attempted determine the effect of non-metal doping on the O$_2$ reduction reaction.
Figure 1.12: The photoactivity of non-metal doped TiO$_2$. a) The effect of B doping on the visible light driven photo-oxidation of toluene, reproduced from Khan et al.\textsuperscript{167} b) The effect of B doping on the ultra-violet light driven photo-oxidation of methylene blue, reproduced from Bettinelli et al.\textsuperscript{168} The effect of N doping on the visible and ultra-violate light driven photo-oxidation of gaseous isopropyl alcohol is shown in c) and d) where c) shows the overall yield of the reactions and d) shows the conversion with time, reproduced from Irie et al.\textsuperscript{169}

1.3.4 Anatase TiO$_2$

The model systems employed in this dissertation are all based on the TiO$_2$ (101) anatase surface, shown in Figure 1.13. Anatase is the major crystalline phase present in P25 TiO$_2$ powders and possesses the highest photoactivity among the three TiO$_2$ crystal structures (anatase, rutile and brookite); the (101) face is the most stable and abundant anatase surface.\textsuperscript{125,173} The TiO2 surface is composed of two and three fold coordinated O atoms and five
and six fold coordinated Ti atoms. The twofold coordinated O atoms and fivefold coordinated Ti atoms, 2f-O and 5f-Ti in Figure 1.13 are like to be the main site for surface reactions because these atoms are under-coordinated. In bulk anatase TiO₂ and Ti atoms are three and sixfold coordinated respectively.

![Figure 1.13](image.png)

**Figure 1.13:** a) top view of the perfect (101) TiO₂ anatase surface, b) side view of the perfect (101) anatase TiO₂ surface. Ti and O atoms are represented by large gray and medium red spheres, respectively.

### 1.4 Thesis Objectives

This thesis investigates four aspects metal oxides catalyst use in renewable energy generation and green chemistry applications. Specifically, it will develop a deeper understanding of two-step metal oxide STWS cycles and photocatalytic organic pollutant degradation. This entails the exploration of the hercynite STWS cycle mechanism and the thermodynamics of STWS cycles, and the determination of the effects of surface decoration and bulk doping of TiO₂ on its photocatalytic organic pollutant degradation rates. These goals are outlined in more detail below, and this thesis addresses each of these objectives in their respective order.
1.4.1 The chemistry of the hercynite solar thermal water splitting cycle

This work aims to determine the reduction/oxidation mechanism of the hercynite cycle under solar thermal water splitting conditions. A combination of experimental and computational techniques was used to assess the reduction and oxidation sources and structures during hercynite cycle based STWS. O₂ release and H₂O reduction were probed using periodic boundary condition density functional theory to assess reaction energies between spinel phases likely to exist in the “hercynite cycle” (CoFe₂O₄, CoAl₂O₄, FeAl₂O₄, and Co₀.₅Fe₀.₅Al₂O₄). Experimentally, in situ high temperature x-ray diffraction probed the Red/Ox phases of the hercynite cycle materials during STWS. Additionally, EDS mapping and Stagnation Flow Reactor water splitting experiments will be used to confirm HT-XRD and DFT results.

1.4.2 Isothermal and near-isothermal solar thermal water splitting

This work aims to determine if the reduction and oxidation steps of solar thermal water splitting can be conducted isothermally and its effects on H₂ production. Water splitting reduction/oxidation cycling was carried out using “hercynite cycle” materials in a stagnation flow reactor under both isothermal (ITWS) and temperature swing (TSWS) conditions. The H₂ production capacities and reaction times under these two operational conditions were compared. The results from this investigation prompted further inquiry into ITWS and near-isothermal water splitting (PITWS).

Because it will be shown that ITWS is possible, see Chapter 4 for details, the design space available for STWS optimization is greatly expanded. This work will therefore also determine the effects of near-isothermal water splitting (NITWS), defined as having a reduction and oxidation temperature difference less than ~150°C, on the quantity and rates of H₂ generation.
1.4.3 Extracting complex gas-solid solar thermal CO\textsubscript{2} splitting reaction kinetic for the hercynite cycle

This work aims to determine the kinetics of the oxidation step of the hercynite based solar thermal CO\textsubscript{2} splitting cycle. Solid state kinetic theory was applied to isothermal CO\textsubscript{2} splitting data; however reactor effects, such as gas dispersion and multiple gas-solid reactions, complicated the extraction of the hercynite oxidation reaction. Therefore reactor dispersive effects were modeled and included in the kinetic models, and solid state kinetic theory was expanded to include multiple simultaneous gas/solid reactions.

1.4.4 The effect of Pt on the photocatalytic activity of TiO\textsubscript{2}.

This work aims to explain the increase and subsequent decrease in the photocatalytic activity of TiO\textsubscript{2} in organic pollutant degradation reactions with increasing Pt loading. Periodic boundary condition based density functional theory was used to examine the rate limiting O\textsubscript{2} reduction reaction step on the TiO\textsubscript{2} surface with and without Pt particles, modeled by the (101) anatase TiO\textsubscript{2} surface and a truncated cuboctahedron Pt cluster with 37 atoms placed on the aforementioned surface. Bader analysis, density of states and bond analysis were used to identify difference in the reduction behavior of O\textsubscript{2} on the decorated and undecorated TiO\textsubscript{2} surfaces. The results of this aim motivated the investigation of other O\textsubscript{2} reduction reaction promoters which was carried out in the second aim.

1.4.5 Altering the photocatalytic activity of TiO\textsubscript{2} via non-metal dopants

This work aims to determine if non-metal dopants can increase O\textsubscript{2} reduction on TiO\textsubscript{2} by introducing dopants that create high energy band gap states. PBC based DFT was used to
examine the O₂ reduction reaction on the TiO₂ surface with non-metal (B, C, N) dopants in surface and sub-surface substitution and interstitial sites to determine their effect on the O₂ reduction reaction. It was hypothesized that dopants which provide electron density to TiO₂ with energy above the π* O₂ orbitals will facilitate O₂ adsorption and reduction.

1.5 References

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Chapter 2: Research Methods

2.0 Overview of thesis methods

In order to investigate light driven metal oxide catalysts of H₂O splitting and organic pollutant degradation reduction/oxidation reactions experimental and computational approaches were used. The solar thermal water splitting work reported here was undertaken using mostly experimental tools, while the development of the understanding of organic pollutant degradation relied solely on density functional theory (DFT)¹,² calculations. In this chapter, the general materials fabrication and testing, and computational approaches will be summarized. For more detailed descriptions of the exact experimental and computational procedures used in individual investigations see the respective chapters.

2.1 Materials fabrication

Water splitting materials were produced by atomic layer deposition (ALD) and the Pechini method. ALD is a materials deposition technique which is tailorable, layer by layer, and pinhole free.³ The Pechini method is a sol-gel type solid materials fabrication technique.⁴ First ALD will be discussed then the Pechini method will be discussed.

2.1.1 Atomic Layer Deposition of hercynite material preparation

Atomic layer deposition is a method where by a single layer of atoms is deposited at a time by sequentially conducting two half-step deposition reactions using non-self-reacting precursors. In general metal oxide ALD, the surface to be deposited on is exposed to an organometallic precursor which reacts with surface reactive groups binding the metal atom to the surface while maintaining a portion of its organic ligands,³ as exemplified in Figure 2.1a using
trimethyl alumina as the organometallic precursor. The remaining organic ligands prevent self-reaction or further precursor/surface interaction. The reaction products and unreacted precursors are swept from the reaction chamber to prevent the organometallic precursor from reacting with the second precursor. After the precursor sweep step is complete the oxidizing precursor is injected into the reactor. This precursor removes the remaining organic groups from the organometallic precursor, deposits an O atom on the surface and reforms the surface groups required for the second ALD cycle, as shown in Figure 2.1b using H$_2$O as the oxidizing agent. As in the first step, an inert gas sweeps the reaction products and unreacted precursor from the reactor before the second cycle begins.

Figure 2.1: Schematic of the ALD process. a) and b) show the first and second half cycle of the Al$_2$O$_3$ deposition process using TMA and water as the reactants.

In the work described here, the ALD reactions are carried out in a vibrating fluidized bed reactor, which is shown in Figure 2.2. The vibrating fluidized bed reactor prevents the particles
from becoming stuck together during deposition.\textsuperscript{5} The extent of the reaction is monitored via an in line mass spectrometer. An example of typical mass spectrometer signals is shown in Figure 2.3 for the CoFe\textsubscript{2}O\textsubscript{4} deposition. The individual half reactions are considered complete when the product production rate decreases and the reactant is detected in the mass spectrometer, which is referred to as precursor brake through. All of the lines are heated to prevent vapor phase precursors from condensing and blocking the lines and valves. All valves and mass flow controllers were controlled via a LabView program.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Diagram of the vibrating bed ALD reactor used in this work. Figure reproduced from King et al.\textsuperscript{5}}
\end{figure}

To produce ALD doped hercynite materials Al\textsubscript{2}O\textsubscript{3} was deposited on a polymer particle support to create a high surface area, high porosity metal oxide base, which was also a reactant in the STWS reaction. After Al\textsubscript{2}O\textsubscript{3} deposition the polymer was removed by combustion. In a second process, CoFe\textsubscript{2}O\textsubscript{4} was deposited on the Al\textsubscript{2}O\textsubscript{3} support.\textsuperscript{6}
Two polymer particles were used as a polymer template: Cavilink™ (∼600 μm, 43.5 m$^2$/g) and DOWEx particles. Both particles were poly-styrene divinylbenzene co-polymers. Unlike the Cavilink™ particles, the DOWEx particles did not have surface reactive groups with which TMA and water could react and bind. Therefore the DOWEx particles were functionalized using nitric or sulfuric acid by boiling the particles in the acid for at least five hours at ~120°C. Al$_2$O$_3$ was deposited on the polymer using trimethyl aluminum (Sigma Aldrich 97% pure) and DI water. The two half-reaction for the deposition of Al$_2$O$_3$ are shown in Equations 1 and 2.\textsuperscript{7,8}

\[
Al(CH_3)_3 + *OH \rightarrow *Al(CH_3)_2 + CH_4(g) \quad (1)
\]

\[
*Al(CH_3)_2 + 2H_2O \rightarrow Al(OH)_2 + 2CH_4(g) \quad (2)
\]

where the * represents a surface bound species. The polymer was combusted away in a furnace heated to above 600°C.\textsuperscript{6,9}
2.1.1.2 CoFe₂O₄ deposition on Al₂O₃ particles

CoFe₂O₄ was deposited on Al₂O₃ using ALD in the same reactor as was used for Al₂O₃ deposition. CoFe₂O₄ was fabricated by depositing alternating layers of CoO and Fe₂O₃ in a 1:1 ratio. ALD was conducted using cobaltocene (Strem Chemicals >98% metal purity), or ferrocene (Strem Chemicals >99% metal purity) as the organometallic precursors for CoO and Fe₂O₃ respectively; O₂ (AirGas UHP) was used as oxidizing precursor for both CoO and Fe₂O₃ deposition. The two half-reaction for the deposition of CoO and Fe₂O₃ are shown in Equations 3 and 4.⁶,¹⁰,¹¹

\[
MCp₂ + 14.5 \cdot O → *MCp + 5CO₂(g) + \frac{5}{2}H₂O(g) \quad (3)
\]

\[
*MCp + (15 + \frac{x}{2})O₂ → *MOₓ + 5CO₂(g) + \frac{5}{2}H₂O(g) \quad (4)
\]

where M is either Co or Fe and Cp is a cyclopentadiene moiety. The exact stoichiometry of the O₂ reaction in Equation 4 depends on the final oxidation state of the metal atom. The CoFe₂O₄ deposition reactions were carried out 350-450°C. An example of the mass spectrometry signals recorded during CoFe₂O₄ ALD is shown in Figure 2.3. After CoO and Fe₂O₃ were deposited the desired ferrite was formed from the constituent oxides either during calcination or the initial reduction step.

2.1.2 Pechini method of hercynite material preparation

The Pechini method was also used to produce spinel materials (FeAl₂O₄ and CoₓFe₁-xAl₂O₄). The Pechini method is a sold-gel method where metal ions are incorporated into an organic polymer, which is removed leaving only a metal oxide.⁴,¹² The inclusion of the cations into the organic polymer helps maintain an even distribution of the various cations throughout
the material, helping to prevent ion and phase segregation. The key to the Pechini method is chelation of the metal ions to an organic group; the chelating agents are then polymerized using a linking agent generally via a polyesterification dehydration reaction, as shown in Figure 2.4. Many flavors of the Pechini method have been developed which differ mainly in the choice of chelating agent and molecule which links the chelating species together. One of the most commonly used pair of chelating and linking molecules are, respectively, citric acid and ethylene glycol;¹² these are the reagents used in this work.

![Cartoon demonstrating the polymerization reactions of the Pechini citrate gel method. The citric acid, ethylene glycol and citric acid chelated metal ion reactants undergo a condensation reaction to form the metal cation containing organic polymer.](image)

**Figure 2.4:** Cartoon demonstrating the polymerization reactions of the Pechini citrate gel method. The citric acid, ethylene glycol and citric acid chelated metal ion reactants undergo a condensation reaction to form the metal cation containing organic polymer. Figure reproduced from Cushing et al.¹²

To perform Pechini fabrication, metal nitrate salts, Fe(NO₃)₃·9 H₂O, Al(NO₃)₃·9H₂O or Co(NO₃)₂·6H₂O (all >98% pure form Alpha Aesar), were dissolved in ethylene glycol (Fisher...
Scientific reagent grade) in a 1:60 molar ratio; subsequently citric acid (Citric Acid monohydrate from Fisher Scientific) was added to the ethylene glycol in a 1:4 citric acid:ethylene glycol ratio. The solution was heated to ~120°C, where upon the citric acid chelates the metal ions and the ethylene glycol polymerize the citric acid into a metal ion containing polymer solid. Excess ethylene glycol was evaporated off. After formation, this organic content of resulting solid was removed via combustion in an air filled furnace at 450 °C for 6 hrs and the resulting oxides were calcined in air at 850°C (the maximum furnace temperature) for 46 hrs.

**2.2 Method for experimental examination of STWS materials**

In investigating the solar thermal water splitting behavior and mechanism of hercynite based STWS H₂O and CO₂ splitting experiments, and materials analysis were conducted. These investigations utilized Stagnation Flow Reactors (SFR) gas splitting experiments, high temperature x-ray diffraction (HT-XRD) and scanning electron microscopy and energy dispersive x-ray spectroscopy. These apparatuses and procedures for these techniques are discussed below in the aforementioned order.

**2.2.1 Stagnation Flow reactor**

A stagnation flow reactor (SFR) was utilized to investigate solar thermal H₂O and CO₂ splitting reactions. Water splitting reactions, as described in Chapters 3 and 4 were carried out at the University of Colorado at Boulder (CU) using an in-house built reactor apparatus and LabView control program. CO₂ splitting reactions, as described in Chapter 5, were carried out at Sandia National Laboratory at Livermore (Sandia). The set-up between the two was similar, and therefore the CU reactor will be described in Sections 2.2.1.1 and 2.2.1.2 and the differences between the CU and Sandia reactors are described in 2.2.1.3.
2.2.1.1 SFR setup and description

All water splitting reactions were carried out in a stagnation flow reactor as shown in Figure 2.5: Schematic of the stagnation flow reactor (SFR) utilized to perform STWS. The dashed line separating the desiccant from the pump indicates an O\textsubscript{2} analyzer by-pass valve which remained closed during redox cycling. The stagnation flow reactor consists of three sections: 1) up-stream gas control, 2) reactor and 3) down-stream gas analysis. The up-stream gas control portion of the reactor set-up consists of gas flow regulators, an up-stream pressure controller, and a steam generator. The gas flow regulators are MKS-mass flow controllers which control the flow of inert and calibration gasses through the reactor system. The pressure controller serves as a safety pressure release system, pressure sensor and reactor by-pass for equilibrating steam flow before it is fed into the reactor. The mass flow and pressure controllers are controlled via an in-house build LabView program, which also recorded the actual flow rates and pressures.

Two separate steam generation systems were utilized. Initially steam was generated using a syringe pump and flash chamber. In this system, water was fed via a syringe pump through a superheated line into a super-heated chamber filled with ceramic beads causing the liquid water to flash vaporize. The ceramic beads served to increase heat transfer, increase the thermal mass of the chamber, and increase the surface area of any liquid water, facilitating vaporization. Generated steam was entrained in an inert sweep gas which entered the bottom of the flash chamber via a dip-tube and exited through the top of the chamber; this provided a counter current flow between the sweep gas and any remaining liquid water. The steam concentration was set by controlling the rate of water injection into the heated vessel. However, water droplets would form at the end of the line connecting the syringe to the steam generating vessel, which, when they dropped into the vessel, caused pressure spikes in the system. This resulted in uneven rates.
of steam delivery. Later a RASIRC RainMaker® steam delivery system was purchased to deliver a steadier stream of steam. The RainMaker® operates by feeding water into an inert stream through a non-pours membrane that rejects the passage of dissolved gasses. The steam concentration is continually monitored via a dew point sensor. The desired dew point can be programmed into the feeder system; the steam concentration is increased or decreased by automatically altering the temperatures of the internal water bath and membrane. The RainMaker® was found to provide a more even steam feed, and therefore was used for all experiments after it was purchased (i.e. the experiments reported in Chapter 3 and Section 4.3.5.1 of Chapter 4).

The actual SFR was composed of two alumina tubes configured to produce an annulus, where the outer tube is sealed at one end, as shown in Figure 2.5. The STWS material is placed in an inert boat which is seated at the bottom of the outer tube. The tubes were arranged such that the exit of the inner tube creates a stagnation zone over the surface of the reacting material minimizing the radial gas concentration gradient across the reactive material surface. The SFR was heated with an electric furnace which was controlled via the LabView program which also recorded the set points and actual temperature within the furnace.
Figure 2.5: Schematic of the stagnation flow reactor (SFR) utilized to perform STWS. The dashed line separating the desiccant from the pump indicates an O\textsubscript{2} analyzer by-pass valve which remained closed during redox cycling.

After exiting the reactor, the gas stream passed through a Drierite (anhydrous CaSO\textsubscript{4}) desiccant column to remove any unreacted steam. The removal of excess steam prevents the cleavage of water in the mass spectrometer which confuses the H\textsubscript{2} production signals and aids in accurate O\textsubscript{2} measurements. A portion of the reactant gas is directed to a mass spectrometer, while the majority is passed through the oxygen analyzer. The pressure in the system was monitored controlled via a downstream pressure controller operated by LabView. H\textsubscript{2} was measured using a Stanford Research QMS200 mass spectrometer with a capillary sampling port, while O\textsubscript{2} was measured using an Advanced Microsystem Instruments Inc. 2001-RS O\textsubscript{2} analyzer. The mass spectrometry data was recorded by a stand-alone program written by Stanford Research, while the O\textsubscript{2} analyzer data was recorded by LabView.
2.2.1.2 General operating procedures of the SFR

In SFR experiments, 0.1-0.2 g of material was loosely placed as thin layer in an aluminum boat which was situated in the SFR. The thin layer helps to prevent gas diffusion limitations into the particle bed. All temperatures were changed at a 15°/min ramp rate. In all experiments the total pressure was maintained at 760 Torr, though the flow rates and gas compositions varied depending on the exact experiment. The inert sweep gas used was UHP He from AirGas. For each experiment, verified content calibration gasses from AirGas were used to calibrate the mass spectrometers and O₂ sensors. For specific operating conditions such as gas flow rates, H₂O/CO₂ concentrations and reduction and oxidation temperatures, see the individual chapters.

2.2.1.3 Differences between the University of Colorado and Sandia National Laboratory SFR

The SFR at CU and Sandia differed only in a few respects. At Sandia, CO₂ was used as the oxidizing gas to eliminate the risk of condensation in system which is inherent to using H₂O. Additionally, the CO and O₂ production rates were measured by a differentially pumped, modulated effusive beam mass spectrometer (Extrell C50, 500 amu). Unreacted CO₂ was removed from the stream exiting the SFR reactor via a liquid nitrogen cooled cryotrap. Additionally, the sample was placed in a zirconia boat rather than an alumina one, as was done at CU. Exact details about the operating conditions can be found in Chapter 5.

2.2.2 High temperature XRD

High temperature x-ray diffraction (HT-XRD) experiments were used to determine the phases present during isothermal doped-hercynite CO₂ splitting and were carried out at Sandia National Laboratory, Albuquerque. CO₂ was employed as the oxidizing gas instead of H₂O to
prevent condensation within the HT-XRD. The XRD patterns were measured using a Scintag PAD X diffractometer (Thermo Electron Inc.; Waltham, MA). The X-rays were produced from a sealed Cu Kα, λ = 0.15406 nm source and were detected using a peltier-cooled Ge solid-state detector. The material was seated on a Buehler hot-stage with Pt/Rh heating strip and surround heater, and was contained in sealed chamber. The X-rays entered through an X-ray-transparent beryllium window. Oxygen was scrubbed from He entering the chamber via an oxygen getter (Centorr TM 1B). O₂ and H₂O were removed from entering CO₂ via an oxygen- and moisture-specific adsorbent purifier bed. An Omega fabricated pyrometer was used to determine the temperature of the sample during experimentation.

Samples of typically 20 – 30 mg material were analyzed as thin layers (ca. 50 – 100 µm) of powder on top of single-crystal <100> 9YSZ platelets (10mm x 10mm x 0.5mm, MTI Corporation). In situ HT-XRD experiments were conducted at atmospheric pressure, under gas flow rates of 150 sccm. Experiments typically involved purging the reaction chamber with He, then ramping the temperature to 1400°C and then held at 1400 °C for three reduction and oxidation cycles. The material was allowed to reduce under He for 50 min, and oxidized under CO₂ for 26 min. Each SRD scan lasted roughly 12 min; there was a 2 min pause between scans when the inlet gas was switched between He and CO₂, and only a few seconds pause between scans when there was no change in the inlet gas. Diffraction patterns were collected at 40 kV and 30 mA using fixed slits over a scan range of 20 – 80 °2θ at a step-size of 0.04 °2θ and a count time of 1 s.

2.2.3 Ion distribution analysis within hercynite material

In order to determine the distribution of ions within the bulk of STWS materials EDS mapping of Fe, Co and Al was conducted after surface material was removed. Focused ion beam
(FIB) milling removed surface layers of metal oxide to expose cross sections of bulk material. FIB milling was carried out using a dual beam FEI Nova 600 Nanolab dual beam imager and milling using a Ga beam for ablation. The milled samples were then Au coated to minimize sample charging. SEM/EDS analysis was conducted using a JEOL JSM-6480LV scanning electron microscope.

2.3 Computational methods

In addition to experimental approaches, DFT calculations were preformed to investigate TiO$_2$ photocatalytic behavior and STWS mechanist behavior.

2.3.1 Background on periodic boundary condition density functional theory

This section will give a brief introduction of DFT and periodic boundary condition (PBC) DFT. For a more complete analysis and development see Cramer, Szabo and Ostlund, Payne et al, or any other number of DFT introductory texts.

The wave function of a system describes the quantum state of that system. Therefore, the wave function of a molecule, surface or bulk material system can be used to determine the relative energies of different atomic configurations and states, which in turn can be used to determine reaction energies, reaction activation energies, spin and oxidation states of constituent atoms and groups, band gaps and electrical properties, and many other useful properties. In general, systems reside in their lowest energy state; therefore the lowest energy wave function of a system can be used to extract information of interest about that system. The Schrödinger equation extracts the energy of a system from its wave function; the time independent version of the Schrödinger equation is shown in Equation 5:

\[
\hat{H} \Psi(r) = E \Psi(r) \quad (5)
\]
where $\Psi$ is the wave function, $E$ is energy, $r$ is position, and $\hat{H}$ is the energy. According to the Born-Openheimer approximation, the wave function of the system can be written as:

$$\Psi = \Psi_{\text{neuc}} \Psi_{\text{elec}} \quad (6)$$

where $\Psi_{\text{neuc}}$ is the nuclear portion of the wave function and $\Psi_{\text{elec}}$ is the electronic portion of the wave function and can be expressed as the Slater determinant\textsuperscript{27} of the wave functions of individual electrons as shown below:

$$\Psi_{\text{elec}} = \left( \begin{array}{ccc}
\phi_{1,1} & \cdots & \phi_{1,n} \\
\vdots & \ddots & \vdots \\
\phi_{n,1} & \cdots & \phi_{n,n}
\end{array} \right) \quad (7)$$

where $\phi_{i,l}$ is the wave function of electron $i$ in orbital, or band $l$. In bulk and surface systems, which are periodic and therefore modeled using periodic boundary conditions, the wave function of individual bands can be described using a summation of plane waves\textsuperscript{15,28} as shown below:

$$\varphi_{i,l} = \sum G c_{i,k,G} e^{i(k + G \cdot r)} \quad (8)$$

where $c$ is the coefficient of electron $i$, at the $k$ $k$-point in reciprocal space, and $G$ is the reciprocal lattice vector of the periodic cell.

The Hamiltonian, $\hat{H}$, is expressed in Equation 9:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (9)$$

where the first term determined the kinetic energy of the system and $\hbar$ is the reduced Planck’s constant, $m$ is the mass of a particle and the second term determined the potential energy of the system and $V$ is the potential felt by a particle at $r$. For electrons, $V(r)$ is composed of electron-electron interactions, electron-nucleus interactions, and particle-external field interactions, which
will be neglected in the rest of this discussion. A similar set of interactions are present for nuclei

The particle-particle potential can be written as follows:

\[ V(r) = -\sum_{i=1}^{n} \sum_{A=1}^{m} \int \frac{Z_A}{r_{iA}} d\tau_i + \sum_{i=1}^{n} \sum_{j=1}^{n} \int \frac{1}{r_{ij}} d\tau_i d\tau_j + \sum_{A=1}^{m} \sum_{B=1}^{m} \frac{Z_A Z_B}{r_{AB}} \] (10)

where \( i \) and \( j \) are electron counters and \( n \) is the total number of electrons, \( A \) and \( B \) count over the nuclei and \( m \) is the total number of nuclei, \( Z_A \) is the nuclear charge of the \( A^{th} \) nucleus, and \( r_{iA}, r_{ij}, \) and \( r_{AB} \) are the electron-nucleus, electron-electron, and nucleus-nucleus distances between \( i \) and \( A \), \( i \) and \( j \), and \( A \) and \( B \) respectively.

However, it is difficult to determine the exact, lowest energy wave function of a system with more than two particles, i.e. electrons and nuclei, because each particle exerts a force on the other particle and they all responds accordingly. By using the Born-Oppenheimer approximation,\(^\text{29}\) which says that because nuclei are so much heavier than electrons the nuclear wave function can be separated from the electronic wave function, the wave function can be determined for a larger number of nuclear particles; however, the number of electrons is still limited. The Hartree-Fock (HF) method attempts to circumvent the problem of finding a multi-electron wave function by transforming a one, \( n \)-body problem into \( n \), one-body problems by employing the mean field approximation and solving for the wave function self consistently.\(^\text{30}\)

The mean field approximation states that the potential of one electron induced on another can be approximated using the mean electron density distribution of the electrons; therefore the electron-electron interaction energy term for electron \( i \) can be calculated using:

\[ V_{e-e} = \sum_{i}^{n} \int \frac{\alpha^2}{r_{ij}} \varphi_i^*(r_i) \varphi_i(r_i) \varphi_j^*(r_j) \varphi_j(r_j) d\tau_i d\tau_j \] (11)
The minimum energy wave function can be found by minimizing the expectation value of the energy for each orbital or band by changing the coefficients for the plane waves:

\[ \frac{d\varepsilon}{d\alpha_k} = \frac{d}{d\alpha_k} \left[ \frac{\langle \sum_i c_i \phi_i | \hat{H} | \sum_j c_j \phi_j \rangle}{\langle \sum_i c_i \phi_i | \sum_j c_j \phi_j \rangle} \right] = 0 \quad (12) \]

where \( \varepsilon \) is the expectation value of the energy. Equation 12 is iterated until a self-consistent solution is reached, i.e. the plane wave coefficients do not change significantly between one iteration and the next. However, as can be seen in Equation 11, calculating all of the electron-electron interactions over all space is computationally intensive due to the double integral and the large number of electrons in a system of even moderate size. This causes the computational costs of the HF method to scale, roughly, as the number of electrons to the fourth power.

Density functional theory, was developed in attempt to lower the computational cost scaling of the HF method by simplifying the manner for calculating the electron-electron integration term from one which requires a summation of double integrals over every pair of electrons to one which requires only one summation of a double integral over the number of electrons. This is accomplished by using the total electron probability density, shown in Equation 13, and using the mean field approximation between a single electron and the electron probability density of all electrons. Equation 14 shows in the Kohn-Sham equation for energy of electron i:

\[ n(r) = \sum_{i=1}^{\n} |\phi_i|^2 \quad (13) \]

\[ \phi^*_i \left( -\frac{\hbar^2}{2m} \right) \nabla^2 \phi_i - \sum_A \int \frac{eZ_A}{r_{iA}} n(r_i) \, dr_i + \frac{e^2}{2} \int \frac{n(r') n(r_i)}{|r_i - r'|} \, dr_i \, dr' + V_{xc}(n(r_i)) = \varepsilon_i \quad (14) \]
where $V_{xc}$ is the exchange and correlation functional, which calculates the electron exchange, electron correlation and corrects for the self-interaction energy which results from the third term of the Equation 14. The method by which $V_{xc}$ is calculated determines the flavor of DFT. $V_{xc}$ is generally calculated using the local density approximation (LDA), which utilizes the exchange energy of a free electron gas at a given density to determine the exchange energy at each point given its local electron density, the generalized gradient approximation (GGA), which utilizes local electron density and its gradient at each point to determine the exchange energy, or hybrid methods of GGA and the HF method. In GGA methods, the relationship between the local electron density and density gradient, and the local exchange energy is a fit set of parameters, where different GGA functionals are fit to different data sets.

In order to further decrease the computational cost of DFT calculations completed in this work utilized the Pseudopotential Approximation. The pseudopotential approximation enables the core electrons to be removed from the calculation while still maintaining computational accuracy. This is can be done because most properties of a material are determined by the valence electrons. However, it is important that the valence electrons in pseudopotential calculations behave like valence electrons of non-pseudopotential calculations. To do this, a radial potential is imposed within a cutoff radius such that the pseudo-wave function matches the true wave function outside of the cutoff radius; as is shown in Figure 2.6. The pseudopotential can be constructed to minimize the wave function nodes within the cutoff radius while matching the behavior of the true wave function as much as possible, which maintains accuracy while decreasing the number of plane waves required to model the system.
In addition to determining the wave function, DFT can be used to determine the nuclear coordinates of the atoms in the system. The forces on the nuclei are determined by differentiating the wave function with respect to the nuclear coordinates, and moving the ions accordingly. After each geometry step, the electronic wave function must be solved again. This is done repeatedly until the forces on the ions, or the change in ionic position approaches zero. The overall process for minimizing the electronic and nuclear geometric energies is shown in Figure 2.7.
2.3.2 Hubbard corrections

GGA functionals, while more accurate than LDA functionals, do not adequately describe the electron correlation in systems with highly correlated electrons such as transition metal oxides. This can result in over delocalization of d-orbital containing bands. A Hubbard correction attempts to improve electron correlation computational accuracy by imposing an energy penalty for electrons occupying the same orbital type on a given atom.\(^\text{32}\) This is referred to as the DFT+U method. In this work, a simplified rotationally invariant method of applying the Hubbard correction is used based on the work of Dudarev et al.\(^\text{33}\) In this implementation the Hubbard correction energy, which is shown in Equation 15 in its non-rotationally invariant form for simplicity, is included in the total energy of the system.

\[
E_{Hubb} = \frac{U_{eff}}{2} \sum_{\sigma} \left( \sum_{m} n_{m}^{\sigma} - \sum_{m} n_{m}^{\sigma^2} \right)
\]  

(15)
where $U_{\text{eff}}$ is the effective Hubbard parameter, $\sigma$ is the spin state (i.e. up or down), and $n$ is occupation number of the $m^{\text{th}}$ state of angular momentum manifold (i.e. s, p, d, etc. orbitals) to be corrected. The inclusion of this term penalizes the partial occupation of a given state and makes it more favorable for the occupation matrix of the angular momentum manifold to be idempotent, or close to idempotent (i.e. populated by eigenvalues of 1 or 0). Traditionally, the Hubbard correction is chosen by fitting a value to obtain a DFT+U calculated property of interest for a known condition, but can also be solved for from first principles.

2.3.3 VASP calculation set up and operation

Plane wave periodic boundary condition DFT simulations were performed using the Vienna Ab initio Simulation Program (VASP).\textsuperscript{34,35} Calculations employed the Perdew-Burke-\textsuperscript{-}Ernzerhof (PBE) generalized gradient approximation (GGA) exchange and correlation functional\textsuperscript{36} coupled with projector augmented wave (PAW) pseudopotentials.\textsuperscript{37} The calculations were performed using the PBE functional rather than the higher level modified Heyd-Scuseria-\textsuperscript{-}Ernzerhof (HSE06)\textsuperscript{38,39} hybrid functional due to its lower computational cost, which scale as $n^3$ rather than $n^4$, and the similar computational results of the DFT+U and HSE06 functionals as described in Chapter 7.

For all computational investigations, plane wave cut-off energy studies and k-point studied were conducted to determine the parameters required accurately model the system. These studies are conducted by incrementally increasing the cut-off energy or number of k-points for a given system then the reaction energy is computed for each of the conditions. The plane wave cut-off energy and number of k-points are determined to be the condition when there is only a very small difference in energy between one set of conditions and a set of more rigorous conditions, i.e. higher cut-off energies and more k-points. All calculations were completed with a
full fast Fourier transform (FFT) grid to ensure accurate transformations between real and reciprocal space.

