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Novel Mixed Metal Ferrites for Hydrogen Production Using Chemical Looping

Victoria J. Aston
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NOVEL MIXED METAL FERRITES FOR HYDROGEN PRODUCTION USING CHEMICAL LOOPING

by

VICTORIA J. ASTON

B.S., New Mexico Institute of Mining and Technology, 2007

M.S., University of Colorado at Boulder, 2010

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Faculty of the Graduate School of the

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of the requirement for the degree of

Doctor of Philosophy

Department of Chemical and Biological Engineering

2013
This thesis entitled:

**Novel Mixed Metal Ferrites for Hydrogen Production Using Chemical Looping**

written by Victoria J Aston

has been approved for the Department of Chemical and Biological Engineering

______________________________________________________________

Alan Weimer (Chair)

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Will Medlin

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.
The chemical looping hydrogen (CLH) process generates pure, separate streams of H₂ and CO₂ from synthesis gas without the use of expensive gas separation equipment. This technology is a potentially efficient method for future H₂ production from coal or biomass with integrated CO₂ capture. In the CLH process, a metal oxide material is reduced through contact with syngas at temperatures between 673 K and 1273 K, fully oxidizing the CO and H₂ in the syngas to H₂O and CO₂. The reduced metal oxide is then contacted with steam to regenerate the metal oxide and produce H₂. The mixed metal ferrites CoFe₂O₄ and NiFe₂O₄ are proposed as alternative metal oxides to the currently used Fe₂O₃. Thermodynamic analysis with the software package FactSage™ predicts high conversions of H₂ and CO to H₂ and CO₂ during the CLH reduction step and complete ferrite regeneration during the H₂O oxidation step. Laboratory experiments with mixed metal ferrites deposited on high surface area ZrO₂ support structures indicate cyclability under CLH conditions, and post-cycling analysis shows complete regeneration of the mixed metal spinel with no detected metal oxide-support interactions. In a packed bed reactor, CoFe₂O₄ and NiFe₂O₄ show superior performance to Fe₂O₃, with over 99% conversion of CO and H₂ to CO₂ and H₂O during reduction. Over 90% of the H₂/CO used to reduce the mixed metal ferrites was recovered as H₂ during H₂O oxidation. For Fe₂O₃, the recovery was only 20%. A kinetic analysis of the oxidation step indicated a dual oxidation mechanism for mixed metal ferrites that involved an order of reaction model followed by a diffusion limited model at higher conversions. Diffusion limitations are attributed to the effect of incorporation of Co²⁺ and Ni²⁺ cations into the spinel lattice. The reduction reaction in a
packed bed reactor is found to follow gas-solid equilibrium conversion values closely at low solid conversions. Analysis of the CLH system using an equilibrium limited model indicates these materials offer significant advantages in H₂ output over Fe₂O₃ at lower reaction temperatures and with high CO₂/CO and H₂O/H₂ syngas.
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Chapter 1: Introduction and Scope

1.1 Current and Future Hydrogen Consumption

Hydrogen, the most abundant element in the universe, makes up about 18% of the atoms in our environment. Present mostly in compounds such as water and hydrocarbons, rather than as gaseous hydrogen (H₂), H₂ must be extracted and separated from other elements. [1] Currently, H₂ production technology is a mature field, and over 20 million tons of H₂ are generated per year, with 9 million tons generated in the United States (U.S.). [1] Half of the current H₂ produced globally is used for ammonia production for the fertilizer industry, and the rest is used in petroleum refining, methanol production, metallurgical processing, and for scientific purposes. [1] Additionally, the “hydrogen economy” has been proposed since the 1970’s as a solution to our nation’s fuel-related environmental and energy security problems. [2] Fuel cells utilizing H₂ are shown to be up to three times more efficient than an internal combustion engine for transportation, producing only H₂O as a product. [3] Hydrogen is hailed as an attractive replacement for gasoline, diesel, natural gas, and other fossil-based fuels that are finite in nature, volatile in price, and leave the U.S. dependent on foreign sources. Over half of the crude oil consumed in the U.S. is imported, leaving the nation vulnerable to price fluctuations resulting from decreased oil production or increased oil demand in other countries. [4, 5]

Shifting to a hydrogen economy for transportation and electricity generation would result in an increase in U.S hydrogen consumption of over 40 million tons per year. [1] Regardless of implementation of a hydrogen economy, the need for fertilizer and petroleum refining will result in a continued increase in the use of H₂ in future years. The expected world population increase of nearly three billion people by 2050 will significantly increase world food and energy

### 1.2 Hydrogen Production Technologies

Current H\textsubscript{2} production technologies include steam-methane reforming and partial oxidation of hydrocarbons, and to a much lesser extent, gasification, pyrolysis and electrolysis. These methods are summarized in Table 1.1. [1]

<table>
<thead>
<tr>
<th>Method</th>
<th>Overall Efficiency (%)</th>
<th>H\textsubscript{2} cost (US$/GJ) (2006)</th>
<th>Total Capital Investment (US$/GJ H\textsubscript{2} capacity)</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>65-75 (LHV)</td>
<td>5-8</td>
<td>9-15</td>
<td>Well-established</td>
<td>Extensive infrastructure</td>
</tr>
<tr>
<td>Partial Oxidation</td>
<td>50 (LHV)</td>
<td>7-10</td>
<td>9-22</td>
<td>Minimal infrastructure, well est., variety of fuels</td>
<td></td>
</tr>
<tr>
<td>Gasification</td>
<td>42-47 (HHV)</td>
<td>9-13</td>
<td>20-42</td>
<td>Minimal infrastructure, CO\textsubscript{2} for sequestration, uses a variety of cheap fuels, could use solar energy</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>48 (HHV)</td>
<td>9-13</td>
<td>15-19</td>
<td>Minimal infrastructure, CO\textsubscript{2} for sequestration, uses a variety of cheap fuels</td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td>35-42 (HHV) (electricity source included), 70 (NG assisted)</td>
<td>20-25 (large) 11-42 (small) 3-30 (large) 32-486 (small)</td>
<td>Potential zero emissions with renewable electricity</td>
<td>Benefits depend on electricity supply, water supply often unreliable</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Current H\textsubscript{2} production methods, adapted from Stiegel, et al., International Journal of Hydrogen Energy, 2006; 65 (Ref. [1]).

Approximately 80% of the H\textsubscript{2} produced worldwide comes from natural gas or oil through the steam methane reforming and partial oxidation of hydrocarbon processes. As a result, the price of H\textsubscript{2} is highly dependent on the price of petroleum. Gasification of coal accounts for nearly all of the remaining H\textsubscript{2} production, and a small fraction is produced using water...
electrolysis technology. [1] Of these technologies, only gasification, pyrolysis, and electrolysis can be applied to renewable fuels and are consequently attractive as long-term H₂ sources. Gasification systems produce electricity, H₂, or other hydrocarbon fuels while utilizing any of a variety of carbon based fuels, including coal, biomass and organic waste material. As the prices of natural gas and oil increase and petroleum supplies eventually become scarcer, coal is projected to become a major source of H₂, especially in countries with an abundance of coal. [7] The known coal reserves in the U.S. are projected to last over 250 years at the current consumption rate. [8] Similar to oil and natural gas, coal is a finite fossil resource; however, it may be vital to aid in the transition between fossil and renewable fuels. The technologies developed for generating fuels from coal will greatly benefit the next generation of fuels from gasification of biomass and waste, while providing the significant volume of fuels necessary to sustain current energy consumption.

1.3 Hydrogen from Gasification

Though not common in the United States, gasification is a well-established technology used in regions where oil and natural gas are expensive, such as China and South Africa. [7] The gasification process, like all other primary H₂ production technologies except electrolysis, generates an intermediate of synthesis gas. Synthesis gas (syngas) is a mixture of CO, CO₂, H₂, and H₂O formed as the organic molecules break apart at the high temperatures and pressures encountered in the gasification process. Coal has a lower H₂/C ratio than natural gas, meaning more CO₂ is generated for each mole of H₂ produced from coal than per mole of H₂ produced from steam methane reforming. [7] Syngas undergoes the water-gas shift reaction (Eq. 1.1) to shift the composition to be high in H₂ and CO₂.

\[
H_2O + CO \leftrightarrow H_2 + CO_2 \quad \text{Eq. 1.1}
\]
The H\textsubscript{2} and CO\textsubscript{2} must then be separated using pressure swing adsorption (PSA), chemical scrubbing (Monoethanolamine or Selexol), or membrane technologies.

Pressure swing adsorption (PSA) has been a state-of-the-art gas separations technology for over 30 years. During the PSA process, CO\textsubscript{2} is adsorbed on physical sorbents, such as silica gel or activated carbon, leaving a purified H\textsubscript{2} stream. [8] The sorbent is regenerated through bed depressurization, which allows the CO\textsubscript{2} and other impurities to desorb. De-pressurization and re-pressurization is highly energy intensive and the process only recovers 70-90% of the H\textsubscript{2} in the feed gas. The remaining H\textsubscript{2} is lost in the waste stream. [9] Membrane separation technologies are attractive due to their simplicity of operation, and are the subject of much current research. However, the full potential of membrane CO\textsubscript{2}/H\textsubscript{2} separation has not yet been realized commercially. [10] Membrane separation results in recovery of between 70-99% of the H\textsubscript{2} in the gas, and often requires highly pressurized syngas and large surface areas for adequate H\textsubscript{2} purity. [11]

The route to H\textsubscript{2} from coal via gasification is inherently more expensive than H\textsubscript{2} production from natural gas due, in part, to the greater capital costs of the gasification reactor and gas cleaning technologies necessary to remove sulfur and other contaminants from coal-derived syngas. [10] Improvements in gasifier technology, gas cleaning technology, and H\textsubscript{2}/CO\textsubscript{2} separation and sequestration technology will decrease the cost of H\textsubscript{2} from coal and make it competitive with current H\textsubscript{2} production methods and affordable for the U.S. consumer. A 60% efficiency for fuels production from coal gasification, with carbon capture, would make these technologies economical. [10]
1.4 CO₂ Sequestration

Carbon capture and storage (CCS) is the separation and capture of CO₂ produced at stationary sources, followed by transport and storage in geological reservoirs to prevent its release into the atmosphere. [11] The cost of CCS is high, but future carbon taxes and fees are proposed to provide incentive to curb the release of large amounts of CO₂ into the atmosphere.

Carbon dioxide prepared for sequestration does contain gaseous impurities that negatively affect the gas transport, injection and storage properties, and ultimately the cost of underground containment. Non-condensable species such as H₂ and N₂ decrease CO₂ storage capacity while increasing the energy required for injection and the volume necessary to store the CO₂. Due to the decreased storage capacity, a CO₂ stream with high impurity (> 15% non-condensable gasses) is estimated to increases the cost of CCS by up to 26%, with an average increase of 6%. [12] The current recommendations for CO₂ purity for CCS are shown in Table 1.2. [12] Conventional CO₂ removal processes are typically focused on the purity of the H₂ rather than the purity of the CO₂ and thus leave significant fractions of impurities in the CO₂. Future separations processes designed to generate CO₂ for sequestration must optimize the purity of the CO₂ in addition to the purity of the H₂.
Chemical looping for H₂/energy generation with integrated CO₂ capture

Chemical looping H₂ production (also known as “syngas chemical looping”, or “chemical looping reforming”, and will be referred to as the CLH process for this thesis) produces H₂, electricity, or both from syngas using cyclic reduction and oxidation of metal oxides. [13-15] The main advantage of the CLH process over conventional water gas shift technologies is the production of pure and separate streams of H₂ and CO₂ from syngas with any composition without the use of complex separations technologies. The overall efficiency of this process is estimated to be 64% with 100% CO₂ capture. A maximum efficiency of 57% for conventional coal-to-hydrogen processes is calculated in the same study. [16]

1.6 Project Scope

Chemical looping hydrogen technology has the potential to bring the H₂ and energy production cost via gasification lower, thus increasing its competitiveness in the current H₂ market and aiding the transition from dependence on foreign fossil fuel to a native fuel supply, and ultimately a renewable fuel supply. The objective of this research is to investigate novel

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>&gt; 95.5 vol%</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2000 ppm</td>
<td>Safety factor of 5 applied due to toxicity, design and operation limit is higher</td>
</tr>
<tr>
<td>H₂S</td>
<td>200 ppm</td>
<td>Safety factor of 5 applied due to toxicity</td>
</tr>
<tr>
<td>CH₄</td>
<td>&lt; 4 vol%</td>
<td>Energy consumption during compression</td>
</tr>
<tr>
<td>H₂O</td>
<td>500 ppm</td>
<td>Below solubility of H₂O in CO₂ to prevent corrosion</td>
</tr>
<tr>
<td>N₂</td>
<td>&lt; 4 vol%</td>
<td>Energy consumption during compression</td>
</tr>
<tr>
<td>Ar</td>
<td>&lt; 4 vol%</td>
<td>Energy consumption during compression</td>
</tr>
<tr>
<td>H₂</td>
<td>&lt; 4 vol%</td>
<td>Energy content of H₂, Energy consumption during compression</td>
</tr>
<tr>
<td>SOx</td>
<td>200 ppm</td>
<td>Prevent dissolution of rocks</td>
</tr>
<tr>
<td>NOx</td>
<td>200 ppm</td>
<td>Prevent dissolution of rocks</td>
</tr>
</tbody>
</table>

Table 1.2: Gaseous impurities in CO₂, and the concentration limits for sequestration. Adapted from Visser et al. Greenhouse Gas Control; 2:478 (Ref. [12]).
materials that allow the CLH process to produce H\textsubscript{2} more efficiently with complete carbon capture. Specifically, the effect of doping conventional ferrite materials used in the CLH process with additional transition metal oxides will be investigated. These materials have the potential to increase the flexibility of the CLH process, allowing greater H\textsubscript{2} recovery at lower material conversions.

This thesis focuses primarily on the mixed metal ferrites CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4}, and their performance in the reduction and oxidation cycles of the CLH process. Due to the lack of demonstrated cyclability properties in the literature under these conditions, NiFe\textsubscript{2}O\textsubscript{4} and CoFe\textsubscript{2}O\textsubscript{4} were synthesized and tested in the laboratory to establish their suitability for the CLH process. Specifically, their ability to regenerate the mixed-metal spinel structure during H\textsubscript{2}O oxidations was investigated. Samples were analyzed with Raman spectroscopy to determine the solid phases present, and interactions between the inert support and metal oxide material were investigated. Additionally, the cyclability of the metal oxides was established through quantifying the total H\textsubscript{2} production of each cycle.

Cyclability and reactivity with H\textsubscript{2}O alone are not sufficient to make NiFe\textsubscript{2}O\textsubscript{4} and CoFe\textsubscript{2}O\textsubscript{4} candidates for the CLH process. An examination of thermodynamic equilibrium between the CO/CO\textsubscript{2} and H\textsubscript{2}/H\textsubscript{2}O systems with the mixed metal ferrites, combined with experimental results in a packed bed reactor, were used to show the benefits of the mixed metal oxides over conventional ferrite materials. Thermodynamic analyses were performed using the Gibbs Free Energy Minimization software package, FactSage\textsuperscript{TM}, and its associated thermodynamic property databases. The reactions in the solid phase were investigated through material analysis with X-ray diffraction and Raman spectroscopy.
In order to understand the rate-limiting mechanisms of the slow reactions involving the mixed metal ferrites, a stagnation flow reactor at Sandia National Laboratories was used to investigate the kinetics of the H₂O oxidation of reduced ferrites. This instrument has many advantages over the packed bed reactor used in the previous step, as it allows one-dimensional homogeneous flow over the sample to sweep away product gasses that inhibit the material forward reaction. Data from this reactor were used to establish the fundamental mechanism controlling the rate of sample reaction, and to calculate the kinetic parameters necessary to model the oxidation reaction over the temperature range of material cyclability. A model that accounts for the dispersion and mixing in the reactor was used to calculate the kinetic parameters that describe the global minimum error, and thus the best fit to considering all the data points. An understanding of the fundamental oxidation mechanisms allows identification of techniques to enhance the reaction rate. Due to the lack of current literature regarding cation diffusion in spinels, the density functional theory (DFT) technique was used to investigate the difference in migration barriers between metallic Fe, Co and Ni, and the spinels Fe₃O₄, CoFe₂O₄, and NiFe₂O₄.

Finally, a model of the system was developed to explore a hybrid H₂O/O₂ oxidation of the mixed metal spinels for the production of H₂/heat, with the goal of optimizing the H₂ and energy output of the CLH process using CoFe₂O₄ and NiFe₂O₄. This model, developed in MATLAB, compared the performance of the novel mixed metal materials with that of the conventional Fe₂O₃ CLH process. The effects of syngas composition and reaction temperature on the material reduction extent, and H₂ and heat generated during H₂O/O₂ oxidation were investigated.
1.7 References


Chapter 2: Literature Review

2.1 Chemical Looping Hydrogen (CLH) Process

In addition to being a possible future energy source for electricity and vehicle transportation, H₂ is necessary for the ammonia production and oil refining industries, which nationally use nine million tons of H₂ every year. [1] Current methods of H₂ production, including steam methane reforming, partial oxidation of hydrocarbons and coal gasification, require the use of the water-gas shift reaction (Eq. 2.1) to produce a mixture of H₂ and CO₂ from the synthesis gas (syngas) that they generate.

\[ \text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2 \quad \text{Eq. 2.1} \]

The reaction in Eq. 2.1 is thermodynamically limited at high temperatures and kinetically limited at low temperatures. Consequently, a two-stage process is required to maximize the amount of H₂ in the syngas. Supplementary purification is then necessary to decrease the amount of CO in the gas stream to the desired level. [2, 3] Additionally, the CO₂ must be separated from the H₂ in the product stream using processes such as Pressure Swing Adsorption (PSA) or Monoethanolamine (MEA) scrubbing, which carry high energy penalties and result in the loss of up to 30% of the produced H₂. [4, 5] Future H₂ generation techniques will need to be capable of efficiently generating a relatively pure and easily-sequestered CO₂ waste stream as monetary penalties for the release of CO₂ take effect.