All atomic configuration visualization were produced using VESTA.\textsuperscript{40}

2.3.4 Charge analysis

Bader charge analysis was utilized to determine the oxidation states of the atoms within the DFT calculations. In Bader analysis all of the electron density of the computation space is assign to one of the nuclei in the system by determining the volume of space surrounding each nucleus whose charge is most associated with that nucleus. The assigned volume is determined by identifying a minimum electron density surface which separates each nucleus from the others.\textsuperscript{24} This is depicted for a water molecule in Figure 2.8. Bader charge analysis was conducted using software from the Henkelman group.\textsuperscript{41,42}

![Figure 2.8: Example of the surface used for dividing the volume of the calculation space and assigning charge to the various nuclei for a H$_2$O molecule in Bader charge analysis. Reproduced from Henkelman et al.\textsuperscript{41}](image-url)
2.4 References


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Chapter 3: Understanding the mechanism of the doped-Hercynite cycle

3.0 Abstract

The doped hercynite solar thermal (STWS) water splitting cycle is of interest because it produces H₂ at the relatively low reduction temperature of 1200°C and does not form slag phases at STWS temperatures. However, the mechanism has not been rigorously determined. This work aims to determine if the hercynite STWS cycle operates through a displacement mechanism (reduction reaction: \( \text{CoFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 \rightarrow 3\text{Co}_{0.33}\text{Fe}_{0.66}\text{Al}_2\text{O}_4 + 1/2 \text{O}_2 \)) or O-vacancy mechanism (reduction reaction: \( \text{Co}_{0.33}\text{Fe}_{0.66}\text{Al}_2\text{O}_4 \rightarrow \text{Co}_{0.33}\text{Fe}_{0.66}\text{Al}_2\text{O}_{4-\delta} + \delta/2 \text{O}_2 \)) using a combination of computational and experimental approaches. Density functional theory (DFT) predicts that a pure displacement type mechanism has insufficient reducing power to split water, but O vacancies in hercynite have sufficient reducing power to split water. The relative H₂ production capacities of iron and cobalt aluminate spinels as predicted by DFT predicted are: \( \text{FeAl}_2\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4 \). High temperature X-ray diffraction experiments indicate that aluminate phases are present under both reducing and oxidizing conditions, but no \( \text{CoFe}_2\text{O}_4 \) was present, suggesting that the displacement mechanism was inactive and suggesting that O-vacancy mechanism was active. EDS of bulk material after hundreds of redox cycles indicates that there was no phase separation of the Fe, Co and Al ions between the reduced and oxidized states, further suggesting that the O-vacancy mechanism was active. Stagnation flow reactor experiments confirmed the DFT predicted relative H₂ production capacities of \( \text{FeAl}_2\text{O}_4 \), \( \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 \), and \( \text{CoAl}_2\text{O}_4 \), which formed an average of 99, 87 and 0 μmol of H₂/g over two STWS cycles. Based on these results, the doped-hercynite cycle operates via an O-vacancy mechanism.
3.1 Introduction

Two-step, metal oxide based solar thermal water splitting (STWS) cycles can broadly be
categorized as operating via one of three mechanisms: 1) volatile displacement chemistries, 2)
non-volatile displacement chemistries, and 3) O-vacancy formation chemistries, as discussed in
Chapter 1. In the first two categories of mechanisms, there is a phase change of the material
during the reduction and oxidation steps, where the newly forming phase displaces the original
phase, as is exemplified by the mixed metal ferrite cycle shown in Equations 1 and 2.\textsuperscript{1}

\begin{align*}
\text{CoFe}_2\text{O}_4(s) & \rightarrow \text{CoO}(s) + 2\text{FeO}(s) + \frac{1}{2} \text{O}_2 \quad (T_{\text{red}} \geq 1400^\circ\text{C}) \quad (1) \\
\text{CoO}(s) + 2\text{FeO}(s) + \text{H}_2\text{O} & \rightarrow \text{CoFe}_2\text{O}_4(s) + \text{H}_2 \quad (T_{\text{ox}} \ll 1400^\circ\text{C}) \quad (2)
\end{align*}

As their names suggest, the difference between the volatile and non-volatile displacement
chemistries is the form of the reduced produce, i.e. is the reaction product a gas (volatile
displacement mechanism) or a liquid or solid (non-volatile displacement mechanism). The O-
vacancy chemistry cycles operate via the formation of oxygen vacancies in host material during
reduction, which are subsequently filled during oxidation, and no phase change occurs. This is
exemplified by the ceria cycle,\textsuperscript{2} shown in Equations 3 and 4.

\begin{align*}
\text{CeO}_2 & \rightarrow \text{CeO}_{2-\delta} + \frac{\delta}{2} \text{O}_2 \quad (3) \\
\text{CeO}_{2-\delta} + \delta\text{H}_2\text{O} & \rightarrow \text{CeO}_2 + \delta\text{H}_2 \quad (4)
\end{align*}

Until 2013, ceria was the only seriously studied cycle which utilized the O-vacancy formation
mechanism.
In 2010, Scheffe et al reported on a new solar thermal water splitting cycled based on a mixture of CoFe$_2$O$_4$ and Al$_2$O$_3$ which was daubed the “Hercynite Cycle”$^3$ as it was reported to operate through the formation of Co doped hercynite (FeAl$_2$O$_4$), as shown in Equations 5 and 6.

\[
\text{CoFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 \rightarrow \text{CoAl}_2\text{O}_4 + 2\text{FeAl}_2\text{O}_4 + \frac{1}{2} \text{O}_2 \quad (T_{\text{red}} \geq 1200^\circ\text{C}) \quad (5)
\]

\[
\text{CoAl}_2\text{O}_4 + 2\text{FeAl}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{CoFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 + \text{H}_2 \quad (T_{\text{ox}} \ll 1200^\circ\text{C}) \quad (6)
\]

where $T_{\text{red}}$ and $T_{\text{ox}}$ are the reduction and oxidation temperatures respectively. This STWS cycle was highly promising as it had the lowest reduction temperature of any two-step metal oxide based STWS cycle reported at that time, undergoing STWS at reduction temperatures ~200°C lower than traditional ferrite cycles and 300°C lower than ceria and ZnO cycles. At the same time, the aluminate reduction products do not melt at temperatures under 1600°C, which meant that this cycle could operate over a wide range of reduction temperatures without the concerns of melting and sintering which plague other ferrite based cycles because of the proximity of their reduction and melting temperatures (<150°C).$^4$ However, while very promising, Scheffe et al did not fully investigate the reaction mechanism; rather they did a precursory investigation of the reduction step, using XRD to determine that after reduction a hercynite like material was formed from the initial mixture of CoFe$_2$O$_4$ and Al$_2$O$_3$; however they neglected to examine the products of the second, oxidation step.$^3$ Because of this finding, and the fact that traditional ferrite based cycles operate via a displacement chemistry mechanism, Scheffe et al suggested that the doped hercynite cycle operates via a non-volatile displacement mechanism.$^3$ This work will determine if the doped hercynite cycle truly operates through a displacement chemistry mechanism, or if the doped hercynite cycle operates through a different mechanism, such as the O-vacancy formation mechanism.
3.2 Methods

To determine the hercynite cycle mechanism, both computational and experimental methods were utilized. Computational methods calculated the energies of different potential reaction schemes while experimentation confirmed computational findings and investigated the long term behavior of the cycling material.

3.2.1 Computational methods

Plane wave periodic boundary condition DFT simulations were performed using the Vienna Ab initio Simulation Program (VASP).\textsuperscript{5,6} Calculations employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange and correlation functional\textsuperscript{7} coupled with projector augmented wave (PAW) pseudopotentials.\textsuperscript{8} PAW’s described the hydrogen 1s; oxygen 2s and 2p; cobalt and iron 4s and 3d; and aluminum 3s and 3p electrons explicitly. All calculations utilize a 500 eV cut off energy based on a cut-off energy study conducted in the range of 450 to 550 eV where a 500 eV cut off energy was determined to be sufficiently accurate, as demonstrated by the 0.29 kJ/mol difference for a CoAl\textsubscript{2}O\textsubscript{4} unit cell when using a 500 and 550 eV cutoff energy. Calculations were conducted using a Γ-point centered 2\times2\times2 Monkhorst-Pack k-point mesh. The effectiveness of this k-point mesh was confirmed by a k-point study that determined that there was only a 0.96 kJ/mol difference when using the 2\times2\times2 Monkhorst-Pack k-point mesh expansion and the more computationally expensive 4\times4\times4 mesh. Bader charge analysis was conducted using software from the Henkelman group.\textsuperscript{9,10} A Hubbard term\textsuperscript{11} of U\textsubscript{eff} = 289 and 193 kJ/mol on the Fe and Co d-electrons, respectively, was included in the calculations because the GGA functional alone does not adequately describe the electron correlation in these systems. The Hubbard correction attempts to describe electron correlation more accurately by imposing an energy penalty for electrons occupying the same orbital type on
a given atom. A Hubbard interaction of 289 and 193 kJ/mol was chosen for U_{eff} because it has been shown to accurately predict the formation energies of Fe and Co based spinels. The spinel super cell was composed of eight (2×2×2) primitive unit cells, as shown in Figure 3.1. For inverse spinels where there are multiple elements on the A site, a random distribution of ions was chosen. The relative energies of the inverse and normal configurations of the spinels considered in this work are shown in Table 3.1. Several spin configurations were attempted for each spinel, including ferromagnetic and multiple anti-ferromagnetic structures; the relative energies of the various spin configuration are shown in Table 3.1.

![Figure 3.1: Representations of a) normal and b) inverse spinel structures. The left cartoon shows the cubic cell representation while the right ball and stick model shows the 2x2x2 primitive unit cell used in this work.](image)
Table 3.1: Relative energies in, kJ/mol, of the spin states for inverse and normal aluminate and ferrite spinels investigated in this work.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Configuration</th>
<th>Co$_3$O$_4$</th>
<th>CoAl$_2$O$_4$</th>
<th>CoFe$_2$O$_4$</th>
<th>Fe$_3$O$_4$</th>
<th>FeAl$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inverse$^a$</td>
<td>All up$^c$</td>
<td>135</td>
<td><strong>0.0</strong></td>
<td>71</td>
<td>52</td>
<td><strong>0.0</strong></td>
</tr>
<tr>
<td></td>
<td>Alternating layers$^d$</td>
<td>57</td>
<td>0.7</td>
<td>19</td>
<td><strong>0.0</strong></td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Tetrahedral and octahedral$^e$</td>
<td>83</td>
<td>N/A</td>
<td><strong>0.0</strong></td>
<td>8</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Other$^f$</td>
<td><strong>0.0</strong></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Normal$^b$</td>
<td>All up$^c$</td>
<td>N/A</td>
<td>19</td>
<td>34</td>
<td><strong>0</strong></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Alternating layers$^d$</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Inversion energy$^g$</td>
<td>85</td>
<td>-14</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inversion parameter (x) at 1200 °C$^h$</td>
<td>0.02</td>
<td>0.85</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Energy difference, in kJ/mol, between spin configurations of the inverse spinel geometry.
$^b$Energy difference, in kJ/mol, between spin configurations of the normal spinel geometry.
$^c$All of the electrons for Co and Fe are initially set to be spin up.
$^d$Every other layer of Co and/or Fe atoms are initially set to alternate spin up and spin down.
$^e$All tetrahedral atoms are initially set to be spin up and all octahedral atoms are initially set spin down.
$^f$The tetrahedral Co are initially set to high spin states ($\mu=3$) and the octahedral Co’s are initially set to low spin states ($\mu=0.1$).
$^g$The energy difference, in kJ/mol, between the lowest energy inverse structure and normal structure. A positive number indicates that the normal structure is energetically preferred, while a negative number indicates that the inverse structure is preferred.
$^h$The inversion parameter was calculated using the method of Wei and Zhang.$^{13}$

Geometric relaxations were carried out using the Quasi-Newton-Raphson method converged to at least 0.1 kJ/mol. The supercell geometry and the internal positions of the atoms were allowed to relax when O-vacancies were created. Reaction energies were calculated using Equation 7 and Equation 8 for displacement reactions and O vacancy formation reactions, respectively.
\[ E_{rx_{disp}} = E_{prod} + n\mu_O - \sum_i E_{react,i} \quad (7) \]

\[ E_{rx_{O-vac}} = E_{vac\ cell} + \mu_O - E_{cell} \quad (8) \]

where \( E_{rx\ disp} \) is the reaction energy of displacement reaction, \( E_{prod} \) is the energy of product material, \( n \) is the number of \( O \) atoms released by the reaction, \( \mu_O \) is the chemical potential of a \( O \) atom and is taken to be the calculated energy of splitting water (i.e. \( \mu_O = \Delta H_{H2O}^{\exp} - E_{H2O}^{DFT} + E_{H2}^{DFT} \)), \( E_{react,i} \) is the energy of the \( i^{th} \) reacting metal oxide, \( E_{O-vac} \) is the \( O \)-vacancy formation energy, \( E_{vac\ cell} \) is the energy of the supper cell containing an \( O \) vacancy, and \( E_{cell} \) is the energy of the supper cell of the material without an \( O \) vacancy.

### 3.2.2 Materials fabrication

Hercynite was produced via atomic layer deposition (ALD) and the Pechini method.\(^{14}\) In ALD fabrication, layers of \( Al_2O_3 \) were deposited on a Cavilink\textsuperscript{TM} polymer support using trimethyl aluminum (Sigma Aldrich 97% pure) and in-house DI water. The polymer was removed and then \( CoFe_2O_4 \) was subsequently deposited on the alumina shell via ALD using cobaltocene (Strem Chemicals >98% metal purity), ferrocene (Strem Chemicals >99% metal purity) and \( O_2 \) (AirGas UHP) as precursors. Further details can be found in Chapter 2 and elsewhere.\(^{15,16}\) This method produced material with 19.8% \( CoFe_2O_4 \) and therefore was 47% active material, where active material is the percent of material which is capable of forming \( Co_{x}Fe_{1-x}Al_2O_4 \), as determined by inductively couple plasma atomic emissions spectrometry (ICP-AES). The ALD material was used in HT-XRD and SEM/EDS experiments.

Pechini fabrication was used to produce several different aluminate materials namely \( FeAl_2O_4 \) and \( (Co_{0.4}Fe_{0.6})_{1.2}Al_{1.8}O_4 \) for use in stagnation flow reactor experiments. \( CoAl_2O_4 \) was also used, but this material was commercially available and therefore purchased from Sigma.
Aldrich. In the Pechini method, metal nitrate salts, Fe(NO$_3$)$_3$·9 H$_2$O, Al(NO$_3$)$_3$·9H$_2$O or Co(NO$_3$)$_2$·6H$_2$O (all >98% pure form Alpha Aesar), were dissolved in ethylene glycol (Fisher Scientific reagent grade) in a 1:60 molar ratio; subsequently citric acid (Citric Acid monohydrate from Fisher Scientific) was added to the ethylene glycol in a 1:4 citric acid:ethylene glycol ratio. The solution was heated to ~120°C, whereupon it formed a metal ion containing polymer and solidified. The organic content of solid was burned out in an air filled furnace at 450 °C for 6 hours and the resulting oxides were calcined in air at 850°C (the maximum furnace temperature) for 46 hours.

### 3.2.3 Experimental methods

Three different experimental approaches were used to characterize the STWS mechanism of the hercynite materials: stagnation flow reactor experiments, high temperature XRD analysis and EDS analysis.

Stagnation flow reactor experiments were used to measure the H$_2$ production capacity of the doped-hercynite material and its components, namely CoAl$_2$O$_4$ and FeAl$_2$O$_4$. The doped and pure hercynite material was produced via the Pechini method and >99% purity CoAl$_2$O$_4$ was purchased from Sigma Aldrich. In these experiments, roughly 0.1 g of material was loosely placed as thin layers in an aluminum boat which was placed in an in-house built stagnation flow reactor. The stagnation flow reactor consists of two alumina tubes configured to produce an annulus where the exit of the inner tube creates a stagnation zone over the surface of the reacting material. The SFR was heated with an electric furnace, and is described in more detail in Chapter 2 and elsewhere. Reduction was carried out at 1350 °C, and a total pressure of 760 Torr; the generated O$_2$ was swept away by a 300 sccm flowrate of He. Oxidation was carried out at 1350°C with a 380 Torr H$_2$O partial pressure, with He making up the balance of the 760 Torr
total pressure. A 300 sccm total flow rate was used during material oxidation. Isothermal operation at 1350°C was chosen because 1350°C is less than the reduction temperature required for ferrite based STWS,\textsuperscript{3} and a high oxidation temperature mitigates kinetic limitations which might be present, as will be discussed in Chapter 4.

High temperature x-ray diffraction (HT-XRD) experiments of were used to determine the phases present during isothermal doped-hercynite CO\textsubscript{2} splitting. CO\textsubscript{2} was employed as the oxidizing gas instead of water to prevent condensation within the HT-XRD. The XRD patterns were measured using a Scintag PAD X diffractometer (Thermo Electron Inc.; Waltham, MA). The X-rays were produced from a sealed Cu K\alpha, \( \lambda = 0.15406 \) nm source and were detected using a peltier-cooled Ge solid-state detector. The material was seated on a Buehler hot-stage with Pt/Rh heating strip and surround heater, and was contained in sealed chamber. The X-rays entered through an X-ray-transparent beryllium window. Oxygen was scrubbed from He entering the chamber via an oxygen getter (Centorr TM 1B). O\textsubscript{2} and H\textsubscript{2}O were removed from entering CO\textsubscript{2} via an oxygen- and moisture-specific adsorbent purifier bed. An Omega fabricated pyrometer was used to determine the temperature of the sample during experimentation.

Samples of typically 20 – 30 mg material were analyzed as thin layers (ca. 50 – 100 \( \mu \)m) of powder on top of single-crystal <100> 9YSZ platelets (10 mm x 10 mm x 0.5 mm, MTI Corporation). In situ HT-XRD experiments were conducted at atmospheric pressure, under gas flow rates of 150 sccm. Experiments typically involved purging the reaction chamber with He, then ramping the temperature to 1400 °C; the chamber was held at 1400 °C for three reduction and oxidation cycles. The material was allowed to reduce under He for 50 min, and oxidized under CO\textsubscript{2} for 26 min. Each XRD scan lasted roughly 12 minutes; there was a 2 minute pause between scans when the inlet gas was switched between He and CO\textsubscript{2}; there were only a few
seconds pause between scans when there was no change in the inlet gas. Diffraction patterns were collected at 40 kV and 30 mA using fixed slits over a scan range of 20 – 80 °2θ at a step-size of 0.04 °2θ and a count time of 1 s.

ALD produced doped hercynite material which had been cycled over 200 times was studied to determine if separate spinel and alumina phases form or whether Fe, Co and Al segregate within a phase during material oxidation and reduction using SEM/EDS. Three samples were produced in the SFR then analyzed via SEM/EDS, a reduced sample, an air-oxidized sample and a CO$_2$ oxidized sample. To produce the reduced sample, hercynite material was heated to 1450°C and reduced under a 300 sccm He flow for four hours to allow the material to reach equilibrium; the material was subsequently cooled to room temperature under inert flow. The oxidized samples were produced by first reducing them, as described above, then oxidizing the reduced material for 4 hours at 1450 °C under an air or CO$_2$ atmosphere before the sample was cooled to room temperature under the same oxidizing environment. In order to determine the distribution of ions within the bulk of the material, surface metal oxide was removed via focused ion beam (FIB) milling to expose cross sections of bulk material. FIB milling was carried out using a dual beam FEI Nova 600 nanolab with a Ga beam for ablation. The milled samples were then Au coated to minimize sample charging. SEM/EDS analysis was conducted using a JEOL JSM-6480LV scanning electron microscope.

3.3 Results

Both the computational and experimental findings will be discussed in relation to the mechanism of doped hercynite cycle based STGS. First, the results of DFT calculations will be described, then the results from experimental work – namely SFR H$_2$ generation experiments,
high temperatures XRD analysis and finally EDS analysis of the materials in oxidized or reduced form, will be discussed.

### 3.3.1 Computed reduction and oxidation energies of possible hercynite cycle redox mechanisms

In STGS, the overall enthalpy (286 kJ/mol) and entropy (44.4 J/mol·K) changes of gas splitting must be met, as shown in Equations 9 and 10. Additionally, STGS only occurs if both the reduction and oxidation half reactions are spontaneous – i.e. have a negative Gibb’s free energy as shown in Equations 11-13.

\[
\Delta H_{cycle} = \Delta H_{TR} + \Delta H_{OX} \geq 286 \text{ kJ/mol} \quad (9)
\]

\[
\Delta S_{cycle} = \Delta S_{TR} + \Delta S_{OX} \geq 44.4 \text{ kJ/mol} \cdot K \quad (10)
\]

\[
\Delta G_{STGS} = \Delta H_{STGS} - T\Delta S_{STGS} < 0 \quad (11)
\]

\[
\Delta G_{TR} = \Delta H_{TR} - T\Delta S_{TR} < 0 \quad (12)
\]

\[
\Delta G_{OX} = \Delta H_{OX} - T\Delta S_{OX} < 0 \quad (13)
\]

where STWGS is the overall reaction, TR is the thermal reduction step and Ox is the H₂ or CO generating material oxidation step. From these equations, several general rules about the half reactions can be developed. Because the formation of H₂ or CO from H₂O or CO₂ is entropically unfavorable (\(\Delta S < 0\)) the material oxidation step must be exothermic (\(\Delta H < 0\)) to proceed if \(\Delta G_{OX}\) is to be negative, as shown in Equation 13. Since the enthalpies of both the reduction and oxidation steps must be greater than the enthalpy of the gas splitting (Equation 9), the reduction enthalpy must be 286 or 284 kJ/mol for H₂O and CO₂ splitting at STP respectively. Therefore, the validity of a possible reduction mechanism is assessable by comparing the reduction enthalpy
to the enthalpy of gas splitting – i.e. if the metal oxide reduction enthalpy is substantially less than the gas splitting enthalpy the suggested mechanism is unlikely to be the experimentally active mechanism. With these restrictions in mind, both displacement and O vacancy based hercynite cycle reaction mechanisms are assessed.

The reduction enthalpy of the hercynite displacement reaction, as shown in Equation 5, is 165 kJ/mol. This is also reported in Table 3.1. The relatively low reduction enthalpy of the displacement mechanism indicates that the hercynite cycle does not have the reducing power to split water (≥286 kJ/mol). Additionally, if the reaction forms a single mixed aluminate the reaction energy is even lower (156 kJ/mol). Therefore a different reaction mechanism must be suggested which is in agreement with the finding that the doped hercynite cycle is STWS active.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reduction Reaction</th>
<th>Reduction energy (kJ/mol)</th>
<th>Water splitting capable</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Displacement</strong></td>
<td>CoFe$_2$O$_4$ + 3Al$_2$O$_3$ $\rightarrow$ CoAl$_2$O$_4$ + 2FeAl$_2$O$_4$ + $\frac{1}{2}$ O$_2$</td>
<td>165</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>CoFe$_2$O$_4$ + 3Al$<em>2$O$<em>3$ $\rightarrow$ Co$</em>{0.33}$Fe$</em>{0.66}$Al$_2$O$_4$ + $\frac{1}{2}$ O$_2$</td>
<td>155</td>
<td>no</td>
</tr>
<tr>
<td><strong>O-vacancy</strong></td>
<td>Co$<em>{0.5}$Fe$</em>{0.5}$Al$<em>2$O$<em>4$ $\rightarrow$ Co$</em>{0.5}$Fe$</em>{0.5}$Al$_2$O$_4$ + $\frac{1}{2}$ O$_2$</td>
<td>One Fe 573</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two Fe 508</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Three Fe 450</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Four Fe 384</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>One Co 621</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two Co 515</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Three Co 436</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Four Co 403</td>
<td>yes</td>
</tr>
</tbody>
</table>

*number and type of non-Al ions neighboring the O to be removed; the total number of neighboring ions is four.

Table 3.2: Comparison of reduction energies of various possible hercynite cycle reaction mechanisms.
If the doped hercynite does not stop reducing after forming the aluminate $(\text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4)$ and forms O-vacancies within the aluminate matrix there is sufficient energy to split water as the O vacancy formation energy is endothermic by at least 384 kJ/mol, as shown in Table 3.2. This indicates that the doped hercynite cycle could operate via an O-vacancy mechanism.

O atoms in the spinel structure are tetrahedrally coordinated to three octahedrally coordinated B site atoms and one tetrahedrally coordinated A site atom. In normal spinels, such as FeAl$_2$O$_4$, CoAl$_2$O$_4$ and Co$_x$Fe$_{1-x}$Al$_2$O$_4$, aluminum atoms occupy the octahedral sites while Co and Fe occupy tetrahedral sites which means that each O atom is nominally coordinated to three Al and one Fe or Co atom. When an O is removed from a configuration where it is coordinated to just one Fe or Co atom the O vacancy formation energy is 508 and 515 kJ/mol. While these sites certainly have the reducing power to split water, the high O-vacancy formation energy suggests that the reduction is unlikely to occur to significant extents with these configurations at STWS temperatures.

At high STWS temperatures, the cations of normal spinels begin to disorder due to entropic driving forces and form structures which are partly normal and partly inverse.$^{19}$ At or near STWS temperatures FeAl$_2$O$_4$ and CoAl$_2$O$_4$ have inversion parameters of 15-20%$^{20}$ and $\sim$5%,$^{21}$ respectively, where the inversion parameter describes the percent of material which has a 2+ ions occupying octahedral sites and 3+ ions occupying both octahedral and tetrahedral sites, as shown in Figure 3.1. These experimental values are in good agreement with the computationally predicted values in Table 3.1 and other computationally determined values.$^{22}$ This suggests that there are likely atomic configurations in the material where an O$^{2-}$ anion neighbors more than one Co or Fe atom. Therefore Al atoms were exchanged for Co or Fe ions.
within the super cell to produced O$^{2-}$ sites that have two, three or four neighboring Co or Fe atoms; the O vacancy formation energy of these O$^{2-}$ sites were determined and are reported in Table 3.3. As the number of non-Al O$^{2-}$ neighbors increases, the O vacancy formation energy decreases because there are fewer Al atoms which are missing O-Al bonds and therefore take on an unfavorable oxidation state of less than +3, as shown in Table 3.3. Additionally, the charge transfer to any single atom decreases, in general, as number of Co and Fe neighbors increase, which lowers the O vacancy formation energy because the Co$^{2+}$ and Fe$^{2+}$ ions do not have to deviate as much from the stable 2+ oxidation state towards the less stable +1 oxidation state. Due to the lowered cost of O vacancy formation at sites with multiple Co or Fe atoms while still having sufficient energy to split water, it is likely that O sites with multiple Co and Fe neighbors are the STWS active sites in doped-hecynite.

The O-vacancy formation energy formation of FeAl$_2$O$_4$ and CoAl$_2$O$_4$ were also investigated to determine if doped hercynite material would operate if segregated phases formed rather than a mixed aluminate phase. The results are shown in Table 3.3. As was found for the doped hercynite material, the O vacancy formation energy was lowest when the O$^{2-}$ ion to be removed neighbored multiple Fe and Co atoms. In general the O-vacancy formation energies of the various spinels were similar at a given number of non-Al nearest neighbors, as shown in Figure 3.2. This would indicate that the doped-hercynite, FeAl$_2$O$_4$ and CoAl$_2$O$_4$ would undergo STWS with relative H$_2$ production capacities and O vacancy formation propensities of: FeAl$_2$O$_4$ > CoAl$_2$O$_4$ ≥ Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$. Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ is predicted here to produce slightly less than H$_2$ than CoAl$_2$O$_4$ using solely the O-vacancy formation energy because O –vacancy formation energy for CoAl$_2$O$_4$ is only 5 kJ/mol higher than Fe neighboring O-vacancy which is within the
estimated DFT accuracy of ~8-12 kJ/mol and there are only half the number of these sites due to the presence of Co ions, which have an O-vacancy formation 14 kJ/mol higher than CoAl₂O₄.

Table 3.3: The effect of the number of non-Al O nearest neighbors on O vacancy formation in spinel aluminates.

<table>
<thead>
<tr>
<th>Spinel Stoichiometry</th>
<th>Type and number of neighboring Fe or Co cations</th>
<th>Relative energy of structure (kJ/mol)</th>
<th>Reduction energy (kJ/mol)</th>
<th>Average change in oxidation after O vacancy formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One Fe</td>
<td>-</td>
<td>573</td>
<td>1.08 0.13 -</td>
</tr>
<tr>
<td></td>
<td>Two Fe</td>
<td>43</td>
<td>508</td>
<td>0.64 0.17 0.46</td>
</tr>
<tr>
<td></td>
<td>Three Fe</td>
<td>75</td>
<td>450</td>
<td>0.49 0.00 0.50</td>
</tr>
<tr>
<td>Co₀.₅Fe₀.₅Al₂O₄</td>
<td>Four Fe</td>
<td>153</td>
<td>384</td>
<td>0.50 - 0.30</td>
</tr>
<tr>
<td></td>
<td>One Co</td>
<td>-</td>
<td>621</td>
<td>0.77 0.11 -</td>
</tr>
<tr>
<td></td>
<td>Two Co</td>
<td>39</td>
<td>515</td>
<td>0.58 0.12 0.49</td>
</tr>
<tr>
<td></td>
<td>Three Co</td>
<td>82</td>
<td>436</td>
<td>0.34 0.00 0.49</td>
</tr>
<tr>
<td></td>
<td>Four Co</td>
<td>135</td>
<td>403</td>
<td>0.37 - 0.26</td>
</tr>
<tr>
<td>FeAl₂O₄</td>
<td>One Fe</td>
<td>-</td>
<td>515</td>
<td>0.85 0.20 -</td>
</tr>
<tr>
<td></td>
<td>Two Fe</td>
<td>-15</td>
<td>518</td>
<td>0.65 0.21 0.38</td>
</tr>
<tr>
<td></td>
<td>Three Fe</td>
<td>66</td>
<td>457</td>
<td>0.54 0.00 0.44</td>
</tr>
<tr>
<td></td>
<td>Four Fe</td>
<td>148</td>
<td>366</td>
<td>0.48 - 0.32</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>One Co</td>
<td>-</td>
<td>578</td>
<td>0.80 0.18 -</td>
</tr>
<tr>
<td></td>
<td>Two Co</td>
<td>64</td>
<td>521</td>
<td>0.54 0.00 0.78</td>
</tr>
<tr>
<td></td>
<td>Three Co</td>
<td>169</td>
<td>443</td>
<td>0.57 0.13 0.30</td>
</tr>
<tr>
<td></td>
<td>Four Co</td>
<td>270</td>
<td>389</td>
<td>0.42 - 0.31</td>
</tr>
</tbody>
</table>

However the energy to exchange an Al atom for Co or Fe atom is not even across the spinels. It is more energetically favorable to form a site where O neighbors four non-Al atoms in FeAl₂O₄ and Co₀.₅Fe₀.₅Al₂O₄ than it is to form a site where O neighbors four Co atoms in CoAl₂O₄ by roughly 120 kJ/mol, as shown in Table 3.3. Therefore the DFT calculations suggest that the aluminates investigated here have the following relative O vacancy and H₂ formation capacities: FeAl₂O₄ > Co₀.₅Fe₀.₅Al₂O₄ > CoAl₂O₄.
Figure 3.2: Calculated O-vacancy formation energy at sites with varying non-Al nearest neighbors. The aluminates are depicted, from left to right: Fe in $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4$, Co in $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4$, FeAl$_2$O$_4$, CoAl$_2$O$_4$.

3.3.2 Analysis of the phases present during doped-hercynite STWS

ALD produced Hercynite material was isothermally cycled in a HT-XRD under He or CO$_2$ atmospheres to determine what phases are present during reduction and oxidation. During cycling the characteristic peaks of an aluminate spinel and alumina are present in both the reduction and oxidation steps, as shown in Figure 3.3. The spinel peaks are aligned with the expected peaks for CoAl$_2$O$_4$ and FeAl$_2$O$_4$. The small 2θ shift between these spinels, and the breadth of the XRD signal make it difficult to determine if a single mixed $\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4$ phase, separate CoAl$_2$O$_4$ and FeAl$_2$O$_4$ phases or only one of these phases are present, however, based on DFT results it is likely that a mixed phase exists. As Figure 3.3 shows, the aluminate peak is present under both reducing and oxidizing conditions, meaning that the Co$_x$Fe$_{1-x}$Al$_2$O$_4$ phase does not form then decompose as the material is cycled. The peaks do, however, shift as the material is cycled. The peak shift indicates that the material contracts during reduction and expands during oxidation, with a measured d-spacing change of roughly 0.005 Å, as shown in
Figure 3.4. This is in accordance with the theory that O vacancies form during reduction and are filled during oxidation. It is interesting to note that the intensity of the Al₂O₃ peak in the hercynite material does not change significantly over the course of cycling, indicating that there is not a significant change in the quantity of Al₂O₃ present during cycling. The intensity and breadth of the hercynite peaks do change during cycling, where the main aluminate peak (2θ ~ 36) intensifies and narrows as it reduces. The lack of aluminate formation and disappearance, and lack of the presence of CoFe₂O₄, suggests that the doped hercynite cycle does not operate via the displacement mechanism as originally proposed, but operates via an O-vacancy mechanism instead.

Figure 3.3: Top: HT-XRD of hercynite materials as they undergo CO₂ splitting cycling. The middle and bottom panels show, respectively, the XRD patterns of Al₂O₃ and various spinels.
3.3.3 Investigation of phase segregation during doped-hercynite STWS

To determine if there is a segregation of Co and Fe from Al after reduction or oxidation, as would be present if the displacement pathway controlled STGS, SEM/EDS analysis was conducted on reduced and oxidized samples. The determination of the internal cation distribution was accomplished by FIB milling, which produced flat cross sections of the internal structure, as shown in SEM images of Figure 3.5a. For the reduced and two oxidized materials there is no significant segregation of the cations as can be seen in Figure 3.5b-e. This suggests that after > 200 cycles the materials are well mixed and there is little segregation. Additionally, because the ion distribution of Co, Fe and Al remain consistent after reduction and oxidation it is unlikely that there is a major phase change between oxidation and reduction steps.
Figure 3.5: SEM and EDS images of bulk hercynite material exposed by FIB milling after the material is reduced, oxidized in CO₂ and oxidized in air. The rows show: a) SEM image of the bulk material, b) Fe ion EDS mapping, c) Co ion EDS mapping, d) Al ion EDS mapping and e) an overlay of the EDS ion maps and SEM image. In e) red, green and blue dots represent Fe, Co and Al EDS signals.
3.3.4 H₂ generation of doped-hercynite and its constituent aluminates

The H₂ production capacity of CoAl₂O₄, FeAl₂O₄ and Co₀.₄Fe₀.₆Al₂O₄ was determined using the SFR. Cycling was operated isothermally at 1350°C and the results are shown in Figure 3.6. CoAl₂O₄ did not reduce and generate O₂ during any reduction step, nor did it produce H₂ during oxidation steps. FeAl₂O₄ underwent significant reduction in the first reduction step, producing 517 µmol of O₂/g of FeAl₂O₄. This could indicate that the material had not fully formed the FeAl₂O₄ phase as the calcination only occurred at 850°C, which is 500°C less than the reduction temperature, and the large O₂ generation is from the formation of FeAl₂O₄ from separate Fe₂O₃ and Al₂O₃ phases. After the initial reduction step, the next two reduction steps produced 38.2 and 54.6 µmol of O₂/g of FeAl₂O₄ the three oxidation steps produced 12, 81.8 and 117.1 µmol of H₂/g of FeAl₂O₄ resulting in H₂/O₂ ratios for the last two cycles of 2.1. The small difference from the ideal H₂:O₂ ratio of 2 could result from the incomplete phase formation or establishment of the final structure after just three cycles. The hercynite had peak H₂ production rates of 0.197 and 0.253 µmol of H₂/s·g of FeAl₂O₄ for the last two cycles.

A similar initially high O₂ release is seen in the cycling of Co₀.₄Fe₀.₆Al₂O₄, though to a lesser extent that for FeAl₂O₄. The doped hercynite material produced 373, 49.6 and 54.8 µmol of O₂/g of Co₀.₄Fe₀.₆Al₂O₄ and 63.6, 89.3 and 84.8 µmol of H₂/g in three cycles. The H₂/O₂ ratios for the doped hercynite material was 0.17, 1.80 and 1.55 for the three cycles examine here. The deviation of the H₂:O₂ from the formal ratio of 2 could be attributed to the incomplete formation of the aluminate phase. In the case of the doped hercynite, the initial reduction step produced significantly less O₂ (373 µmol of O₂/g) than the undoped hercynite (517 µmol of O₂/g) which could indicate that after the one hour under the reducing conditions the initial phases did not convert to doped hercynite as fully as the undoped hercynite. The peak rate of H₂ generation for
doped Co$_{0.4}$Fe$_{0.6}$Al$_2$O$_4$ was faster than FeAl$_2$O$_4$ being 0.27, 0.36, and 0.34 µmol of H$_2$/s·g of Co$_{0.4}$Fe$_{0.6}$Al$_2$O$_4$.

![Figure 3.6](image)

**Figure 3.6:** H$_2$ and O$_2$ production based on Fe, and Co aluminates cycled isothermally at 1350 °C: a) CoAl$_2$O$_4$, b) FeAl$_2$O$_4$ and c) Co$_{0.4}$Fe$_{0.6}$Al$_2$O$_4$ produced via the citrate gel method.

The lower H$_2$ production capacity of the doped hercynite as compared to undoped hercynite could be attributed to several factors. The dope hercynite used in the experiment was
slightly Al poor having a formula of \((\text{Co}_{0.4}\text{Fe}_{0.6})_{1.2}\text{Al}_{1.8}\text{O}_4\). This results in the material being only 90.5% active. Additionally, as discussed in Section 3.3.1, undoped hercynite is predicted to form more O-vacancy active sites (i.e. sites where an O atom is bonded to four Fe or Co atoms) than doped hercynite because they have a lower energy of formation (148 kJ/mol vs 153 kJ/mol) and undoped hercynite has a lower O-vacancy formation energy at these sites (366 kJ/mol vs 384 kJ/mol). This means that there are more sites available to form O vacancies in undoped hercynite and therefore undergo reduction, leading to a higher \(\text{H}_2\) production capacity. Lastly the higher \(\text{H}_2\) production capacity of undoped hercynite could stem from incomplete phase formation and phase ripening. Overall, these experimental findings show that the doped and undoped hercynite material is capable of undergoing STWS while CoAl\(_2\text{O}_4\) is not. This is consistent with the DFT findings that doped-hercynite operates via an O-vacancy STWS mechanism. From these experiments it is unclear if doped or undoped hercynite is a better STWS material because the faster oxidation rate of doped hercynite might result in more efficient \(\text{H}_2\) generation than the slightly higher production capacity of un-doped hercynite.

### 3.4 Conclusions

This work investigated the mechanism of the doped-hercynite solar thermal water splitting cycle. Thermodynamic analysis suggests that the endothermic reduction step requires a reaction energy of at least 286 kJ/mol if water is to be split. DFT calculations show that a displacement reaction mechanism has insufficient reducing power to split water, but O-vacancies formed in the doped-hercynite aluminate have sufficient energy to split water. DFT predicts that the aluminates investigated in this work have relative \(\text{H}_2\) production capacities of \(\text{FeAl}_2\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4\). SFR water splitting reactions confirmed DFT predicted relative \(\text{H}_2\) production capacities of \(\text{FeAl}_2\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4\), indicating that the DFT models
were good predictors of the experimental behavior. HT-XRD analysis shows that no CoFe$_2$O$_4$ was present in the oxidized state; rather a mixed Co$_x$Fe$_{1-x}$Al$_2$O$_4$ phase is present during reduction and oxidation further suggesting that a displacement reaction does not occur. Co$_x$Fe$_{1-x}$Al$_2$O$_4$ expansion and contraction during oxidation and reduction, respectively, suggests that vacancies are forming in the spinel material, lending credence to the DFT results. EDS mapping shows that the Co, Fe and Al ions are well mixed after both reduction and oxidation, further confirming that an aluminate phase does not form and decompose during reduction and oxidation. Overall this work shows that the hercynite cycle operates via an O-vacancy mechanism rather than the displacement reaction initially proposed.

3.5 References


Chapter 4: Efficient Generation of H\textsubscript{2} by Splitting Water with an Isothermal Redox Cycle

4.0 Abstract

Solar thermal water splitting (STWS) cycles have long been recognized as a desirable means of generating sustainable H\textsubscript{2} from water and sunlight. Two-step, metal oxide based STWS cycles generate H\textsubscript{2} by sequential high temperature reduction and water re-oxidation of a metal oxide. The temperature swings between reduction and oxidation steps long thought necessary for STWS have stifled STWS’s overall efficiency because of thermal and time losses that occur during the frequent heating and cooling of the metal oxide. This chapter will show that these temperature swings are unnecessary, and that isothermal water splitting (ITWS) at 1350°C using the “hercynite cycle” exhibits H\textsubscript{2} production capacity >3 and >12 times that of hercynite and ceria, respectively, per mass of active material when reduced at 1350°C and re-oxidized at 1000°C.

4.1 Introduction

As described in Chapter 1 and 3, two-step thermochemical H\textsubscript{2}O splitting based on metal oxide reduction/oxidation (redox) cycles are an attractive option for the production of H\textsubscript{2} at the technically feasible reduction temperatures of 1200° to 1500°C.\textsuperscript{1,2} In traditional two-step temperature swing water splitting (TSWS), O\textsubscript{2} is generated by the reduction of a metal oxide during a high temperature step according to Reaction 1.

\[
\text{MO}_x \rightarrow \text{MO}_{x-\delta} + \frac{\delta}{2} \text{O}_2 \quad \text{T}_{\text{red}} \sim 1200 - 1500 \degree \text{C} \quad (1)
\]
The second step involves lowering the temperature and exposing the reduced metal oxide to water, which reoxidizes the metal oxide and produces H₂ according to Reaction 2:

\[
\text{MO}_{x-\delta} + \delta \text{H}_2\text{O} \rightarrow \delta \text{H}_2 + \text{MO}_x \quad T_{\text{ox}} < T_{\text{red}} \quad (2)
\]

Traditional thermodynamic analysis treats the process as a closed system and suggests that a substantial temperature difference between the oxidation and reduction steps is necessary to split water \(^1,3-5\). However, large temperature swings between the reduction and oxidation steps cause thermodynamic inefficiencies from the irreversible heat losses incurred upon cooling of the active material to the oxidation temperature and the heat required to solely reheat the active material to its reduction temperature. Additionally, thermal stresses arising from the rapid thermal cycling of the system over large temperature differences present engineering and materials challenges in the design of high-temperature redox systems. However, contrary to widely accepted redox gas splitting theory,\(^3\) this chapter will demonstrate that a change in temperature between reduction and oxidation steps is unnecessary, and that isothermal water splitting (ITWS) driven by swings in steam partial pressure not only produces H₂, but outperforms traditional TSWS and provides an opportunity for expanding renewable H₂ generation. This will be examined via temperature-swing and isothermal water splitting using the doped hercynite cycle, as shown in Equations 3 and 4.

\[
\text{CoFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 + \text{heat} \rightarrow 3\text{Co}_{1/3}\text{Fe}_{2/3}\text{Al}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Co}_{1/3}\text{Fe}_{2/3}\text{Al}_2\text{O}_{4-\delta} + \delta/2\text{O}_2 \quad (3)
\]

\[
3\text{Co}_{1/3}\text{Fe}_{2/3}\text{Al}_2\text{O}_{4-\delta} + \delta \text{H}_2\text{O} \rightarrow 3\text{Co}_{1/3}\text{Fe}_{2/3}\text{Al}_2\text{O}_4 + \delta \text{H}_2 \quad (4)
\]
4.2 Experimental Methods

The “hercynite cycle” active material particles were fabricated using atomic layer deposition (ALD) in a fluidized bed reactor by the sequential deposition of CoO and Fe₂O₃ in a 1:2 ratio on Al₂O₃ skeletal supports to produce the desired CoFe₂O₄ stoichiometry on Al₂O₃. CoO and Fe₂O₃ layers were deposited by ALD using cobaltocene and ferrocene (99% purity, form Alfa Aesar®) and O₂. The material is composed of 19.8 wt% CoFe₂O₄ which corresponds to particles with 47 wt% active materials (CoFe₂O₄ + 3 Al₂O₃). Al₂O₃ skeletal supports were fabricated by the ALD of a 15 nm Al₂O₃ film using trimethyl-aluminum and water on high surface area, highly porous polymer particles (Cavilink™) also in a fluidized bed reactor. The particles used in this study underwent aging by performing over 150 reduction/oxidation water splitting cycles prior to their use in this study to ensure that no active material degradation would occur and to simulate long term behavior of the “hercynite cycle” active particles. These particles were used in the TSWS and ITWS experiments.

The same ALD method was used to produce 86% by mass active material; however, the polymer template used was not Cavilink™ but rather a styrene-divinyl benzene copolymer from DOW®, because Cavilink™ product line was discontinued. The styrene-divynal benzene copolymer particles were functionalized by boiling them in H₂SO₄ for at least four hours to functionalize the surface. The surface functionalization was required so that the ALD precursors would have a surface groups with which to react. Inductively coupled plasma atomic emissions spectroscopy was utilized to determine that the final particle composition was [Co₁.1₂Fe₁.8₈O₄][Al₂O₃]₃.₈₉. These particles were used in the near ITWS (NITWS) experiments.

ALD was chosen to produce the “hercynite” cycle materials in order to ensure intimate contact between Al₂O₃ and CoFe₂O₄ while maintaining high porosity and surface area.
Traditionally, for the coating of low surface area substrates, ALD is seen as an expensive production technique that “wastes” a significant fraction of the valuable precursors used to deposit films. However, the use of ALD on particles, as carried out in this work, is efficient as a fluidized bed configuration results in the use of nearly all of the organo-metallic precursor dosed into the ALD reactor. Additionally, while ALD was used to produce the materials for the study reported here, it is not necessary to produce “hercynite cycle” active materials. Depending on the reactor design, desired mechanical properties of the materials, etc., less expensive, simpler fabrication techniques (e.g. spray drying of bulk Fe$_2$O$_3$, CoO, and Al$_2$O$_3$ that are first blended/milled together in the desired stoichiometry, etc.) could be used to produce “hercynite cycle” materials capable of redox.

![Figure 4.1: Schematic of the stagnation flow reactor (SFR) utilized to carry out both ITWS and TSWS. The dashed line separating the desiccant from the pump indicates an O$_2$ analyzer by-pass valve which remained closed during redox cycling.](image)

All water splitting reactions were carried out in a stagnation flow reactor as shown in Figure 4.1. During water splitting cycles, ~0.1 g of the “hercynite cycle” active material was placed in a ZrO$_2$ crucible and situated in the stagnation zone of the stagnation flow reactor. For the O$_2$ generation step, the electric furnace was heated to the desired temperature and the active
material was allowed to reduce for one hour. In ITWS and TWSW the generated \( \text{O}_2 \) was swept from the reactor by a 100 sccm flow of He. For TSWS, the sample was cooled to the oxidation temperature before 100 sccm of steam entrained in 100 sccm He was introduced into the reactor for 25 minutes.

The sample temperature was then raised for the subsequent reduction step. In ITWS, the desired amount of steam entrained in 100 sccm He was injected into the system for 25 minutes without any temperature change; after 25 minutes, a one minute \( \text{H}_2\text{O} \) sweep was carried out by flowing 200 sccm of He through the system to remove any remaining \( \text{H}_2\text{O} \) before the 100 sccm He sweep flow rate was resumed for the reduction step. All temperatures were changed using a 15 \(^\circ\text{C}/\text{min} \) ramp rate. The pressure in the system was maintained at 101.3 kPa.

A similar set of operating conditions were used for NITWS experiments with only a few minor changes. The total flow rate of He (reduction) or He and \( \text{H}_2\text{O} \) (oxidation) was maintained at 300 sccm and the oxidation time was reduced to 15 minutes as the oxidation reaction rates are faster than under TSWS conditions. For these reactions, the cycle was operated under the exact same conditions twice, once with active material and once without active material, generating a blank run. The \( \text{H}_2 \) and \( \text{O}_2 \) production curves were generated by subtracting the blank curves from the material generated curves. In calculating the quantity of gasses produced, baseline shifts were taken into account and removed from the total.

\( \text{O}_2 \) and \( \text{H}_2 \) were measured using an AMI (Advanced Microsystem Instruments Inc.) 2001-RS \( \text{O}_2 \) analyzer and Stanford Research QMS200 mass spectrometer with a capillary sampling port, respectively, after the carrier gas was passed through a Drierite desiccant column to remove any remaining steam. The removal of excess steam prevents the cleavage of water in
the mass spectrometer and accurate O\textsubscript{2} measurements. All H\textsubscript{2} production capacities and rates are referenced to total material (active and inactive). Multiple water splitting cycles were carried out at each operating condition from which H\textsubscript{2} and O\textsubscript{2} production rates and capacities were calculated. Error bars were determined using Student’s t-test and are determined at a 95% confidence interval.

4.3 Results and Discussion

Temperature swing water splitting operating at 1350/1000°C produced 31.4 ± 2.3 µmol of H\textsubscript{2} per gram of total material (see Table 4.1). The extent of reduction and water splitting capacity depends on the reduction temperature. Higher temperatures lead to a larger fraction of reduced Fe\textsuperscript{2+} ions. The number of available Fe\textsuperscript{2+} ions dictates the total H\textsubscript{2} generating capacity of the active material with a maximum ratio of one H\textsubscript{2} molecule produced to every two Fe\textsuperscript{2+} cations. Oxidation at 1000°C was characterized by a slow rate of reaction (a peak H\textsubscript{2} generation rate of 0.06±0.04 µmol/g/s) and is likely surface-reaction limited.\textsuperscript{7} Because the oxidation reaction is slow, it is unlikely that most of the Fe\textsuperscript{2+} ions are re-oxidized to Fe\textsuperscript{3+} during the 25 min, which limits the total H\textsubscript{2} production capacity of the 1350/1000°C TSWS cycle. Higher TSWS reduction and oxidation temperatures result in increased H\textsubscript{2} and O\textsubscript{2} production capacity and water splitting rates. Active material cycled between 1500 and 1200°C produced 93.7 ± 19.2 µmol of H\textsubscript{2}/g with a peak rate of 0.32 µmol H\textsubscript{2}/g·s (see Table 4.1). The higher reduction temperature resulted in more complete reduction of the active material and a larger thermodynamic driving force for H\textsubscript{2}O splitting. The higher rates of H\textsubscript{2} generation at 1500/1200°C resulted from two factors: 1) the intrinsically higher reaction rates which arise from carrying out a kinetically limited process at a higher temperature and 2) the larger thermodynamic driving force for oxidation which comes from the larger extent of reduction. The
ability to perform water oxidation at temperatures above the onset of reduction suggests that isothermal water splitting is possible and that the current understanding of the thermodynamics of STWS is incomplete.

Table 4.1: A comparison of the H₂ production capacities and peak H₂ production rates of solar thermal water splitting cycles operating under both temperature swing and isothermal conditions.

<table>
<thead>
<tr>
<th>Operating temperature conditions (Red/Ox in °C)</th>
<th>Total H₂ generated (µmol/g)</th>
<th>Peak H₂ generation rate (µmol/g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hercynite 1350/1000</td>
<td>31.4 ± 2.3</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>Hercynite 1500/1200</td>
<td>93.7 ± 19.2</td>
<td>0.32 ± 0.01</td>
</tr>
<tr>
<td>Hercynite 1350/1350</td>
<td>102 ± 18</td>
<td>0.55 ± 0.16</td>
</tr>
<tr>
<td>Ceria 1350/1000</td>
<td>16.4 ± 3.6</td>
<td>0.14 ± 0.04</td>
</tr>
</tbody>
</table>

4.3.1 Isothermal water splitting

Hercynite materials split water in a two-step isothermal redox cycle as exemplified by the 1350°C ITWS results shown in Figure 4.2 and Table 4.1. H₂ generation under ITWS conditions was achieved at a temperature above the minimum reduction temperature by first flowing an inert gas through the reactor to sweep away O₂ generated during the reduction step and subsequently injecting steam during the oxidation step to produce H₂. For 1350°C ITWS, the active particles produced 45.1±7.6 µmol O₂/g during 1 hour of reduction and 102±18 µmol H₂/g during a 25 min exposure to 50 vol% steam in He. During reduction, the initial O₂ plateaus arise from incomplete H₂O removal from the system. Once all steam is swept from the reactor, the O₂ peak occurs as the materials reduce followed by the normal exponential decay as the reaction
goes to completion. ITWS at 1350°C produces substantially more O₂ and H₂ than 1350/1000°C TSWS and slightly more O₂ and H₂ than 1500/1200°C TSWS. The slight deviation of the 2.26:1 H₂ to O₂ ratio from the expected 2:1 ratio, though within the error, likely arises from slight differences in the sensitivities and response times of the mass spectrometer used for measuring H₂, and the O₂ analyzer. The higher gas splitting production capacity of ITWS was accompanied by a higher H₂ production rate of 0.55±0.16 µmol H₂ per gram/s.

![Graph showing gas production rates over time](image)

**Figure 4.2:** Isothermal water splitting at 1350°C. The H₂ and O₂ generation rates are shown in red and blue respectively.

### 4.3.2 Developing a thermodynamic model of isothermal water splitting

The ability for a material to undergo ITWS is excluded by the traditional thermodynamic STWS analysis. Traditional TSWS thermodynamic theory uses a closed-system model in which an oxidation temperature lower than the reduction temperature raises the chemical potential of the oxidizing gas and reduced metal oxide above that of the product gases and oxidized material.
in order to drive the oxidation reaction. Therefore, the following Equations dictate the spontaneity of reduction (5) and oxidation (6) reactions:

\[ \Delta G_{TR,TR} = \Delta H_{\text{red}} - T_{TR} \left( \Delta S_{\text{red}} + \frac{1}{2} S_{O_2}^{T_{TR}} \right) \leq 0 \quad (5) \]

\[ \Delta G_{WS,WS} = -\Delta H_{\text{red}} - \Delta H_{f,WS}^{H_2O} - T_{WS} \left( -\Delta S_{\text{red}} + S_{H_2}^{T_{WS}} - S_{H_2O}^{T_{WS}} \right) \leq 0 \quad (6) \]

where \( G \) is the Gibb’s free energy of either thermal reduction (TR) or water splitting (WS). \( H_{\text{red}} \) is the enthalpy of reduction of the metal oxide, \( T \) is the temperature in kelvin, \( S \) is entropy, and \( \Delta S_{\text{red}} \) is the entropy change of the metal oxide incurred by reduction. This gives a required temperature difference between the reduction and oxidation steps in a closed system of:

\[ \Delta T = -\frac{2 \Delta G_{f,WS}^{H_2O} - T_{WS} \Delta S}{S_{O_2}^{T_{TR}} + 2 \Delta S_{\text{red}}} \quad (7) \]

where \( \Delta S \) is the entropy increase of \( O_2 \) as it is heated from \( T_{WS} \) to \( T_{TR} \). This approach is perfectly sound for a closed system. However, STWS reactors are open systems and therefore have flow both into and out of the reactor.

In ITWS, which is an open system, the chemical potential differences that drive the oxidation and reduction steps are achieved by swings in the partial pressure of the oxidizing gas to produce \( H_2 \). In order to account for this and explain ITWS a new set of thermodynamic equations must be developed. For the reactions to occur, the Gibbs free energy of the reactants must be larger than that of the products for there to be a forward reaction as in the traditional analysis. However, Gibb’s free energy can also be defined as:

\[ \Delta G_{rx} = G_{\text{reactants}} - G_{\text{products}} \text{ where } G = PV - TS + \sum_{j=1}^{M} \mu_j N_j \quad (8) \]
where $G$ is still Gibb’s free energy, $P$ is pressure, $V$ is volume, $T$ is temperature, $S$ is entropy, $\mu_j$ is the chemical potential of species $j$ and $N_j$ is the number of species $j$ and the sum is taken over all relevant species. Therefore, the isothermal water splitting reaction is expected when:

$$
-T_{TR}(S_{H_2O} + S_{MOx-\delta}) + \mu_{H_2O}N_{H_2O} + \mu_{MOx-\delta}N_{MOx-\delta} > -T_{TR}(S_{H_2} + S_{MOx}) + \mu_{H_2}N_{H_2} + \mu_{MOx}N_{MOx}
$$

(9)

where $MO_x$ and $MO_{x-\delta}$ are the fully oxidized and the reduced metal oxide species, respectively (for the purpose of simplicity any changes in total system pressure or volume were neglected).

By rearranging Equation 10 the total chemical potential of water required to drive the reaction forward can be calculated:

$$
\mu_{H_2O}N_{H_2O} > -T_{TR}(S_{H_2} + S_{MOx} - S_{H_2O} - S_{MOx-\delta}) + \mu_{H_2}N_{H_2} + \mu_{MOx}N_{MOx} - \mu_{MOx-\delta}N_{MOx-\delta}
$$

(10)

As described in the text, the relevant quantities of $H_2O$ or $H_2$ in the reaction are the number of molecules of each species adsorbed on the surface, which is related to their partial pressure by either Henry’s adsorption constant at low surface concentrations and partial pressures or Langmuir’s model at higher concentrations and partial pressures. Using the simpler Henry’s approximation, Equation 11, (but easily extendable to use Langmuir’s model) an equation can be derived which predicts the spontaneity of the water splitting reaction dependent on partial pressures rather than the number of adsorbed gas molecules (Equation 12):

$$
N_j = \alpha_j P_j
$$

(11)

$$
P_{H_2O} > \frac{\left(\mu_{H_2}a_{H_2}P_{H_2} + \mu_{MOx}N_{MOx} - \mu_{MOx-\delta}N_{MOx-\delta} - T_{Dx}(S_{H_2} + S_{MOx} - S_{H_2O} - S_{MOx-\delta})\right)}{\mu_{H_2O}a_{H_2O}}
$$

(12)
where \( \alpha_i \) and \( P_j \) are, respectively, Henry’s adsorption coefficient and the partial pressure of species \( j \). From this equation, it is easily seen that by keeping the partial pressure of \( H_2 \) low, and the partial pressure of \( H_2O \) high, the oxidation reaction can be driven forward regardless of temperature. In ITWS there is constant flow through the system which sweeps away any \( H_2 \) that is produced by water splitting, and the continuous steam injection into the system maintains the overall number of \( H_2O \) molecules in the reactor. However, higher temperatures require higher \( H_2O \) partial pressure to drive the reaction forward. As the reaction progresses, the difference between the chemical potentials of the reduced metal oxide and the fully oxidized metal oxide shrinks \((N_{MOx}\mu_{MOx} - N_{MOx-\delta}\mu_{MOx-\delta})\). This results in incomplete re-oxidation if the steam partial pressure is low, but complete re-oxidation can be achieved by operating at a higher steam partial pressure.

A similar analysis can be conducted for the reduction reaction, determining when reduction occurs. The result is shown in Equation 13:

\[
P_{O_2} < \frac{\mu_{MOx}N_{MOx}-\mu_{MOx-\delta}N_{MOx-\delta}-T_{TR}(S_{MOx}-S_{MOx-\delta}-S_{O_2})}{\mu_{O_2}a_{O_2}} \tag{13}
\]

From this equation, it is seen that minimizing the \( O_2 \) partial pressure or increasing the reduction temperature drives the reduction reaction. Conversely, as the reduction temperature is reduced, a lower \( O_2 \) partial pressure is required to drive the reduction, therefore more pumping work must be done.

**4.3.3 Effect of \( H_2O \) partial pressure on isothermal water splitting**

The analysis outlined in 5.3.2 suggests that by increasing the partial pressure of the oxidizing gas, water splitting reaction can be driven the further toward the products. Indeed, an
increased partial pressure of water resulted in higher H\textsubscript{2} production capacities at higher rates (see Figure 4.3). For 1350°C ITWS, steam concentrations in He of 33, 43 and 50% (overall pressure held at 101.3 kPa) correspond to H\textsubscript{2} production capacities of 40±9, 72±8 and 102±18 μmol H\textsubscript{2}/g and peak production rates of 0.06±0.02, 0.15±0.07 and 0.55±0.16 μmol H\textsubscript{2}/g·s, respectively. The increased peak production rates correspond to shorter oxidation times, as expected. The higher steam pressure results in a higher water chemical potential on the active material’s surface, which provides a higher thermodynamic driving force for oxidation. Additionally, the higher steam concentrations increase the overall rate of reaction by increasing the reactant concentration. This result suggests that decreases in the time required for the oxidation step and possible increases in the ITWS temperature can be achieved by increasing the partial pressure of the oxidizing gas. Furthermore, as shown in Figure 4.4 and Table 4.1, the ITWS “hercynite cycle” produces > 6 times more H\textsubscript{2} on a total mass basis and > 12 times more H\textsubscript{2} on an active materials basis (47% active) compared to the 1350/1000°C ceria redox cycle which is considered the current state-of-the-art material for TSWS redox processing.

![Figure 4.3: The effect of steam pressure on 1350°C ITWS. The H\textsubscript{2}O partial pressures were, from left to right, 33.7, 43.4 and 50.6 kPa, respectively. H\textsubscript{2} (red) and O\textsubscript{2} (blue).](image-url)
4.3.4 A simple comparison of ITWS and TSWS efficiencies

In order to compare the potential efficiencies of ITWS and TSWS, an energy and mass balance based on a black box reactor system was performed using the operating conditions (reduction/oxidation times and temperatures), production rates and production yields from the stagnation flow reactor (SFR) experiments. Just as in the SFR, a one-hour reduction time was assumed, but the oxidation times were based on the time necessary for 95% completion of the H$_2$ generating reaction. Because many of the energy losses of the system will be similar between ITWS and TSWS for the conditions utilized in the experiments (gas heating/cooling, steam generation, O$_2$/inert separation, etc.) these terms were neglected for this simple comparison. These energy losses will lower the efficiencies of all of the cycles examined here without
significantly affecting the relative efficiencies. The method for calculating the relative efficiencies of ITWS and TSWS will be discussed first, followed by the efficiency calculation results (Table 4.2) and finally these results will be comment on.

4.3.4.1 Method for simple ITWS and TSWS efficiency calculation

Neglecting all gas phase sensible enthalpy, heat of vaporization of steam, separation work, pumping work and all energy losses by mechanisms other than thermal emission, the necessary solar input to the reduction process (per mole of H₂) is taken to be the sum of the emission loss during reduction \( Q_{\text{rad,R}} \), and the heat of reaction for the ideal stoichiometric reduction written in Equation (14).

\[
Q_{s,R} = Q_{\text{rad,R}} + \Delta H_{\text{red}}(T_R)
\]  

(14)

The emission loss (per mole of H₂) during reduction is estimated from Equation 15.

\[
Q_{\text{rad,R}} = \varepsilon\sigma T_R^4 A_{ap} \left( \frac{t_R}{n_{H_2} m_s} \right)
\]  

(15)

In Equation 15, \( t_R \) is the time required to carry out the reduction reaction, \( T_R \) is the reduction temperature, \( n_{H2} \) is the total hydrogen generated per cycle in Table 4.1, \( m_s \) is the total solid mass, and \( \varepsilon \) is the apparent emissivity of the receiver cavity. The aperture is hypothetically sized to accept the requisite solar power at a predefined concentration ratio \( C \) and solar irradiance \( I \):

\[
A_{ap} = \frac{Q_{s,R} n_{H_2} m_s}{IC t_R}
\]  

(16)

The heat produced by the oxidation reaction is assumed insufficient to maintain the elevated oxidation temperature and is further assumed to be rejected to the environment. The solar
requirement for the oxidation reaction is then equated to the emission loss at the oxidation temperature \(T_O\), determined analogously to that for reduction in Equation 17.

\[
Q_{rad,O} = \varepsilon \sigma T_O^4 A_{ap} \left( \frac{t_O}{n_{H_2} m_s} \right) \quad (17)
\]

The reduction and oxidation reactions are assumed to occur within the same vessel; therefore the aperture size is chosen to be identical to that required for the reduction reaction in Equation 16.

The net sensible enthalpy required to raise the temperature of the solid material from \(T_O\) to \(T_R\) is estimated from Equation 18 where \(\hat{C}_{p,s}\) is the mass-weighted averaged heat capacity of the original CoFe\(_2\)O\(_4\)/Al\(_2\)O\(_3\) material and \(\varepsilon_s\) is the solid phase heat recuperation effectiveness. All variations in the heat capacity of the solid material with the extent of reduction or oxidation are neglected. For simplicity, it is assumed that this heat is delivered instantaneously.

\[
Q_{solids} = (1 - \varepsilon_s) \int_{T_o}^{T_R} \frac{\hat{C}_{p,s}}{n_{H_2}} dT \quad (18)
\]

Table 4.2 provides calculated energy inputs for each of the three cases in Table 4.1 with a solar concentration ratio of 1500, uniform irradiance of 1000 W/m\(^2\) and an apparent emissivity of unity.

Inclusion of gas-phase sensible enthalpy requirements resulting from imperfect gas-phase heat recuperation along with the heat of vaporization of the steam inlet stream will increase the total energy requirement substantially above that listed in Table 4.2. However, as uniform flow rates are utilized in each of the three conditions in Table 4.1, the total energy requirement for the
non-isothermal cases will increase relatively more than that for the isothermal case owing to a comparatively higher oxidation time.

4.3.4.2 Results of simple ITWS and TSWS efficiency calculation

As can be seen from Table 4.2, this analysis, although simple, shows that hercynite cycle based ITWS is more efficient than TSWS for the conditions investigated. Because radiation losses scale as temperature to the fourth power, the solar heat required to maintain a 1350°C reduction temperature is much less than a 1500°C reduction temperature. This gives 1350°C ITWS a substantial advantage over 1500/1000°C TSWS even though they produce similar quantities of H₂ per cycle. For all cases studied, the heat input required to counteract the radiation losses during the oxidation step was small in comparison to the other losses. The difference between emission losses during reduction and oxidation for ITWS arises from the comparatively longer reduction time, despite identical reduction and oxidation temperatures. While the decrease in temperature diminishes the radiative heat losses incurred during oxidation for the TSWS cycles (and therefore the solar heat required to maintain the oxidation temperature), the much shorter time required for ITWS oxidation keeps the total solar duty of the oxidation step low, even though ITWS’s oxidation step has a higher rate of heat loss.