The Chemical Looping Hydrogen (CLH) production process is an effective alternative method for generation of pure H₂ from any syngas with integrated CO₂ capture. (Figure 2.1) [2, 6, 7] In the CLH process, syngas leaving a gasifier reduces a metal oxide material at moderate to high temperatures (773 K to 1273 K) (Eq. 2.2-3). The reduced metal oxide is then oxidized
using steam to produce H₂, a process that regenerates the metal oxide to its original state. (Eq. 2.4).

\[
H_2 + MeO_x \leftrightarrow H_2O + MeO_{x-1} \quad K_{Eq,H_2} = \frac{pH_2O}{pH_2} \quad Eq. 2.2
\]

\[
CO + MeO_x \leftrightarrow CO_2 + MeO_{x-1} \quad K_{Eq,CO} = \frac{pCO_2}{pCO} \quad Eq. 2.3
\]

\[
H_2O + MeO_{x-1} \leftrightarrow H_2 + MeO_x \quad K_{Eq,H_2O} = \frac{1}{K_{Eq,H_2}} = \frac{pH_2O}{pH_2} \quad Eq. 2.4
\]

By splitting the water-gas shift reaction into two separate steps, the CLH process takes advantage of fast kinetics at high temperatures without the associated thermodynamic limitations. [2] Furthermore, pure and separate H₂ and CO₂ are produced without complicated and expensive multistep separation processes.

Figure 2.1: Schematic for the ideal chemical looping H₂ production process.

In order to be a viable material for the CLH process, a metal oxide must meet the following criteria: [7]

1) The material must demonstrate fast and stable kinetics over a large number of redox cycles.

2) The reduced form of the metal oxide must be readily oxidized using steam.
3) Thermodynamically, the reaction of the metal oxide with the syngas must be able to convert virtually all of the CO and H$_2$ in the syngas to CO$_2$ and H$_2$O.

2.2 Material Cyclability

Criterion 1, material cyclability and reactivity, is often a property of the material synthesis method and has been studied and demonstrated at length. Consistent cyclability results are difficult to obtain for any one method of sample synthesis, most likely due to differences in preparation method and treatment of the sample before cycling. [4] Commercially available powders categorically have been shown to degrade with cycling as a consequence of sintering of the oxide and subsequent surface area loss. [7-10] Data from bulk commercial Fe$_2$O$_3$ powder cycling in a thermogravimetric analyzer (TGA) are shown in Figure 2.2, demonstrating the diminished reduction and oxidation capacity of the material in each subsequent cycle. [7] Use of such materials results in the need for frequent replacement in an industrial setting, increasing the system cost.

Techniques to stabilize bulk metal oxides for cycling, such as sintering powders into pellets and synthesizing sol-gels, show mixed results. Agglomerated and sieved Fe$_2$O$_3$ powder, stabilized by sintering at 1173 K, shows improved cycle stability for up to six redox cycles at temperatures below 1173 K. [6, 11] However, sintered pellets of Fe$_2$O$_3$ show deactivation in only four cycles at 1023 K. [9] Sol-gel derived Fe$_2$O$_3$ materials show consistent degradation over seven cycles at temperatures between 623 K and 723 K. [12]
To further stabilize the metal oxides, secondary materials are added as binders to serve as supports to maintain metal oxide distribution and pore volume to sustain gas/metal oxide contact, and to increase particle integrity. This approach is implemented in materials synthesis for the chemical looping combustion (CLC) process, which uses O₂ rather than H₂O as an oxidizing agent to produce heat for electricity generation. [13] Binders can be co-precipitated with the metal oxide, included in the sol-gel preparation method, physically mixed with the metal oxide and sintered, or used as a porous substrate onto which the metal oxide is deposited. Two types of binders are considered: inert binders and binders that react chemically with the metal oxide.

The most common inert binder is ZrO₂ or yttria-stabilized ZrO₂ (YSZ). Due to the phase transformation from monoclinic ZrO₂ to tetragonal ZrO₂ near 1273 K, and the associated pore-destroying volume change, yttria is often added to stabilize the zirconia in the tetragonal phase over a wider temperature range. [4] Samples of NiO physically mixed with ZrO₂ and YSZ,
shaped into 2 mm particles and calcined, show significantly improved reduction extent over bulk NiO particles when cycled at 1273 K. [14] Samples of 80% by mass Fe₂O₃ mixed with ZrO₂ made using freeze granulation, a method of forming physically mixed particles of uniform size, show high reduction and oxidation rates at 1223 K. [15] Mixtures of Fe₂O₃ and YSZ cycle over 100 times with excellent repeatability, attributed to the oxygen ion conduction capacity of YSZ. [4] Common binders Al₂O₃ and TiO₂ often react with the metal oxides used in chemical looping processes. Regardless, particles made with reactive binders usually show superior cycling properties to bulk samples. When Al₂O₃ is used as a binder, FeAl₂O₄, MnAl₂O₄, NiAl₂O₄, and CoAl₂O₄ form during reduction, but the reduction extent and cyclability are superior to those of bulk metal oxide materials. These improvements are attributed to the increased stability of pore and particle structures. [14, 16-21] Samples prepared with TiO₂ form FeTiO₂, but still prove highly cyclable, and produce consistent H₂ amounts for five cycles; a result attributed to the enhanced oxygen anion conduction through the TiO₂ phase. [21, 22]

Literature regarding the cyclability and properties of various metal oxide-binder combinations is vast, and more comprehensive summaries are available elsewhere. [4, 23] Regardless of the method of sample production, cyclability is key in the investigation of any new chemistry or material kinetics for the CLH process and should a major study parameter.

2.3 Reaction Thermodynamics

Criteria 2 and 3 are properties of the CO/CO₂ and H₂/H₂O equilibrium with the oxidized and reduced states of a metal oxide, assuming a system with rapid kinetics. The equilibrium constant of Eq. 2.2, $K_{\text{Eq,H}_2} = \frac{p\text{H}_2\text{O}}{p\text{H}_2}$, and that of Eq. 2.3, $K_{\text{Eq,CO}} = \frac{p\text{CO}_2}{p\text{CO}}$ (where p = partial pressure), determine the limiting amount of H₂ and CO remaining in the syngas after the reduction step. [4, 6, 7, 24] Table 2.1 shows the starting oxide stoichiometry, the final reduced
material stoichiometry, and the equilibrium constant at 873 K for the CO and H₂ reduction of metal oxides considered as candidates for chemical looping processes. A large equilibrium constant indicates high conversion of H₂ to H₂O or CO to CO₂ during the reduction reaction, while a small equilibrium constant indicates a lower conversion. This results in a loss of syngas energy content as H₂ and CO are present in the gas exiting the reactor. [24] Equilibrium constants for oxides of Fe, Ni, Co, Cu, and Mn predict nearly 100% conversion of CO and H₂ to CO₂ and H₂O during the reduction step, which would result in a nearly pure CO₂ stream after H₂O condensation. [7]

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Reduction Product</th>
<th>pH₂O/pH₂ (K_{Eq,H₂})</th>
<th>pCO₂/pCO (K_{Eq,CO})</th>
<th>Conversion of H₂O to H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>Ni</td>
<td>250</td>
<td>800</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Cu</td>
<td>1.5x10⁹</td>
<td>1.5x10¹⁰</td>
<td>0</td>
</tr>
<tr>
<td>CoO</td>
<td>Co</td>
<td>44</td>
<td>100</td>
<td>2.3</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>MnO</td>
<td>1.0x10⁵</td>
<td>1.5x10⁴</td>
<td>0</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Fe</td>
<td>1.3</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Fe₃O₄</td>
<td>5.0x10⁵</td>
<td>8.0x10⁵</td>
<td>0</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Sn</td>
<td>2.5</td>
<td>5</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 2.1: Equilibrium constants and H₂ to H₂O conversion at 873 K for common chemical looping candidate metal oxides. [6, 7, 24]

For conventional CLC processes, high conversion of H₂ to H₂O and CO to CO₂ during the reduction step is optimal because the re-oxidation is performed with O₂. For the CLH process, re-oxidation is performed using H₂O, and while high conversion of H₂ to H₂O is desired in the reduction step, the corollary is low conversion of H₂O to H₂ during oxidation. [7] The inverse of Eq. 2.2’s equilibrium constant expresses the equilibrium for the H₂O oxidation of the reduced metal oxide, Eq. 2.3. Low H₂O conversion to H₂ makes regeneration of NiO and CoO difficult, and the regeneration of Cu₂O, Mn₃O₄ and Fe₂O₃ unlikely under reaction conditions. [4] Although the Sn system has reasonable conversion of H₂O to H₂ during oxidation, the amounts
of CO and H\(_2\) that would exit the reactor would be nearly 8%. Additionally, the melting point of Sn is 505 K, significantly below the operating temperature of a CLH reactor. [7]

2.4 Fe-based CLH System

The Fe-based oxide system is unique because of the formation of Fe\(_3\)O\(_4\), an intermediate oxide, between the reduced state, Fe, and the fully oxidized state, Fe\(_2\)O\(_3\). Furthermore, the oxidation of Fe to Fe\(_3\)O\(_4\) is predicted to have a high conversion of H\(_2\)O to H\(_2\): nearly 75%. [7, 25, 26] An O\(_2\) oxidation is necessary to generate Fe\(_2\)O\(_3\) due to the large equilibrium constant for the H\(_2\)O oxidation of Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\). Conversely, the large oxidation equilibrium constant for oxidation of Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\) allows high conversions of H\(_2\) and CO during the reduction of Fe\(_2\)O\(_3\). This intermediate phase allows H\(_2\) production with high H\(_2\)O to H\(_2\) conversion from the reduced metal oxide to form Fe\(_3\)O\(_4\), and a subsequent O\(_2\) oxidation regenerates a phase able to convert nearly all of the H\(_2\) and CO to H\(_2\)O and CO\(_2\) during the reduction step. The phases present in the Fe-based oxide system and the pH\(_2\)O/pH\(_2\) and pCO\(_2\)/pCO ranges in which they are stable are shown in Figure 2.3. The lines represent the equilibrium constants for phase transitions at each temperature. For example, at 673 K (400°C), Fe metal would oxidize to Fe\(_3\)O\(_4\) in a gas with pCO\(_2\)/pCO \sim 1.
Due to these unique equilibrium phases, and its abundance, low cost, and low toxicity, iron (Fe) remains the most studied metal oxide for the CLH process. Consequently, the most common CLH process to date (shown in Figure 2.4) is expressed by the following reactions:

\[ 3\text{Fe}_2\text{O}_3 + 9\text{H}_2 / CO \leftrightarrow 6\text{Fe} + 9\text{H}_2\text{O} / CO_2 \tag{Eq. 2.5} \]

\[ 6\text{Fe} + 8\text{H}_2\text{O} \leftrightarrow 2\text{Fe}_3\text{O}_4 + 8\text{H}_2 \tag{Eq. 2.6} \]

\[ 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow 3\text{Fe}_2\text{O}_3 \tag{Eq. 2.7} \]

The O\textsubscript{2} regeneration step does add complexity to the CLH system and results in a loss of at least 11\% of the potential H\textsubscript{2} production, since the H\textsubscript{2} and CO used to reduce the Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4} cannot be recovered as H\textsubscript{2}. Despite the loss of potential H\textsubscript{2} recovery, the O\textsubscript{2} oxidation of Fe\textsubscript{3}O\textsubscript{4}
has a large reaction enthalpy, allowing the generation of heat, and subsequently electricity, during the cycle. [4, 27]

![Chemical looping diagram]

Figure 2.4: The current state-of-the-art CLH process includes an O₂ oxidation step, in which a portion of possible H₂ production is not utilized.

### 2.5 CLH Reactor Design

The equilibrium conditions between the solid Fe-based oxide and the gas phase necessitate contact with the Fe₂O₃ phase during the reduction step in order for the H₂ and CO to be completely converted to CO₂ and H₂O. [6] Although a high conversion of the metal oxide is desired, more important is maximizing the conversion of H₂ and CO to H₂O and CO₂ during the reduction step. For CO₂ to be sequesterable, the impurity levels must be less than 5%. [28] Additionally, any CO or H₂ that remains unconverted to CO₂ or H₂O becomes unutilized chemical energy.

Typically, a fluidized bed, packed bed, or a moving bed reactor is used for bench-scale chemical looping experiments. [2, 6, 11, 29] During the reduction step, syngas is introduced into the reactor until all the Fe₂O₃ is consumed and breakthrough of H₂ and CO is observed. The reactor is purged, and then steam is introduced to generate H₂. When H₂O oxidation is complete,
O₂ is introduced to regenerate Fe₂O₃, then the reactor is purged of oxidizing gasses and the process is repeated. In a fluidized bed reactor, gas and solid phases are well mixed axially and radially. Gasses entering the reactor are mixed with reacted gasses in the reactor volume, and particles throughout the bed are of uniform conversion due to their exposure to gasses of similar composition. In this configuration, conversion of the Fe₂O₃ beyond Fe₃O₄ before breakthrough of H₂ and CO is difficult to obtain because H₂O/H₂ and CO/CO₂ ratios are high in well-mixed gas. [29] This reaction is sufficient for a CLC process because the desired product is the heat generated during O₂ oxidation of the reduced material. [24] Since Fe₃O₄ cannot be oxidized to produce H₂, the conversion of Fe₂O₃ must be greater for the CLH process, making the fluidized bed a poor choice as a reactor. [29]

Greater conversion is achieved in a packed bed reactor because, ideally, gasses behave as plug flow rather than exhibiting axial mixing. The H₂/H₂O and CO/CO₂ ratios in syngas entering a reactor are often large enough to produce FeO or Fe metal in the first portion of the reactor before all Fe₂O₃ is consumed through the entire bed. [6] A countercurrent moving bed reactor has been shown to have the greatest solid conversion while maximizing the H₂ and CO conversion. [29] Conversion of the solid material is nearly 50% without H₂ or CO breakthrough. An additional benefit to the countercurrent moving bed reactor is that the flows of syngas and steam are continuous, and no high-temperature valves are required to switch gasses entering the reactors.

2.6 Alternative CLH Metal Oxides

Few studies to date comprehensively investigate alternative metal oxides to Fe₂O₃ for the CLH process. A kinetic investigation of the H₂O oxidation of a reduced Cu-Fe-Al₂O₃ co-precipitated material between 550°C and 850°C shows significant H₂ production, but the reduced
and oxidized phases remain unverified, and the conversion of H₂ and CO during the reduction step is unknown, which makes an assessment of the applicability to the CLH process difficult. [30] Similarly, a kinetic investigation of Mn- and Zn- Fe₃O₄ materials, synthesized from physically mixed powders, shows an increase in the oxidation rate and a decrease in the activation energy of the H₂O oxidation between 777 K and 1173 K. However, reduced and re-oxidized products were not identified, and the material equilibrium with the H₂/H₂O and CO/CO₂ systems was not discussed. [31] A study of the reduction and subsequent water oxidation of CoFe₂O₄ and Fe₃O₄ films deposited on high surface area ZrO₂ using atomic layer deposition (ALD) shows excellent cyclability for the CoFe₂O₄ material, which produces twice the amount of H₂ as the Fe₃O₄ under the same cycling conditions. [32] This investigation did not confirm CoFe₂O₄ as the product of the H₂O oxidation, and does not discuss equilibrium with the CO/CO₂ or H₂/H₂O systems, but does identify a CoFe alloy as the reduction product. Unlike the Cu-Fe-Al₂O₃, ZnFe₂O₄, and MnFe₂O₄ systems, the mixed metal spinels CoFe₂O₄ and NiFe₂O₄ have been examined thermodynamically in a study that concluded the systems have promising thermodynamic properties for a CLH process. [33]

Spinels have the structure AB₂O₄, where A is an M²⁺ ion and B is an M³⁺ ion. [34] The spinel Fe₃O₄ contains one Fe²⁺ ion for every two Fe³⁺ ions. In the mixed metal spinels CoFe₂O₄ and NiFe₂O₄, the Co and Ni possess a 2⁺ charge while all the Fe ions exist in the 3⁺ oxidation state. Substitution of Co²⁺ or Ni²⁺ into Fe₃O₄ is known to destabilize the spinel phase, making it easier to reduce, while still being capable of mixed metal spinel regeneration through water oxidation. [35] In high temperature redox cycles, addition of Co²⁺ or Ni²⁺ decreases the temperature necessary to reduce the metal oxide to FeO and CoO, or FeO and NiO from 1760 K
to 1700 K, and mixed metal spinel materials have been investigated several times for these processes. [36-39]

For the lower temperature CLH system, the effect of the Co$^{2+}$ or Ni$^{2+}$ is not as well established. Syngas reduction has the potential to leave the material in a more reduced state than thermal reduction can. Calculations between 300 K and 1000 K predict the reduction of mixed metal spinels containing Fe, Co, and Ni to their metallic states will have higher conversions of H$_2$ to H$_2$O and CO to CO$_2$ than are attainable with Fe$_3$O$_4$, while also having lower H$_2$ to H$_2$O conversions than NiO and CoO. [33] The authors attribute this to a reduced NiO and CoO activity when mixed with a Fe$^{3+}$ material. Similar to the thermal reduction of mixed metal ferrites, this analysis predicts mixed metal ferrite regeneration during H$_2$O oxidation. The referenced study [32] considers stable cycling of these mixed metal spinels to be dubious in the CLH system due to the possibility of preferential oxidation and subsequent phase segregation of the metal oxides Fe$_3$O$_4$, CoO, and NiO. Forming these products rather than the mixed metal spinels would change the equilibrium conversion of gases during reduction and would decrease the H$_2$ yield of the system. Additional H$_2$ production comes from further oxidation of Fe$^{2+}$ ions to Fe$^{3+}$ ions in the mixed metal spinel. No experimental investigation accompanied these calculations and only the equilibria shown in Eq. 2.8 and Eq. 2.9 are considered. Intermediate equilibrium compositions are not investigated.

$$\text{CoFe}_2\text{O}_4 + 4\text{H}_2 / \text{CO} \leftrightarrow 2\text{Fe} + \text{Co} + 4\text{H}_2\text{O} / \text{CO}_2 \quad \text{Eq. 2.8}$$
$$\text{NiFe}_2\text{O}_4 + 4\text{H}_2 / \text{CO} \leftrightarrow 2\text{Fe} + \text{Ni} + 4\text{H}_2\text{O} / \text{CO}_2 \quad \text{Eq. 2.9}$$

2.7 References


Chapter 3: Substrate Selection and Materials Analysis

3.1 Abstract

To establish CoFe$_2$O$_4$ and NiFe$_2$O$_4$ as candidate materials for the chemical looping hydrogen (CLH) process, the mixed metal oxides were deposited on ZrO$_2$ substrates and cycled. The CoFe$_2$O$_4$ and NiFe$_2$O$_4$ phases were identified using Raman spectroscopy before and after cycling, confirming regeneration with H$_2$O oxidation. The absence of a c-ZrO$_2$ phase indicated minimal interaction between the metal oxide and ZrO$_2$ support. Materials proved to be cycleable at 873 K, and oxidation rates were shown to have a clear dependence on H$_2$O concentration and temperature. Post-cycling analysis showed a decrease in material surface area, but the metal cations on the ZrO$_2$ showed no sign of phase segregation.