As expected, the sensible heat necessary to heat the oxidized material back to the reduction temperature exceeds all other energy requirements considered in the simplified analysis. The solar input required ranges from 28% of the total energy required to produce a mole of H₂ in the best scenario modeled here (95% recuperation under 1500/1200°C TSWS conditions) to 77% in the worst scenario modeled here (90% recuperation under 1350/1000°C TSWS conditions). It is important to note that even the worst case scenario provides a generous
coefficient of heat recuperation, which is more typical of fluid phase heat transfer than of solid systems. Additionally, it is worth pointing out that 1350/1000°C TSWS suffers from two

<table>
<thead>
<tr>
<th>Reduction/Oxidation temperature (°C)</th>
<th>1350/1350°C ITWS</th>
<th>1350/1000°C TWSW</th>
<th>1500/1200°C TWSW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Time (min)</td>
<td>12</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>Relative H₂ generation*</td>
<td>1.0</td>
<td>0.27</td>
<td>0.79</td>
</tr>
<tr>
<td>Solid material heat recuperation efficiency</td>
<td>Reaction step</td>
<td>Solar heat input</td>
<td></td>
</tr>
<tr>
<td>ΔH_{red} (kJ/mol H₂)</td>
<td>286.4</td>
<td>286.4</td>
<td>287.8</td>
</tr>
<tr>
<td>Q_{rad,R} (kJ/mol H₂)</td>
<td>101.8</td>
<td>101.8</td>
<td>171.5</td>
</tr>
<tr>
<td>Q_{rad,O} (kJ/mol H₂)</td>
<td>20.4</td>
<td>15.4</td>
<td>28.6</td>
</tr>
<tr>
<td>Q_{solids} (kJ/mol H₂)</td>
<td>0.0</td>
<td>665.8</td>
<td>191.2</td>
</tr>
<tr>
<td>Q_{tot} (kJ/mol H₂)</td>
<td>408.6</td>
<td>1069.5</td>
<td>678.9</td>
</tr>
</tbody>
</table>

\[\varepsilon_s = 0.95\]

| ΔH_{red} (kJ/mol H₂)                 | 286.4            | 286.4            | 287.8            |
| Q_{rad,R} (kJ/mol H₂)               | 101.8            | 101.8            | 171.5            |
| Q_{rad,O} (kJ/mol H₂)               | 20.4             | 15.4             | 28.6             |
| Q_{solids} (kJ/mol H₂)              | 0.0              | 1331.7           | 382.5            |
| Q_{tot} (kJ/mol H₂)                 | 408.6            | 1735.3           | 870.2            |

\[\varepsilon_s = 0.90\]

| ΔH_{red} (kJ/mol H₂)                 | 286.4            | 286.4            | 287.8            |
| Q_{rad,R} (kJ/mol H₂)               | 101.8            | 101.8            | 171.5            |
| Q_{rad,O} (kJ/mol H₂)               | 20.4             | 15.4             | 28.6             |
| Q_{solids} (kJ/mol H₂)              | 0.0              | 1331.7           | 382.5            |
| Q_{tot} (kJ/mol H₂)                 | 408.6            | 1735.3           | 870.2            |

\[\text{Relative H}_2\text{ generation is based upon the total H}_2\text{ that can be produced by the same amount of material in an eight hour day in the same reactor.}\]

negative effects: in addition to requiring a significant amount of heat to change temperatures between 1350 and 1000°C, the total amount of H₂ that 1350/1000°C TSWS can produce is small
and therefore it requires multiple cycles to produce an equivalent quantity of H₂ as 1350°C ITWS or 1500/1200°C TSWS can achieve in a single cycle. This necessitates more cycles, and associated temperature swings, which results in higher heat losses per mole of H₂ produced. ITWS’s higher solar efficiency and specific H₂ production capacity as compared to TSWS for the conditions examined here, suggests that ITWS has the potential to be a game changing technology in the renewable energy and, particularly, H₂ economy fields.

4.3.5 Near isothermal water splitting

Because higher reduction temperatures produce greater extents of reduction, and high oxidation temperatures result in faster kinetics, the effect of operating STWS with reduction temperatures above 1350°C while maintaining the oxidation temperatures at or above 1350°C, or near isothermal water splitting, was investigated. In this investigation reduction was carried out at 1500°C, 1450°C, 1400°C and 1350°C. The same set of temperatures was used during oxidation but the oxidation temperature was never higher than the reduction temperature, i.e. 1500°C/1350°C reduction/oxidation was examined but 1350°C/1500°C reduction/oxidation was not. ITWS was examined for completeness. All NITWS work was conducted using 86% active hercynite material.

4.3.5.1 Near isothermal water splitting

An example of the NITWS gas production operated with a 1500°C reduction temperature is shown seen in Figure 4.5. All H₂ and O₂ production curves are shown in Appendix A Figure A.1-A.3. It can be seen that under identical reduction conditions, having a higher oxidation temperature results in higher rates of reaction, suggested above. However, the total amount of H₂ generated decreases with increase oxidation temperature, for example hercynite cycled at 1500°C
/1500°C and 1500°C /1350°C produced 120±30 µmol of H₂/g and 180± 20 µmol of H₂/g respectively, as shown in Figure 4.6. The decreasing H₂ production capacity with increase oxidation temperature occurs because the higher oxidation temperatures reduce the thermodynamic driving force for the reaction. This is in agreement with Equation 12. This was not seen when the oxidation was operated at <1350°C because the reactions were kinetically limited. The decrease in H₂ production with increased oxidation temperature indicates that at temperatures at or above 1350°C the reactions are no longer kinetically limited.

The H₂ generation capacity of hercynite was also determined at lower reduction temperatures. As the reduction temperature decreases, the H₂ production capacity of hercynite decreases, as was predicted by Equation 13 and shown in Figure 4.6. This trend hold for all the

Figure 4.5: Example of near isothermal water splitting using 86% active hercynite material. All reduction occurred at 1500°C and oxidation occurred at a) 1500°C, b) 1450°C, c) 1400°C, and d) 1350°C. The H₂O partial pressure was 380 Torr. Baseline shifts due to some H₂O getting through the steam trap were subtracted out in determining total gas production.
conditions studied except for 1450°C/1400°C operation, which is also the condition with the largest error. This could indicate that experimental error during this condition, and should be investigated further in future work. Based on these results, small temperature swings of under 150°C may increase overall solar-to-hydrogen efficiency by increasing the H₂ production capacity while maintaining high oxidation rates and minimizing the energy required to heat the material from the oxidation temperature to the reduction temperature. More complete models that the simple model outlined above need to be developed to determine the effects of NITWS on the overall system efficiency.

![Figure 4.6: H₂ production capacities of 86% active hercynite material operated under isothermal or near isothermal conditions.](image)

**Figure 4.6:** H₂ production capacities of 86% active hercynite material operated under isothermal or near isothermal conditions.

### 4.3.5.2 Estimation of near isothermal water splitting kinetics

It is useful to know both the H₂ production capacity of a material and the kinetics of that material. However, the determination of the kinetics of high temperature solid gas reactions can be difficult,⁹ and will be explored in more depth in Chapter 5. However, as a general pass, peak
rate analysis has been carried out on hercynite based STWS to get a rough estimate of the activation energy of ITWS and NITWS.

In peak rate analysis, the initial, peak rate of H₂ generation is used as the kinetic rate in Arrhenius plot analysis. This can be derived as follows, the reaction rate at any point in time is given by Equation 19 and the reaction rate constant is given by Equation 20.

\[ r = k[H_2O]^{\gamma}f(\alpha) \quad (19) \]

\[ k = Ae^{-\frac{E_a}{RT}} \quad (20) \]

where \( r \) is the reaction rate, \( k \) is the reaction rate constant, \( \gamma \) is the STWS reaction order with respect to the H₂O concentration and \( f(\alpha) \) is an equation which models the consumption of the reduced material, where \( \alpha \) is the reaction extent as is reviewed in Khawam et al.,\(^{10}\) \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the universal gas constant and \( T \) is temperature. These equations can be combined and rearranged to relate the reaction rate to the activation energy, as shown in Equation 21.

\[ \ln \left( \frac{r}{[H_2O]^{\gamma}f(\alpha)} \right) = \frac{1}{T} \cdot \frac{-E_a}{R} + \ln A \quad (21) \]

By conducting this analysis at the beginning of the reaction, i.e. at the peak rate, the steam concentration and reaction extent can be considered a constant. Therefore these terms can be factored out of the left hand side of the equation and combined with the \( A \) term giving Equation 22.

\[ \ln(r_{peak}) = \frac{1}{T} \cdot \frac{-E_a}{R} + \ln A + \ln([H_2O]^{\gamma}f(\alpha)) = \frac{1}{T} \cdot \frac{-E_a}{R} + b \quad (22) \]

where \( b \) include the \( A, H_2O \) and \( f(\alpha) \) terms.
The peak rate Arrhenius plot for hercynite based NITWS is shown in Figure 4.7. The activation energy of NITWS is found to be $130 \pm 20$ kJ/mol and $120 \pm 50$ kJ/mol for reduction at 1500°C and 1450°C respectively. As can be seen in Figure 4.7, one of the data points for 1450°C/1400°C operation resulted in a reaction rate much higher than the other reaction rates; if this data point is removed from the line fitting, the activation energy determined from the Arrhenius plot for NITWS after 1450°C reduction is $120 \pm 30$ kJ/mol. Therefore, based on the 95% confidence intervals the calculated activation energies are the same. This is because the reaction mechanism should be the same regardless of the reduction temperature. The reduction temperature does, however, alter the initial extent of reduction, or $\alpha_0$, which is contained in the y-intercept term. This is seen in the decrease in the reaction rate at any given oxidation temperature with reduction temperature, as shown in Figure 4.7.

![Figure 4.7: Peak rate analysis of hercynite based near-isothermal water splitting using 86% active material.](image-url)
4.4 Conclusions

Isothermal water splitting is not only technically feasible, but appears to be superior to temperature swing operation using “hercynite cycle” material. When operating isothermally at 1350°C the hercynite cycle material produced 102 µmol/g, which is more than hercynite cycled at 1350°C /1000°C (31.4 µmol/g) and roughly the same material cycled at 1500°C /1200°C (93.7 µmol/g). The increased H₂ production is attributed to the increased reaction rates caused by higher oxidation temperatures. Unlike temperature swing water splitting, which as the name suggests, is driven by a temperature difference between the reduction and oxidation step, isothermal water splitting is driven by changes in oxygen partial pressure.

Near isothermal water splitting combines the benefits of TSWS and ITWS by driving re-oxidation with both pressure and temperature swing, while maintaining the high reaction rates of high oxidation temperatures and high H₂ production capacities of high reduction temperatures. Operating under NITWS conditions, 86% active material was able to produce up to 180± 20 µmol of H₂/g operating at 1500°C/1350°C conditions. The activation energy of NITWS was determined to be 130± 20 kJ/mol. Overall, isothermal water splitting and near isothermal water splitting is highly promising for efficient and economical H₂ production.

4.5 References

Chapter 5: Extracting Complex Gas-Solid Solar Thermal CO₂ Splitting Reaction Kinetic
for the Hercynite Cycle

5.0 Abstract

A new approach for extracting gas-solid kinetic information from convoluted experimental data is developed and demonstrated via the extraction of kinetic parameters for isothermal carbon dioxide splitting at high-temperature using CoFe₂O₄/Al₂O₃ (i.e., hercynite cycle based on Co-doped FeAl₂O₄) active material. The reaction kinetics equations derived account for competing side reactions, namely catalytic CO₂ splitting and O₂ oxidation on doped hercynite, in addition to CO₂ splitting driven by the oxidation of oxygen-deficient doped hercynite. The model also accounts for experimental effects, such as detector dead time and gas mixing downstream of the reaction chamber, which obscure the intrinsic chemical processes with the raw signal. A second-order surface reaction model in relation to extent of unreacted material, and a 2.4ᵗʰ order model in relation to CO₂ concentration, were found to best describe the CO generation behavior of the doped hercynite. In accordance with previously predicted behavior, the CO production capacity increases with increasing reduction temperature and CO₂ partial pressure. The method outlined in this paper is generally applicable to the analysis of other convoluted gas-solid kinetics experiments.

5.1 Introduction

As shown in Chapter 4, hercynite material based high temperature isothermal or near isothermal solar thermal gas splitting (STGS), as shown in Equations 1 and 2, is both feasible and a potentially game changing energy production technology. In the design of reactors where
these processes are to take place, it is desirable to know the intrinsic kinetics of the individual reactions in order to confidently apply kinetic models derived from bench-scaled experiments to new reactor and process designs. To date no study has been undertaken to examine the kinetics of hercynite based STGS, let along isothermal STGS.

$$\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4 \rightarrow \text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4-\delta + \delta/2 \text{O}_2 \quad (1)$$

$$\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4-\delta + \delta \text{CO}_2 \rightarrow \text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4 + \delta \text{CO} \quad (2a)$$

$$\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4-\delta + \delta \text{H}_2\text{O} \rightarrow \text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4 + \delta \text{H}_2 \quad (2b)$$

While very useful, detailed kinetic information can be difficult to extract, especially at the high-temperature conditions required for some of these reactions, and particularly when solids are reacting with gases. Many reported studies of high-temperature gas-solid reactions rely either on thermogravimetric analysis (TGA), or modeling of flow-reactor data, to extract kinetic information. In TGA experiments, the solid is contained in a crucible and held in a furnace which brings the material to the desired temperature under various reactive atmospheres. The crucible is connected to a quartz crystal micro balance that measures the differential mass change of the solid during reaction. Kinetic models and their associated parameters are then routinely derived from these data. In the flow-reactor method, either the solid is passed through the reactor, or the gas is passed over the solid, and the products are measured. Separately, a computer simulation is developed to model the mass and energy transfer of the system inclusive of kinetic governance. Kinetic parameters are then obtained from best fits to the experimental data. In the STWS research community, solid-state models that describe various rate-limiting phenomena are often employed.
The aforementioned approaches suffer from experimental and numerical shortcomings that often lead to erroneous results, such as misidentification of the true rate governing mechanism and its associated energetics. For example, diffusion of the reactant or product gases to and away from the solid in a TGA experiment is not instantaneous, and the rate or extent of mixing is rarely taken into account when conducting the kinetic analysis. This may mislead researchers into incorrectly ascribing the rate-limiting step in the solid-state reaction to a diffusion-like process.\textsuperscript{17,18} Similar problems plague flow-reactor modeling, even when heat and mass transfer are correctly included in the analysis. The dispersion of the gaseous products in the lines between the exit of the flow reactor and the gas analyzer is seldom accounted for, and can result in the erroneous assignment of a diffusion-based kinetic model to the reaction. Even in cases where all gaseous dispersion effects are accurately taken into account,\textsuperscript{19,20} the individual solid-state reaction models reviewed by Khawam et al.\textsuperscript{16} are not always sufficient to describe all of the processes occurring when, for example, multiple gas-solid reactions are occurring simultaneously. These are widely recognized problems, especially with thermal analysis techniques,\textsuperscript{21} and have recently been addressed using model-free approaches.\textsuperscript{22} With this in mind, a new method of kinetic data extraction from a complex, high-temperature gas-splitting process that occurs in the presence of multiple parasitic gas-solid reactions while preserving the model-based approach will be developed in order to determine the kinetic parameters of hercynite based STGS.

Several steps occur during the oxidation of reduced STGS materials. CO\textsubscript{2} or H\textsubscript{2}O gas adsorbs to the surface and splits into free O atoms and other surface-bound reactive intermediates that are precursors to the desorbed product gas, CO or H\textsubscript{2}. The free O atom then migrates into solid solution, diffusing into the material and oxidizing the bulk Fe\textsuperscript{2+} atoms back to Fe\textsuperscript{3+} at the
reaction front. Any of these steps, surface reaction, diffusion or bulk oxidation at the reaction front can be rate-limiting.

This work develops a kinetic model of CO₂ splitting on doped hercynite and incorporate them into the gas dispersion correction method described by Scheffé et al. CO₂ was chosen as a stand in for H₂O because it behaves similarly and eliminations the possibility that the unreacted gas would condense in the reactor lines or worse in the mass spectrometer used in this work. Here a set of gas/solid reaction mechanism equations are developed that account for multiple gas-solid reactions. Solid-state kinetic theory is used to describe the chemical transformation of the redox material itself, as prescribed by Khawam et al., but the equation which represents the oxidation reaction is comprised of a system of equations representing a parallel reaction network. This approach provides a road map for the extraction of relevant kinetic data from convoluted, high-temperature data sets not only for STGS but for any reaction where multiple gas-solid reactions occur simultaneously.

5.2 Experimental Methods

In this section both the methods of kinetic modeling as well as the experimental data acquisition methods.

5.2.1 Kinetic modeling methods

An overall reactor model was developed to elucidate the kinetic behavior of a high-temperature, multiple oxidative species gas-solid reactions. Scheffé et al. have shown that experimental artifacts such as the finite time required to introduce oxidizing gas into the reacting volume; detector time lag; and the dispersion and mixing of gases downstream of the reaction must be accounted for when developing a kinetic model for gas/solid reactions. If not removed,
these effects cause the gas production curve, i.e. CO generation rate, to broaden in time, which depresses the peak rate while preserving total area under the curve. Scheffe et al. developed a rigorous numerical approach that models the dispersive experimental effects in addition to the kinetic processes occurring in the solid state, allowing the determination of the intrinsic solid-state kinetics. This is the basis for the kinetics extraction method that will be developed here.

The numerical model consists of three parts: 1) gas injection dispersion, 2) solid-state reaction, and 3) mixing of the gases downstream of the reaction site before the detector. The behavior of CO$_2$ injection is modeled by a sigmoidal error function that includes a detector time delay. The oxidation reaction is based on the solid-state models reviewed by Khawam et al., weighted by the concentration of CO$_2(t)$ and given generally in Equation 3; the nature of the kinetic model $f(\alpha)$ functional and kinetic constants are the information that the experiments and modeling presented in this work aim to determine.

$$\frac{da}{dt} = k_o[Y_{oxid}(t)]^\gamma f(\alpha)$$  \hspace{1cm} (3)

where $k_o$ is the kinetic rate coefficient, $Y_{oxid}$ is the concentration of oxidizing gas fed to the reactor (in this case CO$_2$), $\gamma$ is reaction order of the oxidative species, $f(\alpha)$ is the kinetic model under consideration, which may be any of those listed in Table 5.1, and $\alpha$ is the extent of oxidation of the active material. The reaction modes considered here are the shrinking area or volume ($R_2$ or $R_3$), diffusion family ($D_n$) and reaction order family ($F_n$) where $n$ is the order of the reaction. A full development of the new set of reaction modeling equations is given in Section 3.2.

The downstream dispersion is modeled using a variable number of consecutive continuously stirred tank reactors (CSTR), which are characterized using step changes of an
argon tracer gas at each experimental condition. Of the dispersive effects which confound the reaction rate, downstream mixing constitutes the majority of the gas dispersion and is mainly attributable to turbulence in the large volume of the cryogenic CO$_2$ trap. To determine the kinetic rate expression, the parameters of various solid-state reaction models are stochastically fit to the experimental CO generation rates via a minimization of the sum of squares error after the concentration of generated CO has been acted on by the diffusion models.

**Table 5.1:** List of the solid state reaction models in differential form used in this work as taken from Khawam et al.\textsuperscript{16}

<table>
<thead>
<tr>
<th>Model Name</th>
<th>Description</th>
<th>Equation [ f(α) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_n$\textsuperscript{a}</td>
<td>Reaction order</td>
<td>$(1 - α)^n$</td>
</tr>
<tr>
<td>$D_1$</td>
<td>1-D diffusion</td>
<td>$\frac{1}{2α}$</td>
</tr>
<tr>
<td>$D_2$</td>
<td>2-D diffusion</td>
<td>$\frac{-1}{\ln(1 - α)}$</td>
</tr>
<tr>
<td>$D_3$</td>
<td>3-D diffusion</td>
<td>$\frac{3 * (1 - α)^{2/3}}{2 * (1 - (1 - α)^{1/3})}$</td>
</tr>
<tr>
<td>$D_4$</td>
<td>4-D diffusion</td>
<td>$\frac{3}{2 * ((1 - α)^{-1/3} - 1)}$</td>
</tr>
<tr>
<td>$R_2$</td>
<td>Contracting area</td>
<td>$2 * (1 - α)^{1/2}$</td>
</tr>
<tr>
<td>$R_3$</td>
<td>Contracting volume</td>
<td>$3 * (1 - α)^{1/3}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Where the reaction order is n

The following set of equations was solved to determine the sum of squares error:

\[
\frac{dα_i}{dt} = k_i [Y_{CO_2,0}(t - t_s)]^{Y_{CO_2,i}} f(α_i) \quad (4)
\]

\[
\frac{dα_{tot}}{dt} = \sum_i \frac{dα_i}{dt}; \; α_{tot} \leq 1 \quad (5)
\]
\[
\frac{dY_{\text{CO},n}}{dt} = \tau_n (Y_{\text{CO},n-1} - Y_{\text{CO},n}) \quad (6)
\]

\[
Y_{\text{CO},0} = \left(\frac{V_{\text{CO}}}{F_{\text{tot}}}ight) \left(\frac{d\alpha_{\text{tot}}}{dt}\right) \quad (7)
\]

\[
RSSQ = \sum_t \omega_{\text{CO}} [\bar{Y}_{\text{CO}}(t) - Y_{\text{CO},n=\text{last}}(t)]^2 \quad (8)
\]

Where \(\alpha_i\) is the extent of reaction of species \(i\), \(Y_{i,n}\) is the concentration of species \(i\) in the \(n^{th}\) reactor, \(\tau_n\) is the space velocity of the \(n^{th}\) CSTR reaction, \(V\) is the standard volume of the \(i^{th}\) species, \(F_{\text{tot}}\) is the total flow rate, and \(\omega\) is the a weighting factor at each time point. In this work, a broader set of reaction models which replace Equation 4 is developed. This system of equations was implemented in the computational tool Mathematica®\textsuperscript{35} which numerically solves the system of governing equations (NDSolve), produces a value for the RSSQ shown in Equation 7, and then passes this information to a numerical minimization routine (NMinimize). The fitting routine uses a Differential Evolution algorithm native to Mathematica® that stochastically solves a constrained, mixed-integer optimization problem. Differential weighting is also applied to data points surrounding the peak in \(H_2\) signal, and to a lesser extent, the tails observed. In this work, each individual reaction condition was fit independently, with activation energies and pre-exponential factors determined by an Arrhenius plot; however, Equation 4 could be altered to include these kinetic parameters, and Equation 8 could be expanded to include the entire set of experimental runs such that the activation energy and pre-exponential factor could be fit by Mathematica®\textsuperscript{35} as well.

### 5.2.2 Experimental methods

Active doped hercynite materials were produced via atomic layer deposition (ALD) on a highly porous, high surface area, poly-styrene-divinylbenzene support as described in detail elsewhere.\textsuperscript{32,36} Layers of \(\text{Al}_2\text{O}_3\) were deposited on the polymer support which was subsequently
removed leaving nanometer thickness walls onto which CoFe$_2$O$_4$ was deposited via alternating CoO and Fe$_2$O$_4$ ALD processes. The material was cycled many times before use in the work described here; this eliminates structural changes in the material, which are observed in initial cycles, and, therefore, can affect the kinetic analysis.

Isothermal CO$_2$ splitting experiments were carried out using an idealized stagnation flow reactor (SFR), which has been described elsewhere.$^{20}$ In each experiment, approximately 150 mg of active material (loosely packed in a shallow bed) was placed in a zirconia boat at the stagnation point in the flow field. This ensured that all redox active surfaces were exposed to the oxidizing stream with minimal inter-particle transport resistance. In a given CO$_2$ splitting reaction, the STGS material was heated from room temperature to the desired reduction temperature and allowed to reduce for 30 min; then, while maintaining the temperature, CO$_2$ carried in He was injected into the system for 20 min with an overall flow rate of 500 sccm, allowing the material to re-oxidize and generate CO. The effluent stream was scrubbed of unreacted CO$_2$ using a liquid nitrogen cooled cryogenic trap before the product gases from the reactor were analyzed by a differentially pumped, modulated effusive beam mass spectrometer (Extrell C50, 500 amu). CO$_2$ splitting reactions were conducted over a 1280°C to 1420°C temperature range and a 310 Torr to 576 Torr CO$_2$ partial pressure range. The total overall pressure was 760 Torr. The specific operating conditions were chosen using a central composite experimental design with k=2, as shown in Figure 5.1a.
Control runs without the active oxide were conducted at each reaction condition to determine the CO\textsubscript{2} splitting attributable to the reactor itself. At each operating condition, the blank CO generation curve was subtracted from the CO generation curve obtained when doped hercynite was present resulting in a CO generation rate that is attributable solely to the active material. This will be referred to as the “corrected CO curve”. A similar process was attempted with the O\textsubscript{2} generation curve, but resulted in a temporal anomaly that will be described in further detail in the Results and Discussion section. The CO production curves presented here are analyzed with respect to the total doped hercynite mass.

5.3 Results

The results and discussion section is organized as follows. First the general findings of isothermal CO\textsubscript{2} splitting are discussed, which motived the further development of gas-solid reaction models. Then an expansion of the single solid-state kinetic model id developed before
finally the result of applying the expanded solid state kinetic model to our CO₂ splitting data is reported.

5.3.1 Solar thermal CO₂ splitting motivation to expand the solid-state reaction model

Isothermal based CO₂ splitting using the stagnation flow reactor results in significant CO production, as shown in Figure 5.1b for a CO₂ splitting process at 1400 °C and 350 Torr of CO₂. In addition to the high peak CO production rate, after roughly 300 seconds of reaction the CO production continues in an apparently catalytic fashion along with concomitant production of O₂. As shown in Figure 5.1c (blank run), a significant quantity of CO was produced from CO₂ reduction on the walls of the SFR, which confounds interpretation of the CO₂ splitting behavior of doped hercynite. The CO₂ splitting in the absence of reactive material is attributed to catalytic activity on the reactor walls and zirconia boat. At the high experimental temperatures, between 1280°C and 1420°C, the alumina walls become catalytic and split the CO₂ into CO and O₂. The small volume in the SFR and relatively high flow rate make it possible to rapidly quench the gas-phase recombination of CO and O₂, otherwise this chemistry would go unnoticed.

In order to differentiate between the CO produced from splitting by the reactor walls and the CO produced from the oxidation of doped hercynite, the respective signals from blank runs were subtracted from the overall CO and O₂ signals, as demonstrated in Figure 5.1c and d. Even after correcting for CO₂ splitting caused by the reactor itself, there is CO production for the duration of the oxidation step, long after the initial CO production peak has subsided. This is attributed to the catalytic splitting of the CO₂ on the surface of the active material. At the reaction temperatures, the highly redox active surface provided by the material becomes catalytic. The assertion that the continued CO production is due to catalytic behavior is substantiated by the fact that after the oxidation reaction is complete, the CO and O₂ are
generated in a 2:1 ratio, which is expected for CO\textsubscript{2} decomposition. The sources and sinks of CO\textsubscript{2}, CO and O\textsubscript{2} in the SFR are shown schematically in Figure 5.2a.

![Figure 5.2: a) Schematic of the sources and sinks of CO\textsubscript{2}, CO, and O\textsubscript{2} in the stagnation flow reactor b) Schematic of the surface and bulk oxidation reactions occurring during material re-oxidation. The F-family of models consists of the various reactions on the surface including CO\textsubscript{2} and O\textsubscript{2} adsorption and dissociation, as well as CO desorption. Ion diffusion, as modeled by the D-family of equations, can be oxygen ion diffusion into the bulk, as shown here, or cation diffusion. The R-family models describe interfacial reactions such as movement of ions from the re-oxidized material to the reduced material, and phase change across the interface.](image)

As mentioned previously, correction of the oxygen signal by subtracting the blank-run data created a temporal anomaly in the product evolution curve. A time delay is observed in the O\textsubscript{2} production rate as compared to the blank (Δt in Figure 5.1d) when hercynite was present in the SFR. Subtracting the blank-run O\textsubscript{2} data gives a negative production rate at early times. The delay likely stems from the oxidation of the active material by the O\textsubscript{2} that was formed from catalytic CO\textsubscript{2} splitting on the reactor walls. The O\textsubscript{2} oxidation of the reactive material consumes a
portion of the reduced material, thereby decreasing the overall CO production capacity and the rate of CO production. As suggested above, the continued O₂ production at a rate higher than that found for the blank is due to catalytic behavior where the CO and O₂ are generated in a 2:1 ratio. Because of these complications, new reaction equations that take into account the oxidation of the hercynite material by CO₂ and O₂, and included catalytic splitting on the surface of the hercynite material, need to be incorporated into the analysis.

### 5.3.2 Expanded solid-state reaction model development

The complicated reaction behavior described above, namely catalytic CO₂ splitting and co-oxidation of the active material by O₂ and CO₂, makes direct use of a single solid-state reaction model inadequate. This is exemplified in Figure 5.3 where a single traditional solid-state reaction model (F1, F2, D1, D2, etc.) attempted to predict the CO production data using the numerical method described above. As can be seen, the predicted CO generation is unable to match either the initial CO generation peak or the catalytic CO production. These shortcomings arise because neither O₂ oxidation of the material nor catalytic CO₂ splitting on the doped hercynite is included in the reaction model.

To account for catalytic CO₂ splitting, and O₂ uptake by the reduced oxide, additional terms were included in the equations modeling CO generation and the overall reaction progress (α). The new equations for modeling the CO₂ splitting behavior that replace Equation 4 are developed as follows. The oxidation of hercynite by CO₂ and the resulting CO generation is described by Equation 9.

\[
\frac{d\alpha_1}{dt} = \frac{d[CO]_1}{dt} = k_1 Y_{CO_2}^{\alpha_1} f_1(\alpha)
\]  

(9)
where $\alpha$ is the total extent of hercynite re-oxidation, $\alpha_1$ is the extent of re-oxidation due to oxidative CO$_2$ splitting, $\frac{d[CO]}{dt}$ is the rate of CO generation attributable to oxidative CO$_2$ splitting, $t$ is time, $k_1$ is the kinetic rate coefficient for oxidative CO$_2$ splitting, $Y$ is the CO$_2$ concentration, $\gamma_1$ is the reaction order with respect to the CO$_2$ concentration, and $f_1(\alpha)$ is the gas/solid reaction model.

The catalytic portion of the CO$_2$ splitting is modeled by a zeroth order reaction (with respect to $\alpha$) as shown in Equation 10.

$$\frac{d[CO]}{dt} = k_2 Y_{CO_2}^{\gamma_2}$$

where $\frac{d[CO]}{dt}$ is the rate of CO generation attributable to catalytic CO$_2$ splitting, and $k_2$ is the

![Figure 5.3: Stochastically fit CO generation to a single F_s model a) without the inclusion of catalytic CO$_2$ splitting and b) with catalytic CO$_2$ splitting.](image-url)
kinetic rate coefficient of catalytic CO\textsubscript{2} splitting.

The re-oxidation of hercynite by O\textsubscript{2} released from the walls of the reactor is accounted for by Equation 11.

\[
\frac{d\alpha_3}{dt} = k_3 Y_{O_2}^{\gamma_3} f_3(\alpha) \tag{11}
\]

where \(\alpha_3\) is the rate of the doped hercynite oxidation by O\textsubscript{2}, \(k_3\) is kinetic rate coefficient of O\textsubscript{2} oxidation, \(Y_{O_2}\) is the concentration of O\textsubscript{2} in the system, \(\gamma_3\) is the reaction order with respect to the O\textsubscript{2} concentration, and \(f_3(\alpha)\) is the reaction order model for O\textsubscript{2} oxidation. The two unknowns in Equation 11 are the rate-limiting step behavior, i.e. \(f_3(\alpha)\) and the concentration of O\textsubscript{2} at the surface of the active material, i.e. \(Y_{O_2}\). In choosing an equation to model O\textsubscript{2} uptake by the active material, it is important to remember that both O\textsubscript{2} and CO\textsubscript{2} are oxidizing gases, and, the set of potential equations that model CO\textsubscript{2} oxidation also necessarily model O\textsubscript{2} oxidation. Therefore, the same reaction models described by Khawam et al.\textsuperscript{16} were used as potential models for \(f(\alpha_3)\).

Because the thermodynamics and kinetics of CO\textsubscript{2} interacting with the reactor wall and splitting in the reactor volume are time independent and are related to the CO\textsubscript{2} concentration in the reactor, the O\textsubscript{2} concentration was related to CO\textsubscript{2} by Equation 12.

\[
Y_{O_2} = \beta Y_{CO_2} \tag{12}
\]

where \(\beta\) is a constant which takes into account the thermodynamics, kinetics, surface area of the reactor wall and reactor volume before the CO\textsubscript{2} and O\textsubscript{2} reach the reactive material.

Equations 9-12 can be combined to model the rate of CO generation and hercynite re-oxidation. Equation 13 shows the overall rate of CO production.

132
\[
\frac{d[CO]}{dt} = \frac{d[CO]_1}{dt} + \frac{d[CO]_2}{dt} = k_1 Y_{CO_2}^Y f_1(\alpha) + k_2 Y_{CO_2}^Y (13)
\]

Combining Equations 9, 11 and 12 results in an overall rate expression for material re-oxidation, as shown in Equation 14.

\[
\frac{d\alpha}{dt} = \frac{d\alpha_1}{dt} + \frac{d\alpha_2}{dt} = k_1 Y_{CO_2}^Y f_1(\alpha) + k_3 Y_{CO_2}^Y f_3(\alpha) = k_1 Y_{CO_2}^Y f_1(\alpha) + k_3 Y_{CO_2}^Y f_3(\alpha) (14)
\]

As described above, the individual reaction steps that occur during doped hercynite re-oxidation can be described by the F-family of models (surface reactions), the D-family of models (O diffusion) or the R-family of models (reaction at the oxidation reaction front), as shown schematically in Figure 5.3b. This does not mean that the simultaneous CO\(_2\) and O\(_2\) oxidation behaviors are independent of one another and can or should be modeled by different solid-state reactions.

Of the three solid-state model behaviors, the D- and R-families have identical reaction rates for both CO\(_2\) and O\(_2\) oxidation with the caveat that the CO\(_2\) and O\(_2\) oxidation produce different surface O concentrations. The degenerate activation energies and pre-exponential factors arise because the source of O atoms only affects the concentration of surface O atoms, and not the barrier for a bulk O atom to hop between vacancies (diffusion limited), or across a reaction front (reaction front limited), nor the frequency with which that O atom vibrates within the lattice. Therefore, diffusion cannot be the rate-limiting step for oxidation by O\(_2\) while interfacial reaction is the rate-limiting step for oxidation by CO\(_2\), or vice versa. This eliminates the need to consider both a diffusion and reaction interface model in predicated the behavior of the active materials under simultaneous oxidation by CO\(_2\) and O\(_2\). If diffusion or the interfacial reaction is the slow step for both O\(_2\) and CO\(_2\) oxidation, that reaction step is logically the rate-
limiting step for simultaneous oxidation and Equation 14 collapses into Equation 15 which has a single $f(\alpha)$ term modeling the reaction.

$$\frac{d\alpha_0}{dt} = k_4(k_1Y_{CO_2}^r + k_3'Y_{CO_2}^r)f(\alpha_0) \quad (15)$$

In Equation 15, the dependence of the reaction rate on the CO$_2$ and O$_2$ concentration stems from thermodynamic adsorption considerations, shown by $k_1$ and $k_3$, and the diffusion or interfacial reaction kinetics, such as hopping frequencies or interfacial reaction kinetics, the information of which is contained in $k_4$. The $k_1$ containing terms can then be used to determine the CO generated from material oxidation.

If the O$_2$ and CO$_2$ oxidation reactions are governed by a mixture of surface and bulk based reactions, the overall rate model should still collapse into Equation 15 due to unequal surface reaction competition. For example, if the rate-limiting step for CO$_2$ oxidation is diffusion, but, the rate-limiting step for O$_2$ oxidation is a surface reaction, then the CO$_2$ surface decomposition reaction must be faster than O$_2$ oxidation, because they have the same diffusion rate. Therefore, the CO$_2$ splitting reaction will be the dominant surface reaction, covering the surface in O atoms and preventing the O$_2$ surface oxidation reaction, but the CO$_2$ reaction will still be limited by diffusion. This will result in large quantities of CO production which is modeled by Equation 15 where the CO production is diffusion-limited with almost no O$_2$ oxidation reaction occurring ($k_3' \approx 0$). A similar, but converse argument can be made with O$_2$ as the main species oxidizing the surface resulting in little or no CO generation and, therefore, reaching the conclusion that Equation 15 still holds. The same analysis can be done with an interfacial reaction rather than a diffusion-based model. Therefore, only the doped hercynite
material oxidation to a single $f(\alpha)$ model, as shown in Equation 15, was used for the cases of diffusion- and interfacial reaction-limited processes.

If, however, the reaction is surface limited (F-family) for both CO$_2$ and O$_2$ oxidation, the modeling equation does not necessarily collapse into a single $f(\alpha)$ model as is the case for D- and R-family models. This is because the number of surface sites required for adsorption and decomposition of O$_2$ and CO$_2$ are potentially different, and the number of surface sites required is related to the order of the model and, therefore, the exponent in the governing equation [i.e. $f_1(\alpha) = (1-\alpha)^{n_1}$ and $f_3(\alpha) = (1-\alpha)^{n_2}$, where $n_1 \neq n_2$]. Therefore, the $f(\alpha)$ term cannot be factored out of the concentration and rate constant terms as was done to derive Equation 15. Modeling surface-limited reactions, then, requires two F-family models to characterize simultaneous CO$_2$ and O$_2$ oxidation of the active material, as shown in Equation 16.

$$\frac{d\alpha_0}{dt} = k_1 Y_{CO_2}^{\gamma_1} (1 - \alpha_0)^{n_1} + k_3 Y_{CO_2}^{\gamma_3} (1 - \alpha_0)^{n_3} \quad (16)$$

From Equation 16, the CO$_2$ and O$_2$ contributions to oxidation of the doped hercynite materials are easily discernable; where the terms containing subscripts 1 and 3 represent CO$_2$ and O$_2$ based oxidation, respectively.

**5.3.3 Application of the expanded kinetic model to CO$_2$ splitting using doped hercynite**

The collapsed diffusion and reaction interface, and surface reaction models, as shown in Equations 15 and 16 respectively, were used to fit the CO generation rates found in the SFR experiments. Examples of the resulting CO production predicted by these models are shown in Figure 5.4 for the experiment conducted at 1350°C and 450 Torr CO$_2$. Fits to the R- and D-family of models are shown in Appendix B Figure B.1. The F-family based model outperforms the D- and R-family of models via inspection and sum of squares error. This result agrees with
previous findings for STGS materials, which have determined that the F-family or mixed F- and D-family of models best describe CO$_2$ oxidation behavior.$^{18,19,37-39}$ Based on these results, the F-family of models was used to stochastically fit the CO production profile for each of the CO$_2$ splitting conditions examined in this work. As mentioned above, each reaction condition was fit individually, but in future work this method could be expanded to fit all of the conditions simultaneously.

![Figure 5.4: Stochastically fit CO generation curves at 1350°C and 450 Torr P$_{CO_2}$ including both CO$_2$ and O$_2$ oxidation using an a) F$_3$ model; b) D$_2$ model; and c) R$_3$ model.](image)
The peak CO production rate increases with both increased reaction temperature and increased partial pressure of CO$_2$, as shown in Figure 5.5. All fitted CO production curves can be found in Appendix B Figure B.2- B.10. These figures also show that it is necessary to account for downstream diffusion when conducting kinetic analysis; without including dispersion, it would appear that CO$_2$ splitting at 1350°C and 576 Torr P$_{CO2}$ is slower than at 1350°C 450 Torr P$_{CO2}$ or even 310 Torr P$_{CO2}$ due to the increased dispersion when the CO$_2$ partial pressure increases. The increased CO production with increasing temperature is expected because the higher reaction temperatures increase the extent of reduction in the oxide, thereby, increasing the

![Figure 5.5: Stochastically fit CO generation at the material surface using an F$_n$ model including both CO$_2$ and O$_2$ oxidation reactions at 450 Torr P$_{CO2}$ and a) 1420°C, b) 1350°C and, c) 1280 °C; and at 1350°C and d) 576 Torr P$_{CO2}$, e) 450 Torr P$_{CO2}$ and f) 310 Torr P$_{CO2}$. The inserts show the measured CO production rates (solid dots) and the model predictions (solid lines) that account for reaction and dispersion.](image)
overall CO production capacity of the material while simultaneously increasing the oxidation driving force and rate of oxidation. Similarly, the increase in CO production with increased CO$_2$ partial pressure stems from the increased driving force for oxidation, which has been described before,$^{33}$ as well as increasing the rate of the reaction.

The overall kinetic parameters found in this work are shown in Table 5.2. It is important to note that while these models offer a reasonably good fit to the experimental data, they are not necessarily unique solutions and therefore interpreting the implicit kinetics of the material derived from these findings must be approached with caution. However, the broad findings are useful in illustrating the new gas-solid reaction models, developing a general understanding of the active material behavior and, potentially, for use in basic reactor and system modeling. The apparent reaction order with respect to the extent of reduced doped hercynite oxidation ($\alpha$) was found to be n~2 and n~1.5 for CO$_2$ and O$_2$ oxidation, respectively, suggesting that oxidation requires two surface sites for adsorption and reaction. This is in agreement with previous investigations of CO$_2$ splitting on ceria$^{40}$ and oxidation reactions on ferrite materials.$^{20}$ The reaction order with respect to the CO$_2$ concentration was found to be ~2.5. The distribution in the predicted reaction order is likely attributable to the differing initial extents of reduction of the materials, for example materials reducing at 1420°C are more reduced than materials reduced at 1280°C, and therefore, have a higher CO production capacity and differing initial reaction driving forces.
Table 5.2: Stochastically fit parameters for CO$_2$ splitting modeled using Equation 16.

<table>
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<th>T (°C)</th>
<th>$P_{\text{CO}_2}$ (kPa)</th>
<th>Log $k_1$</th>
<th>$\gamma_1$</th>
<th>$n_1$</th>
<th>Log $k_2$</th>
<th>$\gamma_3$</th>
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</tr>
</tbody>
</table>

The reaction rate constants, on the other hand, span a larger range of values. This stems from the Arrhenius like behavior of reaction rate constants, which vary from one oxidation temperature to the next. The determination of a pre-exponential factor and activation energy based on the reaction rate constants is complicated by the different reduction extents described above and the simultaneous oxidation by O$_2$ and catalytic CO production. To a rough estimate, however, the predicted pre-exponential factor and activation energies for the CO$_2$ splitting reaction are $88.2[\text{CO}][\text{CO}_2]^{-2}[\text{O}_2]^{-1.5}$ s$^{-1}$ and 80.0 kJ/mol, respectively based on apparent reaction rate constants and an Arrhenius plot, as shown in Figure 5.6. The activation energy is reasonably close to the activation energy ($E_a=53.9$ kJ/mol) of the F$_2$ reaction path for water-splitting on CoFe$_3$O$_4$ on YSZ.$^{20}$
The extraction of the activation energy from the \( \text{O}_2 \) oxidation reaction is complicated by the fact that the \( \text{O}_2 \) concentration at the reaction surface are not know because the \( \text{O}_2 \) concentration was related to the \( \text{CO}_2 \) concentration via \( \beta \), which was then combined with the reaction rate constant to give an effective rate constant. Similarly, it is challenging to determine the reaction order with respect to \( \text{O}_2 \) concentration. Therefore, the analysis of the \( \text{O}_2 \) oxidation is left for doped hercynite to future work, where \( \text{O}_2 \) is used as the sole oxidizing gas. With the estimates of reactions orders, and activation barriers for the \( \text{CO}_2 \) splitting reaction developed in this work, doped hercynite materials can now be simulated in reactor design models.

### 5.4 Conclusions

In this work, a set of gas-solid reaction equations was developed and employed to determine the kinetic parameters of isothermal \( \text{CO}_2 \) splitting using doped hercynite materials over the temperature range of 1280-1420°C and \( \text{CO}_2 \) partial pressure range of 310-576 Torr. The expanded set of gas-solid reaction equations was required to account for CO production from both material oxidation and catalytic \( \text{CO}_2 \) splitting on the active material’s surface and
simultaneous O₂ oxidation of the hercynite material. The experimental CO production rates were fit using the updated models and a second order surface reaction (F-family) model was found to best fit the reaction with respect to the extent of re-oxidation, with an apparent activation energy and pre-exponential factor of 80.0 kJ/mol and 88.2[CO][CO₂][O₂]⁻¹.⁵ sec⁻¹. While these models offer a reasonably good fit, they are not necessarily unique fit solutions and, therefore, cannot be used to infer implicit kinetics of the material and process but are suitable for reactor design and modeling using doped hercynite. The models, and method for developing the models, described here are applicable not only to the STGS community, but to the gas-solid reaction community at large, particularly to reactions which are more complicated than a single gas species reacting along a single reaction path.

5.5 References


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Chapter 6: The Effect of Surface Deposited Pt on the Photocatalytic Activity of TiO₂

6.0 Abstract

The roles of deposited Pt clusters and adsorbed O₂ in the photoactivity of anatase TiO₂ (101) surfaces have been studied using density functional theory. O₂ only adsorbs to TiO₂ surfaces when excess negative charge is available to form O-Ti bonds, which can be provided by a photoexcited electron or subsurface oxygen vacancy, in which cases the adsorption energies are -0.94 eV and -2.52 eV, respectively. When O₂ adsorbs to a subsurface defect, it scavenges extra electron density and creates a hole that can annihilate excited electrons. In aqueous solutions, O₂ interactions with the TiO₂ surface are rare because water preferentially adsorbs at the surface. Pt clusters on TiO₂ significantly enhance O₂ adsorption providing many adsorption sites with adsorption energies up to -1.69 eV, stronger than the -0.52 eV adsorption energy of H₂O on the Pt cluster. Consequently, Pt increases the rate of electron scavenging by O₂ relative to that of undoped TiO₂ leading to enhanced photocatalytic performance. Pt states completely bridge the band gap and act as electron-hole recombination centers, which are deleterious to the photoactivity of TiO₂. The initial rise and subsequent fall in TiO₂’s photoactivity with Pt loading results from the competition between enhanced electron scavenging due to increased O₂ adsorption and increased electron-hole recombination.

6.1 Introduction

The mechanism for the increase and decrease in TiO₂ photocatalytic activity with increasing Pt content is still not clearly understood. To explain the effect of Pt loading on
photoactivity some reports have suggested that Pt clusters act as an electron-hole (e-h) separation center and therefore inhibit e-h recombination at low Pt loadings, but that at high loadings Pt acts as an e-h recombination center.\textsuperscript{3,9,10,13,14} Unfortunately, this suggestion has not been verified or explained mechanistically, leaving the field with no proven, fundamental explanation for the mechanism by which Pt affects the photoactivity of TiO\textsubscript{2}.

To investigate the role of Pt on the photoactivity of TiO\textsubscript{2} the electronic structure and energy of O\textsubscript{2} adsorbed to and scavenging electrons from the Pt/TiO\textsubscript{2} system was calculated and analyzed, because this has been shown to be the rate limiting step in aerobic, TiO\textsubscript{2} based photocatalytic organic degradation.\textsuperscript{13,14} Moreover, because the photocatalysis reaction investigated here occurs in solution H\textsubscript{2}O adsorption was also investigated on the TiO\textsubscript{2} and Pt/TiO\textsubscript{2} surfaces. This study provides a first principles description of fundamental phenomena involved in photocatalytic degradation of organic pollutants. Furthermore, it provides principles and an approach that might be applied to understand and investigate other TiO\textsubscript{2} or Pt related catalytic and photocatalytic processes, such as photocatalytic water splitting on Pt/TiO\textsubscript{2} and Pt catalyzed oxygen reduction in fuel cells.

6.2 Computational Methods

Plane wave periodic boundary condition DFT simulations were performed using the Vienna Ab initio Simulation Program (VASP).\textsuperscript{28,29} Calculations employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange and correlation functional\textsuperscript{30} coupled with projector augmented wave (PAW) pseudopotentials.\textsuperscript{31} In this case, PAW’s were used to describe the hydrogen 1s; oxygen 2s and 2p; titanium 3p, 4s and 3d; and platinum 6s and 5d electrons explicitly. All calculations utilize a 400 eV cut off energy based on a cut off energy study conducted in the range of 200 to 500 eV where a 400 eV cut off energy
was determined to be sufficiently accurate. All calculations were conducted at the Γ-point as extensive Brillouin zone folding for large supercells enables the Γ-point to span a larger fraction of k-space without the added computational expense of a k-point expansion. This was confirmed by a k-point study that demonstrated that the Γ-point calculation was of sufficient accuracy for these supercells; for a unit cell containing a single Pt atom on a 144 atom TiO₂ slab DFT predicted a Γ-point cell energy of -1,272.43 eV, only 0.05 eV lower than the cell energy obtained using a 2×2×2 Monkhorst-Pack k-point mesh expansion. Bader charge analysis was conducted using software from the Henkelman group.³²,³³ Additionally, GGA+U calculations were completed to investigate the effect of electron localization on the TiO₂ systems studied.²¹ A Hubbard term³⁴ of Uₜₐₜₐₜ = 3.5 eV on the Ti d-electrons was included for calculations where the GGA functional alone did not adequately describe the electron correlation in the system. The Hubbard correction attempts to describe electron correlation more accurately by imposing an energy penalty for electrons occupying the same orbital type on a given atom. A Hubbard interaction of 3.5 eV was chosen for Uₜₐₜₐₜ because it has been shown to most accurately represent the electronic structure of TiO₂.²¹

The model systems employed in this work are all based on the TiO₂ (101) anatase surface, as shown in Figure 6.1. Three different supercells were utilized in this study to represent the (101) anatase surface. For single molecule adsorption on the (101) surface a 3×2 supercell slab consisting of 108 atoms, corresponding to a 3×1 slab cut along the [010] and [10̅1] directions, was employed. A 4×2 supercell consisting of 144 atoms was used for studies of the effect of co-adsorbed H₂O on the behavior of O₂ on TiO₂. Both of these slabs consisted of three Ti-O double-layers. This thickness allows for the creation of a subsurface vacancy without
interfering with the frozen bottom layer. Previous work has shown that three-layers are sufficient for calculations involving subsurface defects.\textsuperscript{21,35}

![Diagrams of TiO\textsubscript{2} and Pt clusters](image)

**Figure 6.1:** a) top view of the perfect (101) TiO\textsubscript{2} anatase surface, b) side view of the perfect (101) anatase TiO\textsubscript{2} surface, c) side view of the (101) anatase surface with a subsurface O vacancy with the location of the defect marked with a dashed square, d) top view of (101) anatase with a subsurface O vacancy. Ti and O atoms are represented by large gray and medium red spheres, respectively.

To investigate the role of Pt on the photoactivity of TiO\textsubscript{2}, a 37 atom Pt cluster supported on TiO\textsubscript{2} (101) anatase was employed as the model system. A 37 atom Pt cluster was selected because its diameter of 1.4 nm is similar to that of Pt clusters observed experimentally\textsuperscript{12} and because a 37 atom structure corresponds to a hemispherical fragment of the 55 atom magic number FCC Pt nanoparticle.\textsuperscript{27} For calculations of supported platinum clusters a 144 atom (4×3) supercell slab consisting of two Ti-O double-layers was employed. The (4×3) supercell model provides adequate surface area for the 37 atom platinum cluster. Furthermore, the slab with two Ti-O double-layers was chosen because it reproduced the electronic, geometric and energetic results of a model consisting of Pt on a five Ti-O double-layer slab. All cells had at least a 15 Å vacuum gap between the adsorbed species and the backside of the periodic image of the slab.
The active side of the slab was allowed to relax, while the atoms of the bottom double-layer for all supercells were frozen in their bulk positions to mimic a bulk-like layer. Geometric relaxations were carried out using the Quasi-Newton-Raphson method converged to at least $1 \times 10^{-3}$ eV. The energy of defect formation was calculated using Equation 4, and all adsorption energies were calculated using Equation 5:

$$E_{\text{vac}} = E_{\text{surf} \cdot \text{vac}} + \frac{1}{2} E_{\text{O}_2} - E_{\text{surf}}$$  \hspace{1cm} (4)$$

$$E_{\text{ads}} = E_{\text{surf} \cdot \text{mol}} - (E_{\text{surf}} + E_{\text{mol}})$$  \hspace{1cm} (5)$$

where $E_{\text{vac}}$ is the vacancy formation energy, $E_{\text{surf} \cdot \text{vac}}$ is the energy of the bare surface with an O vacancy, $E_{\text{O}_2}$ is the energy of O$_2$ in vacuum, and $E_{\text{surf}}$ is the energy of the perfect surface. $E_{\text{ads}}$ is the energy of adsorption, $E_{\text{surf} \cdot \text{mol}}$ is energy of the surface of interest with an adsorbate, $E_{\text{surf}}$ is the energy of the surface of interest without an adsorbate, and $E_{\text{mol}}$ is the energy of the molecule alone in vacuum. A negative adsorption energy indicates that the process is exothermic and hence favorable.

6.3 Results

In order to determine the effects of Pt clusters on the photocatalytic activity of TiO$_2$ the O$_2$ reduction reaction on the undecorated surface was examined before discussing the way in which Pt clusters interact with the TiO$_2$ and the O$_2$ reduction reaction.

6.3.1 Adsorption of O$_2$ on TiO$_2$

In the absence of Pt, a reduction reaction must occur on the TiO$_2$ surface to maintain the overall charge neutrality of the TiO$_2$. In the presence of O$_2$, O$_2$ acts as the electron scavenger.
First the electron transfer on the perfect TiO$_2$ surface will be discussed and then at surface defect sites.

6.3.1.1 Adsorption of O$_2$ on the Perfect (101) Anatase Surface.

The perfect anatase TiO$_2$ (101) surface, shown in Figures 6.1a and b, has a stepped structure with coordinatively unsaturated ions. It consists of: Ti atoms with two different coordinations: a 5-fold-coordinated Ti (5f-Ti) located nearer the surface; and a 6-fold (fully) coordinated Ti (6f-Ti) located below 5f-Ti atoms; and three different O atoms: a 2-fold-coordinated bridging O (2f-O) located furthest into the vacuum, and two different 3-fold coordinated O atoms, 3f-O, and 3f'-O, which differ mainly in the extent to which they extend into the vacuum. Previous reports have demonstrated that although some GGA methods accurately predict the geometric structures of H$_2$O and O$_2$ adsorbed on TiO$_2$, they do not accurately represent the electronic structure of the TiO$_2$ system.$^{21}$ To accurately describe the electronic structure, a Hubbard correction of $U_{\text{eff}} = 3.5$ eV was imposed on the Ti atoms in calculations of interactions of O$_2$ with the TiO$_2$ surface. As such, all the data and figures reported for O$_2$ adsorbed on TiO$_2$ were calculated using the Hubbard term.

As shown previously, O$_2$ does not adsorb to a perfect, neutral TiO$_2$ surface.$^{14,19,21,23}$ DFT calculations also show that when O$_2$ is placed on the TiO$_2$ surface, it relaxes into the vacuum rather than adsorbing. However, upon addition of one electron to simulate O$_2$ interacting with a photoexcited electron in TiO$_2$, O$_2$ gains electron density provided by the additional electron and chemisorbs to the surface with an adsorption energy of -0.95 eV. Before O$_2$ adsorption the additional electron resides at the conduction band minimum (CBM), which is comprised primarily of Ti d character. Modeling the photoexcited system by adding an extra electron that populates the CBM assumes that the photoexcited electron and, the negatively charged adsorbed
O₂ do not strongly interact with the photoexcited hole, thus avoiding the need for an expensive excited state calculation. This was tested by Di Valentin et al. who demonstrated that the photoexcited hole and electron do not strongly interact because they remain well localized on individual atoms independent of whether the electron and hole are simulated individually or as an exciton. Additionally, Dupuis et al. calculated that the diffusion rates of excited holes and electrons through bulk anatase are both fast with diffusion barriers of only 0.17 eV and 0.30 eV, respectively, although they point out that electron transfer is expected to be even faster than the rate suggested by the 0.30 eV activation barrier owing to factors not accounted for in their simulations. Thus, because of their fast migration, photoexcited electrons and holes are both likely to reach the surface.

The -0.95 eV O₂ adsorption energy is lower in magnitude than that calculated by Filippone. This difference may stem from their inclusion of ancillary ions in the unit cells to provide the negative charge for TiO₂ rather than the method of directly adding electrons to the slab. Additionally, both the model supercell and the separation between slabs are substantially larger than those employed by Filippone et al., leading to smaller spurious interactions between periodic images. The adsorbed O₂ is bound to a surface Ti atom in the 5f-Ti site and lies parallel to the rows of bridging surface oxygen atoms as shown in Figures 6.2a and b. Both O atoms are 2.08 Å from the Ti atom they are bound to, while the O-O bond lengthens from the 1.23 Å bond length of gas phase O₂ to 1.33 Å upon adsorption. This indicates the formation of the superoxide state of oxygen characterized by an O-O bond length of 1.33 Å. Upon O₂ adsorption, the 5f’-Ti atom bound to the adsorbed O₂ relaxes into the vacuum and its bond to the subsurface O atom lengthening from 1.84 Å to 2.15 Å. This indicates a significant weakening of the Ti-O bond.
between the surface Ti to which O₂ adsors and the subsurface O atoms to which this Ti atom is bound.

Table 6.1: The charge gain of O₂ determined by a Bader charge analysis and the O-O, O-Ti and O-Pt bond lengths upon O₂ adsorption on various surfaces under different charge conditions.

<table>
<thead>
<tr>
<th>system</th>
<th>perfect TiO₂</th>
<th>TiO₂ with subsurface vacancy</th>
<th>Pt/TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>system charge</td>
<td>-1</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>O₂ charge gain upon adsorption (e⁻)</td>
<td>0.52</td>
<td>1.05</td>
<td>0.98</td>
</tr>
<tr>
<td>O-O bond length (Å)</td>
<td>1.33</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>O-Ti/O-Pt bond length (Å)</td>
<td>2.05</td>
<td>1.86</td>
<td>1.84</td>
</tr>
</tbody>
</table>

*Positive charge values indicate an increase in the electron density. The neutral perfect TiO₂ surface is not applicable because O₂ does not adsorb to this surface.

Although O₂ formally gains a full electron relative to O₂ upon O₂ adsorption to the negatively charged surface to form the superoxide O₂⁻, Bader charge analysis of the adsorbed state estimates that the adsorbing O₂ gains only 0.55 e⁻ as seen in Table 6.1. The gain of only 0.55 e⁻ is attributable to the fact that a fraction of the extra electron density is localized on the surface 5f⁻.
Ti atom to form bonds to the adsorbing O\textsubscript{2}. The projected density of states (PDOS), shown in Figure 6.3a, indicates that the highest energy occupied band is composed of O 2p character from the adsorbed O\textsubscript{2} and Ti 3d character from the 5f\textsuperscript{-}-Ti atom to which the O\textsubscript{2} adsors. This suggests that the Ti-O bonds are of d-p π character. The d-p π bond between the d\textsubscript{xz} orbital of the 5f-Ti titanium atom and the π\textsubscript{z}\textsuperscript{*} antibonding orbital of O\textsubscript{2} leads to additional occupation of what was originally one of the two degenerate partially occupied π\textsuperscript{*} highest occupied molecular orbitals (HOMO’s) of O\textsubscript{2}. A illustration of the bond is shown in the insert of Figure 6.3a. This additional occupation of the O\textsubscript{2} π\textsubscript{z}\textsuperscript{*} antibonding orbital increases the O\textsubscript{2} bond length to that of superoxide.

The lowest energy unoccupied band is composed mostly of O 2p\textsubscript{y} character from the O\textsubscript{2} π\textsubscript{y}\textsuperscript{*} antibonding orbital with contributions of Ti d\textsubscript{xy} character, also shown in Figure 6.3a. The transfer of only 0.55 e\textsuperscript{-} to O\textsubscript{2} is a characteristic of the Ti-O\textsubscript{2} d-p π bond that forms between the Ti d\textsubscript{xz}-orbital and the O\textsubscript{2} π\textsubscript{z}\textsuperscript{*} antibonding orbital.

**Figure 6.3:** Projected density of states (PDOS) of O\textsubscript{2} adsorbed on the perfect (101) anatase surface with one additional electron (a) and two additional electrons (b). Insert: illustrates the bonds between the adsorbed O\textsubscript{2} and the surface as indicated by the orbital character of the highest energy occupied band of the DOS.

Upon the addition of a second electron to the supercell model of the TiO\textsubscript{2} surface, adsorbed O\textsubscript{2} acquires an additional 0.50 e\textsuperscript{-}, for a total of 1.05 e\textsuperscript{-}. Furthermore, the O-O bond lengthens further to 1.46 Å (see Table 6.1 for a comparison of bond lengths); approximately the
length of the peroxide bond (1.49 Å) and the magnitude of the adsorption energy increases to -1.63 eV. As indicated by the PDOS analysis shown in Figure 6.3b, the second additional electron occupies the state that arises from the O₂ πₚ* antibonding orbital composed of O 2pₚ orbitals and Ti 3dₓᵧ orbitals that are orthogonal to the 5f-Ti dₓz-πₚ* bond. The lower energy of the Ti dₓz-O πₚ* bonding state relative to the Ti dₓy-O πₚ* bonding state (see Figure 6.3b) is expected because of the larger overlap between the orbitals making up the bond relative to the overlap between the Ti dₓy and O πₚ* orbitals, leading to the increased strength of the Ti dₓz-O πₚ* bond.

The presence of O₂⁻ on the perfect surface when free electrons are available is consistent with the observations of Berger et al.³⁹ They observed a greater increase in the O₂⁻ signal in the EPR spectra upon TiO₂ UV irradiation during exposure to O₂ than that obtained upon UV irradiation of TiO₂ after O₂ was evacuated from the chamber. If O₂ is removed before irradiation, it can only adsorb at defects, leading to a small number of adsorbed oxygen species. In contrast, if irradiation by light of sufficient energy to cause photoexcitation of TiO₂ occurs in the presence of O₂, then O₂ at the surface can acquire electron density by electron transfer and adsorb, leading to higher O₂⁻ concentrations on the surface. This could describe the mechanism for electron scavenging in air where a significant flux of impinging O₂ increases the probability that an excited electron is transferred to O₂, hence allowing it to adsorb. In contrast, the probability that O₂ interacts with a free electron in TiO₂ is greatly decreased in an aqueous environment because the concentration of O₂ near the surface and flux of O₂ to the surface are low when it is covered by water (vide infra).

6.3.1.2 Adsorption of O₂ onto (101) anatase at subsurface O vacancies

Aschauer et al. originally demonstrated that O₂ readily adsorbs to TiO₂ surfaces that possess subsurface defects.²¹ The TiO₂ surface with a subsurface O vacancy is illustrated in
Figures 6.1c and 1d. The 6f'-Ti atom is positioned above the subsurface O vacancy. The Ti atom positioned below the subsurface O vacancy is labeled B-Ti. Figure 6.2b shows the structure of O\textsubscript{2} adsorbed to the 5f'-Ti atom that neighbors the 6f'-Ti atom above the O vacancy. The equilibrium O vacancy concentration is relatively low owing to the high O vacancy formation energy of 4.70 eV (3.87 eV calculated without a Hubbard correction). The O\textsubscript{2} adsorption energy at the 5f'-Ti atom was calculated to be -2.53 eV. Upon adsorption, the O-O bond lengthens from its gas phase value of 1.23 Å to 1.45 Å, in good agreement with previous studies.\textsuperscript{21} Because this bond is almost the same length as the 1.49 Å O-O bond length of peroxide (O\textsubscript{2}\textsuperscript{2-}), one might expect that the adsorbed O\textsubscript{2} would have an overall charge of 2 e\textsuperscript{-}. However, Bader charge analysis predicts that O\textsubscript{2} gains only 0.98 e\textsuperscript{-} upon adsorption. As discussed above, this can be explained as arising from O\textsubscript{2} sharing the electrons in the two d-p π bonds, d\textsubscript{xy}-π\textsubscript{*} and d\textsubscript{yz}-π\textsubscript{y}* formed with the surface Ti atom. Because two d-p π bonds are formed by O\textsubscript{2} adsorbed at the defect and O\textsubscript{2} acquires ~0.5 e\textsuperscript{-} per bond, the adsorbed O\textsubscript{2} acquires a charge of ~1 e\textsuperscript{-} upon adsorption at the subsurface O vacancy. This explains why Ti-O\textsubscript{2} bonds for O\textsubscript{2} adsorbed at the defect are 0.21 Å shorter and 1.6 eV stronger than Ti-O\textsubscript{2} bonds on the perfect surface with one photoexcited electron. It is worth noting that the electron density associated with the 5f'-Ti atom to which O\textsubscript{2} adsorbs does not change after O\textsubscript{2} adsorption (an increase of only 0.002e\textsuperscript{-} from a Bader charge analysis). This is because upon O\textsubscript{2} adsorption the O atom below the 5f'-Ti atom descends to partially fill the original sub-surface vacancy, dissociating from the 5f'-Ti atom. Thus, as O\textsubscript{2} adsorbs the 5f'-Ti atom forms new bonds to the adsorbing O\textsubscript{2} replacing the bonds to the subsurface O that dissociates.

This raises two questions: first, \textit{because there is no change in the electron density around the Ti atom at which O\textsubscript{2} adsorbs, what provides the electron density that is transferred to O\textsubscript{2}}
upon adsorption?, and second, because O₂’s π* orbitals are filled when it is bound to a 5f’-Ti atom, what occurs when this adsorbed O₂ encounters an excited electron? To answer the first question, Bader analysis was carried out before and after O₂ adsorption. This shows that before oxygen adsorption, the 6f’-Ti and B-Ti atoms that are directly above and below the O vacancy (see Figure 6.1c) possess the extra electron density provided by the creation of the subsurface oxygen vacancy, as seen by the increase of ~0.3 e⁻ on each of these Ti atoms relative to the perfect surface. The localization of only ~0.6 e⁻ at the O vacancy can be attributed to inability of the Hubbard correction to fully account for electron correlation and exchange. Upon O₂ adsorption, these two Ti atoms both lose their additional ~0.3 e⁻ electron density to have a charge nearly equal to those of the other Ti atoms in the system. While the O₂ gains 0.98 e⁻ as it adsorbs, the two Ti atoms directly above and below the oxygen vacancy together lose their additional 0.60 e⁻. This indicates that, even with the limits of the Hubbard correction the two Ti atoms neighboring the subsurface vacancy are the primary electron donors. Therefore, O₂ adsorbs to the surface with subsurface oxygen vacancies as a result of O vacancies providing electron density localized on the 6f’-Ti and B-Ti Ti atoms to the absorbing O₂ as it forms an O₂-Ti bond.

To address the second question of what occurs when O₂ adsorbed at a subsurface O vacancy encounters an excited electron, an extra electron was added to the slab. Upon addition of an extra electron, O₂ does not become significantly more strongly adsorbed to the surface; the adsorption energy of O₂ is -2.64 eV compared to -2.53 eV without the additional electron. This indicates that significant additional electron density has neither been transferred to O₂ nor to the Ti-O₂ bond because significant density transfer would have likely increased the adsorption energy, as discussed for O₂ adsorption on the perfect surface. This was confirmed using Bader analysis, which shows that adsorbed O₂ only gains 0.04 e⁻ upon addition of the electron to the
slab with the subsurface oxygen vacancy. Instead, the added electron delocalizes over the Ti atoms of the supercell. Projection of the highest occupied states, which now lie at the bottom edge of the conduction band, onto atomic states shows an increase in electron density primarily on Ti atoms at the frozen face (backside) of the slab. However, the second lowest unoccupied band is localized on the B-Ti atom located below the O subsurface vacancy. This is the lowest unoccupied band that is not located on the frozen face, and indicates that the lowest lying unoccupied band in the actual system is primarily composed of d-states from the Ti atom located directly below the O vacancy.