3.2 Introduction

The chemical looping hydrogen (CLH) process generates pure and separated streams of H$_2$ and CO$_2$ from syngas from any source, and it is proposed as a method of H$_2$ production with integrated CO$_2$ capture for future gasification systems.[1] The process involves a metal oxide material that is first reduced simultaneously with H$_2$ and CO, then oxidized in H$_2$O to generate H$_2$ and regenerate the original metal oxide.[2] Iron is the current state-of-the art material for the CLH process due to its favorable thermodynamics, low toxicity, and low cost. [1] The mixed metal spinels NiFe$_2$O$_4$ and CoFe$_2$O$_4$ are possible metal oxides for the CLH process; however, the investigation of these materials to date includes only preliminary thermodynamic results and limited cycling data. One concern with these materials is the preferential re-oxidation of the respective metals, which could inhibit regeneration of the mixed metal spinel. [3] Success at cycling CoFe$_2$O$_4$ is reported, though regeneration of the mixed metal spinel after cycling was not confirmed. [4] No investigation into NiFe$_2$O$_4$ is reported in literature to date. A comprehensive
study, including cyclability analysis and phase identification, is necessary to confirm the candidacy of these mixed metal ferrites for the CHL process and to justify further investigation of the materials.

The specific goals of this study were to investigate the cyclability characteristics of CoFe$_2$O$_4$ and NiFe$_2$O$_4$, to determine if the H$_2$O oxidation regenerates the mixed metal spinels CoFe$_2$O$_4$ and NiFe$_2$O$_4$, and to perform preliminary investigations into the effects of H$_2$O concentration, temperature, and metal oxide composition on the oxidation process. The H$_2$ production was used as a metric to determine the material cyclability; a material with consistent H$_2$ production peak values and total H$_2$ production per cycle was considered to be cycle stable. In accordance with the overall goal of H$_2$ production, material performance was assessed based on H$_2$ production capacity, cyclability, and ability to regenerate the mixed metal oxide phase. Based on previous literature suggesting successful material cycling with metal oxides supported on ZrO$_2$, an inert binder was chosen to minimize the binder-metal oxide interaction and to allow unhindered investigation into the nature of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ reduction and oxidation cycles.

### 3.3 Materials and Methods

#### 3.3.1 Samples

Metal oxide samples were prepared in the laboratory using the incipient wetness method. [5, 6] Iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Sigma Aldrich, 98%), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O, Alfa Aesar, 98%), and cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O, Alfa Aesar, 98%) were dissolved in de-ionized water to form 2 molar aqueous solutions of metal cations. Catalyst pellets made of approximately 20 nm sintered ZrO$_2$ spheres (Alfa Aesar, 99%, 0.31 cc/g, 50 m$^2$/g), were crushed and sieved to 110 – 175 μm diameter particle size and subsequently mixed with the aqueous metal nitrate solutions of the desired stoichiometry. Solution volumes equal to the calculated
pore volume of the ZrO$_2$ samples were added using a calibrated pipette. Samples were dried at 333 ± 5 K in a vacuum oven for eight hours after each addition of the nitrate solution. When the desired mass percent of metal oxide (20%) was reached, the samples were calcined at 873 ± 10 K in air for eight hours.

3.3.2 Sample Characterization

The metal oxide mass percents and cation ratios were confirmed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Phase identification before and after cycling was performed with a Raman spectrometer using a 532 nm Nd:YAG laser with a 1 μm spot size. Calibrations were performed with a with a neon lamp. Multiple sites on each material were sampled to ensure sample conformity. Surface areas were measured using Brunauer-Emmett-Teller (BET) surface area analysis, and crushed samples were examined visually using a Philips CM 100 Transmission Electron Microscope. Samples were also examined with a JSM-7401F field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDS) for surface elemental analysis and mapping.

3.3.3 Sample Cyclability

Cyclability analysis was performed in a stagnation flow reactor, shown in Figure 3.1.[4] Reactant gas flow, controlled using calibrated mass flow controllers, proceeded through an insulated and heated stainless steel manifold to the reactor tube. A shallow, loosely packed bed of ferrite sample was placed on a flat ZrO$_2$ sample holder positioned at the bottom of the vertically oriented, closed-end Al$_2$O$_3$ reactor tube. Reactant gases entered the reactor and impinged on the sample through an Al$_2$O$_3$ tube situated concentrically inside an outer closed-end tube. After contact with the sample, the gases exited the reactor by flowing up between the tubes and out the top of the reactor. Exiting gas concentrations were measured with a differentially
pumped, modulated effusive beam mass spectrometer (Extrell C50, 500 amu), which was
designed to increase detection sensitivity in the presence of background gases. The mass
spectrometer was calibrated daily using analytical standard gases, with 4-point calibrations in the
H₂, CO, and CO₂ partial pressure ranges observed during reduction and oxidation reactions. To
prevent H₂O from entering the mass spectrometer during oxidation, steam was cryogenically
removed from the gas stream in a liquid nitrogen cooled trap prior to gas sampling. A vacuum
pump and pressure controller were used to maintain a constant 1 kPa pressure in the system
during the reaction.

Figure 3.1: Stagnation flow reactor. Gases flow through the center tube and onto the sample at
the bottom of the closed end tube. Dimensions are such to minimize velocity gradients across the
sample, from Schefte et al. Chemistry of Materials.2010;23 (Ref. [4]).
In accordance with chemical looping conditions, samples were reduced for ten minutes at 873 K using a syngas mixture containing 2% CO\textsubscript{2}/2% H\textsubscript{2}/2% CO/Balance He to simulate reduction conditions during the CLH process. Oxidations under 10% H\textsubscript{2}O/balance He followed and continued until the H\textsubscript{2} levels returned to baseline as observed before cycling. Steam was generated at 348 K using a RASIRC steam generation unit incorporating a humidity sensor that allowed accurate water flow rate control and recording during the reaction.

### 3.4 Experimental Results and Analysis

#### 3.4.1 Sample Characterization

Sample surface areas and mass percents are listed in Table 3.1. The surface area of the ZrO\textsubscript{2} substrate was 49.1 m\textsuperscript{2}/g prior to deposition. Surface areas decreased with the addition of the metal oxide due to both the addition of mass and to pore blocking in the substrate. Mass percents of metal oxide and cation ratios, measured with ICP-AES, were verified to be similar to the values calculated from the volumes of nitrate solution used in synthesis. Samples at 10X magnification show 100-200 μm particles, which are uniform in color. (Figure 3.2 a) Visual examination of crushed particles revealed consistent coloring throughout, confirming dispersion of the metal oxide into the interior of the particle. Analysis of the crushed particle with EDS confirmed uniform distribution of cations throughout the particle. Inspection of the particle exterior and interior using SEM revealed a rough, porous surface. (Figure 3.2 b) Visual TEM

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Percent metal oxide</th>
<th>Cation Ratio</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank ZrO\textsubscript{2}</td>
<td>none</td>
<td>none</td>
<td>49.1</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>20.7</td>
<td>All Fe</td>
<td>35</td>
</tr>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4}</td>
<td>18.7</td>
<td>2.1:1 Fe:Co</td>
<td>33.3</td>
</tr>
<tr>
<td>NiFe\textsubscript{2}O\textsubscript{4}</td>
<td>21.6</td>
<td>2:1 Fe:Ni</td>
<td>38.9</td>
</tr>
</tbody>
</table>

Table 3.1: Sample mass percents and surface areas.
inspection of a blank ZrO$_2$ sample confirmed the morphology of the ZrO$_2$ substrate material as sintered ~20 nm particles. (Figure 3.2 c) Similar images of an annealed and crushed Fe$_2$O$_3$ sample showed metal oxide materials exist as 100-200 nm agglomerates. (Figure 3.2 d) Nitrogen Leco analysis confirmed complete removal of nitrogen from the samples during annealing.

Figure 3.2: (a) NiFe$_2$O$_4$ deposited on ZrO$_2$ (10X) (b) SEM image of NiFe$_2$O$_4$ particle surface (c) TEM image of ZrO$_2$ blank shows ~20 nm sintered particles (d) Annealed and crushed Fe$_2$O$_3$ sample shows 100-200 nm metal oxide agglomerates.

3.4.2 Phase Identification

Spinels have the composition AB$_2$O$_4$, where A is an M$^{2+}$ ion and B is an M$^{3+}$ ion. [7] The spinel Fe$_3$O$_4$ contains one Fe$^{2+}$ ion for every two Fe$^{3+}$ ions, while in the mixed metal spinels NiFe$_2$O$_4$ and CoFe$_2$O$_4$, the Ni and Co possess a 2+ charge and all the Fe ions exist in the 3+
oxidation state. In a normal spinel material, all 2+ cations occupy tetrahedral sites, where the neighboring atoms are four oxygen anions and all the 3+ atoms occupy octahedral sites, where the neighboring atoms are six oxygen anions. The ferrites Fe$_3$O$_4$, NiFe$_2$O$_4$, and CoFe$_2$O$_4$ are all inverse spinels, meaning that all of the 2+ cations occupy octahedral sites with half of the 3+ cations, while half of the 3+ cations occupy tetrahedral sites. [8]

Each crystal structure has unique vibrational properties that depend on the structure and composition of the material. Raman spectroscopy uses inelastic light scattering caused by the excitation or de-excitation of vibrational modes in crystals to produce a spectrum that is used to identify the metal oxide phase present in a material. [9] Group theory classifies spinels as the cubic space group Fd3m, and predicts spinel materials will have five Raman active vibrational modes (F$_{2g}(1)$, E$_g$, F$_{2g}(2)$, F$_{2g}(3)$, and A$_{1g}$). [10, 11] In a spinel, the A$_{1g}$, F$_{2g}$, and E$_g$ peaks are often attributed solely to bonds between tetrahedral cations and their corresponding oxygen anions; however, much experimental evidence indicates that the octahedral cation affects peak placement as well. [9, 11, 12] A comparison of the wavenumber of the A$_{1g}$ peak between multiple inverse spinels should show no shift due to Fe$^{3+}$ in the tetrahedral sites for each if the position is solely dependent on the tetrahedral cation, yet the peak shifts by as much as 40 cm$^{-1}$. Because of this, the A$_{1g}$ peak position is thought to depend on the divalent octahedral cation in the inverse spinel structure. [13] A shoulder on the CoFe$_2$O$_4$ and NiFe$_2$O$_4$ A$_{1g}$ peak is often seen, and attributed to the trivalent cation in the octahedral site. [14] Due to fast electron hopping between the Fe$^{2+}$ and Fe$^{3+}$, a shoulder is not seen on the A$_{1g}$ peak of Fe$_3$O$_4$ even though it is also an inverse spinel. [9] Additionally, peaks other than the A$_{1g}$ peak are often weak in the Fe$_3$O$_4$ spectra and not observed above the experimental noise.
The potential compositions of the mixed metal ferrites include \( \alpha\)-Fe\(_2\)O\(_3\), \( \gamma\)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), NiFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\), Co\(_3\)O\(_4\), CoO, and NiO. Peak positions from literature sources for each of these materials used to identify the composition of these samples are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>( F_2g(1) )</th>
<th>( E_g )</th>
<th>( F_2g(2) )</th>
<th>( F_2g(3) )</th>
<th>( A_{1g} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_3)O(_4)</td>
<td>193</td>
<td>306</td>
<td>538</td>
<td>668</td>
<td>[10]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>193</td>
<td>308</td>
<td>540</td>
<td>670</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>312</td>
<td>477</td>
<td></td>
<td>687</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>NiFe(_2)O(_4)</td>
<td></td>
<td>460sh, 492</td>
<td>574sh, 595</td>
<td>654sh, 702</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>339</td>
<td>490</td>
<td>579</td>
<td>700</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td></td>
<td>481</td>
<td>521</td>
<td>689</td>
<td>[12]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Non-spinel metal oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha)-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>( \gamma)-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>NiO</td>
</tr>
<tr>
<td>CoO</td>
</tr>
</tbody>
</table>

Table 3.2: Raman peaks for materials of interest.

Due to the known difference in composition between an O\(_2\) oxidized Fe-only sample (Fe\(_2\)O\(_3\)) and an H\(_2\)O oxidized Fe-only sample (Fe\(_3\)O\(_4\)), the Fe-only samples were analyzed with Raman after H\(_2\)O oxidation to ensure formation of the Fe\(_3\)O\(_4\) phase. The observed \( A_{1g} \) peak located at \( \sim 670 \) cm\(^{-1}\), and the \( F_2g \) located at 542 cm\(^{-1}\), correspond with literature values for Fe\(_3\)O\(_4\), confirming the presence of the spinel material. (Figure 3.3 a)

Raman spectra of the NiFe\(_2\)O\(_4\) sample taken before and after cycling showed the same peaks and peak positions present in each sample. Peaks at 500 cm\(^{-1}\) and 698 cm\(^{-1}\) correspond with literature values for the locations of the NiFe\(_2\)O\(_4\) \( F_2g \) and \( A_{1g} \) peaks, respectively. (Figure 2b) Similarly, Raman data taken before and after cycling the CoFe\(_2\)O\(_4\) samples showed unchanged peak positions (Figure 2c). The \( A_{1g} \) and \( F_2g \) peaks appear where expected from literature values, at 698 cm\(^{-1}\) and 487 cm\(^{-1}\). These spectra indicate that the NiFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\)
phases were regenerated, after reduction, with only H₂O oxidation. This is an important finding in light of the concern that preferential oxidation hinders the formation of the mixed metal spinel. [3] Phase segregation resulting from preferential oxidation would result in the phases Fe₃O₄ and CoO or NiO after oxidation. The peaks identified do not correspond to peaks from these metal oxide phases, but rather solely to the mixed metal spinel phases.

![Raman spectra](image_url)

Figure 3.3 Raman spectra of a) Fe₃O₄, b) NiFe₂O₄ samples, and c) CoFe₂O₄. d) Position of each peak for comparison with Table 3.2.


3.3.3. Interaction with ZrO$_2$

Although ZrO$_2$ is considered an inert support material, Fe, Ni, and Co cations are soluble in ZrO$_2$ and require higher temperatures to reduce once they are dissolved in ZrO$_2$. The solubility limits of Fe and Co in ZrO$_2$ are 25% and 15%, respectively. Dissolved cations are easily be detected through conventional materials analysis, as even 1% dissolved cations in the ZrO$_2$ matrix stabilizes the cubic ZrO$_2$ phase, which has distinctively different XRD spectra and Raman spectra from the monoclinic phase of ZrO$_2$. [23, 24]

Dissolved cations are easily be detected through conventional materials analysis, as even 1% dissolved cations in the ZrO$_2$ matrix stabilizes the cubic ZrO$_2$ phase, which has distinctively different XRD spectra and Raman spectra from the monoclinic phase of ZrO$_2$. [25]

Due to the non-uniform nature of the metal oxide deposition on the ZrO$_2$ support, and the large diameter of the laser used in Raman analysis in comparison to the size of the metal oxide particles, a signal from the ZrO$_2$ substrate was observed in addition to the metal oxide spectra in many spectra collected from the samples. All materials examined showed evidence of only an m-ZrO$_2$ phase, characterized by two peaks near 200 cm$^{-1}$. (Figure 3.4) A large c-ZrO$_2$ peak at 500 cm$^{-1}$ is obscured by the F$_{2g}$(2) spinel peak. Formation of c-ZrO$_2$ exhibits broad peaks at 250 cm$^{-1}$ and 350 cm$^{-1}$. The surface is the most likely region of the sample for c-ZrO$_2$ to form, due to the immediate contact with the metal cations. The absence of the c-ZrO$_2$ phase near the surface allows us to assume that the amount of cations dissolved in the ZrO$_2$ is not significant. Phase analysis of the material bulk using XRD also failed to detect a c-ZrO$_2$ phase.
Cyclability was established before investigating the effects of steam concentration and temperature on the oxidation, since material degradation masks the effects of changes in cycle conditions. Being the current state-of-the-art material, samples of Fe$_3$O$_4$ were cycled as a baseline material with which to compare total H$_2$ production and oxidation characteristics. (Figure 3.5 a) These samples showed an initial sharp decrease in total H$_2$ production and peak H$_2$ production between the first and second cycles. Subsequent cycles showed a stabilization of total H$_2$ production and peak H$_2$ production. The total amount of H$_2$ produced was approximately 1 mmol H$_2$ per gram metal oxide in the sample. Transient H$_2$ production behavior showed rapid oxidation that was complete in less than 100 sec. This behavior was similar to the
behavior observed using samples of Fe$_3$O$_4$ films deposited using ALD, which had total H$_2$ production amounts near 1 mm/g, but with lower peak rates. [4]

Cycling of the NiFe$_2$O$_4$ samples (Figure 3.5 b) showed an initial decrease in total H$_2$ production and peak H$_2$ production, similar to the Fe-only material. After the third cycle, the material appears to stabilize, producing consistent total H$_2$ amounts and H$_2$ peak production values. The amount of H$_2$ produced was five times greater than the amount produced from the Fe$_3$O$_4$ sample, nearly 6 mmol/g metal oxide, though oxidation took longer to complete. Complete oxidation is not shown in Figure 3.5 b, as the H$_2$ levels do not return to baseline until after 800 s.