To ensure that the B-Ti atom gains the extra electron in the physical system, a four double-layer thick slab was created in which the bulk positions of the third double-layer was frozen, and the back side of the slab, which is now the fourth double-layer, was allowed to relax to stabilize the high energy dangling bonds. Bader charge analysis on the surface possessing the subsurface O vacancy before O$_2$ adsorption shows that the excess electron density near the oxygen vacancy is mainly distributed over the 5f'-Ti and the B-Ti atoms (an additional $\sim$0.3 e$^-$ compared with the rest of the Ti atoms in the system), with some density distributed over the 6f'-Ti atom and the Ti atom located directly below the 5f'-Ti atom (an additional $\sim$0.09 e$^-$ and 0.08 e$^-$, respectively). After O$_2$ adsorption to a subsurface defect on the four double-layer thick slab (adsorption energy of -2.62 eV, in good agreement with the three double-layer thick slab), the four Ti atoms surrounding the vacancy lose 0.63 e$^-$ to the O$_2$, which itself gains 0.99 e$^-$. The 5f'-Ti atom and the B-Ti atom loose the most electron density; -0.2 e$^-$ and -0.35 e$^-$, respectively. The projection of the DOS of the additional electron, simulating a photoexcited electron, shows that it is mostly localized on the B-Ti atom, confirming the conclusion reached using the three double-layer thick slab.
The fact that O\textsubscript{2} withdraws electron density from the Ti\textsuperscript{3+} atoms directly above and below the O subsurface vacancy, and that the lowest unoccupied bands (excluding those localized on the frozen face) are localized on these same Ti atoms, suggest that O\textsubscript{2} adsorbed at defects acts as an electron scavenger by creating high energy holes in TiO\textsubscript{2} that can annihilate excited electrons. Based on these results it is proposed that O\textsubscript{2} acts as an electron scavenger through the following mechanism:

\[ 2\text{Ti}^{3+} + \text{Ti}^{4+} + \text{O}_2 \text{(gas)} \rightarrow 2\text{Ti}^{4+} + (\text{O}_2^{2-})\cdot\text{Ti}^{4+} \quad (6) \]

\[ 2\text{Ti}^{4+} + 2\text{e}^- \rightarrow 2\text{Ti}^{3+} \quad (7) \]

Where, in 6, the Ti\textsuperscript{3+} are the 6f'-Ti and B-Ti titanium atoms neighboring the oxygen vacancy and Ti\textsuperscript{4+} is the 5f'-Ti atom to which O\textsubscript{2} adsorbs and in 7 the Ti\textsuperscript{4+} atoms are the 6f'-Ti and B-Ti titanium atoms neighboring the oxygen vacancy. 7 can be split into two individual reduction steps, each occurring as a Ti\textsuperscript{4+} atom encounters an excited electron.

In the oxidation of organic pollutants in aqueous systems, the perfect TiO\textsubscript{2} surface is covered with adsorbed H\textsubscript{2}O as a result of the favorable adsorption energy of H\textsubscript{2}O on the perfect TiO\textsubscript{2} surface. DFT calculations predict H\textsubscript{2}O adsorption energies of -0.88 eV for a single H\textsubscript{2}O molecule and -0.86 eV per H\textsubscript{2}O for a 2\times2 monolayer of water on the perfect TiO\textsubscript{2} surface, in agreement with past studies.\textsuperscript{40} These results, coupled with the low concentrations of O\textsubscript{2} in aqueous phases and transport limitations of O\textsubscript{2} in liquid, suggest that the probability of O\textsubscript{2} striking a perfect TiO\textsubscript{2} surface and interacting with an excited electron is negligible. Additionally, there is only a small thermodynamic driving force of 0.12 eV for O\textsubscript{2} to displace one of the waters on the surface even when an additional electron is added to the slab, which is within the error bars of DFT. Consequently, the most likely locations for O\textsubscript{2}/TiO\textsubscript{2} interactions,
and hence electron transfer, are at defects that are not occupied by H$_2$O. The calculations show that the adsorption energy per H$_2$O for a monolayer of H$_2$O on the surface with subsurface O vacancies is -0.92 eV, in comparison to -0.86 eV on the perfect surface, suggesting only a slight possible preference for adsorption on and around the defect site. In contrast, O$_2$ does not adsorb to the perfect, neutral surface, but strongly adsorbs near subsurface O vacancies with a calculated adsorption energy of -2.52 eV. However, when a monolayer of adsorbed water surrounds an O$_2$ adsorbed at the O vacancy site the adsorption energy of O$_2$ increases to -2.82 eV. Consequently, the displacement of an adsorbed water molecule by O$_2$ at this defect site is exothermic by -1.87 eV. Because O$_2$ displacement of adsorbed H$_2$O from the perfect surface is unlikely, the energetic favorability for displacement of an H$_2$O molecule adsorbed at a defect site by O$_2$ further suggests that electron scavenging by O$_2$ adsorbed near subsurface O vacancies is the main pathway for electron scavenging by O$_2$ in aqueous TiO$_2$ systems.

6.3.2 The electronic structure of Pt on TiO$_2$

In order to study the effect of Pt on TiO$_2$, a truncated cuboctahedron Pt cluster with 37 atoms was constructed on the (101) anatase TiO$_2$ surface slab. The Pt cluster has three atomic layers (as shown in Figures 6.4a and b), with 19 atoms in the hexagonally shaped bottom layer, 12 atoms in the middle layer, and 6 atoms in the top layer. The cluster has an fcc structure with each layer composed of a (111) close-packed plane. A Hubbard interaction term on the Ti atoms in the Pt/TiO$_2$ system was tested to determine whether it affects the predicted structure and merits the increase in computational expense of including this term. Because Hubbard on-site interaction terms do not localize electrons in metallic systems, no significant effect on structure was found upon inclusion of the Hubbard interaction. Thus, a Hubbard term was not included in
the following calculations because they involve interactions of O\(_2\) and H\(_2\)O with the TiO\(_2\) supported Pt cluster and not direct interactions with the semiconducting TiO\(_2\) surface.

*Figure 6.4:* a) Side view of the Pt\(_{37}\) cluster on the anatase (101) surface, b) top view of the Pt\(_{37}\) cluster on (101) anatase, c) side view of O\(_2\) adsorbed on the Pt\(_{37}\) cluster with E\(_{ads}\) = -1.69 eV, and d) side view of H\(_2\)O adsorbed on the Pt\(_{37}\) cluster with E\(_{ads}\) = -0.52 eV. Gray, red, green and white atoms represent Ti, O, Pt and H atoms, respectively.

Bader charge analysis was performed to analyze the electronic properties of the Pt cluster supported on TiO\(_2\). As the results in Table 6.2 show, the Pt cluster is positively charged by ~ 1 e\(^+\) when it is supported on the neutral, ground state TiO\(_2\) surface. A detailed delineation of the charge of each atom shows that the positive charge does not distribute itself equally among the Pt atoms of the cluster, but instead localizes on the Pt atoms in the bottom layer of the cluster that are directly bonded to O atoms of TiO\(_2\). This results from the higher electronegativity of O relative to Pt, causing Pt atoms to lose electron density to neighboring oxygen atoms. On the other hand, the Pt atoms at the interface with TiO\(_2\) adjacent to Ti atoms are slightly negatively charged as they accept electron density from Ti, although significantly less than the charge.
withdrawn by interfacial O atoms. These results are analogous to those obtained for the interface between Ru and HfO$_2$.\textsuperscript{41}

**Table 6.2:** The change in charge of the Pt$_{37}$ cluster and the TiO$_2$ surface on which it is supported upon the addition of an electron or hole to the slab determined by a Bader charge analysis.

<table>
<thead>
<tr>
<th>system charge</th>
<th>charge difference\textsuperscript{a} (e\textsuperscript{-})</th>
<th>Pt</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0\textsuperscript{b}</td>
<td>-0.98</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>-1\textsuperscript{c}</td>
<td>0.57</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>+1\textsuperscript{c}</td>
<td>-0.59</td>
<td>-0.40</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Positive values indicate a gain of electron density. \textsuperscript{b}The neutral row shows changes in charge with respect to the isolated Pt$_{37}$ cluster and isolated TiO$_2$ slab. \textsuperscript{c}System charges of -1 and +1 represent the addition of an e\textsuperscript{-} and h\textsuperscript{+}, respectively, for which the change in charge relative to the uncharged system is reported.

To model excitation under UV illumination, an extra electron or hole is added to the supercell. The Pt cluster shows similar electron and hole trapping ability, with 0.57 e\textsuperscript{-} of the added electron and 0.59 e\textsuperscript{+} of the added hole distributed over the Pt cluster. The balance of the extra electron/hole is located in TiO$_2$’s metal induced band gap states and are due to the permittivity of TiO$_2$ that allows metal states to penetrate into the dielectric, similar to what is found for Ru on HfO$_2$.\textsuperscript{41} Although the added electron or hole are not entirely localized within the Pt cluster when these charges are added to the system separately, the Coulombic attraction of the electron-hole pair makes it likely that Pt fully localizes both the hole and electron if they are near the Pt cluster. The predicted equal electron and hole trapping ability indicates that the Pt cluster does not act solely as an electron trap as most previous reports have suggested.\textsuperscript{3,9,13,14}
Figure 6.5 shows the PDOS plots of the bare TiO$_2$ and the Pt/TiO$_2$ structures. The energy scale was shifted to align the TiO$_2$ valence band maxima of the two structures. The Fermi level of bare TiO$_2$ is at the valence band edge. The band gap of (101) anatase TiO$_2$ was calculated to be 2.1 eV, which is lower than the experimental value of 3.2 eV. The underestimation of band gaps by DFT is well known, and is primarily caused by the inaccuracy in describing unoccupied bands (virtual states) and hence an inability to accurately describe the energy required to promote an electron to unoccupied bands. The valence band of TiO$_2$ is comprised mainly of oxygen 2p character with a minor contribution from Ti 3d orbitals while the conduction band is primarily comprised of contributions from Ti 3d orbitals with smaller contributions from O 2p orbitals. Adding the Pt cluster to the TiO$_2$ surface introduces a continuum of Pt states within the bandgap and shifts the Fermi level up towards the TiO$_2$ conduction band, although the distribution of the O and Ti states remain in similar locations relative to one another with and without the presence of the supported Pt cluster. The similar

![Figure 6.5](image.png)

*Figure 6.5: a) PDOS for a TiO$_2$ surface and b) PDOS for the Pt$_{37}$ cluster on the (101) anatase surface. The valance band maximums (VBM) of TiO$_2$ are aligned. The solid vertical lines indicate the VBM and the conduction band minimums (CBM) and the vertical dashed lines the Fermi levels of each system.*
location of Ti and O states with and without Pt results from the fact that the platinum cluster primarily interacts with only those Ti and O atoms to which it is directly bonded, leaving the majority of states unperturbed. Thus, the bandgap of bulk TiO$_2$ does not change upon the addition of Pt; instead new states are introduced throughout the bandgap so that no gap exists for the overall Pt/TiO$_2$ system.

The states with energies near the Fermi level are predominately of Pt 5d character. Consequently, when e-h pairs are generated in TiO$_2$, it is favorable for both the electron and hole to transfer to the Pt cluster as it is energetically favorable for the electron to fill low energy states and holes to fill states that are high energy for electrons. This is consistent with the results of a Bader analysis that shows that the Pt cluster is both an electron and a hole trap. Furthermore, because Pt states completely bridge TiO$_2$’s band gap, excited electrons and holes can easily relax through the non-segmented density of state, suggesting that Pt clusters act as e-h recombination centers.

Additionally, the electronic structure of a 7 Pt atom cluster on two TiO$_2$ supercells of different sizes were calculated; one TiO$_2$ supercell containing 144 Ti and O atoms leading to a Pt cluster-cluster distance of 16.5 Å, and a TiO$_2$ supercell containing 72 Ti and O atoms leading to a Pt cluster-cluster distance of 11.0 Å. The PDOS of both Pt/TiO$_2$ systems show that the Pt states completely fill the bandgap of TiO$_2$. This indicates that the complete bridging of TiO$_2$’s bandgap for clusters as small as 7 Pt atoms is not an artifact of periodic boundary conditions imposed on moderately sized supercells. Additionally, Han et al. suggests that the bandgap of the Pt/TiO$_2$ system disappears for Pt cluster sizes as small as trimers. Considering that Pt deposition on TiO$_2$ produces Pt clusters with average diameters of ~2 nm, corresponding to at most a hundred Pt atoms, it is concluded that Pt clusters act as electron-hole recombination centers independent
of loading contrary to claims that Pt becomes an electron-hole recombination center only after the Pt loading exceeds a specific level.

The PDOS of Pt/TiO$_2$ suggests that Pt on TiO$_2$ adsorbs visible light as the Pt metal states allow for the absorption of any wavelength light because there is no gap between occupied and unoccupied Pt states for Pt clusters of at least three atoms. From these calculated PDOS it is concluded that visible light absorption does not result in visible light photoactivity. If an electron-hole pair is generated from the absorption of visible light by Pt, it rapidly recombines within the Pt cluster before it can migrate into TiO$_2$ as there are no barriers to recombination. This hypothesis is tested experimentally and reported in a separate study.

### 6.3.3 Adsorption of O$_2$ on Pt particles supported on anatase

As discussed above, Pt particles on TiO$_2$ act as electron-hole recombination centers independent of Pt loading, which is deleterious to the photoactivity of TiO$_2$. However, it is well known that Pt enhances the photoactivity of TiO$_2$ up to an optimal loading. Consequently, at low Pt loadings Pt clusters on TiO$_2$ must possess an ability to enhance the photoactivity that successfully competes with its acceleration of electron/hole pair annihilation. Unfortunately, no evidence supporting the mechanism for this effect has been reported. In an attempt to identify the source of the enhanced photoactivity, the adsorption characteristics of O$_2$ and H$_2$O on Pt clusters supported on TiO$_2$ was investigated using DFT. Several different configurations and positions for O$_2$ adsorbed to the 37 atom Pt cluster were considered, including a bridging site on top of the cluster, as well as adsorption on the sides and edges of the cluster. All configurations led to O$_2$ adsorption after the starting structures were allowed to relax with the bridge site on the top surface of the Pt cluster found to be the most energetically favorable, in agreement with previous work on O$_2$ adsorption on Pt clusters.$^{45-47}$ As illustrated in Figure 6.4c, each of the two O atoms
form covalent bonds to its neighboring Pt atom of length 1.98 Å where the O-O bond lies parallel to the Pt-Pt axis between the two Pt atoms to which O₂ adsorbs. The predicted adsorption energy is -1.69 eV, which is significantly stronger than that of O₂ chemisorbed on the negatively charged (101) anatase surface (-0.94 eV), and adsorption on the perfect neutral surface to which O₂ has no inclination to adsorb (Table 6.3). The quantity of O₂ adsorbed on Pt relative to adsorption on TiO₂ near O vacancies is likely large because adsorption on Pt is highly favorable, there are a large number of adsorption sites provided by Pt and there is a low concentration of O vacancies in TiO₂ at equilibrium. In contrast, O₂ on bare TiO₂ requires either photoexcited electrons or defects that provide free electron density. This partly explains the ability of Pt to enhance the net rate of electron scavenging by O₂.

Table 6.3: Binding energies in eV for O₂ and H₂O adsorption on the perfect TiO₂, defective TiO₂ and Pt/TiO₂ surfaces. Defect TiO₂ refers to TiO₂ with subsurface O vacancies. No adsorption energy is reported for O₂ adsorption on the neutral and positively charged perfect TiO₂ surfaces because O₂ does not adsorb to them.

<table>
<thead>
<tr>
<th>system charge</th>
<th>0</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>system</td>
<td>perfect TiO₂</td>
<td>defect TiO₂</td>
<td>Pt/TiO₂</td>
</tr>
<tr>
<td>O₂ (eV)</td>
<td>N/A</td>
<td>-2.52</td>
<td>-1.69</td>
</tr>
<tr>
<td>H₂O (eV)</td>
<td>-0.88</td>
<td>-0.88</td>
<td>-0.52</td>
</tr>
</tbody>
</table>

The O-O bond distance of a bridge site adsorbed O₂ is 1.40 Å, which is longer than that of superoxide (1.32 Å), but shorter than that of peroxide (1.49 Å). Furthermore, Bader charge analysis (Table 6.4) shows that O₂ gains 0.65 e⁻ upon adsorption to Pt, which is more than the
0.55 e\textsuperscript{−} gained when O\textsubscript{2} adsorbs in a superoxide-like state and less than the 0.98 e\textsuperscript{−} O\textsubscript{2} gains in a peroxide-like state, as discussed above. This suggests that O\textsubscript{2} can adsorb to Pt because Pt is able to donate electron density to O\textsubscript{2}, which partially fills its second π\textsuperscript{*} orbital, and suggests that O\textsubscript{2}'s π\textsuperscript{*} states lie below the highest lying Pt occupied states. The 0.65 e\textsuperscript{−} gain in charge by O\textsubscript{2} upon adsorption to Pt is primarily withdrawn from the Pt cluster; Bader charge analysis shows that 0.62 e\textsuperscript{−} of the 0.65 e\textsuperscript{−} gained by O\textsubscript{2} is provided by Pt. This leaves the Pt cluster positively charged with a “hole”. Furthermore, population analysis shows this electron density is mostly provided by the two Pt atoms to which the O\textsubscript{2} molecule adsorbs, with each losing \~0.3 e\textsuperscript{+}. The O-O bond length and charge density of O\textsubscript{2} on Pt is between that of the superoxide and peroxide states, as described above and reported in the literature, indicating a different bonding mechanism than for O\textsubscript{2} adsorption to the TiO\textsubscript{2} surface.

An examination of the bonds for O\textsubscript{2} adsorbed on Pt indicates that the individual O’s are most likely bonded to separate Pt atoms, rather than forming a three-center bonding orbital. It is difficult to determine the extent to which the O atoms are bonded to different Pt atoms owing to the extensive state broadening caused by the metallic Pt states. When an extra electron is subsequently added to the system to mimic a photoexcited electron, it is not transferred to the adsorbed O\textsubscript{2}, as evidenced by only an additional 0.04 e\textsuperscript{−} localized on the O\textsubscript{2}, as shown in Table 6.4. Instead, the additional electron primarily fills the hole in Pt, as explained by the fact that the LUMO is comprised of Pt states and that the unoccupied O\textsubscript{2} states are located at higher energies. This is further evidenced by only a slight increase in the O-O bond length after addition of an extra electron to 1.41 Å versus 1.40 Å for the neutral system. This suggests that the electron scavenging mechanism involves O\textsubscript{2} removing electrons from Pt to produce a negatively charged O\textsubscript{2} species and a hole in the Pt cluster that can then be annihilated by a photoexcited electron,
similar to the mechanism identified for electron scavenging from subsurface O vacancies near the TiO$_2$ surface. Consequently, it is proposed that Pt increases the photoactivity of TiO$_2$ by providing many favorable adsorption sites for O$_2$ and coupling adsorption to electron transfer, which leads to increased electron scavenging and OH• formation, both of which are key to photocatalytic activity.

Table 6.4: Charge gain or loss upon O$_2$ and H$_2$O adsorption onto the Pt$_{37}$ cluster supported on TiO$_2$ and the effects of adding an e$^-$ or h$^+$ to the system, determined by Bader charge analysis.

<table>
<thead>
<tr>
<th>System charge</th>
<th>charge gain/loss upon O$_2$ adsorption to Pt (e$^-$)</th>
<th>charge gain/loss upon H$_2$O adsorption to Pt (e$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_2$</td>
<td>Pt</td>
</tr>
<tr>
<td>0$^a$</td>
<td>0.65</td>
<td>-0.62</td>
</tr>
<tr>
<td>-1$^b$</td>
<td>0.04</td>
<td>0.50</td>
</tr>
<tr>
<td>+1$^b$</td>
<td>-0.05</td>
<td>-0.55</td>
</tr>
</tbody>
</table>

$^a$ Positive values indicate an increase in the electron density. $^b$ The change in charge upon addition of an e$^-$ or h$^+$ is relative to the neutral system.

When an electron is removed from the supercell model of O$_2$ adsorbed to Pt, the majority of the added hole still accumulates within the 37 atom Pt cluster; the added hole is not repelled by the Pt cluster, despite the cluster already being positively charged by O$_2$ adsorption, as shown in Table 6.4. This indicates that even with O$_2$ adsorbed on the Pt cluster, both electrons and holes are attracted to the cluster, ruling out the possibility that O$_2$ adsorbed on Pt prevents the cluster from acting as a recombination center. Therefore, O$_2$ adsorption does not change the function of Pt as an e-h recombination center, although it facilitates the scavenging of electrons that significantly reduces e-h recombination so long as a hole does not encounter the Pt cluster. When the rate of electron scavenging due to the O$_2$ adsorption is faster than the rate of e-h
recombination, the photoactivity is enhanced; if on the other hand O₂ adsorption is limited or Pt loading is too high, e-h recombination dominates and thus photoactivity decreases.

Because many metal based catalysts allow adsorbed species to “spill over” onto the support, the ability of O₂ to adsorb onto the TiO₂ surface near the Pt cluster was also investigated. As it has been shown that O₂ adsorption onto the TiO₂ surface is coupled with electron density transfer, and the highest concentration of available electron density is TiO₂ adsorption sites is nearest the Pt cluster, O₂ adsorption was studied at the neighboring Ti atom that is closest to the Pt cluster. The adsorbed O₂ O-O bond length is 1.43 Å, indicating that O₂ gains a significant amount of electron density when adsorbed at this site. On adsorption of O₂ the O₂ bond axis rotates relative to the row of bridging oxygen atoms, positioning one of the O atoms closer to the Pt cluster, as shown in Figure 6.6. This leads to an asymmetry of the O atoms, with one O atom 1.89 Å from the Ti adsorption atom, and 3.11 Å from the nearest Pt atom, while the other O atom lays nearly equidistant from the Pt and the Ti atom (2.18 Å and 2.15 Å, respectively). However, Bader analysis shows equal charge on both O atoms and predicts that upon adsorption O₂ gains 0.92 e⁻ with 0.69 e⁻ being transferred from the Pt cluster and the remaining density provided by the TiO₂ slab. While the electron density transferred from the

Figure 6.6: a) Side and b) top views of O₂ spillover from the Pt₁₇ cluster on the anatase (101) surface. O₂ adsorbs at a spillover site with E_{ad} = -1.47 eV. Gray, red, green and white spheres represent Ti, O, Pt and H atoms, respectively.
TiO$_2$ surface is significant, it is highly delocalized with no atom donating more than 0.06 e\textsuperscript{−}. On the other hand, most of the hole created in the Pt cluster by O$_2$ adsorption localizes on the Pt atom to which the oxygen atom nearest the cluster bonds.

The adsorption energy for O$_2$ at the spillover site is -1.47 eV, which is lower than that found for adsorption at an O defect site (-2.52 eV), and adsorption to the TiO$_2$ surface with two added electrons (-1.63 eV), despite the electron density transferred to O$_2$ being roughly the same. This adsorption energy is also lower than that of O$_2$ directly adsorbed on the Pt cluster (-1.69 eV), although more electron density is transferred to O$_2$ adsorbed at the spillover site. The lower adsorption energy can be attributed to the long O-Pt and O-Ti bonds involving the adsorbed oxygen atom located between the Pt and Ti, as shown in Figure 6.6. The bonds are respectively lengthened by 0.20 Å and 0.26 Å from their lengths for O$_2$ adsorbed directly to the Pt cluster or the perfect TiO$_2$ surface with two added electrons. The attraction between the negatively charged O atom and the hole on the Pt cluster results in a competition between Pt and Ti for bonds with this oxygen atom, straining the O-Pt and O-Ti bonds and lowering the O$_2$ adsorption energy. The fact that the negatively charged adsorbed O$_2$ is attracted to Pt and O$_2$ adsorbed at the spillover site possesses a lower adsorption energy suggest that the Pt cluster has a limited range over which it can transfer electron density so that O$_2$ adsorption facilitated by Pt clusters will likely only occur near the Pt cluster. The ability for the Pt cluster to facilitate O$_2$ adsorption on the adjacent TiO$_2$ surface is further evidence that O$_2$ adsorption depends on electron density transfer to O$_2$, and shows that Pt increases O$_2$ adsorption not only by providing sites for adsorption on the cluster, but also by donating electron density to neighboring surface Ti atoms to transform them into potential O$_2$ adsorption sites.
Because O$_2$ directly interacts with the TiO$_2$ surface, a Hubbard correction was added to determine whether there were any significant differences in the calculated properties; no differences were found (adsorption energy of -1.44 eV and O$_2$ electron gain of 0.94 e$^-$). This suggests that O$_2$ spillover onto the TiO$_2$ surface does not affect the electronic occupation of the Ti d-states because the adsorbed O$_2$ behaves more like O$_2$ adsorbed on a Pt cluster than on the TiO$_2$ surface. This is expected because the Pt cluster provides the electron density that enables O$_2$ to adsorb.

### 6.3.4 Adsorption of H$_2$O on Pt particles supported on Anatase

Water adsorption on Pt was also calculated for a single H$_2$O molecule adsorbed on the Pt cluster, as shown in Figure 6.4d. Adsorbed H$_2$O aligns so that the O atom is located directly above a Pt atom. The H-O-H plane is tilted by 12.5$^\circ$ from the Pt surface plane. The O-H bond length is 0.98 Å, and 0.96 Å for gas phase H$_2$O while the H-O-H angle is 104.4$^\circ$ for the adsorbed molecule and 104.5$^\circ$ for the gas phase molecule. Consequently, the molecularly adsorbed state is only slightly perturbed from the gas phase molecule. The long O-Pt distance of 2.26 Å suggests that one of oxygen’s lone pairs donates into an empty d-orbital of Pt to form a dative “donor-acceptor” bond, implying weak chemisorption. The calculated H$_2$O adsorption energy is -0.52 eV, weaker than the -0.88 eV adsorption energy for H$_2$O adsorbed on bare TiO$_2$, and much weaker than the -1.69 eV adsorption energy for O$_2$ adsorbed at bridge sites on Pt. Because H$_2$O does not adsorb as strongly to Pt as it does to TiO$_2$, nor as strongly as O$_2$ adsorbs to Pt, H$_2$O does not prevent O$_2$ from adsorbing on Pt. As H$_2$O adsorbs on Pt, it does not accept significant charge, irrespective of whether the system is neutral, or positively or negatively charged, as shown in Table 6.4. This suggests that H$_2$O does not accept the holes that are localized within the Pt cluster. This leaves direct hole transfer to organic pollutants as a possible mechanism for hole
removal from the Pt cluster, ignoring recombination, which is not a hole transfer process. However, because H₂O concentrations are generally significantly higher than that of organic contaminants in aqueous solutions, and because Pt is likely to be covered with H₂O and O₂, the probability of an organic molecule adsorbing to Pt and scavenging a hole is low. Thus, the main pathway for hole removal is likely through acceptors on the TiO₂ surface rather than on the Pt surface.

6.4 Discussion

As described above, O₂ does not readily adsorb on the neutral perfect (101) anatase surface, although it does adsorb to the negatively charged surface, where the electron density transfer to O₂ during the adsorption process is analogous to the adsorption of O₂ onto the neutral TiO₂ surface with a photoexcited electron. While this is likely when TiO₂ is exposed to air, the probability is reduced significantly in aqueous solutions where H₂O bonds readily to the TiO₂ surface, blocking O₂ from accepting electron density from a photoexcited electron at the surface. For neutral TiO₂ surfaces without an excited electron, O₂ only adsorbs at defect sites where electron density is available to form bonds between the surface and O₂, such as near subsurface O vacancies where O₂ adsorption is more favorable than H₂O adsorption (as shown schematically in Figure 6.7). O₂ scavenges electrons by accepting electron density associated with the O vacancy creating high-energy holes located on the Ti atoms neighboring the O vacancy that photoexcited electrons can then annihilate (process 1 in Figures 6.7a and b). While these defects provide sites at which O₂ can adsorb to the TiO₂ surface, their equilibrium concentration is low owing to their high formation energy. This limits the extent to which O₂ removes excited electrons from surfaces with subsurface vacancies. In contrast, water readily adsorbs to TiO₂ and acts as a hole acceptor (process 2 in Figures 6.7a and b). However, because
electron scavenging by $O_2$ is limited due to the low number of $O_2$ adsorption sites on TiO$_2$, a large number of excited electrons are present in TiO$_2$ that can recombine with holes limiting TiO$_2$’s photocatalytic activity (process 3 in Figures 6.7a and b).

The DFT calculations show that Pt clusters deposited on TiO$_2$ increase $O_2$ adsorption by providing electron density for $O_2$ adsorption and many favorable $O_2$ adsorption sites, leading to a significant increase in TiO$_2$ photoactivity at low Pt loadings. This is significant because electron scavenging by oxygen is the rate-limiting step in semiconductor photocatalysis and because $O_2$ reduction provides the species responsible for pollutant degradation. When $O_2$ adsorbs on the supported Pt cluster, it scavenges electrons from Pt creating charged oxygen species that can then produce hydroxyl radicals and high energy holes in Pt. When an excited electron encounters...
the now electron deficient Pt cluster, the excited electron annihilates the hole in Pt created by O\textsubscript{2} adsorption (process 4 in Figure 6.7b). As a result, in addition to forming charged oxygen species, the removal of excited electrons reduces the rate of electron-hole recombination in TiO\textsubscript{2} (processes 3 in Figure 6.7). However, the Pt cluster is itself an e-h recombination center independent of Pt loading; when photoexcitation generates an e-h pair, both the electron and hole readily accumulate on Pt clusters with nearly equal energetics, thus enhancing recombination and reducing the photoactivity of TiO\textsubscript{2} (processes 5 in Figure 6.7b) in competition with Pt’s effect of increasing photoactivity through enhancing O\textsubscript{2} adsorption and electron scavenging.

Overall, when the Pt loading is low, excited electrons either interact with O\textsubscript{2} at defect sites, annihilate holes in Pt clusters created by O\textsubscript{2} adsorption or recombine with holes in TiO\textsubscript{2} or the Pt cluster. Because the concentration of defect sites is low and excited holes are more likely to encounter and be scavenged by H\textsubscript{2}O adsorbed on TiO\textsubscript{2} than they are to encounter a Pt cluster and recombine with electrons there, the fate of the photoexcited electron is most likely to fill the holes created in Pt by the electron scavenging of adsorbed O\textsubscript{2}. In contrast, photogenerated holes at low Pt loadings most likely transfer to H\textsubscript{2}O adsorbed to the TiO\textsubscript{2} surface. Thus, at low Pt loadings the effect of increased O\textsubscript{2} adsorption on Pt particles outweighs the enhancement of e-h recombination by Pt resulting in higher photoactivity.

At high Pt loadings Pt clusters reduce the exposed TiO\textsubscript{2} surface area upon which H\textsubscript{2}O molecules can adsorb. This increases the likelihood that holes encounter and transfer to the Pt cluster rather than encountering and being scavenged by an H\textsubscript{2}O molecule adsorbed on TiO\textsubscript{2}. This consequently increases the rate of electron-hole recombination. Furthermore, because fewer adsorbed H\textsubscript{2}O molecules on TiO\textsubscript{2} are available to remove holes, the rate of electron-hole recombination in TiO\textsubscript{2} and Pt itself increases. Thus, at high Pt loadings the increased e-h
recombination rate in Pt clusters has a larger deleterious effect than the increased O₂ adsorption on Pt which enhances photoactivity. This competition between enhanced O₂ electron scavenging, reduced H₂O hole scavenging and e-h recombination in Pt and TiO₂ results in the observed enhanced photoactivity at low Pt loadings and decreased photocatalytic activity at high Pt loadings.

6.5 Conclusions

This study presents a fundamental description of the principles governing the photocatalytic activity of Pt on TiO₂ and aims to provide insight into the effects of deposited Pt, clarifying several long-held assumptions about this process. For example, several researchers have suggested that the initial increase and subsequent decrease of the photoactivity of TiO₂ with increasing Pt loading results from supported Pt clusters separating electron-hole pairs at low loadings, and transforming into electron-hole recombination centers at high Pt loadings. These calculations demonstrate that this description provides an inaccurate picture of the role of Pt in altering the photocatalytic activity of TiO₂.

Our results show that excess electron density must be present at the TiO₂ or Pt surfaces for O₂ to adsorb, and that this electron density is scavenged by O₂ as it adsorbs. Electron density can be provided by photoexcited electrons, excess electrons localized near surface defects, such as O vacancies in TiO₂, or by Pt clusters. In the latter two cases, a photoexcited electron annihilates the holes created by the adsorbed oxygen. As few near surface O vacancies likely exist in TiO₂ at equilibrium, Pt’s primary role in increasing photocatalytic activity is to provide electron density, and hence O₂ adsorption sites, that in effect allows O₂ to interact with the TiO₂ surface. However, Pt also acts as an electron hole recombination center at all Pt loadings. The increase and subsequent decrease in photocatalytic organic degradation with Pt loading stems
from the initial increase in the rate of \( O_2 \) reduction, due to increased \( O_2 \) adsorption and electron scavenging enabled by Pt, which outweigh the increase in electron hole recombination at low Pt loadings; however, the enhanced rate of electron hole recombination with increased Pt loading eventually outweighs the effect of the increased \( O_2 \) adsorption. This clarifies the role of Pt doping on the photoactivity of TiO_2, contributing to the fundamental understanding of this important process.