Cycling of the CoFe$_2$O$_4$ materials (Figure 3.5 c) showed that the incipient wetness CoFe$_2$O$_4$ samples were highly cycleable, with little change detected in eight cycles and consistent peak heights and total H$_2$ production. The amount of H$_2$ produced was nearly eight times greater than from the Fe$_3$O$_4$ sample, at 8 mmol/g metal oxide, though the production took nearly 500 s to reach completion.
A direct comparison of all the materials (Figure 4 d) shows that both NiFe$_2$O$_4$ and CoFe$_2$O$_4$ offer significant improvements over conventional Fe$_3$O$_4$ in total H$_2$ production and peak rate of H$_2$ production. Greater H$_2$ production from CoFe$_2$O$_4$ in comparison to Fe$_3$O$_4$ was attributed to the ability of the Co$^{2+}$ ion to reduce to a metallic state under conditions where the Fe$^{3+}$ ion reduced no further than Fe$^{2+}$. [4] Metallic Co and Fe are generated from CoFe$_2$O$_4$ during reduction conditions that form FeO from a Fe$_3$O$_4$ sample, as identified using in-situ XRD. The cycling conditions in the present study use the same gas composition as the previously mentioned study, thus the reduction products are assumed analogous to those seen by Scheffe, et
al. Reduction to a metallic state, rather than to the FeO state, accounts for the increased H\textsubscript{2} production of both mixed metal spinels in comparison to the Fe-only sample.

3.4.5 Characterization of Cycled Materials

Surface areas after cycling, shown in Table 3.3, indicate surface area loss for each sample. To distinguish between the effects of the surface area loss of the substrate and the surface area loss of the metal oxide, blank ZrO\textsubscript{2} substrate was cycled at 873 K and subsequently analyzed. The surface area of the substrate was unchanged; therefore, surface area loss during cycling was attributed to the metal oxide, most likely due to sintering and agglomeration of the metal oxide particles. Visual examination of the sample with TEM after reduction showed an increase in the metal oxide agglomerate size to a few hundred nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area before cycling (m\textsuperscript{2}/g)</th>
<th>Surface Area after cycling (m\textsuperscript{2}/g)</th>
<th>Change in surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-ZrO\textsubscript{2}</td>
<td>49 ± 2</td>
<td>49 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>35 ± 2</td>
<td>24 ± 2</td>
<td>-11</td>
</tr>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4}</td>
<td>33 ± 2</td>
<td>23 ± 2</td>
<td>-10</td>
</tr>
<tr>
<td>NiFe\textsubscript{2}O\textsubscript{4}</td>
<td>39 ± 2</td>
<td>17 ± 2</td>
<td>-22</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison between initial sample surface area and ample surface area after cycling

Examination of the material surface with SEM analysis showed no observable difference between cycled and uncycled materials, and EDS analysis of cycled materials showed homogeneous dispersion of the Co, Ni, and Fe, as was seen in the initial EDS analysis. The absence of distinct zones of ZrO\textsubscript{2} and metal cations, combined with the Raman data showing the presence of the CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4} phases, was evidence that phase segregation did not occur during reduction and oxidation cycling.
3.3.6 Effect of H$_2$O Concentration and Temperature on Oxidation

To establish the limits of cyclability for these CoFe$_2$O$_4$ and NiFe$_2$O$_4$, samples were cycled under different H$_2$O concentrations and at different temperatures. As shown in Figure 3.5, data show a clear relationship between H$_2$O concentration and the peak rate of H$_2$ production, indicating that the process limiting the kinetic rate of oxidation for these materials has a dependence on H$_2$O concentration. Oxidation data at different temperatures indicate a clear relationship between reaction temperature and oxidation rate, as expected in any solid-gas reaction due to the increased rate at which solid state processes occur at higher temperatures. [26] These two factors will be investigated in more detail in Chapter 6. The reaction temperature also affected the total H$_2$ production. This total difference in H$_2$ was hypothesized to be due to a combination of two factors: different reduction extents resulting from reduction at different temperatures, and incomplete oxidation due to slower kinetic processes at lower temperatures. Materials proved to be cycleable between the temperatures of 773 K and 873 K; however, at temperatures above 873 K material degradation was observed for all samples. Blank ZrO$_2$ supports cycled at 1073 K showed a decrease in surface area from 49 m$^2$/g to 37 m$^2$/g, indicating substrate instability at high temperatures. The remainder of studies in this thesis were conducted between 773 K and 873 K to preserve the cyclability of the metal oxides.
3.4 Conclusions

This investigation showed the regeneration of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ from reduced material solely through H$_2$O oxidation. Additionally, the reduced material was highly reactive with H$_2$O, producing H$_2$ with peak rates near or greater than that of Fe-only materials. The mixed metal spinels showed cycle stability, and the regeneration of the mixed metal spinel was confirmed after several cycles. The substrate m-ZrO$_2$ was identified as a non-reactive and stable platform for deposition of the mixed metal ferrites. Materials prepared using incipient wetness showed no interactions with the ZrO$_2$ substrate as only m-ZrO$_2$ was detected at the surface and in the material bulk. Sample surface areas decrease with cycling, most likely due to the observed sintering and agglomeration of the metal oxide. No metal cation segregation was detected with SEM EDS analysis, though the resolution of this technique is on the order of 1 μm. The detection of the mixed metal spinel phase with Raman analysis after cycling supports the conclusion that no significant phase segregation was occurring in the materials. Based on the results from this analysis, a comprehensive kinetic study investigating the oxidation of these materials should incorporate their response to both temperature and H$_2$O concentration.

3.5 References


Chapter 4: Novel Mixed Metal Ferrites for H₂ Production through Chemical Looping

4.1 Abstract

The mixed metal ferrites NiFe₂O₄ and CoFe₂O₄ are candidate materials for the Chemical Looping Hydrogen (CLH) process, which produces pure and separate streams of H₂ and CO₂ without the use of complicated and expensive separation equipment. In the CLH process, syngas reduces a metal oxide, oxidizing the H₂ and CO in the syngas to H₂O and CO₂, and stores the chemical energy of the syngas in the reduced metal oxide. The reduced metal oxide is then oxidized in steam to regenerate the original metal oxide and produce H₂. In this study, we report thermodynamic modeling and experimental results regarding the syngas reduction and H₂O oxidation of NiFe₂O₄ and CoFe₂O₄ to determine the feasibility of their use in the CLH process. Modeling predicts the oxidation of nearly all the CO and H₂ in syngas to H₂O and CO₂ during the reduction step for both materials, and regeneration of the mixed metal spinel phase during oxidation with excess H₂O. Laboratory tests in a packed bed reactor confirmed over 99% conversion of H₂ and CO to H₂O and CO₂ during reduction of NiFe₂O₄ and CoFe₂O₄. Powder XRD analysis of the reduced materials showed, in accordance with thermodynamic predictions, the presence of a spinel phase and a metallic phase. High reactivity of the reduced NiFe₂O₄ and CoFe₂O₄ with H₂O was observed, and XRD analysis confirmed re-oxidation to NiFe₂O₄ and CoFe₂O₄ under the conditions tested. When compared with a conventional Fe-based CLH material, the mixed metal spinels showed a higher extent of reduction under the same conditions, and produced at least four times the H₂ per mass of active material than the Fe-based material. Analysis of the H₂ and CO consumed in the reduction, and the H₂ produced during the oxidation, showed over 90% conversion of the H₂ and CO in syngas back to H₂ during oxidation.
4.2 Introduction

In addition to being a possible future energy source for electricity and vehicle transportation, hydrogen (H₂) is necessary for ammonia production and oil refining, which nationally use nine million tons of H₂ every year. [1] Current methods of H₂ production, including steam methane reforming, partial oxidation of hydrocarbons, and coal gasification, require use of the water-gas shift reaction (Eq. 4.1) to produce a mixture of H₂ and CO₂ from the synthesis gas (syngas) that they generate.

\[
H_2O + CO \leftrightarrow H_2 + CO_2 \quad \text{Eq. 4.1}
\]

The reaction in Eq. 1 is thermodynamically limited at high temperatures and kinetically limited at low temperatures. Consequently, a two stage process is required to maximize the amount of H₂ in the syngas. Supplementary purification is then necessary to decrease the amount of CO in the gas stream to the desired level. [2, 3] Additionally, the CO₂ must be separated from the H₂ in the product stream using processes such as Pressure Swing Adsorption (PSA) or Monoethanolamine (MEA) scrubbing, which carry high energy penalties and can result in the loss of up to 30% of the produced H₂. [4, 5] Generation of a pure and easily sequestered CO₂ waste stream is important, as pressure is increasing on industries to curtail the release of CO₂ into the atmosphere.

The Chemical Looping Hydrogen (CLH) production process is an effective alternative method for generation of pure H₂ and a separate stream of pure and easily sequestered CO₂ from any syngas. [2, 6, 7] In the CLH process, syngas reduces a metal oxide material at moderate to high temperatures (500°C to 800°C) as it leaves a gasifier (Eq. 4.2-3). The reduced metal oxide can then be oxidized using steam to produce H₂ and regenerate its original oxide form (Eq. 4.4).
\[ H_2 + MeO_x \leftrightarrow H_2O + MeO_{x-1} \quad Eq.4.2 \]

\[ CO + MeO_x \leftrightarrow CO_2 + MeO_{x-1} \quad Eq.4.3 \]

\[ H_2O + MeO_{x-1} \leftrightarrow H_2 + MeO_x \quad Eq.4.4 \]

Pure and separate H₂ and CO₂ are produced without complicated or expensive multistep separation processes.

In order to be a viable material for the CLH process, a metal oxide must meet the following criteria:

1) Thermodynamically, the reaction of the metal oxide with the syngas must be able to convert almost all of the CO and H₂ in the syngas to CO₂ and H₂O.

2) The reduced form of the metal oxide must be readily oxidized using steam.

3) The material must demonstrate fast and stable kinetics over a large number of redox cycles.

[7] The first two criteria are intrinsic properties of the metal oxide, and can be altered by changing or doping the metal oxide in use with additional metallic constituents. The third criterion, often a property of the material synthesis method, has been studied and demonstrated at length. [7-9]

Of the potential CLH metal oxide candidates, iron (Fe) remains the most studied due to its abundance, low cost, low toxicity, and overall favorable thermodynamics. [2, 7, 9] When compared thermodynamically to specific oxides of Ni, Cd, Cu, Co, Cr, Mn, and Sn, Fe₂O₃ showed the most promising theoretical maximum conversion of CO and H₂ to CO₂ and H₂O.
Furthermore, the oxidation of FeO and Fe to Fe$_3$O$_4$ has a high conversion of H$_2$O to H$_2$. [7, 10, 11] Consequently, the most common CLH process to date is expressed by the following reactions:

$$3\text{Fe}_2\text{O}_3 + 9\text{H}_2 / \text{CO} \leftrightarrow 6\text{Fe} + 9\text{H}_2\text{O} / \text{CO}_2 \quad \text{Eq. 4.5}$$

$$6\text{Fe} + 8\text{H}_2\text{O} \leftrightarrow 2\text{Fe}_3\text{O}_4 + 8\text{H}_2 \quad \text{Eq. 4.6}$$

$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow 3\text{Fe}_2\text{O}_3 \quad \text{Eq. 4.7}$$

The O$_2$ oxidation (Eq. 7) is necessary because Fe$_3$O$_4$ is unable to split water to regenerate Fe$_2$O$_3$. Unlike Fe$_2$O$_3$, Fe$_3$O$_4$ is thermodynamically unable to oxidize much of the CO and H$_2$ in syngas to CO$_2$ and H$_2$O, which leaves a significant portion of un-reacted CO and H$_2$ in the syngas exiting the reactor. Experimentally, this is observed as immediate CO and H$_2$ breakthrough when testing a packed bed of Fe$_3$O$_4$ particles. [2] Therefore, the Fe$_2$O$_3$ phase must be regenerated with O$_2$ before the reduction step. [7, 11, 12] The H$_2$ and CO used to reduce the Fe$_2$O$_3$ to Fe$_3$O$_4$ is not recovered as H$_2$, which results in a loss of potential H$_2$ production. Regardless of the associated H$_2$ loss, the O$_2$ oxidation is exothermic and produces a significant amount of heat, which is used to generate electricity and heat process streams. [7]

In addition to Fe$_2$O$_3$/Fe$_3$O$_4$, the mixed metal spinels NiFe$_2$O$_4$ and CoFe$_2$O$_4$ have been suggested as possible CLH materials. [10] These spinels have the composition AB$_2$O$_4$, where A is an M$^{2+}$ ion and B is an M$^{3+}$ ion. [13] The spinel Fe$_3$O$_4$ contains one Fe$^{2+}$ ion for every two Fe$^{3+}$ ions. In the mixed metal spinels NiFe$_2$O$_4$ and CoFe$_2$O$_4$, the Ni and Co possess a 2+ charge while all the Fe ions exist in the 3+ oxidation state. Thermodynamic studies conducted between 127°C and 727°C predict a higher conversion of H$_2$ to H$_2$O and CO to CO$_2$ during the reduction
of mixed metal spinels containing Fe and Ni or Fe and Co than are attainable with Fe$_3$O$_4$. Predictions show the mixed metal ferrite will regenerate during H$_2$O oxidation, unlike Fe$_2$O$_3$. [10] The referenced study [10] regards the mixed metal spinels with caution due to the hypothesis that the metal oxides Fe$_3$O$_4$, CoO, and NiO would segregate upon cycling rather than regenerate the mixed metal spinel phase. Oxidation to NiFe$_2$O$_4$ or CoFe$_2$O$_4$, rather than NiO/Fe$_3$O$_4$ or CoO/Fe$_3$O$_4$, increases the oxidation H$_2$ yield by 8% if the starting composition is a stoichiometric mixture of 2:1 Fe:Ni or 2:1 Fe:Co in their metal states. This additional H$_2$ production comes from the further oxidation of Fe$^{2+}$ ions to Fe$^{3+}$ ions in the mixed metal spinel.

In a recent study of the reduction and subsequent water oxidation of CoFe$_2$O$_4$ and Fe$_3$O$_4$ films deposited on high surface area substrates using atomic layer deposition (ALD), CoFe$_2$O$_4$ produced twice the amount of H$_2$ as the Fe$_3$O$_4$ under the same cycling conditions, and maintained excellent cyclability for up to the seven cycles tested. [14] Additional H$_2$ production was attributed to the ability of the Co$^{2+}$ to cycle between the metallic state and the +2 oxidation state under the conditions tested. Though successfully demonstrating that the mixed metal ferrites can have beneficial cycling properties, this investigation did not confirm CoFe$_2$O$_4$ as the product of the oxidation and did not consider the limits of H$_2$ and CO conversion during the reduction step of the cycle. No such data have been reported for NiFe$_2$O$_4$.

The present study seeks to investigate the feasibility of utilizing mixed metal spinels, specifically NiFe$_2$O$_4$ and CoFe$_2$O$_4$, in the CLH process. The ability of these materials to convert CO and H$_2$ to CO$_2$ and H$_2$O during the reduction step and the reactivity of the reduced materials with water to produce H$_2$ were examined using thermodynamic databases in the FactSage program, then experimentally investigated and compared with the properties of Fe-based materials. While conventional CLH processes are focused on Fe$_2$O$_3$ to produce H$_2$, CO$_2$, and
heat, this mixed metal ferrite-based process is focused on maximizing the amount of \( \text{H}_2 \) produced, with \( \text{H}_2 \) production demonstrated at four times that of the conventional \( \text{Fe}_2\text{O}_3 \) processes under operating conditions.

### 4.3 Materials and Experimental Methods

#### 4.3.1 Thermodynamic Analysis

Thermodynamic calculations were performed using the FactSage\textsuperscript{TM} program (Version 6.2), which uses Gibbs free energy minimization calculations and extensive thermodynamic property databases for thermodynamic modeling. Multiple studies show the FactSage program correctly models the phase and composition of mixed metal spinels during thermal reduction and \( \text{H}_2\text{O} \) oxidation. [15, 16] Including solution phases from the FactSage oxide solution database (version 5.3) in thermodynamic calculations, rather than only stoichiometric line compounds, significantly affects the accuracy of the thermodynamic calculations. [15] FactSage is able to reproduce thermodynamic properties, activities, \( \text{M}^{2+}/\text{M}^{3+} \) ratios, solution sublattice cation distributions, and partial pressures of equilibrium gases from compiled experimental data using these databases. [17]

In addition to pure solids and gases from the Fact 5.3 database, spinel and metal oxide solution phases were included for this study and are shown in Table 1. The FactSage spinel solution phase uses the compound energy formalism model to describe the distribution of cations over spinel tetrahedral and octahedral sites. Vacancies in the octahedral sublattice allow oxygen non-stoichiometry and deviations from the ideal \( 2+/3+ \) cation ratio in the spinel phase model 
\[
(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{M}^{2+}, \text{M}^{3+})_7[\text{Fe}^{2+}, \text{Fe}^{3+}, \text{M}^{2+}, \text{M}^{3+}, \text{Va}]_2\text{O}_4.
\] [18] The metal oxide solution phase is modeled as a random solution of \( \text{M}^{+2}, \text{Fe}^{+2}, \) and \( \text{Fe}^{+3} \) ions on cation sites. Vacancies associated with \( \text{Fe}^{+3} \) ions on cation sites allow for excess Fe cations in the wustite (\( \text{Fe}_{1-x}\text{O} \)) phase. [15, 19]
These models have been optimized over the temperatures and compositions examined in this chapter. [17, 20]

<table>
<thead>
<tr>
<th>Solution Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
</tr>
<tr>
<td>[Co(II),Co(III),Fe(II),Fe(III)]</td>
</tr>
<tr>
<td>[Co(II),Co(III),Fe(II),Fe(III),Vacancy]2O4/</td>
</tr>
<tr>
<td>[Ni(II),Fe(II),Fe(III)]</td>
</tr>
<tr>
<td>[Ni(II),Fe(II),Fe(III),Vacancy]2O4</td>
</tr>
<tr>
<td>MeO (Me=Co/Ni)</td>
</tr>
<tr>
<td>Fe2O3, MeO</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gases</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>CO2</td>
</tr>
<tr>
<td>H2</td>
<td>CO</td>
</tr>
<tr>
<td>O2</td>
<td>Fe</td>
</tr>
<tr>
<td>O</td>
<td>Ni/Co</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>Fe</td>
</tr>
</tbody>
</table>

Table 4.1: Compounds, gases and solution species considered in thermodynamic calculations using FactSage.

As in previous literature, the H2/H2O and CO/CO2 systems were considered independently in calculations. [7, 21-23] The activity of the reducing gas, held constant, defined the activity of the oxidizing gas. These model conditions simulate the continuous flow of a constant composition syngas over the metal oxide, such that the gaseous reaction products do not inhibit forward reactions. This allowed the calculation of predicted solid products in the limiting case of excess gaseous reactants. Gases involved behave as ideal gases at both the reference temperature and the evaluated temperature, so gas pressures are reported instead of gas activities. [7, 11, 24, 25]

4.3.2 Ferrite Sample Preparation

Samples of Fe2O3, NiFe2O4, and CoFe2O4 were prepared via the incipient wetness method. [26, 27] Iron nitrate (Fe(NO3)3·9H2O, Sigma Aldrich, 98%), nickel nitrate (Ni(NO3)2·6H2O, Alfa Aesar, 98%), and cobalt nitrate (Co(NO3)2·6H2O, Alfa Aesar, 98%) were
dissolved in de-ionized water to form 2 molar aqueous solutions of metal cations. Catalyst pellets made of approximately 20 nm sintered ZrO$_2$ spheres (Alfa Aesar, 99%, 0.31 cc/g, 50 m$^2$/g), were crushed and sieved to 110 – 175 µm diameter particle size and subsequently mixed with the aqueous metal nitrate solutions of the desired stoichiometry. Solution volumes equal to the calculated pore volume of the ZrO$_2$ samples were added using a calibrated pipette. Samples were dried at 60°C in a vacuum oven for eight hours after each addition of the nitrate solution. When the desired mass percent of metal oxide (30%) was reached, the samples were calcined at 600°C in air for eight hours.

4.3.3 Material Characterization

Sample mass loadings and deposited cation ratios were confirmed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Phase identification was performed using X-Ray diffraction (XRD, Scintag PAD5 Powder Diffractometer, CuKα1 radiation, $\lambda$=1.5406 Å, scan rate 0.5°/min, step size 0.02°). Surface areas were measured using Brunauer-Emmett-Teller (BET) surface area analysis, and crushed samples were examined visually using a Philips CM 100 Transmission Electron Microscope.

4.3.4 Chemical Cycling

Selected test samples were used to form a packed bed in a 0.64 cm OD/0.32 cm ID (0.25” OD/0.125” ID) Al$_2$O$_3$ tube, as shown in Figure 4.1. A metal filter gasket in a 0.32 cm (0.25”) ID ultra-torr fitting was secured at one end of the tube, which was subsequently filled to the center with 0.16 cm (0.0625”) diameter ZrO$_2$ spheres. Approximately 600 mg of sample material was placed in the tube on top of the ZrO$_2$ spheres to form a bed of active material. A small piece of
ZrO$_2$ felt (Zircar Zirconia) between the spheres and the sample ensured the sample placement at the center of the bed. A second piece of ZrO$_2$ felt at the opposite end of the sample ensured sample packing. The tube was placed in a horizontal furnace constructed using a 1.27 cm OD/0.95 cm ID (0.5” OD/0.375” ID) Al$_2$O$_3$ tube wrapped in nichrome wire secured using a high temperature ceramic epoxy and wrapped in insulation. An Omega CNi16 process controller module was used to control the temperature of the reactor, which was monitored using a thermocouple placed between the furnace tube and the Al$_2$O$_3$ reactor tube.

Calibrated MKS 1179A mass flow controllers delivered gases to the system. A New Era NE-1000 syringe pump delivered water to heated coils and a stream of Ar carrier gas to generate steam for the oxidation step. A constant stream of Ar purged the reactor before and after delivery of reactant gases. The reducing syngas mixture and oxidizing steam mixture equilibrated on a separate pressure controlled reactor bypass line for fifteen minutes prior to introduction contact with the sample. Upon completion of each reaction step, the Ar purge immediately resumed. A column of drierite removed H$_2$O from the gas stream before the mass spectrometer. Pressure controllers and a vacuum pump maintained a constant pressure on the bypass and reactor lines, and the bypass line pressure controller monitored the upstream pressure during the reactions.

A downstream absolute pressure of 81.3 ± 0.03 kPa (610 ± 0.2 Torr set point) was maintained during reduction and oxidation of the sample. A flowrate of 24 sccm of syngas and steam in Ar created a 13 - 20 kPa (100 - 150 Torr) pressure drop across the reactor. Syngas was composed of 8.7% H$_2$, 8.7% CO, 13% CO$_2$, in Ar, a composition appropriate for reducing Fe$_2$O$_3$ to FeO. [14] Reduction to FeO rather than to Fe metal mitigates the degradation of the material cyclability and the deposition of carbon. [6] Reduction and oxidation reactions were performed
at a furnace temperature of $873 \pm 1.5 \, K$. Steam production occurred at $110^\circ C$ by injecting 0.002 mL/min or 0.006 mL/min of H$_2$O into 20 sccm of Ar in heated coils. The resulting mixture was estimated to be 10% and 30% steam in Ar, respectively. All gas lines were maintained at a temperature of 993 K to avoid condensation of H$_2$O before the drierite column. Oxidations continued until H$_2$ levels returned to their baseline as measured before reaction.

![Diagram of reactor system](image)

**Figure 4.1: Reactor system used for chemical reduction and H$_2$O oxidation.**

### 4.3.5 Gas Analysis

A Stanford Research Systems QMS 200 mass spectrometer monitored reaction products in each experiment. In some experiments a California Analytic Instruments non-dispersive infrared detector (NDIR) obtained secondary data for the CO and CO$_2$ concentrations during reaction. For NDIR analysis, 475 sccm of Ar diluted the reaction product stream after the drierite column and mass spectrometer capillary port to meet the flow minimum of 500 sccm required for instrument operation. Five point calibrations, performed each day for H$_2$, CO, and CO$_2$ with each instrument used, covered the gas parts-per-million (ppm) ranges observed in reactor operation. The mass spectrometer had a detection limit of 3000 ppm for CO and CO$_2$, and 500 ppm for H$_2$. The NDIR had a detection limit of 600 ppm for both CO and CO$_2$. 
4.4 Results and Discussion

4.4.1 Thermodynamic modeling

Figure 4.2 a) and b) show the results of the FactSage equilibrium calculations. Plotted are the equilibrium moles of spinel and metal oxide solution phases and the metallic phase as a function of gas compositions, $p_{CO}/p_{CO_2}$ and $p_{H_2}/p_{H_2O}$ for NiFe$_2$O$_4$ and CoFe$_2$O$_4$. Additionally, the predicted equilibrium cation fractions in the spinel are plotted as a function of gas composition.

Calculations show that NiFe$_2$O$_4$ in contact with gases containing $p_{CO}/p_{CO_2}$ ratios less than 0.002 and $p_{H_2}/p_{H_2O}$ ratios less than 0.005 show the formation of a small amount of NiO. The amount of Ni in the NiO phase at equilibrium increases with increasing $p_{H_2}/p_{H_2O}$ and $p_{CO}/p_{CO_2}$, and reaches a maximum of about 7% of the total Ni content at $p_{CO}/p_{CO_2} = 0.0019$ and $p_{H_2}/p_{H_2O} = 0.0049$. At these gas compositions, the Fe cations are predicted to remain in the spinel phase to form an Fe-rich spinel with stoichiometry between NiFe$_2$O$_4$ and Ni$_{0.93}$Fe$_{2.07}$O$_4$. At $p_{CO}/p_{CO_2}$ ratios greater than 0.002, and $p_{H_2}/p_{H_2O}$ ratios greater than 0.005, FactSage calculations show the disappearance of the NiO phase and the formation of a Ni metal phase with the Fe-rich spinel phase. The amount of Ni in the metallic phase increases with increasing $p_{H_2}/p_{H_2O}$ and $p_{CO}/p_{CO_2}$ ratios until the Ni in the spinel is exhausted near a $p_{CO}/p_{CO_2}$ ratio of 0.8 or a $p_{H_2}/p_{H_2O}$ ratio of 1.5.
Figure 4.2: FactSage modeling results for the a) NiFe$_2$O$_4$ system and b) CoFe$_2$O$_4$ system. The total moles of spinel, MeO, and metallic phases, as well as the fraction of each cation in the spinel phase are shown as a function of pH$_2$/pH$_2$O and pCO/pCO$_2$.

Similarly, CoFe$_2$O$_4$ in contact with gases containing pCO/pCO$_2$ ratios less than 0.01, and pH$_2$/pH$_2$O ratios less than 0.03, forms a CoO phase in equilibrium with an Fe-rich spinel phase. The amount of Co in the CoO phase reaches a maximum of 12% of the total Co, forming a spinel with a composition Co$_{0.87}$Fe$_{2.13}$O$_4$. At pCO/pCO$_2$ ratios greater than 0.01 and pH$_2$/H$_2$O ratios greater than 0.03, the CoO phase disappears and a Co metal phase appears. The amount of Co in the metal phase increases, but the Fe cations are predicted to remain in the spinel phase until pCO/pCO$_2 = 1$ or pH$_2$/pH$_2$O = 1.5, forming an increasingly Fe-rich spinel.
These calculations show that in both the Co/Fe system and the Ni/Fe system, each composition of spinel is in equilibrium with a unique \( p\text{CO}/p\text{CO}_2 \) or \( p\text{H}_2/p\text{H}_2\text{O} \) ratio, as expressed in Equations 4.8 and 4.9. In a reactor system with sufficiently high kinetic rates, the ratios of \( p\text{CO}/p\text{CO}_2 \) and \( p\text{H}_2/p\text{H}_2\text{O} \) in the syngas exiting a reactor containing fully oxidized NiFe\(_2\)O\(_4\) or CoFe\(_2\)O\(_4\) could be quite low: less than 0.002. In accord with the equilibrium constants between the gas and solid for each intermediate spinel composition of each material, gradual breakthrough of CO and H\(_2\) would be observed, along with a gradual decrease in produced CO\(_2\) and H\(_2\)O. Under the same conditions, CoFe\(_2\)O\(_4\) is expected to show H\(_2\) and CO breakthrough at lower material conversions than NiFe\(_2\)O\(_4\) due to the higher overall \( p\text{H}_2/p\text{H}_2\text{O} \) and \( p\text{CO}/p\text{CO}_2 \) values at the same M\(_{1-0.75\delta}\)Fe\(_{2\delta}\)O\(_{4.5}\) composition.

In contrast to the mixed metal spinels, equilibrium constants predict that reduction of Fe\(_3\)O\(_4\) to FeO occurs when the ratio of \( p\text{H}_2/p\text{H}_2\text{O} \) is 2.3 and the ratio of \( p\text{CO}/p\text{CO}_2 \) is 0.85 (Eq. 4.10a). In a system with sufficiently fast kinetics, syngas in equilibrium with the reduction of Fe\(_3\)O\(_4\) to FeO will maintain this composition until complete conversion of Fe\(_3\)O\(_4\) to FeO and then change abruptly. Similarly, no intermediates exist between Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\); therefore, a sharp change in gas composition is expected at the reactor exit when Fe\(_2\)O\(_3\) is exhausted (Eq. 4.10b).

As the spinel compositions shown in Figure 4.2 imply, FactSage predictions show regeneration of NiFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\) with H\(_2\)O oxidation; however, an excess of H\(_2\)O is necessary. The H\(_2)/H_2\text{O} \) equilibrium constants for Equations 8 and 9 govern the amount of H\(_2\)O excess necessary for full oxidation.
Table 4.2: Chemical equations for spinel reduction as predicted with FactSage. Mixed metal spinels (Eq.4.8, 9) reduce to form a Fe-rich spinel and ultimately a metallic phase. Each spinel composition is in equilibrium with a unique gas composition.

4.4.2 Material Characterization

Sample surface areas and mass percents are listed in Figure 4.3. The surface area of the ZrO₂ substrate was 49 ± 2 m²/g prior to deposition. Surface areas decreased with the addition of the metal oxide due to both the addition of mass and to pore blocking in the substrate. Mass percents of metal oxide and cation ratios, measured with ICP-AES, were verified to be as calculated from the volumes of nitrate solution used in synthesis. Powder XRD analysis confirmed only the spinel phase and the m-ZrO₂ phase after annealing. Visual inspection of annealed and crushed samples with a TEM, displayed in Figure 3, show 100-200 nm metal oxide agglomerates. Nitrogen Leco analysis confirmed complete removal of nitrogen from the samples during annealing.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass percent of metal oxide</th>
<th>Cation composition</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>30.6%</td>
<td>Only Fe</td>
<td>29</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>28.0%</td>
<td>Fe:Co=2.1:1</td>
<td>26</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>31.1%</td>
<td>Fe:Ni=1.9:1</td>
<td>36</td>
</tr>
</tbody>
</table>

Figure 4.3: TEM of crushed and annealed incipient wetness prepared sample, surface areas and mass percents for each sample tested.

4.4.3 Reduction Step

Initial experiments using Fe₂O₃ and Fe₃O₄ validated the previously mentioned apparatus and procedures by confirming equivalent results with previous literature, and provided a comparison for the NiFe₂O₄ and CoFe₂O₄. Figures 4.4a and 4.4b show the composition of syngas exiting the reactor during the reduction step as a function of time for samples of Fe₂O₃ and Fe₃O₄. Samples were reduced for a total of fifteen minutes at 873 K. Flow of syngas to the reactor began at t = 0 s, and the gases took 275 s to travel from the mass flow controllers to the mass spectrometer capillary port. For the Fe₂O₃ sample, from t = 275 s to t = 425 s (the region labeled “1” in Figure 4.4a), CO₂ was the only reactant or product gas through the reactor due to the oxidation of CO to CO₂ as CO reduced the metal oxide. The reduction product H₂O, also expected, was removed in the drierite column before the mass spectrometer to prevent condensation in the capillary tube. A sharp breakthrough of CO and H₂ was observed at approximately t = 425 s (the beginning of region 2, Figure 4.4a), signaling that all the Fe₂O₃ had been consumed and converted to Fe₃O₄ or FeO. As discussed, equilibrium constants for the reduction of Fe₂O₃ to Fe₃O₄ are large (Kₑₒ,CO = pCO₂/pCO = 100,000, Kₑₒ,H₂ = pH₂O/pH₂ = ...
33,000 at 600°C), which indicates that the reaction can proceed until essentially all H\(_2\) or CO is consumed. [6, 7] Analysis of pre-breakthrough effluent gases (gas composition in region 1, Figure 4.4a) confirmed greater than 99% conversion of H\(_2\) and CO, indicating H\(_2\) levels less than 500 ppm and CO levels less than 650 ppm.

Oxidation of the reduced Fe\(_2\)O\(_3\) sample in H\(_2\)O formed Fe\(_3\)O\(_4\), which was verified using XRD. As expected, upon subsequent reduction, this sample showed immediate simultaneous CO, H\(_2\), and CO\(_2\) breakthrough (beginning of region 1, Figure 4b). In this experiment, the measured pCO\(_2\)/pCO ratio was 1.17 and the pH\(_2\)O/pH\(_2\) ratio was 0.45 (H\(_2\)O values were calculated assuming all H\(_2\) not observed with the mass spectrometer was oxidized to H\(_2\)O), which both agree with the theoretical values K\(_{eq}\) (pCO\(_2\)/pCO) = 1.2 and K\(_{eq}\) (pH\(_2\)O/pH\(_2\)) = 0.43. A similar equilibrium was observed after breakthrough for the Fe\(_2\)O\(_3\) samples. These results for Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\), shown in Figures 4.4a and 4.4b, agree well with previously published literature. [2, 6, 28]

Figure 4.4c and 4.4d shows the composition of syngas exiting the bed as a function of time for samples of NiFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\) during fifteen minute reductions. To ensure the CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) samples were in oxidation states achievable with only steam oxidation, the samples were reduced and subsequently oxidized in steam before these data were collected.

From t = 275 s to t = 625 s, the NiFe\(_2\)O\(_4\) effluent gas contained only CO\(_2\) (region 1, Figure 4.4d). All H\(_2\)O was removed in the drierite column. At t = 625 s, breakthrough of CO and H\(_2\) was observed and the CO\(_2\) level decreased (region 2, Figure 4.4c). Breakthrough of CO and H\(_2\) occurred simultaneously and increased at nearly identical rates, thus the mass spectrometer traces lie almost directly on top of each other in Figure 4.4c. Gas analysis during
region 1 indicated less than 500 ppm H\textsubscript{2} and 800 ppm CO in the effluent gas, an H\textsubscript{2} and CO conversion greater than 99%.

From \( t = 275 \) s to \( t = 400 \) s the CoFe\textsubscript{2}O\textsubscript{4} effluent gas contained only CO\textsubscript{2} (region 1, Figure 4.4c). Again, H\textsubscript{2}O was expected, but was removed in the drierite column. At \( t = 600 \) s,
the CO₂ level decreased and breakthrough of CO and H₂ was observed (region 2, Figure 4.4c). Breakthrough of H₂ occurred more rapidly than breakthrough of CO, in accordance with the FactSage predictions discussed in Section 3.1. As with NiFe₂O₄, gas analysis during region 1 during CoFe₂O₃ reduction indicated less than 500 ppm H₂ and 800 ppm CO in the effluent gas, an H₂ and CO conversion greater than 99%.