6.6 References


Chapter 7: Increasing the Photocatalytic Activity of Anatase TiO₂ through B, C and N Doping

7.0 Abstract

Density functional theory (DFT) was used to systematically investigate the ability of B, C and N interstitial and O substitutional surface and near-surface dopants in TiO₂ to facilitate O₂ reduction and adsorption. Periodic boundary condition calculations based on the PBE+U DFT functional show that dopants that create filled band gap states with energies higher than that of the near surface O₂ πₓ* molecular orbital enable O₂ adsorption and reduction. Sites that create unoccupied band gap states with energies below that of the O₂ πₓ* orbital reduce TiO₂’s reduction ability as these states result in photoexcited electrons with insufficient reduction potential to reduce O₂. B dopants in interstitial and relaxed substitutional sites, whose gap states lie > 1.5 eV above the valence band maximum (VBM) and hence above O₂’s πₓ* level, reduce O₂ to the peroxide state with adsorption energies on TiO₂ of -1.22 to -2.77 eV. However, N dopants, whose gap states lie less than ~1 eV above the VBM do not facilitate O₂ adsorption or reduction; O₂ on N doped (101) anatase relaxes away from the surface. Interstitial and substitutional N dopants require two photo-excited electrons to enable O₂ adsorption. C doping, which introduces gap states between those introduced by N and B, enables O₂ adsorption as a peroxide for interstitial doping, although substitutional C does not enhance O₂ adsorption. Dopants for photocatalytic O₂ reduction in order of predicted effectiveness are interstitial B, relaxed substitutional B, and interstitial C. In contrast, substitutional C, and interstitial and substitutional N hinder O₂ reduction despite increasing visible light absorption. Dopants within the surface layer likely deactivate quickly due to the high exothermicity of O₂ reacting with them to form BO₂, CO₂, and NO₂.
7.1 Introduction

As described in Chapter 4, density functional theory (DFT) calculations based on the PBE+U Hubbard corrected exchange-correlation functional to show that Pt particles deposited on TiO$_2$ increase photocatalytic activity by enhancing O$_2$ adsorption, and consequently increasing the rate of O$_2$ reduction upon illumination with UV light.$^1$

Although O vacancies and Ti interstitials in TiO$_2$, and Pt clusters on the (101) anatase surface promote O$_2$ reduction, new approaches to enhance ORR and OPD could overcome major challenges in TiO$_2$ photocatalysis, including the high cost of Pt. One of the most straightforward ways to modify TiO$_2$ involves inducing defects by doping TiO$_2$ with either non-metals, such as B, C, N, S and P$^{12-13}$ or other transition metals such as V, Fe, Cr, Nb, and Mn.$^{14-18}$ Although modified TiO$_2$ materials are often created in an attempt to enable visible light photoactivity, B doped TiO$_2$ outperforms undoped TiO$_2$ even under UV illumination and specific reaction and preparation conditions;$^{19,20}$ in contrast, N doping was shown to have a detrimental effect on UV light photoactivity.$^{19,21,22}$ While many theoretical studies have examined the effect of doping on the band structure of TiO$_2$, from which O$_2$ reduction and photocatalytic behavior has been hypothesized (where high energy states and band gap lowering dopants are associated with increasing the catalytic rates), to date no study has attempted to prove or quantify these effects. The objective of this investigation is to use quantum chemical calculations of the adsorption and reduction of O$_2$ on B, C and N doped (101) anatase to: a) develop a fundamental description of the effect of these dopants on O$_2$ reduction on TiO$_2$ and b) provide governing principles for developing effective and practical reduction photocatalysts for ORR, and hence OPD.
7.2 Computational Methods

Calculations of TiO$_2$ surfaces were performed using the PBE+U method, which combines the Perdew-Burke-Ernzerhof (PBE) DFT generalized gradient approximation (GGA) exchange correlation functional$^{23}$ with a Hubbard onsite Coulomb repulsion term.$^{24}$ Slab supercell models of the (101) anatase surface were described using plane wave periodic boundary condition calculations within the Vienna Ab initio Simulation Program (VASP).$^{43,44}$ Projector augmented wave (PAW) pseudopotentials$^{25}$ that explicitly describe the 2s and 2p electrons of boron, carbon, nitrogen and oxygen atoms, as well as the 3p, 4s and 3d electrons of titanium atoms were used to reduce the computational cost of the calculations. All calculations utilized a 400 eV cut off energy as determined by a convergence analysis conducted over a range of 200 to 500 eV and were conducted at the Γ-point rather than using a k-point expansion because extensive Brillouin zone folding for larger supercells results in the Γ-point spanning a large fraction of k-space without the added computational expense of an explicit k-point expansion.

DFT calculations of first row transition metal oxides such as TiO$_2$ require careful treatment of onsite correlation effects, which often lead to partial occupancies of degenerate 3d states, and thus self-interaction errors, when treated by various DFT functionals. To avoid these errors the GGA+U method was employed with an onsite Hubbard correction U to treat correlation of the 3d electrons at Ti sites. A Hubbard term$^{24}$ of $U_{\text{eff}} = 3.5$ eV was used to incorporate the onsite correlation effects on Coulomb repulsion between Ti d-electrons occupying the same d-orbitals. This value for $U_{\text{eff}}$ for the rotationally invariant formulation of the on-site Hubbard-U term was chosen as a compromise between accurate reaction energies and band gaps,$^{26}$ and has previously been used to describe O$_2$ interactions with the anatase (101) surface.$^{27}$ The DFT+U method was chosen over more demanding methods such as HSE06 due to
the impractically high computational costs of full HSE06 electronic and geometric optimizations of the 192 atom supercells with 15 Å of vacuum space utilized in this work. To validate the use of the DFT+U functional, the adsorption energy of O$_2$ on TiO$_2$ doped with a B atom occupying interstitial site 7 was calculated at the HSE06 level at the PBE+U geometry and found to be -1.70 eV. The PBE+U method predicts an adsorption energy of -1.76 eV, suggesting that PBE+U results in similar O$_2$ adsorption energies at significantly lower computational costs.

The (101) anatase TiO$_2$ surface was modeled using a four double-layer thick (101) slab consisting of a 4 × 2 primitive cell containing 192 atoms, as shown in Figure 7.1. All four double layers were allowed to relax. The four double layer slab representation of the (101) surface enables a reliable description of bulk properties (for example, 3.878 Å inter layer Ti-Ti distance for the second and third double layer of the slab compared to a 3.836 Å inter layer Ti-Ti distance in the bulk), while simultaneously correcting the energy of dangling bonds of frozen surface atoms by allowing both slab surfaces to relax. For instance, a single N dopant in an interstitial bulk position in an equivalent three layer thick slab with a frozen backside double layer exhibits

![Figure 7.1: a) The 4x2x4 anatase TiO$_2$ slab which was used to represent the (101) surface. Small red spheres are O atoms and large gray spheres are Ti atoms. b) Density of states plot of the slab showing the oxygen dominated valence band (VB) and Ti dominated conduction band (CB). The solid gray line shows the total density of states, the red short dashed line shows the O states and the blue long dashed line shows the Ti states.](image)
O shoulder states associated with the frozen surface atoms that extend into the band gap, as shown in Appendix C, Figure C.1. All supercells employ a 15 Å vacuum gap between the top surface and the backside of the periodic image of the slab. Increasing the vacuum gap to 20 Å changed the O\textsubscript{2} adsorption energy to the B doped interstitial 7 site by less than 0.003 eV, and therefore the less computationally demanding 15 Å vacuum gap was utilized. Geometric relaxations were carried out using the Quasi-Newton-Raphson method and were converged to at least 1×10^{-3} eV. All electron density changes were determined using a Bader charge analysis using software from the Henkelman group\textsuperscript{28,29}. The density of states plots presented in this work were shifted to align the Ti 2p states, which are the lowest energy states in the system.

Dopant formation energies are calculated by Equations 1 and 2 for interstitial and substitutional dopants respectively:

\[ E_{doping\_int} = E_{doped\_int} - (E_{bulk} + \mu_{dopant}) \]  

\[ E_{doping\_sub} = E_{doped\_sub} + \mu_{O} - (E_{bulk} + \mu_{dopant}) \]

where \( E_{doping\_int} \) and \( E_{doping\_sub} \) are the enthalpies of doping, \( E_{doped\_int} \) and \( E_{doped\_sub} \) are the calculated energies of the doped cell for interstitial and substitutional dopants, \( E_{bulk} \) is the energy of the undoped surface, \( \mu_{dopant} \) is the chemical potential of the dopant. \( \mu_{dopant} \) is taken to be a fixed value, which is calculated to be a) half of the PBE energy of an N\textsubscript{2} molecule (\( \mu_{N} = \frac{1}{2} E_{N2} \)), the b) energy of a C atom in graphite (\( \mu_{C} = E_{C\text{ in graphite}} \)) or c) the calculated energy of a B atom in B\textsubscript{2}H\textsubscript{6} (\( \mu_{B} = \frac{1}{2} E_{B2H6} - 3/2 E_{H2} \)) for N, C and B dopants, respectively. \( \mu_{O} \) is given by \( \mu_{O} = \frac{1}{2} E_{O2} + \mu_{O}^{'} \), where \( E_{O2} \) is the calculated energy of an isolated O\textsubscript{2} molecule and -2 eV < \( \mu_{O}^{'} \) < 0 eV. The relationship between reference \( \mu_{O}^{'} \) temperature and pressure values and actual equivalents was derived by Reuter et al\textsuperscript{30}. 

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O₂ adsorption energies were calculated using Equation 3:

\[ E_{ads} = E_{surf \cdot O_2} - (E_{surf} + E_{O_2}) \] (3)

where \( E_{ads} \) is the energy of adsorption, \( E_{surf \cdot O_2} \) is energy of the surface of interest with an adsorbed O₂, and \( E_{O_2} \) is the energy of the isolated triplet O₂ molecule. A negative energy indicates that the process is exothermic, although more favorable adsorptions are often described as having “larger” adsorption energies.

In order to avoid expensive excited state calculations photoexcited electrons were modeled by adding additional electrons (at most two) to the slab model. This results in the “excited” electron occupying the lowest previously unoccupied band. Modeling a photoexcited electron simply by the addition of an extra electrons is valid if the photoexcited electron and the photoexcited hole do not strongly interact. In the case of TiO₂, Di Valentin et al. have demonstrated that photoexcited electrons and holes do not strongly interact and behave similarly regardless of whether they are modeled as individual quasi-particles, or by adding or removing an electron from the TiO₂ supper cell or as an exciton.³¹

7.3 Results

In this work, both interstitial and O-site substitutional B, C and N dopants on the surface and in the first subsurface layer were considered as shown in Figure 7.2. As expected, due to their low coordination with other atoms, all dopant atoms initially located at interstitial positions 2, 3 and 6 on the surface are unstable and relax away from the surface and into the vacuum upon geometry optimization. In contrast, dopants initially placed at interstitial sites 1, 4, 5 and 7 and all substitutional sites are stable upon relaxation and are examined further. The formation energies for these defects at 227 °C and an O₂ partial pressure of 0.1 atm are reported in Table
for the doping energies at various $O_2$ chemical potentials see Appendix C Figure C.2 and for the $O_2$ pressure at which a substitutional dopant is more favorable than an interstitial dopant see Appendix C Table C.1. It is worth noting that for C and B dopants, the most favorable substitutional dopant is not favored over the least favorable interstitial dopant at all temperatures under $727^\circ C$ and $O_2$ partial pressures above $1 \times 10^{-18}$ atm. In the case of N doping, the most favorable substitutional doping location (substitutional site 5) only becomes favorable over the least favorable interstitial location (non-NO$_3$ form of interstitial site 7) at $227^\circ C$ and 0.1 atm. Before discussing the effect of TiO$_2$ doping of B, C and N on its $O_2$ reduction activity, first the adsorption and reduction of $O_2$ on undoped TiO$_2$ are briefly summarize to establish the basic mechanism of $O_2$ adsorption and reduction. TiO$_2$ structures that exhibit strong $O_2$ adsorption and reduction indicate that those sites will be active ORR sites and therefore facilitate OP degradation reactions.
Table 7.1: Formation energies of B, C and N dopants at various stable or metastable doping sites at 227 °C and 0.1 atm of O₂

<table>
<thead>
<tr>
<th></th>
<th>B (eV) (^{a})</th>
<th>C (eV)</th>
<th>N (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial 1</td>
<td>-0.37</td>
<td>1.15</td>
<td>2.68</td>
</tr>
<tr>
<td>Interstitial 4</td>
<td>1.01</td>
<td>1.75</td>
<td>4.35</td>
</tr>
<tr>
<td>Interstitial 5</td>
<td>3.57</td>
<td>2.0</td>
<td>4.34</td>
</tr>
<tr>
<td>Interstitial 7</td>
<td>0.66</td>
<td>1.91</td>
<td>4.30 (^{b})</td>
</tr>
<tr>
<td>Substitutional 1</td>
<td>5.67 (7.72)</td>
<td>4.62</td>
<td>4.88</td>
</tr>
<tr>
<td>Substitutional 2</td>
<td>5.74 (7.85)</td>
<td>4.52</td>
<td>4.94</td>
</tr>
<tr>
<td>Substitutional 3</td>
<td>5.31 (8.27)</td>
<td>4.75</td>
<td>4.79</td>
</tr>
<tr>
<td>Substitutional 4</td>
<td>5.48 (7.85)</td>
<td>4.46</td>
<td>4.77</td>
</tr>
<tr>
<td>Substitutional 5</td>
<td>5.78 (7.73)</td>
<td>4.49</td>
<td>4.66</td>
</tr>
</tbody>
</table>

\(^{a}\)The substitutional dopants are RSS dopants while MSS dopants are shown in parenthesis.

7.3.1 Adsorption and Reduction of O₂ on Undoped TiO₂

Here, the adsorption and reduction of O₂ on the undoped (101) TiO₂ anatase surface are briefly summarize to establish a point of comparison for the reactivity of doped TiO₂ surfaces. A more extensive description of the adsorption of O₂ on TiO₂ can be found elsewhere.\(^{1,27,32,33}\) As has been previously described,\(^{1,27,34,35}\) O₂ does not adsorb to the defect free TiO₂ surface unless sufficient electron density is present in the conduction band to enable the formation of Ti-O bonds between the adsorbing O₂ molecule and a Ti atom on the surface while concomitantly reducing O₂. An O₂ molecule near the non-photoexcited TiO₂ surface does not adsorb, but rather relaxes into the vacuum space. The two half-occupied degenerate O₂ \(\pi^*\) molecular orbitals are, however, lower in energy when O₂ is near a surface Ti atom than when it is far from the surface; additionally these \(\pi^*\) levels split, such that the \(\pi^*\) orbital lies lower in energy than the \(\pi^*_y\)
orbital, as shown in Figure 7.3a and Appendix C Figure C.3. Near-surface, but

unadsorbed O₂ was modeled using an O₂ molecule 2.07 Å from a surface Ti atom oriented parallel to the [010] row of surface Ti atoms. At this position, O₂ has a calculated O-O bond length of 1.24 Å, compared to a calculated bond length of 1.23 Å in the gas phase. Splitting of the O₂ π* orbitals to break their degeneracy is caused by interactions with the Ti surface atom’s unfilled 3d orbitals; the lower energy O₂ π*ₜₙ orbitals relative to the O₂ π*ₚ orbitals results from larger overlap between the O₂ π*ₜₙ and Ti d_yz orbitals than between the π*ₚ and the Ti d_xy orbital. When an electron is in the conduction band, for example after promotion from the valence band by photoexcitation, it provides electron density to O₂ π*ₚ-Ti d_yz bonding orbitals, thus allowing

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**Figure 7.3:** Density of states plot for undoped TiO₂. a) an O₂ molecule near the TiO₂ surface where the O₂ is free to relax along the O-O bond but constrained from relaxing either towards or away from the surface. For an O₂ molecule far above the TiO₂ surface see Appendix C Figure C.3. b) O₂ adsorbed to the (101) anatase TiO₂ surface when one excited electron is present in the slab. The insert shows the electron density isosurface for the highest occupied band and the characteristic ~1.33 Å O-O bond length of a super oxide species. c) O₂ adsorbed to a (101) surface TiO₂ anatase surface with two excited electrons present in the slab. The inserts show the isosurface for the two highest occupied bands and the characteristic ~1.44 Å O-O bond length of a peroxide species. d) (101) anatase slab with a sub-surface oxygen vacancy. For all DOS plots, the solid gray line indicates the total density of states, the red short dashed line indicates O₂ states and the blue long dashed line indicates Ti states. In d) the red short dashed line shows the O atoms’ of the TiO₂ slab. The total density of states has been reduced 15 fold in a and c, and 20 fold in b in order to highlight the details in the PDOS lines.
O\textsubscript{2} to adsorb ($E_{\text{ads}}$=-1.10 eV), as shown in the insert of Figure 7.3b and Table 7.2. O\textsubscript{2} adsorption to the (101) anatase surface with one photoexcited electron results in the superoxide state, O\textsuperscript{2-}, as indicated by lengthening of the O\textsubscript{2} O-O bond to 1.33 Å. When a second electron is present near the adsorbing O\textsubscript{2}, it is further reduced to the peroxide state, O\textsubscript{2}\textsuperscript{2-}, by the formation of a second bond, O $\pi^*$-Ti $d_{xy}$, as shown in the insert of Figure 7.3c.

Electron density provided by occupied defects states, such as those accompanying subsurface O vacancies, facilitates O\textsubscript{2} adsorption to undoped TiO\textsubscript{2} when these states have sufficient reducing potential to reduce adsorbing O\textsubscript{2}. Oxygen vacancies facilitate O\textsubscript{2} adsorption because they provide high energy electron density which is localized on the Ti atoms neighboring the O vacancy. This electron density occupies gap states with an energy 1.68 and 2.08 eV above the VBM, as shown in Figure 7.3d, and 0.28 and 0.68 eV above the near surface O\textsubscript{2} molecule’s $\pi_y^*$ and $\pi_z^*$ molecular orbitals, respectively. Consequently, the excess electron density provided by vacancies a few layers below the surface lies sufficiently close to the surface and sufficiently high in energy to transfer electron density to an adsorbing O\textsubscript{2}, resulting in an $E_{\text{ads}}$ of -2.59 eV. Although near-surface vacancies are predicted to act as O\textsubscript{2} reduction sites, their low equilibrium concentration in TiO\textsubscript{2} and the relatively low kinetic barriers to fill these vacancies with O atoms in the presence of O\textsubscript{2}\textsuperscript{36,37} render an approach using O vacancies to enhance O\textsubscript{2} adsorption impractical. This study aims to determine if near surface dopants that possess occupied gap states with energies greater than that of the O\textsubscript{2} $\pi^*$-Ti $d_{yz}$ LUMO indeed facilitate O\textsubscript{2} adsorption and reduction, the rate-limiting step of photocatalytic organic pollutant degradation, and therefore provide a predictive method and design principles for surface modifications to increase photoactivity.
Table 7.2: \( \text{O}_2 \) adsorption characteristics on undoped TiO\(_2\)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Singly photo-excited electron</th>
<th>Doubly photo-excited electron</th>
<th>Subsurface O vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy (eV)</td>
<td>-1.10</td>
<td>-1.74</td>
<td>-2.59</td>
</tr>
<tr>
<td>O-O bond length (Å)</td>
<td>1.33</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>( \text{O}_2 ) charge (e(^{-}))(^{a})</td>
<td>0.53</td>
<td>1.02</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\(^{a}\)The reported charge is relative to triplet (ground state) \( \text{O}_2 \) in the vacuum

7.3.2 Adsorption and Reduction of \( \text{O}_2 \) on Boron Doped TiO\(_2\)

Introducing B atoms into the surface and near subsurface layers of TiO\(_2\) results in B dopants nominally located in either interstitial or oxygen substitutional positions. However, B atoms positioned at O substitutional sites on the O sublattice are only metastable and upon relaxation move into interstitial BO\(_2\)-like sites and in the process create an O vacancy. This is demonstrated by the relaxation of a B atom initially placed at O substitutional site 3, as shown in Figures 7.4a and b. The O sublattice substitutional site is referred to as a meta-stable substitutional site (MSS) and the relaxed structure as a relaxed substitutional site (RSS). The calculated relative energies of B dopants are reported in Table 7.1. An O atom from either an

![Figure 7.4](image)

**Figure 7.4:** Example geometries for the B doped TiO\(_2\) slab showing the a) RSS 3 and b) interstitial 7 sites. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.
H$_2$O or O$_2$ molecule, upon encountering a B RSS dopant, readily fills the O vacancy created by the RSS B atom, to create a shallow interstitial B defect and no O vacancy. Because B migration from a MSS to a RSS is exothermic by at least 1.89 eV, and filling the RSS O vacancy with an oxygen atom from O$_2$ is exothermic by at least 6.29 eV, this thesis will focus on interstitial B dopants and how they affect TiO$_2$ photocatalytic activity.

Interstitial and substitutional B defects in bulk TiO$_2$ decrease its effective band gap by inducing gap states near the conduction band minimum (CBM), as shown previously.$^{38,39}$ Figure 7.5 illustrates the projected density of states (PDOS) for the representative interstitial site 7 and

![PDOS plot](image)

**Figure 7.5:** Density of states plots for B doped TiO$_2$ for a) RSS 3 and b) interstitial 7 sites. The solid gray line indicates the total density of states, the red short dashed line the O states, the blue long dashed line the Ti states and the pink dotted line represents B states. The total density of states has been reduced 15 fold in order to highlight the details in the PDOS lines.
substitutional site 3; the DOS plots for all B dopant sites can be found in Appendix C, Figure C.4-C.6 and the relaxed positions of all dopants can be seen in Appendix C, Figure C.7-C.9. The differences in the character of the dopant induced band gap states between the various dopant sites arise from the nature of the interactions between the B dopant atom and the surrounding TiO$_2$ material. When a B atom resides in the BO$_3$-like interstitial position the neighboring O atoms relax away from the Ti atoms to which they are bound (the Ti-O bonds elongate from 2.11 Å to 2.14-2.25 Å) and towards the interstitial B atom forming bonds with an ~1.40 Å B-O bond distance. A Bader charge analysis indicates that in the BO$_3$ interstitial structure all three of B’s valence electrons are transferred to its three O nearest-neighbors. Because the B interstitial atom donates electron density towards filling the valence orbitals of its nearest-neighbor O atoms, the O atoms draw less electron density from their neighboring Ti atoms. The Ti atoms, therefore, retain more of their valence electron density, giving rise to occupied Ti states in the band gap near the conduction band. An examination of these gap states shows that in fact, they are not solely localized on the Ti atoms nearest to the B dopant, but are instead distributed over the Ti atoms of the slab. This stems from the large number of Ti atoms within the supercell model that are second nearest-neighbors to the B dopant, and whose initially unoccupied 3d states at the CBM are stabilized by delocalization of the electron density provided by the B dopant.

Unsurprisingly, because the structure of RSS B defects involves a BO$_3$-like structure paired with an O vacancy it gives rise to gap states similar to those produced by oxygen vacancy defects as well as unique states associated with B-O interactions in the BO$_3$ structures. The highest energy gap states are comprised of Ti 3d states of the Ti atoms neighboring the O vacancy while the states that lie ~ 1 eV above the VBM in Figure 7.5b originate from the B atom bound to two O atoms and two Ti atoms. When in the RSS the B atom is only partially oxidized
where Bader analysis predicts that it has only lost between 1.5 and 1.7 e$^-$s, significantly less than the three electron oxidation of B that occurs when it resides in an interstitial position. This is because the B atom is only bound to two O atoms rather than the three O atoms of the interstitial site, which lessens the amount of charge B transfers to O atoms, and because the Ti atoms supply B with some electron density through the B-Ti bonds.

Boron dopants in metastable substitutional sites (MSS) give rise to donor states in the gap that lie just below the high-energy states induced by interstitial B dopants. The initial metastable B substitutional defect places B on the oxygen sublattice where it interacts with two nearest-neighbor Ti atoms. The gap states resulting from the MSS B dopant are comprised mainly of B 2s and 2p character and Ti 3d character contributed by B’s nearest-neighbor Ti atoms; these gap states correspond to Ti-B bonds. The Ti-B bonds are more covalent than ionic as evidenced by B only gaining ~0.5 e$^-$ as indicated by Bader charge analysis, whereas the O atom replaced by the B substitutional atom accepts 1.2 electrons from its nearest-neighbors in TiO$_2$. This is not unexpected. Whereas O is significantly more electronegative than Ti, B has an electronegativity similar to and slightly higher than that of Ti, resulting in more charge sharing and less electron transfer in Ti-B bonds.

The high energy occupied states introduced by B doping in TiO$_2$, which are predicted to have similar energies to the band gap states created by O vacancies, suggest that B doping provides electron density with sufficient reducing potential to reduce adsorbing O$_2$ and thus that B doping enhances the photocatalytic activity of TiO$_2$. DFT calculations predict O$_2$ adsorbs exothermically to B doped TiO$_2$ with adsorption occurring at Ti sites, as discussed in detail below. However, for B doping on the surface at oxygen substitutional sites 1 and 2 and at interstitial site 5, O$_2$ adsorbs directly to the B dopant atom to form a BO$_3$ species, as shown in
Appendix C Figure C.10a. Although adsorption of $O_2$ to B at surface substitutional sites 1 and 2 and at interstitial site 5 is highly favorable, these surface sites are directly exposed to the aqueous solvent; the high solubility of $B_2O_3$ in water suggests that exposed $BO_3$ structures will dissolve in aqueous conditions and that their dissolution will lead to the deactivation of these dopant structures. Consequently, these structures will not be discussed further except to mention that they will contribute to the catalytic activity until they dissolve.

Interstitial B dopants give rise to high energy occupied gap states that enable strong $O_2$-$TiO_2$ bonding with adsorption energies of $-1.56$, $-2.77$ and $-1.76$ eV for interstitial sites 1, 4 and 7, respectively. The strong adsorption of $O_2$ on interstitial B doped $TiO_2$ corresponds to the formation of surface peroxide species by reduction of $O_2$. This is evident from both the characteristic $\sim 1.45$ Å O-O bond length and the $\sim 0.95$ e$^-$ charge of the adsorbed $O_2$ molecule, as shown in Table 7.3 and Figure 7.6a for interstitial site 7. $O_2$ gains only $\sim 0.95$ e$^-$, in stark contrast to the nominal two electrons $O_2$ gained to form the peroxide species because the adsorbed $O_2$

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure7.6.png}
\caption{$O_2$ adsorption to B doped $TiO_2$ anatase (101) surface at a) interstitial 7 and b) RSS 3 sites. The O-O bond length is indicated in the right hand panels. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.}
\end{figure}
molecule bonds to a Ti surface atom with which it shares electron density through an $O_2 \pi^* \rightarrow \text{Ti} d_{yz}$ and an $O_2 \pi^* \rightarrow \text{Ti} d_{xy}$ bond, analogous to the $O_2$-$\text{Ti}$ bond formed upon $O_2$ adsorption on the perfect surface as illustrated by the inset of Figure 7.3c. The highly favorable adsorption of $O_2$ to interstitial site 4 ($E_{\text{ads}} = -2.77$ eV) arises from interactions between $O_2$ and the partial vacancy created by a surface O atom that relaxes into the bulk to associate with the B atom at interstitial site 4, as seen in Appendix C Figure C.10b. When the $O_2$ molecule adsorbs, it rotates away from being parallel to the row of Ti atoms to point towards the descended surface O atom (see Appendix C Figure C.10b).

<table>
<thead>
<tr>
<th>Site</th>
<th>$O_2$ adsorption energy (eV)</th>
<th>$O_2$ bond length (Å)</th>
<th>$\text{B charge before } O_2$ adsorption (e$^-$)</th>
<th>$\text{B charge after } O_2$ adsorption (e$^-$)</th>
<th>$O_2$ charge (e$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inter. 1</td>
<td>-1.56</td>
<td>1.45</td>
<td>0.0</td>
<td>0.0</td>
<td>0.93</td>
</tr>
<tr>
<td>Inter. 4</td>
<td>-2.77</td>
<td>1.45</td>
<td>0.0</td>
<td>0.0</td>
<td>1.02</td>
</tr>
<tr>
<td>Inter. 7</td>
<td>-1.76</td>
<td>1.45</td>
<td>0.0</td>
<td>0.0</td>
<td>0.96</td>
</tr>
</tbody>
</table>

$^a$O$_2$ forms BO$_2$ at interstitial site 5

When $O_2$ adsorbs to the B doped TiO$_2$ surface electron density from the highest energy occupied gap states, which are localized over the Ti atoms of the TiO$_2$ slab, transfers to the adsorbing $O_2$. It is important to mention here that the highest occupied band after $O_2$ adsorption to the B doped TiO$_2$ surface is not comprised of Ti-$O_2$ bonds (Appendix C, Figure C.4d); instead, it is composed of the same Ti 3d states distributed throughout the slab that provide the electron density to the adsorbing $O_2$. Because each B dopant donates three electrons to the unit cell of our supercell model of the TiO$_2$ surface and only two electrons are required to fully reduce $O_2$, one electron is expected to remain in the high energy Ti states. This indicates that each interstitial B
provides electron density capable of reducing more than one adsorbing O₂; and indeed when a
second O₂ molecule is placed near the interstitially B doped TiO₂ surface it does in fact adsorb
exothermally by -1.01 eV relative to only one adsorbed O₂ on the surface (Appendix C Figure
C.10c).

Substitutional B dopants in RSS positions also provide electron density which is capable
of enabling O₂ adsorption. Like interstitial B atoms, O₂ adsorption to TiO₂ surfaces containing
RSS B dopants results in a peroxide O₂ species, as demonstrated for RSS 3 as shown in Figure
7.6b. Appendix C Table C.2 reports the adsorption energies and bond lengths for O₂ adsorbed to
TiO₂ containing B in RSSs. As mentioned above, before O₂ adsorption the high energy states are
Ti 3d states localized on the Ti atoms neighboring the O vacancy; therefore, upon O₂ adsorption
electron density is transferred to O₂ from these Ti states and not the B dopant, which Bader
analysis predicts retains its charge of ~1.2 e⁻’s after adsorption of O₂. The low energy band gap
state corresponding to the B-O bond is still present after O₂ adsorption, (Appendix C Figure
C.5e).

In contrast to RSS B dopants, the MSS B dopant possess less reducing potential than the
RSS and interstitial B dopants and so O₂ adsorption near MSS B atoms results in less stable O₂
adsorbates, as shown in Appendix C Table C.1. O₂ adsorbed near an MSS B dopant forms a
superoxide species as indicated by both the shorter 1.32 Å O-O bond length, and the fact that O₂
gains only 0.51-0.58 e⁻’s, depending on B dopant location, upon adsorption. Of the ~0.55 e⁻
gained by the adsorbing O₂, roughly 0.25 e⁻ is provided directly from the MSS B dopant while
the remaining ~0.25 e⁻ is provided by the Ti atoms of the slab.
Not only does B doping facilitate O\textsubscript{2} absorption to the TiO\textsubscript{2} surface regardless of doping structure, but excited electrons also increase the O\textsubscript{2} adsorption strength and reduce the B dopant to facilitate additional O\textsubscript{2} reduction. When an excited electron encounters an O\textsubscript{2} adsorbed to the anatase surface doped with an interstitial B the excited electron backfills the hole created in the previously occupied gap states oxidized upon reducing O\textsubscript{2}. For the interstitial B case the photoexcited electron slightly stabilizes the Ti-O\textsubscript{2} adsorbate, which increases the adsorption energy from -1.76 to -1.88 eV; additionally, rather than further reducing the adsorbed O\textsubscript{2}, the excited electron backfills the Ti 3d state that provided electron density to the adsorbing O\textsubscript{2} molecule.

When an excited electron encounters an O\textsubscript{2} adsorbed to the MSS B-doped TiO\textsubscript{2} surface, the O\textsubscript{2}-Ti bond is significantly strengthened. In the case of an O\textsubscript{2} adsorbed to the B dopant in a MSS, for example substitutional site 3, the adsorption energy increases in magnitude from -0.47 eV to -0.90 eV when a photo-excited electron is present; nevertheless the resulting adsorbed species is still a superoxide. Rather than the photoexcited electron localizing on the adsorbed O\textsubscript{2}, which only gains an additional 0.03 e\textsuperscript{-}, it localizes on the B dopant as indicated by a 0.26 e\textsuperscript{-} increase in electron density as determined by Bader analysis. A second photoexcited electron does not significantly increase the magnitude of the O\textsubscript{2} adsorption energy in the MSS case, but instead acts to fully reduce the O\textsubscript{2} to the peroxide state, which is evidenced by the 1.45 Å O-O bond length and by 1.02 e\textsuperscript{-}’s localized on the adsorbed O\textsubscript{2}.

Overall, doping the TiO\textsubscript{2} surface with B facilitates O\textsubscript{2} adsorption and consequently, oxygen reduction regardless of the doping site. Therefore, our results predict that B doping is an effective approach for increasing the photoactivity of TiO\textsubscript{2}. However, it is worth noting that because B dopants create gap states, which at the surface or near surface enhances O\textsubscript{2} adsorption,
bulk B dopants also act as electron/hole recombination centers that lower the number of excited electrons and thus hinder electron transfer to the surface and lower the overall photochemical efficiency. Further study is required to quantify these effects. Therefore, to the degree that it is practical, B dopants should be introduced in the near surface region where they act as both O$_2$ adsorption sites and as reducing agents.

7.3.3 Adsorption and Reduction of O$_2$ on Carbon Doped TiO$_2$

Both near surface substitutional and interstitial C atoms introduce states into the band gap of TiO$_2$ where interstitial C doping generally introduces states that lie higher in the band gap than substitutional C, as previously predicted for bulk structures$^{40}$ and shown for near surface C dopants in Figures 7.7 and 7.8, respectively. Density of states plots and geometries of all structures considered can be found in Appendix C, Figures C.11-C.12 and C.13-C.14, respectively.

Interstitial C atoms introduce occupied gap states with energies that lie between 1.16 and 1.59 eV above the VBM, which are predicted to be sufficiently high in energy to reduce O$_2$ and thus enable its adsorption. In contrast, substitutional C atoms introduce both occupied and unoccupied gap states. The occupied states possess energies between 0.29 eV and 1.02 eV above the VBM, which is predicted to lie below the O$_2$ $\pi^*$ LUMO energy, and thus do not have sufficient reducing potential to reduce O$_2$ and consequently are unable to facilitate O$_2$ adsorption. The unoccupied gap states induced by interstitial C lie higher in the gap at approximately 2 eV above the VBM. The predicted formation energies of C dopants are reported in Table 7.1.