These data confirm the thermodynamic prediction that fully oxidized NiFe₂O₄ and CoFe₂O₄, like Fe₂O₃, are capable of oxidizing essentially all the H₂ and CO in the syngas to H₂O and CO₂. Unlike the sharp breakthrough of H₂ and CO during Fe₂O₃ reduction, the CO and H₂ breakthroughs were gradual for NiFe₂O₄ and CoFe₂O₄, and H₂ and CO values continued to rise until the end of the reduction. Before the reduction was terminated, the pCO/pCO₂ and pH₂/pH₂O ratios increased to values near 0.2 for both NiFe₂O₄ and CoFe₂O₄. In this gas composition range, FactSage predictions show formation of a Fe-rich spinel and Ni or Co metal. As FactSage predicted, under the same conditions, breakthrough of H₂ and CO were observed earlier for CoFe₂O₄ than for NiFe₂O₄ because of higher overall pH₂/pH₂O and pCO/pCO₂ values at the same M₁₋₀.₇₅₅Fe₂O₄₋δ composition.

4.4.4 XRD and Raman Analysis

X-ray diffraction spectra of NiFe₂O₄ and CoFe₂O₄ materials after three minutes of reduction, after twelve minutes of reduction, and after complete H₂O oxidation are shown in Figure 4.5a. For these experiments, 0.4 g of previously cycled sample were loaded into the reactor, and the material for XRD analysis was taken from the middle of the bed after the reactor was cooled under a continuous Ar purge.
As seen in Figure 4.5a, the H₂O oxidation products for NiFe₂O₄ were the spinel phase and the monoclinic ZrO₂ phase (ICCD-JCPDS 13-0307). The lack of a discernible NiO peaks indicates that the fully oxidized material does not exhibit significant phase segregation, and the

Figure 4.5: XRD data for a) NiFe₂O₄ and b) CoFe₂O₄ samples. The spinel phase is regenerated during H₂O oxidation for each sample, and a metallic phase forms during reduction.

As seen in Figure 4.5a, the H₂O oxidation products for NiFe₂O₄ were the spinel phase and the monoclinic ZrO₂ phase (ICCD-JCPDS 13-0307). The lack of a discernible NiO peaks indicates that the fully oxidized material does not exhibit significant phase segregation, and the
amount of NiO remaining due to equilibrium is negligible or too small to detect with this instrument.

Analysis of reduced NiFe$_2$O$_4$ shows that a metallic phase was formed during the three minute reduction, detectable from a reflection near $2\theta = 44^\circ$. This metallic phase grew at the expense of the spinel phase between three and twelve minutes of reaction time for both samples. The XRD patterns for the cubic spinels Fe$_3$O$_4$ and NiFe$_2$O$_4$ are nearly identical; however, small peak shifts occur in the XRD reflections due to small changes in the spinel lattice constant, $a$, when a Ni$^{2+}$ is substituted for an Fe$^{2+}$ in the lattice. [29] These differences are slight but evident in the standard spinel (311) lattice plane reflection seen at $2\theta = 35.42^\circ$ for Fe$_3$O$_4$ (ICCD-JCPDS #19-0629) and at $2\theta = 35.68^\circ$ for NiFe$_2$O$_4$ (ICCD-JCPDS #44-1485). Figure 4.5a shows the (311) peak for the NiFe$_2$O$_4$ sample when fully oxidized, after three minutes of reduction, and after twelve minutes of reduction. A peak shift from $2\theta=35.67^\circ$ when fully oxidized to $2\theta=35.48^\circ$ after twelve minutes of reduction is observed, which indicates the expected shift in spinel composition from NiFe$_2$O$_4$ to one enriched in Fe. The formation of a metallic phase and an iron-rich spinel phase are evidence that the reduction of these two mixed metal ferrites proceeds as FactSage calculations predict under these conditions. This phenomena has also been observed using Mossbauer spectroscopy in the reduction of a 4:1 Fe:Ni catalyst to form a Fe$_3$.\_$_{y}$Ni$_{y}$O$_4$ and a metallic phase. [30] The difference in energy between Ni-O and Fe-O bonds could cause the preferential loss of oxygen from the Ni in the spinel before the Fe rather than equally from both the cations to form an oxygen deficient 2:1 Fe:Ni spinel.

Bond strength in crystals depends on the bond length and the electronegativities of each atom. [31, 32] In NiFe$_2$O$_4$, the Ni$^{2+}$ ion sits in an octahedral site, while the Fe$^{3+}$ occupies both the octahedrally and tetrahedrally coordinated sites. A Ni$^{2+}$ atom has radius of 0.069 nm in the
octahedral spinel position, while the Fe\textsuperscript{3+} ion has a radius of 0.049 nm in the tetrahedral coordination and 0.0645 Å in the octahedral coordination. [33] A greater bond strength would be expected between an Fe cation and an O anion due to the higher charge density on the Fe\textsuperscript{3+} ion. This is consistent with calculations based on density functional theory, which showed that the energy required to form an Fe vacancy is always greater than the energy required to form an Ni vacancy. [34] Oxygen anions bonded with Ni\textsuperscript{2+} cations will be more easily removed by H\textsubscript{2} and CO on the surface, leaving Ni in a reduced state before removing the O bonded to Fe\textsuperscript{3+} in the spinel phase.

A similar argument can be made for the reduction of CoFe\textsubscript{2}O\textsubscript{4}, which has also been shown to have a mostly inverse structure. [29] In the inverse structure, an octahedrally coordinated Co\textsuperscript{2+} ion has a radius of 0.072 Å, while the tetrahedrally coordinated Fe\textsuperscript{3+} ions have a radius of 0.049 Å, and octahedrally coordinated Fe\textsuperscript{3+} ions have a radius of 0.065 Å. The resulting charge density is lower for the Co\textsuperscript{2+} ion, and oxygen anions bonded to a Co\textsuperscript{2+} cation will be more easily removed than those bonded to an Fe cation in CoFe\textsubscript{2}O\textsubscript{4}. Reduction and in-situ XPS analysis of a mixed Fe-Co spinel at 543 K shows complete reduction of Co at the surface after one hour, while a significant amount of Fe on the surface remains bonded to oxygen anions. After five hours of reduction, only metallic Fe and Co are detectable on the surface. [35] Diffraction data from samples for our study (shown in Figure 4.5b) indicated formation of a metallic phase during the three minute and twelve minute reductions of CoFe\textsubscript{2}O\textsubscript{4}. Although an Fe-rich spinel was expected to form, a peak shift was not observed for the CoFe\textsubscript{2}O\textsubscript{4} (311) reflection. Since the reflection is at 2\theta = 35.42° for Fe\textsubscript{3}O\textsubscript{4} (ICCD-JCPDS #19-0629) and 2\theta = 35.44° for CoFe\textsubscript{2}O\textsubscript{4} (ICCD-JCPDS #22-1086), the diffraction resolution for these materials is
believed to be too poor to capture the expected shift. [36] The H2O oxidation regenerates the spinel phase, as shown in Figure 4.5b.

Since the data from Raman spectroscopy are not solely reliant on the lattice parameter of the material, but rather on the vibrational modes of the lattice, the Fe3O4 and CoFe2O4 Raman spectra have different A1g, F2g, and Eg peak positions. [37, 38] The fully oxidized CoFe2O4 and the CoFe2O4 reduced for three minutes were examined using Raman spectroscopy and compared to know samples shown in Figure 4.6. The peak positions of the A1g and F2g(3) reflections for the fully oxidized material align with those of the CoFe2O4 sample. The A1g peak position of the reduced sample shift left, indicating a change in the octahedral divalent cation. [39-41] In CoFe2O4, this cation is Co2+, while in Fe3O4 this cation is Fe2+. The peak shift indicates that the material does not retain a 2:1 Fe:Co ratio. The shift towards the Fe3O4 peak implies a replacement of the Co2+ octahedral cations with Fe2+ cations and formation of a Fe-rich spinel.
Figure 4.6: Raman spectra of fully oxidized CoFe$_2$O$_4$ and a CoFe$_2$O$_4$ sample reduced for three minutes. The peak shift to the left indicates a change in octahedral divalent cation from Co$^{2+}$ to Fe$^{2+}$.

4.4.5 Oxidation Step

To investigate and compare the reduced ferrite reactivity with steam, sample materials were reduced for twelve minutes, then oxidized in 10% H$_2$O until H$_2$ levels returned to the baseline measured before reaction. Plots of the H$_2$ generation during H$_2$O oxidation and the total amounts of H$_2$ generated for each material are shown in Figure 4.7. Oxidation of the Fe-based material was rapid, with complete oxidation to Fe$_3$O$_4$ occurring in less than 30 min. Reduced CoFe$_2$O$_4$ took approximately 100 min to oxidize, while reduced NiFe$_2$O$_4$ took over eight hours to completely oxidize (the entire oxidation is not shown in Figure 4.6. For NiFe$_2$O$_4$ and CoFe$_2$O$_4$ oxidation, an initial peak transitioned into a long tail portion at about 25 min, and then H$_2$ levels slowly returned to baseline. Despite their lengthy oxidations, the total H$_2$ production per mass of material was factors of several greater for NiFe$_2$O$_4$ and CoFe$_2$O$_4$ than for Fe$_2$O$_3$. 


The solid material extent of reduction (X) was calculated from

\[ X = \frac{\text{Moles } H_2 \text{ produced during oxidation}}{\text{Total active moles of } O \text{ in sample}} \] \hspace{1cm} \textit{Eq. 11}

The total active moles of O were calculated for each sample from the measured sample mass, with the assumption that Fe$_2$O$_3$, NiFe$_2$O$_4$, and CoFe$_2$O$_4$ are the fully oxidized phases and Fe, Co, and Ni metals are the fully reduced phases. The Fe$_2$O$_3$ sample reached a conversion of 17%, while the CoFe$_2$O$_4$ sample conversion was 53% and the NiFe$_2$O$_4$ sample conversion was 68%. The high conversion of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ in comparison to that of Fe$_2$O$_3$ was not surprising given FactSage thermodynamic predictions and supporting XRD data. Syngas entering the reactor is able to reduce both the Fe$^{3+}$ and Fe$^{2+}$ ions in the spinel when the ratios of pH$_2$/pH$_2$O and pCO/pCO$_2$ are high. As the reacting syngas is oxidized, these ratios fall below the minimum levels to reduce Fe$^{3+}$ and Fe$^{2+}$. In the case of Fe$_3$O$_4$, the syngas would cease to change the composition of the metal oxide through the remainder of the bed, as the gas phase would be in contact with only Fe$^{2+}$ and Fe$^{3+}$ ions. However, with NiFe$_2$O$_4$ and CoFe$_2$O$_4$, the oxidized syngas is still able to reduce the Ni$^{2+}$ and Co$^{2+}$ ions, leaving an Fe-rich spinel in the remainder of the bed. The Ni$^{2+}$ and Co$^{2+}$ ions are reduced throughout the entire bed, allowing a higher material conversion. This will be shown in more detail in Chapter 6.
Figure 4.7: H₂ production comparison for Fe-only, NiFe₂O₄ and CoFe₂O₄ samples after 12 minutes of reduction. Each material proved to be reactive with H₂O, and NiFe₂O₄ and CoFe₂O₄ produce significantly more H₂ than the Fe-only material under these conditions.

Literature regarding the oxygen oxidation of NiFe and CoFe alloys indicates the long oxidation times are due to the incorporation of dopant cations Co²⁺ and Ni²⁺ into the spinel structure, a process that decreases the cation diffusion rates. [42] Oxygen oxidation experiments of NiFe alloys at 973 K show the formation of an outer layer of Fe₃O₄ in contact with a Ni-enriched alloy phase after only fifteen minutes. Almost 90 h into the oxidation, the Ni begins to be incorporated into the spinel layer. [43] Oxygen oxidation of 20% Fe/80% Ni alloy films at temperatures between 473 K and 673 K confirms the development of an outer layer of iron oxide and a metallic inner layer which is depleted of Fe during the oxidation process. [44, 45] The oxygen oxidation of a 48.7% Fe/49.3% Co/2% V alloy at temperatures between 773 K and 873 K results in the preferential oxidation of Fe, leaving a Co/V-enriched metal phase. A
CoFe$_2$O$_4$ phase formed upon further oxidation. [46] Although these referenced experiments were conducted with bulk samples in an oxygen environment, rather than sub-micron sized particles in a steam environment, they still illustrate the relative rates at which these processes occur.

As expected, regardless of the length of time required to fully oxidize the reduced materials, the experiments indicated complete oxidation was vital for complete conversion of H$_2$ and CO during the following reduction step. When oxidation reactions were terminated before H$_2$ levels returned to baseline, high levels of CO and H$_2$ were subsequently observed during the next reduction reaction because the spinel was left in an oxidation state with equilibrium pH$_2$/pH$_2$O and pCO/pCO$_2$ ratios higher than 0.005. Since the production of steam for the oxidation process is energy intensive, long oxidation times can be prohibitive in an industrial setting. Consequently, the effect of H$_2$O concentration during oxidation and the effect of a surface catalyst should be explored to determine if the oxidation kinetics can be improved for these materials.

4.4.6 Cyclability

Multiple cycles were performed on each sample to determine the long term cyclability of NiFe$_2$O$_4$ and CoFe$_2$O$_4$. Materials were reduced for three minutes, then oxidized in 30% H$_2$O in Ar. Cycles are shown in Figure 4.8. Both materials prove to be highly cyclable with consistent H$_2$ production amounts. In contrast, under the same conditions the Fe-only material produced 0.9 mmH$_2$/g, only about 25% of the H$_2$ produced using NiFe$_2$O$_4$ and CoFe$_2$O$_4$. 
Figure 4.8: Cyclability of the a) NiFe$_2$O$_4$ and b) CoFe$_2$O$_4$ samples. Each was cycled over 20 times with stable H$_2$ production totals and peak rates.

4.4.7 Effect of Metal Oxide Choice on H$_2$ Recovery

The CLH process uses a reduction step to store the chemical energy of syngas in the reduced metal oxide material, leaving a stream of only H$_2$O and CO$_2$, and then releases that energy in the form of pure H$_2$ during the oxidation step. Ideally, every mole of H$_2$ and CO used to reduce the metal oxide in the first step is converted to H$_2$ in the second step. With Fe$_2$O$_3$, this is not possible, as the H$_2$ and CO used to reduce Fe$_2$O$_3$ to Fe$_3$O$_4$ is not recovered.

Figure 8 shows how the pre-breakthrough percent conversion of H$_2$/CO in the syngas back to H$_2$ during H$_2$O oxidation varies as a function of the conversion of Fe$_2$O$_3$. This assumes uniform conversion throughout the sample. Up to 11% conversion of Fe$_2$O$_3$ results in 0% conversion of the syngas back to H$_2$ as this leaves a mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$, which is unable to split water. Once FeO begins to form, water splitting is possible and H$_2$ can be generated from the chemical energy stored during the reduction step. The maximum theoretical conversion of H$_2$ and CO in the syngas to H$_2$ during oxidation is 89%, which occurs at full conversion of the
Fe₂O₃ to Fe. With NiFe₂O₄ and CoFe₂O₄, 100% conversion of H₂ and CO in the syngas to H₂ at all extents of reduction are theoretically possible since NiFe₂O₄ and CoFe₂O₄ can be regenerated with H₂O alone.

To investigate this possibility, material balances were performed on the data taken to evaluate material cyclability, which were three minute reductions and subsequent oxidations in 30% H₂O. Total moles of H₂/CO fed to the reactor during reduction were calculated, and any H₂ or CO detected during the reduction step was quantified and subtracted from the calculated total amount fed. The resulting number was the amount of H₂ and CO consumed in the reaction. A carbon mole balance was generally closed to within 5%, calculated by comparing the amounts of CO and CO₂ measured during the reduction with the amount of CO and CO₂ fed to the reactor. The total amount of H₂ generated during the oxidation was then used to calculate how much of the H₂ and CO consumed in the reduction was recovered as H₂ during the H₂O oxidation. This ratio is called the syngas conversion efficiency

\[
Conversion\ Efficiency\ (\%) = \frac{\text{Moles } H_2\ generated\ during\ oxidation}{\text{Moles } H_2\ and\ CO\ consumed\ in\ reduction} \times 100 \quad Eq.\ 12
\]

Values calculated for Fe₂O₃, CoFe₂O₄, and NiFe₂O₄ are plotted in Figure 8. In these experiments, the Fe₂O₃ sample showed 18% solid conversion, calculated from the amount of H₂ and CO consumed in the reaction, and ~22% conversion efficiency. The NiFe₂O₄ and CoFe₂O₄ showed conversion efficiencies of nearly 90% and 95%, respectively, even though the solid conversion was only 22% and 24%, respectively. The highest reported conversion of solids in a packed bed without syngas breakthrough is 49%, achieved in a reactor optimized for the CLH process with counter-flow moving solids and gas. [12] This mixture was determined to be 74.6% FeO and 25.4% Fe, resulting in a potential conversion efficiency of 78%, though figures
concerning oxidation were not published in the study. Unlike the highly exothermic O$_2$ oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$ ($\Delta H = -84.5$ kJ/mole Fe$_2$O$_3$ at 873 K), the H$_2$O oxidation of Fe$_3$O$_4$ and Ni to NiFe$_2$O$_4$ and Co, and Fe$_3$O$_4$ to CoFe$_2$O$_4$, are only slightly exothermic ($\Delta H = -9.4$ kJ/mol NiFe$_2$O$_4$ at 873 K, $\Delta H = -7$ kJ/mol CoFe$_2$O$_4$ at 873 K). The trade-off between heat generation and additional H$_2$ production would need to be evaluated depending on the specifics of the system and the desired products, but NiFe$_2$O$_4$ and CoFe$_2$O$_4$ provide an option for significantly higher H$_2$ recovery that Fe-only materials cannot.

Figure 4.9: Conversion efficiency of Fe-based materials (- -) and mixed metal ferrites (-), and experimental results from laboratory packed bed reactor. Mixed metal ferrites approach the theoretical value of 100% conversion efficiency, while Fe-based materials approach their theoretical maximum of 25% conversion efficiency.
4.5 Conclusions

Investigation of NiFe₂O₄ and CoFe₂O₄ as CLH materials has shown both fully oxidized mixed metal spinels are indeed capable of oxidizing the H₂ and CO in syngas nearly fully to H₂O and CO₂, and behave comparably to Fe₂O₃ during the reduction step. Findings are in accordance with thermodynamic predictions, which indicate syngas compositions between approximately 0.005-1 pCO/pCO₂ and 0.005 - 1.5 pH₂/pH₂O will form a metallic phase and an Fe-enriched spinel phase. Analysis of the materials at three minutes and twelve minutes into the reduction showed the presence of a spinel structure and a metal phase at both times. Reduced NiFe₂O₄ and CoFe₂O₄ were highly reactive with steam and able to regenerate the mixed-metal spinel structure. The total H₂ production per mass of mixed metal spinel was four times greater than that of the Fe₂O₃ samples due to complete oxide regeneration in steam. In these experiments, Fe₂O₃ had a conversion efficiency of 22%, whereas NiFe₂O₄ and CoFe₂O₄ had conversion efficiencies of nearly 100%. Further research will focus on better understanding the rate limitations of the water oxidation step for the mixed metal ferrite, as well as further investigating the trade-off between heat/electricity production of the conventional Fe-based CLH process and the additional H₂ production with the novel mixed metal ferrites.

4.6 Acknowledgements

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References


Chapter 5: Investigation of the H₂O Oxidation Kinetics of Reduced Fe₃O₄, CoFe₂O₄ and NiFe₂O₄ in a Stagnation Flow Reactor

5.1. Abstract

The oxidation kinetics of NiFe₂O₄, CoFe₂O₄, and Fe₃O₄ in H₂O at temperatures between 773 K and 873 K were investigated in a stagnation flow reactor. Thin films of metal oxides were deposited on higher surface area ZrO₂ substrates using atomic layer deposition (ALD) to minimize the effect of diffusion in the metal oxide oxidation. Materials were reduced in a syngas mixture, then oxidized in 10%, 20%, and 30% steam/He mixtures. The Fe₃O₄ sample showed no diffusion limitation during oxidation, instead following an order of reaction model with an $E_a = 78 \pm 10$ kJ/mol. This is believed to describe a surface reaction limitation. The mixed metal oxides also followed an order of reaction model with similar activation energies for the initial oxidation, followed by a diffusion limited reaction model with $E_a = 122 \pm 10$ kJ/mol (CoFe₂O₄) and $148 \pm 15$ kJ/mol (NiFe₂O₄). The diffusion limitation is believed to come from a decrease in the cation diffusion coefficient through the spinel as the concentration of the secondary cation increases. This eventually causes cation diffusion in the spinel to be slower than the initially limiting surface reaction.

5.2. Introduction

Mixed metal ferrites in the CLH process produce over three times the quantity of H₂ per cycle than conventional Fe-based materials. Although the materials look promising as candidate CLH metal oxides, the steam oxidation of the mixed metal ferrites in a packed bed reactor has been shown to take significantly longer than the oxidation of Fe-only material. A fundamental understanding of the mechanism of this slow oxidation and the factors that affect it would allow the development of superior materials and better utilization of active metal oxide.
Metal oxidation reactions are usually controlled by one of three processes: solid state diffusion, a surface reaction, or a reaction at the gas/solid or solid/solid interface (phase boundary). Solid state diffusion involves the migration of atoms through the lattice via defects, and is influenced by the type of atom moving and the number defects. [1] Surface reactions are numerous and depend upon the reactant species, but may include the adsorption of a reactant, rate of bond cleavage of the reactant \((H_2O \rightarrow OH(a)_+O(a))\), or desorption of a reaction product. [2] For either of these processes to be rate-limiting, the chemical reaction in the solid must be rapid so the rate is controlled by reactants reaching or products leaving the reaction site. When the reaction itself is the slow step, a phase boundary control is typically observed since the reaction is usually occurring at a gas/solid or solid/solid boundary. [3]

In the case of iron, cobalt, and nickel metal oxidation, a scale of oxidized material (CoO, NiO, and Fe3O4) is formed over the top of un-oxidized metal. [4] In order for the metal to continue oxidizing, oxygen anions must diffuse through the scale through defects or metal cations and electrons must diffuse outwards through the scale through defects and holes to react with oxygen at the surface. [3] As the scale grows thicker, the additional diffusion distance decreases the oxidation rate. In each of these metals, the diffusion of oxygen through the metal oxide lattice has a lower diffusion coefficient due to a significantly higher energy barrier associated with the movement of large anions through the lattice. It is often assumed that the reaction between oxygen anions and metal cations takes place near the metal oxide surface rather than at the metal-oxide interface. [3] In support of this theory, outward diffusion of the metal cations has been found to be the rate controlling process for metal oxidation reactions when a compact scale is formed. [2, 5] The diffusion of the metal ions away from the metal and towards the surface can leave a void space after significant oxidation has occurred; however, at
small thicknesses, plastic deformation of an unconstrained scale allows continued contact with the metal. [2]

The O₂ and H₂O oxidation of Fe-, Co-, and Ni-only materials has been studied at length and some oxidation parameters found in literature are summarized in Table 5.1. Limited literature regarding the oxidation to mixed metal spinels exists in the literature, leaving the effect of the secondary cation on the oxidation unclear. The goal of this study is to investigate the effect of the Co and Ni cations on the kinetics of H₂O oxidation of Fe materials and to determine the rate-limiting mechanism during the oxidation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidizer</th>
<th>Temperature (K)</th>
<th>Mechanism</th>
<th>Activation Energy (Eₐ) (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
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<td>H₂O</td>
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<td>Diffusion</td>
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<td>[6]</td>
</tr>
<tr>
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<td>Diffusion</td>
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<tr>
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<td>102.3</td>
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<tr>
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<td>1073 – 1400</td>
<td>Surface reaction</td>
<td>76</td>
<td>[7]</td>
</tr>
<tr>
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<td>H₂O</td>
<td>973-1073</td>
<td>Surface reaction</td>
<td>47</td>
<td>[8]</td>
</tr>
<tr>
<td>FeO</td>
<td>CO₂</td>
<td>973-1073</td>
<td>Surface reaction</td>
<td>73</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Diffusion</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Experimental rate-limiting mechanisms and activations energies for Fe oxidation.

5.3. Materials and Methods

5.3.1. Sample Preparation

Since diffusion is often found to be rate-limiting for the oxidation of metals and metal oxides, materials with very small diffusion distances, like thin films, could improve the rates at which oxidation occurs. To generate metal oxides with small diffusion distances, samples were made using atomic layer deposition (ALD). The ALD process is a self-limiting deposition technique that allows metal oxide films to be deposited over high surface area substrates with precise control of the film thickness. [10] During the ALD process for metal oxide deposition, a
precursor containing the metal ion is dosed and reacts with hydroxyls on the surface of the material, leaving the surface covered with metal precursor molecules. Once all surface hydroxyls have been consumed or blocked due to steric hindrance from the attached metal precursor, no additional metal precursors attach to the surface. The reactor is purged and a second precursor is introduced to react with the ligands of the metal precursor, removing them and leaving hydroxyls on the surface. [11] After a purge step, the cycle is repeated. Film thickness increases layer-by-layer, allowing precise control over film thickness and mass percent of the metal oxide. Films are often amorphous as deposited, so calcination in air or an inert is necessary to form the desired metal oxide phase. [12]

Films of NiFe$_2$O$_4$, CoFe$_2$O$_4$, and Fe$_3$O$_4$ were deposited using ALD on crushed and sieved 50 m$^2$/g monoclinic zirconia. The support was identical to the support used for incipient wetness samples in the packed bed proof of concept study. Five grams of the substrate material were placed in a fluidized bed ALD reactor where they were alternatingly dosed with a metal precursor and O$_2$ at a temperature of 723 K and a pressure of 0.13 kPa. Metal precursors ferrocene, cobaltocene, and nickelocene were dosed from bubblers heated to 353 K. [12] During dosing, N$_2$ flowing through the bubbler was saturated with vapor and carried to the reactor. In-situ mass spectrometry was used to ensure that breakthrough was reached for each cycle. Between 20 and 35 total ALD cycles were performed on each sample, forming a 2-5 nm conformal metal oxide film over the surface of the support. The samples were annealed at 873 K for eight hours before characterization.

5.3.2 Material Characterization

Sample mass loadings and deposited cation ratios were confirmed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Phase identification before and after
cycling was performed with a Raman spectrometer using a 532 nm Nd:YAG laser with a 1 μm spot size, calibrated with a neon lamp. Multiple sites on each material were sampled to ensure sample conformity. Surface areas were measured using Brunauer-Emmett-Teller (BET) surface area analysis. Samples were also examined with a JSM-7401F field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDS) for surface elemental analysis and mapping.

5.3.3. Kinetic Analysis in Stagnation Flow Reactor

Kinetic parameters for each metal oxide were investigated using a stagnation flow reactor (SFR) system at Sandia National Laboratories, as shown schematically in Figure 5.1. [13] Reactant gas flow, controlled using calibrated mass flow controllers, proceeded through an insulated and heated stainless steel manifold to the reactor tube. A shallow, loosely packed bed of ferrite sample was placed on a flat ZrO$_2$ piece positioned at the bottom of the vertically oriented, closed-end, Al$_2$O$_3$ reactor tube. Reactant gases entered the reactor and impinged on the sample through an Al$_2$O$_3$ tube situated concentrically inside the outer closed-end tube. This inner tube was positioned such that gases exited it 8 mm above the sample surface, forming a region of uniform stagnation flow, thus eliminating velocity gradients over the top of the sample and allowing diffusive transport to dominate in reaction control volume. [13] The lack of thermal and velocity gradients allow the sample to be in contact with a uniform gas composition, providing an ideal environment for kinetic analysis. [14]
After contact with the sample, the gases exited the reactor by flowing up between the tubes and out the top of the reactor. Exiting gas concentrations were measured with a differentially pumped, modulated effusive beam mass spectrometer (Extrell C50, 500 amu) designed to increase detection sensitivity in the presence of background gases. The mass spectrometer was calibrated daily using analytical standard gases, with four-point calibrations in the H$_2$, CO, and CO$_2$ partial pressure ranges observed during reduction and oxidation reactions. To prevent H$_2$O from entering the mass spectrometer during H$_2$O oxidation, H$_2$O was condensed out of the gas stream in liquid nitrogen cooled cryogenic trap prior to gas sampling.

Figure 5.1: Stagnation flow reactor. Gases flow through the center tube and onto the sample at the bottom of the closed-end tube. Dimensions are such to minimize velocity gradients across the sample. From Scheffe et al. Chemistry of Materials 2011;23:2030 (Ref. [13])
A vacuum pump and pressure controller were used to maintain a constant 1 kPa pressure in the system during the reaction. Samples were reduced for ten minutes at 873 K using a syngas mixture containing 2% CO₂/2% H₂/2% CO/Balance He to simulate reduction conditions during the CLH process. [15] Oxidation of the reduced material occurred at temperatures between 773 K and 873 K in 10% H₂O in Helium for Fe–only samples, and in 10%, 20%, and 30% H₂O in Helium for CoFe₂O₄ and NiFe₂O₄. Steam was generated at 348 K using a RASIRC steam generation unit incorporating a humidity sensor that allowed accurate water flow rate control and recording during the reaction. Oxidations were continued until the H₂ signal returned to its baseline, usually after 10 to 30 minutes of oxidation.

5.3.4. Method of Kinetic Analysis

5.3.4.1 Mathematical Model of Reactor

The measured H₂ production (MH₂(t), in moles), as monitored by mass spectrometry, was used to hypothesize a reaction model for each material using standard solid state kinetic models.[16] These models assume that the rate of reaction, and therefore H₂ production, is governed by non-equilibrium processes on the material surface or in the material bulk. [17] Solid state reaction rates are generally expressed as follows:

\[ \frac{d\alpha}{dt} = k f(\alpha) \quad Eq. 5.1 \]

where \( \alpha \) is the material conversion, \( \frac{d\alpha}{dt} \) is the reaction rate, and \( k \) is a temperature dependent Arrhenius kinetic expression, \( A e^{-\frac{E_a}{RT}} \), where \( A \) is the pre-exponential constant, \( E_a \) is the activation energy for the reaction, \( R \) is the ideal gas constant, and \( T \) is the reaction temperature in Kelvin. Material conversion, \( \alpha(t) \), at time \( t \) is calculated for these experiments using:
\[ \alpha(t) = \frac{\int_0^t MH_2(t) \, dt}{\int_0^{t_f} MH_2(t) \, dt} \quad (0 \leq \alpha \leq 1) \quad \text{Eq. 5.2} \]

The \( t_f \) term indicates the time that oxidation is complete, such that \( \alpha(t) \) represents the ratio of moles of hydrogen produced at time \( t \) to the total moles of hydrogen produced when the reaction has finished. Since the moles of H\(_2\) generated during oxidation is equivalent to the moles of oxygen gained by the sample, H\(_2\) measurement can be used as an analogue to calculate material conversion. In Eq. 10, the \( f(\alpha) \) term represents the reaction model, which expresses how the reaction rate changes as a function of the conversion. [18] Models for \( f(\alpha) \) are mathematically derived based on common reaction pathways such as nucleation and growth throughout a particle, surface nucleation and growth according to a particle geometry, diffusion through a product layer, or rate proportional to the amount of unreacted material. [16] Common \( f(\alpha) \) terms are shown in Table 5.2.

<table>
<thead>
<tr>
<th>Common Reaction Pathway Models</th>
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<tbody>
<tr>
<td>Model</td>
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<td>------------------------------</td>
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<tr>
<td>Power Law (P2)</td>
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<tr>
<td>Contracting Volume</td>
</tr>
<tr>
<td>1-D Diffusion</td>
</tr>
<tr>
<td>Second Order</td>
</tr>
<tr>
<td>Third Order</td>
</tr>
</tbody>
</table>

Table 5.2: Common \( f(\alpha) \) terms that express how the rate of reaction changes with reaction extent.

As described by Scheffe, et al., [14] in the SFR the transient nature of the H\(_2\) generated during oxidation is distorted due to the time lag before the H\(_2\)O impinges on the sample, the detector time lag, and the dispersion of the gases as they flow through the reactor tube, manifold, and the volume of the liquid nitrogen water trap, as shown in Figure 5.2. These effects can have a significant impact on the shape of the H\(_2\) generation curve and on the solid state model that is
found to best describe the reaction, and thus the determined rate-limiting oxidation mechanism. To account for the effects of these reactor-specific phenomena, the models developed in [14] for the water-delivery to the reactor and for the dispersion of the $H_2$ downstream of the reactor were used in this analysis. A simulation of the water delivery through the manifold and reactor tube provided an expression for a time-dependent water flow to the sample, and a simplified model of the reactor volume, cryogenic trap, and downstream manifold as a series of CSTR’s accounted for the dispersion of the $H_2$ before the detection, as well as the time lag to reach the detector. The number of CSTR’s, the space velocity ($\tau$), and the detector time lag ($t_s$) were determined with $H_2$ pulse experiments through and around the reactor and cryogenic trap.

![Diagram of system components](image)

**Figure 5.2:** Each component of the system introduces dispersion, which affects the measured peak shape and kinetic model if not accounted for in analysis.

The equations used to model the system are shown in Table 5.3. Equation 5.3 shows the extent of reaction of the material based on a solid state reaction model, and Equation 5.4 shows
the total extent of reaction if more than one reaction occurs simultaneously. The water mole fraction, $Y_{H_2O,k}$, includes the time-dependent correction from the steam delivery system simulation. Equation 5.6 expresses a series of n CSTR’s and is used to model the dispersion of H$_2$ and detector lag time, and Equation 5.6 relates the H$_2$ mole fraction and the reaction extent. The experimental H$_2$ mole fraction detected at the mass spectrometer, $Y_{H_2,k}$ is compared with the predicted H$_2$ mole fraction, $Y_{H_2,n=last,k}$, and the residual sum squared error is used to optimize the kinetic parameters $A_i$, $E_i$, and $\gamma$ for given solid state models $f(\alpha_i)$.

A Mathematica script was written to read kinetic data at different temperatures and H$_2$O concentrations, guess model values of A, Ea, and $\gamma$, and solve the differential equations in Table 5.3 using the NDSolve function. The model then compares predicted H$_2$ mole fraction to the measured H$_2$ mole fraction and minimizes Equation 5.7 using the NMinimize numerical minimization routine. This analysis led to the global best-fit mechanism and parameters, as the error associated with every data point was included in the minimization.
\[
\frac{d\alpha_{i,k}}{dt} = A_i \left[ Y_{H_2O,k}(t - t_{ex}) \right]^{y_{H_2O_i}} \exp \left( \frac{-E_i}{RT} \right) \ast f(\alpha_i) \quad \text{Eq. 5.3}
\]

\[
\frac{d\alpha_{tot,k}}{dt} = \sum_i \frac{d\alpha_{i,k}}{dt}, \quad \alpha_{tot,k} \leq 1
\quad \text{Eq. 5.4}
\]

\[
\frac{dY_{H_2,n,k}}{dt} = \tau_k \ast (Y_{H_2,n-1,k} - Y_{H_2,n,k})
\quad \text{Eq. 5.5}
\]

\[
Y_{H_2,0,k} = \frac{v_{H_2,k}}{F_{tot,k}} \ast \frac{d\alpha_{tot}}{dt}
\quad \text{Eq. 5.6}
\]

\[
RSSQ = \sum_k \sum_t \omega_{H_2,k} \ast \left[ \tilde{Y}_{H_2,k} - Y_{H_2,n=last,k} \right]^2
\quad \text{Eq. 5.7}
\]

| \(i\) | Reaction model (process) |
| \(k\) | Experiment number (run #) |
| \(\alpha\) | Extent of reaction |
| \(A\) | Pre-exponential factor (1/s) |
| \(E\) | Activation Energy (kJ/mol) |
| \(\gamma\) | Reaction Order |
| \(Y_{H_2O}\) | Mole Fraction H\(_2\)O |
| \(\tau\) | Space velocity (1/s) |
| \(t\) | Detector time lag (s) |
| \(V\) | Standard volume (scm\(^3\)) |
| \(F\) | Standard total flow rate (scm\(^3\)/s) |
| \(\omega\) | Weighting factor |

Table 5.3: Equations used in modeling the oxidation kinetics.