The gap states induced by interstitial C consist of both C-O bonds as well as higher energy states with electron density distributed over the Ti atoms within the supercell model,
analogous to interstitial B dopants. The occupied gap states induced by C interstitials lie at molecular O$_2$’s LUMO, as shown in Figure 7.6, which suggests that O$_2$ will adsorb to the TiO$_2$ surface near C interstitials. On the other hand, where substitutional B atoms rapidly relax from

![Figure 7.7](image-url)  
**Figure 7.7:** Density of states plots for interstitial site 7 C doped TiO$_2$ (101) anatase. a) before O$_2$ adsorption and b) after O$_2$ adsorption. The solid gray line indicates the total density of states, the blue long dashed line the Ti states, the brown dotted line represents C states, and the red short dashed line the a) near surface O$_2$ states before O$_2$ adsorption and b) O$_2$ states after adsorption. O$_2$ states before adsorption and shown in a) are taken from Figure 7.3a. The O atoms of the near surface O$_2$ are 2.07 Å from a surface Ti atom of an undoped TiO$_2$ slab and the O$_2$ has an O-O bond length of 1.23 Å. The total density of states has been reduced 30 and 20 fold in a and b respectively in order to highlight the details in the PDOS lines. c) Geometry of the O$_2$ adsorption to interstitial site 7. Large gray spheres represent Ti atoms, medium brown spheres represent B atoms, and small red spheres represent O atoms.
the initial MSS on the oxygen sublattice to interstitial like RSS positions, C substitutional atoms at oxygen positions do not relax off these sites. Rather they remain on the oxygen sublattice and gain significant electron density (~0.8 e⁻’s). The gap states induced by C substitutional doping are comprised of C 2s and 2p character and Ti 3d contributions; that is, these states correspond to

Figure 7.8: Density of states plots for substitutional site 4 C doped (101) anatase TiO₂. a) before O₂ adsorption and b) after O₂ adsorption. The solid gray line indicates the total density of states, the blue long dashed line shows Ti states, the brown dotted line represents B states, and the red short dashed line the near O₂ states a) before O₂ adsorption and b) after O₂ adsorption to the surface with an excited electron. O₂ states in a) before adsorption are taken from Figure 7.3a. The total density of states has been reduced 15 and 20 fold in a and b respectively in order to highlight the details in the PDOS lines. c) Geometry of the thermoneutral O₂ adsorption to (101) anatase doped with C in substitutional site 4 and in the presence of a photoexcited electron. Large gray spheres represent Ti atoms, medium brown spheres represent B atoms, and small red spheres represent O atoms.
bonds between the substitutional C dopant and its neighboring Ti atoms.

The relative energies of interstitial C’s occupied gap states compared to O$_2$’s $\pi^*$ orbitals indicate that O$_2$ adsorption to the (101) anatase surface is only facilitated by C dopants positioned at interstitial sites 1, 4 and 7 because only these C interstitial defects induce occupied gap states with adequate reducing potential to reduce O$_2$. When an O$_2$ molecule is initially placed on the (101) surface near all other substitutional or interstitial C defects it relaxes away from the surface and into the vacuum, or, as in the case of C in substitutional sites 1 and 2 and interstitial sites 1 and 5, it forms CO$_2$, thus eliminating these defects as viable ORR and OPD reaction sites. Our geometry optimizations predict that O$_2$ does not adsorb to surfaces with dopants that do not induce occupied states with energies above the states corresponding to O$_2$’s $\pi^*$ orbitals, that is that lack sufficient reducing potential to transfer electrons to O$_2$, and corroborate our predictions based on the calculated relative energies of the filled electronic energy levels. O$_2$ adsorbed at interstitial sites 4 and 7 adsorbs favorably by -1.92 and -1.84 eV, has calculated O-O bond lengths of 1.45 and 1.44 Å, a ~1.88 Å Ti-O bond length and accepts 0.95 and 0.97 of an electron, respectively, as reported in Table 7.4. The electron density transferred to O$_2$ is partially provided by the interstitial C dopant. A C atom in interstitial site 4 donates 0.87 e$^-$ to the adsorbing O$_2$ molecule while a C atom in interstitial site 7 only loses 0.22 e$^-$ and the remaining electron density donated to the adsorbing O$_2$ molecule is provided by Ti 3d states. Similar to O$_2$ adsorption on surfaces containing interstitial and RSS B atoms, O$_2$ adsorbs as a peroxide on interstitially C doped TiO$_2$ and forms Ti d$_{xy}$-O$_2$ $\pi^*$ and Ti d$_{xy}$-O$_2$ $\pi^*$ bonds to surface Ti atoms. Our results predict that C interstitials give rise to occupied states sufficiently high in the band gap to reduce O$_2$, and thus facilitate O$_2$ adsorption and reduction, whereas substitutional C atoms do not. The \textit{ab initio} description of the electronic structure of C doped TiO$_2$ clearly establishes how the
calculated density of states induced by dopants predicts whether a specific dopant enables O₂ adsorption; the calculated energy of occupied gap states of dopants that provide electron density with energy in excess of the O₂ π* LUMO indicates favorable O₂ adsorption and reduction, while occupied gap states calculated to lie below O₂’s LUMO predict that O₂ will not adsorb, as shown in Figures 7.7 and 7.8.

Table 7.4: O₂ adsorption characteristics on interstitially C doped TiO₂

<table>
<thead>
<tr>
<th>Site</th>
<th>O₂ adsorption energy (eV)</th>
<th>O₂ bond length (Å)</th>
<th>C charge before O₂ ads (e⁻)</th>
<th>C charge after O₂ ads (e⁻)</th>
<th>O₂ charge (e⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inter. 4</td>
<td>-1.92</td>
<td>1.45</td>
<td>3.17</td>
<td>2.30</td>
<td>0.95</td>
</tr>
<tr>
<td>Inter. 7</td>
<td>-1.84</td>
<td>1.44</td>
<td>2.16</td>
<td>1.94</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*O₂ does not adsorb to the substitutionally C doped TiO₂ and forms CO₂ at interstitial site 5.

Photoexcited electrons are necessarily present under photocatalytic conditions and because of the presence of unoccupied gap states associated with substitutional C doping, they are predicted to have an effect on the O₂ adsorption behavior on C doped TiO₂. Therefore, these interactions are discussed in some detail. Generally, C atoms in interstitial sites induce occupied gap states sufficiently high in the gap to reduce O₂. However, substitutional C provides both occupied gap states that are too low in energy to reduce O₂ and unoccupied gap states that are predicted to be capable of reducing O₂ when occupied by photoexcited electrons. Indeed, the presence of a photoexcited electron strengthens the O₂-Ti bonds of interstitially C doped TiO₂, where the O₂ adsorption energy changes from -1.75 eV to -1.85 eV. Although substitutional C atoms enable O₂ adsorption when coupled with photoexcited electrons, O₂ adsorption is only thermoneutral. In the case of C in substitutional site 4, both one and two photoexcited electrons results in thermoneutral O₂ adsorption in the peroxide state (1.33 Å O-O bond length and ~0.6 e⁻).
’s transferred to O2). The thermoneutral nature of O2 adsorption on photoexcited substitutionally C doped TiO2 suggests that the increase in energy of the electron in the half occupied O2 \( \pi^* \) orbital due to Ti-O bond formation involves an energy penalty similar to the energy decrease of the photoexcited electron due to relaxation of the electron from the C induced gap state to the O2–Ti \( \pi^* \)-d\(_{xy}\) bond. The transfer of less than one electron to O2 adsorbing on the doubly photoexcited TiO2 surface with a substitutional C atom (~0.6 e−’s transferred to O2) suggests that the photoexcited electron occupying the normally vacant second induced gap state above the Fermi energy does not have sufficient reducing power to transfer electron density to O2; i.e. one photoexcited electron lies higher in energy than the O2 \( \pi^*_z\)-Ti d\(_{xy}\) bond, but the second photoexcited electron occupies a level lower in energy than the O2 \( \pi^*_y\)-Ti d\(_{xy}\) bond, as shown in Figures 7.8b and c. However, the formation of interstitial C defects, which facilitate O2 reduction, is energetically favored over the formation of substitutional C dopants. Similar to the B doped (101) anatase surface, C doping likely increases O2 reduction most effectively for dopants located in the near surface region where electron trapping promotes O2 reduction rather than electron hole recombination, but further study is required to quantify electron hole recombination kinetics.

**7.3.4 Adsorption and Reduction of O2 on Nitrogen Doped TiO2**

Substitutional and interstitial N doping of bulk and surface TiO2 was previously shown\(^{41,42}\) to decrease the band gap of TiO2 by introducing states that create a shoulder in the DOS at the VBM or that induce states in the band gap near the VBM, as shown in Figure 7.9. DOS plots and N geometries for all dopant sites are shown in Appendix C Figures C.15&C.16 and C.17&C.18, respectively. The smaller band gap explains the visible light photocatalytic activity of N doped TiO2.\(^{43}\) The position of the highest lying occupied states introduced by both the interstitial and
substitutional N dopants are found to lie within 1 eV of the VBM where interstitial sites create distinct, occupied band gap states while substitutional sites create shoulder states. Additionally,

**Figure 7.9:** Density of states plots for N doped TiO$_2$ in a) substitutional site 4, b) interstitial site 7 and c) the N$_2$/O$_2$ structure. The solid gray line indicates the total density of states, the dark blue long dashed line Ti states, the bright blue dotted line N states, the light red short dashed line near O$_2$ states before O$_2$ adsorption and the dark red dashed line in c) indicates the O atom in the pore. The O$_2$ states before adsorption are taken from Figure 7.3a. The total density of states has been reduced 15 (a and b) and 2 (c) fold in order to highlight the details in the PDOS lines.
substitutional N dopants induce empty levels that also lie only ~1 eV above the VBM. Interstitial and substitutional N atoms induce states that are significantly lower in the band gap of TiO$_2$ than the other dopants investigated, however, because they lie below O$_2$’s lowest lying empty $\pi^*$ orbitals they have insufficient reducing potential to reduce O$_2$, although they do significantly redshift TiO$_2$’s excitation energy. Thus, N doping that forms substitutional and interstitial dopant structures are not predicted to enhance O$_2$ adsorption and thus, do not facilitate the ORR more than merely enabling visible light photoactivity.

In contrast to B and C dopants, Bader charge analysis predicts that substitutional N atoms gain between 0.97 and 1.18 e”’s and that interstitial N atoms gain between 0.33 and 0.46 e”’s, whereas B and C dopants only gain electron density when located in substitutional sites. Interstitial N atoms gain electron density because they form covalent N-O bonds and both the N and the O atoms are bound to Ti atoms; in contrast, B and C only bond to O atoms. Interstitial and substitutional N atoms induce states that significantly lower the band gap of TiO$_2$ and therefore redshift TiO$_2$’s excitation energy, however, because they lie below O$_2$’s lowest lying empty $\pi^*$ orbitals they have insufficient reducing potential to reduce O$_2$.

In addition to substitutional and interstitial structures, N dopants also form a structure in the near-surface region named the N$_o$/O$_v$ structure where O atoms near N interstitials relax into the TiO$_2$ pore (see Figure 7.9). This relaxation reduces steric repulsion within the N$_o$/O$_v$ structure to stabilize it by 0.60 eV relative to N in interstitial site 7. This relaxation involves significant displacement of surface Ti and O atoms into the vacuum, which is precluded for bulk relaxation of the N$_o$/O$_v$ dopant structure. This structure induces occupied gap states that lie 1.3 eV above the VBM, significantly higher than the states induced by other N dopant structures. Nevertheless, our results predict that these energy levels lie too low in the band gap to facilitate O$_2$ adsorption.
The relaxation of O$_2$ into the vacuum in geometry optimizations where O$_2$ is initially placed on the interstitial and substitutional N doped (101) anatase surface corroborates the prediction that this doping induces gap states that lie too low in the band gap to facilitate O$_2$ adsorption. This occurs for N doping at all substitutional and interstitial sites with the exceptions of N occupying interstitial sites 1 and 5, where instead NO$_2$ is formed, and interstitial site 7, where O$_2$ forms a metastable adsorbate with an endothermic adsorption energy of 0.10 eV, as referenced to the N$_o$/O$_v$ structure. Upon O$_2$ adsorption at interstitial sites 1 and 5 NO$_2$ is formed, which makes this site inactive for further reaction. The inability of O$_2$ to favorably bond to the TiO$_2$ surface in the presence of near surface N dopants results from the high energy of O$_2$’s $\pi^*$ orbitals relative to the energies of the highest occupied gap states induced by N doping; thus, occupied gap states induced by N doping have insufficient reducing potential to reduce O$_2$ and enable O$_2$ adsorption and ORR.

Although N dopants increase photoexcited electron density in TiO$_2$ by decreasing its band gap to therefore allow absorption of longer wavelength solar photons, even singly excited TiO$_2$ near a N dopant does not aid O$_2$ adsorption because when a photoexcited electron encounters a N dopant it loses reduction potential by relaxation to the lower energy N induced empty gap states. Instead of adsorbing, O$_2$ relaxes into the vacuum when initially placed on singly photoexcited (101) anatase near substitutional N dopants. To enable O$_2$ adsorption on substitutionally N doped TiO$_2$, two photoexcited electrons must be added to the slab: one that fills the lower energy gap state, and a second that occupies the second lowest normally unoccupied states that lie at the CBM and which possess sufficient reducing potential to reduce adsorbing O$_2$. Because O$_2$ reduction in the presence of N dopants requires a second photoexcited electron, N doping hinders O$_2$ reduction and, in the case of UV light photoexcitation, is worse
than no doping at all, which only requires a single photoexcited electron to enable the adsorption of O₂. Only N dopants that form the N₀/Oᵥ structure enable a single photoexcited electron to reduce O₂ and facilitate its adsorption, which is exothermic by -0.48 eV. O₂ adsorption at N₀/Oᵥ sites occurs because the initially unfilled N-O π* states lie above the O₂ LUMO, as shown in Figure 7.9. These results suggest that although N doping lowers TiO₂’s band gap, N’s propensity to act as a low energy electron trap hinders the ability of TiO₂ to reduce oxygen such that overall the effect of N on TiO₂’s UV photocatalytic activity is detrimental, as is observed experimentally.

7.4 Conclusions

In this work calculated electronic structures of doped TiO₂ surfaces to elucidate how doping affects O₂ adsorption and reduction and to predict that doping the TiO₂ surface with elements that create filled gap states with energy greater than the near surface O₂ π* molecular orbital (O₂ LUMO) increases O₂ adsorption and reduction, the rate-limiting step in photocatalytic organic pollution degradation and other photocatalytic processes. However, sites that create empty states lower than the O₂ π* orbitals handicap TiO₂’s reduction abilities, as these states decrease the photoexcited electron’s reduction potential. The most effective dopants for photocatalytic ORR in order of predicted effectiveness are interstitial B, substitutional (relaxed) B, interstitial C, and substitutional C. Our calculations predict that interstitial N and substitutional N are in fact deleterious to O₂ adsorption and reduction, despite their effect of lowering the band gap of TiO₂. In contrast, B dopants increase O₂ adsorption regardless of whether the dopant is in a substitutional or interstitial site, although B atoms in substitutional sites will likely rapidly relax to the more stable interstitial sites. C dopants enhance O₂ reduction depending on the dopant location with the more stable interstitial sites enhancing adsorption with
or without photoexcited electrons. Although N doping has previously been used in attempts to enhance the ORR by increasing the visible light photoactivity of TiO$_2$, these results predict that it generally hinders O$_2$ adsorption and reduction and therefore limits UV photocatalytic ORR, although as intended, they do enable visible light photoactivity by lowering the band gap. To increase UV activity, it is important that B and C dopants reside near the surface where they act as O$_2$ reduction sites rather than in the bulk where they act as electron traps or worse, electron-hole recombination centers. This work also demonstrated that the likelihood of photocatalytic oxygen reduction can be predicted by calculating the relative energies of the highest occupied band and the O$_2$ $\pi_z^*$ molecular orbital. This enables the rapid evaluation and screening of dopants and catalysts for oxygen reduction reactions and is applicable to TiO$_2$ OPD and to ORR on other substrates and reactions.

7.5 References


Chapter 8: Conclusions and Recommendations for Future Work

8.1 Conclusions

This work investigated two light driven metal oxide catalysts for renewable H₂ production and organic pollutant degradation. A hercynite material was investigated for use in solar thermal water splitting and TiO₂ was investigated for use in photocatalytic organic pollutant degradation (OPD). Computational and experimental methods were undertaken to develop a deeper understanding of the mechanisms involved in these processes. This understanding will further the ability of the scientific community to develop more effective, efficient and economic routes to H₂ generation and organic pollutant remediation. The findings of the individual objectives are briefly summarized below, for a full set of finding please refer to the individual Chapters addressing the individual objectives.

8.1.1 The chemistry of the hercynite solar thermal water splitting cycle

This work investigated the operating mechanism of the hercynite solar thermal water splitting cycle using computational and experimental methods. The hercynite cycle was found to operate via an O-vacancy mechanism rather than the previously reported displacement mechanism. Density functional theory predicted that the O-vacancies in hercynite have the reduction power to split water, while displacement reactions do not. This finding was confirmed by high-temperature XRD and EDS studies which did not detect the displacement reaction products and SFR water splitting experiments.
8.1.2 Isothermal and near-isothermal solar thermal water splitting

This work investigated isothermal and near isothermal water splitting, which was previously thought to be thermodynamically non-viable. Not only was it shown that isothermal water splitting is possible, but that the hercynite cycle based ITWS was capable of producing more H₂ than traditional temperature swing water splitting operations. This is due to kinetic limitations of the hercynite material. Near isothermal water splitting, where the oxidation temperature was greater than or equal to 1350°C was found to produce even more H₂ than ITWS. In the future, it is likely that STWS cycles will operate isothermally or near-isothermally.¹

8.1.3 Extracting complex gas-solid solar thermal CO₂ splitting reaction kinetic for the hercynite cycle

This work investigated the kinetics of the oxidation step in hercynite based isothermal CO₂ splitting. Stagnation flow reactor experiments were conducted and a mathematical method was used to determine the oxidation rates from the CO generation data. Kinetic solid state theory was expanded to enable its use in this work. Oxidation was found to be a surface controlled process with an activation energy of 80 kJ/mol.²

8.1.4 The effect of Pt on the photocatalytic activity of TiO₂.

This work investigated the mechanism by which Pt increases and then decreases the photocatalytic activity of TiO₂ with increasing Pt loading using DFT. Without Pt, O₂ does not readily adsorb to the TiO₂ surface because there are no electrons available to form O₂-TiO₂ bonds; this hinders OPD. Pt facilitates O₂ adsorption and reduction on the TiO₂ surface by providing high energy electrons which can form O-Pt bonds, which increases the photocatalytic activity of TiO₂. However, Pt bridges the band gap of TiO₂ enabling electron hole
recombination. At low Pt loadings, the increased O$_2$ adsorption increases the photocatalytic rate more than Pt increases electron-hole recombination. At high Pt loadings, the increased electron-hole recombination decreases the photocatalytic rate more than the increased O$_2$ adsorption increases the photocatalytic rate.$^3$

8.1.5 Altering the photocatalytic activity of TiO$_2$ via non-metal dopants

This work investigated the use of non-metal dopants to enhance photocatalytic OPD by providing high energy electron density to increase the O$_2$ reduction reaction. B, and interstitial C dopants induced electron filled high energy band gap states which were found to facilitate O$_2$ adsorption, and reduction and therefore OPD. Substitutional C dopants and N dopants induced band gap states which are either too low in energy to reduce O$_2$ and, hence, form an O$_2$ surface bond, or are unfilled and therefore did not facilitate O$_2$ reduction and in the case of N doping actually hindered O$_2$ reduction.$^4$

8.2 Recommendations for Future Work

The work presented in this dissertation provides a deeper understanding of STWS and photocatalytic OPD and lays the groundwork for continued improvements in the efficiency and effectiveness of STWS and photocatalytic materials. Areas of research to further advance the understanding developed in this work, and potential new avenues of investigation will briefly be suggested below.

8.2.1 Future STWS investigations

This fundamental work on the hercynite STWS material and the potential for its use in isothermal or near isothermal water splitting only touches on two of the three inter-related, aspects of STWS that need to be considered and improved upon if STWS is to become an
efficient and commercially viable process: 1) STWS materials, as discussed in this work; 2) systems operations, which includes isothermal, near isothermal or temperature swing operations as discussed in this work but also includes vacuum or inert sweep gas methods to reduce the O\textsubscript{2} partial pressure which was not investigated; and 3) STWS reactor design which was also not investigated in this work.

The hercynite materials should be further investigated to determine its kinetic properties and to identify dopants which may improve its performance. Water splitting and hercynite reduction kinetic parameters should be determined. To do this the method developed for CO\textsubscript{2} splitting in Chapter 5 should be used. In investigating the oxidation reaction it may be necessary to first develop a kinetic expression for hercynite re-oxidation by O\textsubscript{2}. This would help reactor designers model this material and developed the most efficient reactor configurations possible. Additionally, other hercynite materials, such as Ni doped hercynite or undoped hercynite, should be investigated for STWS properties, because, as was seen in Chapter 3, Co increased the reaction rate over undoped hercynite but the undoped-hercynite produced more H\textsubscript{2}.

In addition to hercynite, other new O-vacancy mechanism materials should also be investigated, particularly perovskite materials, which have a formula of ABO\textsubscript{3}, and have the capacity for high O-vacancy concentrations while remaining stable. These have recently been shown to reduce at similar temperatures to hercynite\textsuperscript{5-7} and many combinations of elements can take on the perovskite structure meaning there is a large material design space to be explored.

More accurate solar to H\textsubscript{2} efficiency models need to be developed for simulating the operation of STWS plants so that efficient modes of operation can be identified. Currently, the field uses broad and varied assumptions in modeling overall systems efficiency which make it
difficult to compare results between groups;\textsuperscript{8-13} a standardized set of assumptions and values should be developed. Additionally, it is still unclear if removing the generated O\textsubscript{2} from the reduction reaction by vacuum pump or an inert sweep gas is more efficient because models to date have not included mass and heat transport effects\textsuperscript{14-16} which likely have an effect the overall system efficiency.

Solarthermal water splitting reactors also require research attention. Without an efficient reactor, even a perfect STWS active material will be unable to meet the economic, efficiency, or production capacity milestones necessary for commercialization. In order to generate H\textsubscript{2} efficiently, a STWS reactor must be designed to deliver solar heat and steam to the reactive materials without requiring unnecessary energy, requiring significant amounts of external work, while being resistant to structural failure. Many current designs rely on complex mechanically moving parts operating at STWS temperatures,\textsuperscript{17-19} and are therefore prone to mechanical failure, or monoliths of materials\textsuperscript{20,21} which can have heat and mass transfer limitations. A new design that avoids these problems should be developed.

\subsection*{8.2.2 Future photocatalytic OPD investigations}

Understanding the role of Pt and non-metal dopants in facilitating the oxygen reduction reaction in OPD was an important first step in increasing the effectiveness of photocatalytic organic pollution remediation; however there are more steps along the oxidizing agent formation path that should be investigated and more complex catalysts which could increase these reaction rates should also be investigated.

Further surface and near surface doping of TiO\textsubscript{2} should be investigated. This work investigated only metallic Pt clusters and B, C and N surface dopants; however there are many
other available elements. Many other metals, and possibly even high work function metal oxides, could be investigated for use as surface catalyst while non-Pt metals and non-metals could decrease the TiO$_2$ band gap or produce surface sites for O$_2$ adsorption. A more extensive study of surface catalysts and dopants should be conducted.

The work carried out here studied only a single non-metal surface dopant; in reality there may be several dopant atoms in the near surface region which interact and therefore affect the dopant energies states. In addition to multiple dopant atoms of the same time, there could be beneficial effects of co-doping multiple element types. These possibilities should be investigated to determine their effect on the surface O$_2$ adsorption and reduction reaction.

The oxygen reduction reaction is only the first step in the OPD pathway. After it forms, O$_2^{2-}$ reacts with two H$^+$ to form the H$_2$O$_2$ that is the organic pollutant degrading species. The proton addition reactions, and H$_2$O$_2$ desorption steps should be investigated on the doped TiO$_2$ surface to ensure that the new catalysts developed do not bind the products so strongly that the degradation reaction does not occur. Additionally, the water oxidation reaction should be investigated on the doped surfaces.

8.3 References


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Appendix A: Near isothermal gas production rates

Figure A.1: Near isothermal water splitting using 85% active hercynite material. All reduction occurred at 1450°C and oxidation occurred at a) 1450°C, b) 1400°C, and c) 1350°C. The H₂O partial pressure was 380 Torr.
Figure A.2: Near isothermal water splitting using 85% active hercynite material. All reduction occurred at 1400°C and oxidation occurred at a) 1400°C, and b) 1350°C. The H₂O partial pressure was 380 Torr.

Figure A.3: 1350°C isothermal water splitting using 85% active hercynite material. The H₂O partial pressure was 380 Torr.
Appendix B: Fit CO₂ production rates

Figure B.1: The predicted CO generation for isothermal CO₂ splitting by the hercynite material at 1350 °C and 450 Torr CO₂ using different models. a) F1.5, b) R3, c) D1, d) D2, e) D3, f) D4.
Figure B.2: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1280 °C and 450 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).

Figure B.3: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1300 °C and 350 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).
Figure B.4: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1300 °C and 550 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).

Figure B.5: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1350 °C and 310 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).
Figure B.6: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1350 °C and 450 Torr CO₂. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).

Figure B.7: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1350 °C and 576 Torr CO₂. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).
Figure B.8: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1400 °C and 350 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).

Figure B.9: The predicted CO generation for isothermal CO2 splitting by the hercynite material at 1400 °C and 550 Torr CO2. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).
Figure B.10: The predicted CO generation for isothermal CO₂ splitting by the hercynite material at 1420 °C and 450 Torr CO₂. The left frame shows the CO generated at the material surface and the right frame shows the actual CO generated (dots) and the predicted CO generated (dots) and the predicted CO generated corrected for dispersion (solid line).
Appendix C: Additional Figures and Tables Concerning Increasing the Photocatalytic Activity of Anatase TiO$_2$ through B, C and N Doping

Figure C.1: Comparison of three and four layer thick interstitial N doped TiO$_2$. a) three layer thick slab with the bottom layer frozen, b) four layer thick slab completely relaxed, and c) four layer thick bulk slab. The solid gray curve shows the total density of states, the red short dashed curve shows surface O states and the light blue dotted curve shows N states.
Figure C.2: Formation energies of surface doped TiO$_2$ at various O chemical potentials for a) B doped TiO$_2$, b) C doped TiO$_2$ and c) N doped TiO$_2$. 
Figure C.3: Comparison of the density of states of an O$_2$ molecule a) near the TiO$_2$ surface and b) in vacuum far from the TiO$_2$ surface. The solid gray curve shows the total density of states, the red short dashed curve shows the O$_2$ molecule’s states and the light blue dashed curve shows N states.
Figure C.4: Density of states plots for interstitial B dopants investigated. a) interstitial site 1, b) interstitial site 5, c) interstitial site 4, and d) interstitial site 7 after O\textsubscript{2} adsorption. The gray curve shows the total density of states, and the pink curve represents B states. The dashed red curve in d represents adsorbed O\textsubscript{2}.
Figure C.5: Density of states plots for RSS B dopants investigated. a) RSS 1, b) RSS 2, c) RSS 4, d) RSS 5 and e) RSS 3 after O\textsubscript{2} adsorption. The gray curve shows the total density of states, and the pink curve represents B states. The dashed red curve in c represents adsorbed O\textsubscript{2}.
Figure C.6: Density of states plots for MSS B dopants investigated. a) MSS 1, b) MSS 2, c) MSS 4, and d) MSS 5. The gray curve shows the total density of states, and the pink curve represents B states.
Figure C.7: Interstitial B doped TiO$_2$. a) interstitial 1, b) interstitial 3, c) interstitial 4, and d) interstitial 5. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.
Figure C.8: RSS B doped TiO₂. a) RSS 1, b) RSS 2, c) RSS 4, and d) RSS 5. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.
Figure C.9: B doped TiO$_2$: a) MSS 1, b) MSS 2, c) MSS3, d) MSS 4, and e) MSS 5. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.
Figure C.10: a) O$_2$ adsorption to interstitial site 5, resulting in BO$_3$ formation, b) O$_2$ adsorption to a TiO$_2$ surface with a B dopant in an interstitial 4 site, c) double O$_2$ molecule adsorption to a TiO$_2$ surface with a B dopant in an intestinal 7 site and d) O$_2$ adsorbed to a TiO$_2$ surface with a B dopant in an MSS 3 site. Large gray spheres represent Ti atoms, medium pink spheres represent B atoms, and small red spheres represent O atoms.
Figure C.11: Density of states plots for interstitial C dopants investigated. a) interstitial site 1, b) interstitial site 4, c) interstitial site 5, and d) interstitial site 7. The gray curve shows the total density of states, and the brown curve represents C states.
Figure C.12: Density of states plots for substitutional C dopants investigated a) substitutional site 1, b) substitutional site 2, c) substitutional site 3, d) substitutional site 4, and e) substitutional site 5. The gray curve shows the total density of states, and the brown curve represents C states.
Figure C.13: Interstitial C doped TiO$_2$, a) Interstitial 1, b) Interstitial 4, and c) Interstitial 5. Large gray spheres represent Ti atoms, medium brown spheres represent C atoms, and small red spheres represent O atoms.
Figure C.15: Density of states plots for N dopants investigated. a) interstitial site 1, b) interstitial site 5, and c) interstitial site 7.
Figure C.16: Density of states plots for N dopants investigated. a) substitutional site 1 b) substitutional site 2, c) substitutional site 3, d) substitutional site 4, e) substitutional site 5.
Figure C.17: N doped TiO$_2$. a) Interstitial 1, b) Interstitial site 4, c) Interstitial site 5 and d) Interstitial site 7. Large gray spheres represent Ti atoms, medium blue spheres represent N atoms, and small red spheres represent O atoms.
Figure C.18: N doped TiO$_2$. e) Substitutional 1, a) Substitutional 2, b) Substitutional 3, c) Substitutional 4, and d) Substitutional 5. Large gray spheres represent Ti atoms, medium blue spheres represent N atoms, and small red spheres represent O atoms.
Table C.1: $O_2$ pressure at which a substitutional dopant is favored over an interstitial dopant

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>N-dopant$^a$</th>
<th>C-doping$^b$</th>
<th>B-doping$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$3.8 \times 10^{-53}$</td>
<td>$6.7 \times 10^{-275}$</td>
<td>$&lt;1 \times 10^{-300}$</td>
</tr>
<tr>
<td>200</td>
<td>$2.1 \times 10^{-22}$</td>
<td>$2.8 \times 10^{-133}$</td>
<td>$3.7 \times 10^{-244}$</td>
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<td>300</td>
<td>$8.2 \times 10^{-12}$</td>
<td>$9.8 \times 10^{-68}$</td>
<td>$1.2 \times 10^{-159}$</td>
</tr>
<tr>
<td>400</td>
<td>$2.9 \times 10^{-06}$</td>
<td>$1.0 \times 10^{-61}$</td>
<td>$3.8 \times 10^{-117}$</td>
</tr>
<tr>
<td>500</td>
<td>$9.6 \times 10^{-3}$</td>
<td>$9.8 \times 10^{-68}$</td>
<td>$1.9 \times 10^{-91}$</td>
</tr>
<tr>
<td>600</td>
<td>$1.5 \times 10^{0}$</td>
<td>$1.6 \times 10^{-37}$</td>
<td>$1.8 \times 10^{-74}$</td>
</tr>
<tr>
<td>700</td>
<td>$7.5 \times 10^{1}$</td>
<td>$1.6 \times 10^{-30}$</td>
<td>$3.3 \times 10^{-62}$</td>
</tr>
<tr>
<td>800</td>
<td>$1.4 \times 10^{3}$</td>
<td>$2.7 \times 10^{-25}$</td>
<td>$5.1 \times 10^{-53}$</td>
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<tr>
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<td>$1.8 \times 10^{4}$</td>
<td>$4.1 \times 10^{-21}$</td>
<td>$9.5 \times 10^{-46}$</td>
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<tr>
<td>1000</td>
<td>$1.1 \times 10^{5}$</td>
<td>$7.3 \times 10^{-18}$</td>
<td>$4.9 \times 10^{-40}$</td>
</tr>
</tbody>
</table>

$^a$ The pressure at which Sub. Site 5 is more stable than interstitial site 5  
$^b$ The pressure at which Sub. Site 5 is more stable than interstitial site 7  
$^c$ The pressure at which Sub. Site 3 is more stable than interstitial site 4

Table C.2: $O_2$ adsorption characteristics on MSS and RSS B doped TiO$_2$

<table>
<thead>
<tr>
<th>Site</th>
<th>$O_2$ adsorption energy (eV)</th>
<th>$O_2$ bond length (Å)</th>
<th>B charge before $O_2$ adsorption (e$^-$)</th>
<th>B charge after $O_2$ adsorption (e$^-$)</th>
<th>$O_2$ charge (e$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSS 3</td>
<td>-0.52</td>
<td>1.33</td>
<td>3.57</td>
<td>3.26</td>
<td>0.52</td>
</tr>
<tr>
<td>MSS 4</td>
<td>-3.05</td>
<td>1.33</td>
<td>3.53</td>
<td>3.24</td>
<td>0.52</td>
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<tr>
<td>MSS 5</td>
<td>-2.26</td>
<td>1.32</td>
<td>3.56</td>
<td>3.32</td>
<td>0.51</td>
</tr>
<tr>
<td>RSS 3</td>
<td>-1.62</td>
<td>1.45</td>
<td>1.28</td>
<td>1.15</td>
<td>0.97</td>
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<tr>
<td>RSS 4</td>
<td>-1.22</td>
<td>1.45</td>
<td>1.49</td>
<td>1.48</td>
<td>0.96</td>
</tr>
<tr>
<td>RSS 5</td>
<td>-1.74</td>
<td>1.45</td>
<td>1.41</td>
<td>1.33</td>
<td>0.96</td>
</tr>
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</table>

$^a$O$_2$ forms BO$_2$ at interstitial site 5