5.3.4.2. Determination of \(\tau\) and \(t_{\text{shift}}\)

To determine the dispersion of the H\(_2\) through the system and cryotrap, pulses of H\(_2\) were sent through the system, measured with the mass spectrometer, and the H\(_2\) was modeled as the output of a series of CSTR’s. The variables \(\tau\), \(t_{\text{shift}}\), and the number of CSTR’s were determined by a least squares analysis that compared the predicted H\(_2\) response with the measured H\(_2\) signal from the reactor. With higher H\(_2\)O concentrations, larger deviation from the original pulse was observed due to higher dispersion in the cryotrap as an increased volume of gases were condensed out of the gas flow, as evident in the values of \(\tau\) required in the model to obtain a good fit with the pulse data.
5.4 Results and Discussion

5.4.1 Material Characterization

Sample properties are shown in Table 5.4. After deposition of the metal oxides and annealing, surface areas were between 35 and 40 m²/g. Metal oxide phases CoFe₂O₄ and NiFe₂O₄ were identified using Raman Spectroscopy to confirm formation of the mixed metal spinel phase before and after cycling, as shown in Chapter 3. In accord with the incipient wetness samples, no evidence of cation interaction with, or diffusion into, the ZrO₂ lattice was observed for the ALD materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Oxide (Mass %)</th>
<th>Cation ratio</th>
<th>Surface Area (m²/g) (before cycling)</th>
<th>Surface Area (m²/g) (after cycling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe₂O₄</td>
<td>12.2</td>
<td>2.15:1 Fe:Co</td>
<td>41 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>18.3</td>
<td>2.3:1 Fe:Ni</td>
<td>36 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>13.1</td>
<td>All Fe</td>
<td>39 ± 2</td>
<td>17 ± 2</td>
</tr>
</tbody>
</table>

Table 5.4: Mass % metal oxide, cation ratio, and surface areas of ALD materials used in the kinetic study.

5.4.2 Material Cyclability

Before kinetic analysis, cyclability of the ALD material was established to ensure that changes in the transient nature of H₂ production were due solely to kinetic changes. The CoFe₂O₄ showed excellent cyclability, as shown in Figure 5.3. The NiFe₂O₄ and Fe₂O₃ materials showed more variability from cycle to cycle, which added additional error to their determined kinetic parameters. These samples also showed an initial decrease in peak H₂ production, but stabilized after a few cycles. This was most likely due to sintering and the associated surface area decrease of the metal oxides in the first few cycles since ZrO₂ substrate itself does not see a significant surface area change at 873 K. As shown in Table 5.4, the surface areas of the samples decrease to around 20 m²/g during cycling.
Figure 5.3: Cyclability of CoFe₂O₄ sample

5.4.3 Kinetic Analysis

Analysis using the method described in Section 5.3.4 shows that a second order reaction model gave a minimum global error for the oxidation of reduced Fe₂O₄, with an activation energy of 78 ± 10 kJ/mole. This second order reaction model is similar to kinetic models used in homogeneous gas phase kinetics, and indicates that the reaction rate is proportional to the amount of unreacted iron in the sample. [16] Figure 5.4 shows the quality of fit over the temperature range investigated.
As seen in the packed bed experiments reported previously in Chapter 3, the NiFe$_2$O$_4$ and CoFe$_2$O$_4$ oxidations were initially rapid, but H$_2$ production slowed before returning to baseline, especially for the NiFe$_2$O$_4$ material, and shows a long plateau of H$_2$ production before the reaction is stopped. This is again in contrast with the rapid oxidation of the Fe-only material under the same conditions.

Analysis of the NiFe$_2$O$_4$ using only one model did not give an adequate fit over the entire time domain of the reaction. Figure 5.5 shows the best fit with a third order reaction model, the
single model with the lowest error. While this model predicts the peak H₂ production with some accuracy, it fails to capture the long-term slow H₂ production observed after the initial peak. A diffusion limited model predicts peak H₂ production uncharacteristic of the observed peak behavior, but accurately describes the tail portion of the reaction. A model that includes these two simultaneous reaction mechanisms fits the data with lower global error than the single model. Figure 5.5 shows the best fit for the data in this range. Although the diffusion limited model does not appear to add significant H₂ at any single point in time, the small production over the time during which it is active results in nearly 20% of the total H₂ production of the material. The reaction order model was found to have an $E_a = 68 \pm 13$ kJ/mol, and the diffusion-based model had an $E_a = 148 \pm 15$ kJ/mol. At near complete conversion, the parabolic rate equation no longer accurately described the rate of H₂ production, indicating an additional rate controlling mechanism change. This may due to a thermodynamic limitation. The equilibrium constant for

![Figure 5.5](image.png)

Figure 5.5: a) An order of reaction model fits the reaction peak, while a diffusion model fits the long-term H₂ production b) A combination of two kinetic models gives the best fit for the NiFe₂O₄ material.
H₂O oxidation of the nearly-fully oxidized NiFe₂O₄ is small, and at some point the amount of H₂O supplied will not be sufficient to observe a kinetic limitation.

Analysis of CoFe₂O₄ kinetic data similarly showed that a single model systematically under predicted the H₂ production after 200 s of oxidation. A dual model analysis found the best fit for CoFe₂O₄ data to be a second order reaction model with an $E_a = 79 \pm 8$ kJ/mol, and a diffusion based model with an $E_a = 122 \pm 10$ kJ/mol.

The activation energies calculated in this study are reasonable when compared with literature values for similar materials shown in Table 5.1. Activation energies for FeO, MnFe₂O₄, and ZnFe₂O₄ oxidation with H₂O are reported between 78 and 110 kJ/mol. [19] Oxidation of ZnFe₂O₄ with CO₂ has an activation energy of $73.4 \pm 8.5$ kJ/mol. [20]
The Fe oxidation to Fe$_3$O$_4$ is consistently found to follow a diffusion-limited mechanism after an initial rapid surface oxidation. [8, 9] A spectral emissivity study of the air oxidation of polished Fe discs at temperatures between 688 K and 843 K shows oxide film thickness increases as predicted by the parabolic model for up to 24 h with an $E_a$ of 155 ± 15 kJ/mol. [21] Oxidation of Fe rods in 5% H$_2$O at temperatures between 623 K and 823 K show adherence to a surface-limited reaction mechanism followed by a parabolic diffusion mechanism at high temperatures. The $E_a$ value for the surface limited reaction is calculated to be 47 kJ/mol. [8] A study of the CO$_2$ oxidation of ~50 μm diameter FeO powder at temperatures between 923 K and 1473 K shows the reaction to be controlled initially by a surface reaction with an $E_a$ of 73.4 ± 8.5 kJ/mol, followed by a parabolic reaction with an $E_a$ of 106.4 ± 8.8 kJ/mol. [9] Steam oxidation of 100-150 μm reduced Fe$_2$O$_3$ particles follows a diffusion limited model, the Jander equation, with an $E_a$ of 77.9 kJ/mol between 773 K and 1173 K; however, the quality of fit is poor in this study. [6] Further support for an initial surface reaction limitation is found in literature reporting success in the use of surface catalysts to enhance the H$_2$O oxidation of

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Type</th>
<th>$E_a$ (kJ/mol)</th>
<th>Region 2</th>
<th>Reaction Type</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Second Order</td>
<td>78 ± 10</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>Third Order</td>
<td>68 ± 13</td>
<td></td>
<td>Parabolic diffusion</td>
<td>148 ± 15</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>Second Order</td>
<td>79 ± 8</td>
<td></td>
<td>3D diffusion</td>
<td>122 ± 10</td>
</tr>
</tbody>
</table>

Table 5.5: Models and activation energies determined experimentally for the oxidation of Fe$_2$O$_3$, CoFe$_2$O$_4$, and NiFe$_2$O$_4$ materials.
reduced metal oxides. [22] Deposition of Rh, Pt, and Ru decrease the temperature at which H₂ is evolved during H₂O oxidation of Fe materials; however, a mechanism is not proposed in the referenced study.

Experiments in this study showed that solid state diffusion effects during oxidation were eliminated from the Fe₃O₄ samples under these reaction conditions. Instead, an order of reaction model is observed, with an Eₐ comparable to the surface reactions reported in [8] and [9]. We believe that due to the thin film materials on high surface area supports, oxidation of these materials remains in the surface reaction limited regime for the entire extent of the reaction. Materials that reported parabolic diffusion limitations in Fe₃O₄ were using materials with longer diffusion distances than the ALD-prepared materials. The smallest metal oxide particles were 50 μm in diameter. Although we expect some sintering and agglomeration of the ALD films during cycling, we do not expect the metal oxide agglomerates to reach sizes larger than a few μm due to the substrate material and the sample mass loadings. In fact, images from SEM analysis before and after cycling, shown in Figure 5.7, demonstrate the development of ~ 1 μm agglomerates of metal oxide during cycling. Under these conditions, the cation diffusion in the Fe₃O₄ film material is rapid enough to not be rate controlling.

While diffusion effects were successfully eliminated from the Fe₃O₄ samples, kinetic fits with the lowest global error for the similarly prepared thin film CoFe₂O₄ and NiFe₂O₄ samples contained a diffusion limited model at high conversions during oxidation under the same conditions. The best fit combination of models could be considered a completely empirical method of describing these complex reactions; however, literature regarding the oxidation of mixed metal oxides indicates that a two stage model can be a reasonable approximation of the solid state processes occurring during oxidation.
Figure 5.7: a) SEM image of uncycled sample b) SEM image of sample after 20 cycles. 1 μm agglomerates of metal oxide form during cycling.

Although only a small amount of data regarding oxidation of reduced NiFe$_2$O$_4$ or CoFe$_2$O$_4$ at temperatures between 773 K and 873 K are published in the literature, data regarding alloy oxidation can address the observed mechanism change to a diffusion limited reaction at high conversions. When mixed metals are oxidized, the metal with the most negative Gibb’s free energy of oxidation, $\Delta G_{\text{oxid}}$, will usually oxidize first and form a protective scale, a process called selective oxidation. [3] Observed in materials such as steel, selective oxidation of one alloy constituent leaves an alloy enriched in the second alloy constituent. The second metal will also eventually oxidize, if able, and will form a thermodynamically stable oxide phase. [2] Thermodynamic analysis predicts the scale and alloy composition at equilibrium conditions, though knowledge of the diffusion processes in both the alloy and the scale is key to developing an understanding of the oxidation kinetics. Similar to the oxidation of pure metals, several possible rate-limiting steps exist for the oxidation of alloys: diffusion in the scale, diffusion in the alloy, or an alloy/scale or scale/gas interface reaction. A scale will only form and continue to grow if diffusion is rapid in the alloy, allowing the more easily oxidized metal to be replenished at the scale-alloy interface. In this case, the reaction at the scale/alloy interface or diffusion
through the scale is rate-limiting. If diffusion in the alloy is slow, then the alloy/scale interface becomes depleted and the diffusion in the alloy becomes rate-limiting. [2]

At 873 K, the $\Delta G_{\text{oxd}}$ for the Fe to Fe$_3$O$_4$ oxidation is -414 kJ/mol $O_2$, for the oxidation of Ni to NiO it is -320 kJ/mol $O_2$, and for Co to CoO it is -345 kJ/mol $O_2$. [2] These values indicate that if preferential oxidation occurs in a NiFe alloy or CoFe alloy, Fe would be the first metal to oxidize. Experimentally, oxygen oxidation experiments of NiFe alloys at 793 K show the formation of an outer layer of Fe$_3$O$_4$ in contact with a Ni-enriched alloy phase after fifteen minutes. At longer oxidation times, Ni was incorporated into the spinel. [23] Oxygen oxidation of 20% Fe/80% Ni alloy films at temperatures between 473 K and 673 K confirms the initial development of an outer layer of iron oxide and a metallic inner layer that is depleted of Fe during the oxidation process. [24, 25] Similarly, the oxygen oxidation of a 48.7% Fe/49.3% Co/2% V alloy at temperatures between 773 K and 873 K results in the preferential oxidation of Fe, leaving a Co/V-enriched metal phase. A CoFe$_2$O$_4$ phase forms upon further oxidation. [26]

To determine the phases present in the reduced NiFe$_2$O$_4$ sample when the reaction mechanism changes from a third order reaction to a diffusion controlled reaction, oxidation of the reduced NiFe$_2$O$_4$ was stopped immediately following the peak $H_2$ production. Analysis of the resulting material with XRD indicated the presence of only Fe$_3$O$_4$ and a metallic phase. Since the material was partially oxidized without formation of an oxidized Ni phase, such as NiFe$_2$O$_4$ or NiO, we believe preferential oxidation of the reduced Fe may have occurred. A similar analysis could not be completed for CoFe$_2$O$_4$ due to the inability to differentiate between CoFe$_2$O$_4$ and Fe$_3$O$_4$ with XRD.

In our analysis, the initial peak observed in CoFe$_2$O$_4$ and NiFe$_2$O$_4$ oxidation is best described with an “order of reaction” model, similar to the oxidation of the Fe-only material, with
measured E_a values close to that of the Fe-only material (79 ± 8 kJ/mole and 68 ± 13 kJ/mole in comparison to 78 ± 10 kJ/mol). This indicates a similar process controls the reaction rate for each of these materials during the peak of H_2 production, most likely a surface reaction with H_2O as observed in the oxidation of Fe.

Studies of vacancy formation and migration in CoFe_2O_4 at high temperatures (1473 K) show that diffusion occurs by migration through cation vacancies at high O_2 activities. [27] As the spinel becomes less Fe-rich at the same O_2 activity, the overall defect concentration decreases, an affect attributed to the increasing difficulty of oxidizing Me^{2+} to Me^{3+} as the cobalt concentration increases. These defect changes cause the measured cation tracer diffusion rate to decrease two orders of magnitude as the composition of the spinel changes from Fe_3O_4 to CoFe_2O_4 at 1473 K.

Oxygen activity dependence of the rate-limiting cation migration mechanism has also been observed in Fe_3O_4 between the temperatures of 773 K and 1473 K, and several studies all indicate the same type of materials behavior as a function of O_2 activity, regardless of the temperature. [5, 28, 29] For Fe_3O_4, low temperature data agree with data extrapolation from higher temperature studies to lower temperature studies. Similarities between the behavior of Co and Ni tracers in Fe_3O_4 and Fe self diffusion in Fe_3O_4 indicate that the mechanism is the same for cation transport of each through the spinel lattice. [30]

Although no comprehensive data regarding the diffusion mechanisms in CoFe_2O_4 and NiFe_2O_4 at 873 K exist in literature, the similarities between Fe_3O_4 and CoFe_2O_4 diffusion data indicate that high temperature CoFe_2O_4 data may be accurately extrapolated to lower temperatures. In this case, the diffusion limitation seen in the kinetic analysis presented here is most likely related to the decrease in cation vacancies as the secondary cation content of the
Fe₃O₄ increases. As the secondary cation concentration increases in the oxidized layer, the diffusion coefficient decreases until it becomes the rate-limiting process and H₂ production reflects the controlling mechanism change. The Ea for the diffusion–limited portion increases between CoFe₂O₄ and NiFe₂O₄, which may be due to a difference in the energy of formation of vacancies between the two oxides, or in the difference in energy barriers of cation migration in NiFe₂O₄ in comparison to CoFe₂O₄. A diffusion limitation involving the metal atoms through the un-oxidized phase, as mentioned above, is also possible. Vacancy formation enthalpies and migration barriers for pure Co, Fe and Ni and their corresponding alloys, as well as the spinel phases Fe₃O₄, NiFe₂O₄ and CoFe₂O₄, were investigated using density functional theory calculations. As detailed in Appendix A, the migration barriers were found to be greater in the spinel phase than in the metallic phase for each system, confirming diffusion in the spinel phase as the most likely kinetic limitation.

5.5 Conclusions

Using the ALD method as a sample preparation technique was generally successful in eliminating the diffusion effects often found to limit metal oxidations in H₂O. The Fe-only sample showed no diffusion limitations during oxidation and was shown to fit a reaction order model with an Ea of 78 ± 10 kJ/mol, consistent with other observed surface reaction–limited behavior. The CoFe₂O₄ and NiFe₂O₄ sample oxidations were initially limited by the reaction order model, similarly to the Fe₃O₄ sample and with nearly identical Ea’s (79 ± 8 kJ/mol and 68 ± 13 kJ/mol). Despite identical sample preparation and cycling techniques, the CoFe₂O₄ and NiFe₂O₄ samples showed a diffusion limitation during the last portion of the oxidation. This is believed to be caused by a decrease in the diffusion coefficient through Fe₃O₄ as the concentration of a secondary cation increases. As the Co and Ni are incorporated into the spinel, the cation
diffusion rate decreases, eventually becoming slower than the surface reaction and affecting the rate of $\text{H}_2$ production. The $E_a$ for diffusion in the NiFe$_2$O$_4$ layer is greater than the $E_a$ for diffusion in the CoFe$_2$O$_4$ layer ($148 \pm 15 \text{kJ/mol}$ vs. $122 \pm 10 \text{kJ/mol}$).

5.6 Acknowledgements

The author wishes to thank Tony McDaniel at Sandia National Laboratories in Livermore, CA for the use of the excellently maintained stagnation flow reactor, as well as for the Mathematica script files for analysis of the data generated at the facility.

5.7 References


Chapter 6: A Thermodynamic Investigation of the Chemical Looping Hydrogen Process:  
Comparison of Novel Mixed Metal Oxides

6.1 Abstract

The mixed metal spinels CoFe$_2$O$_4$ and NiFe$_2$O$_4$ have been shown to produce about four times the amount of H$_2$ compared to conventional Fe-based materials during the CLH process in laboratory experiments. In addition, these mixed metal spinels have been shown to be capable of complete regeneration during steam oxidation unlike Fe-based materials. Materials with such improved properties could increase the flexibility of the CLH process, allowing more H$_2$ production than is currently possible with the Fe-based materials while maintaining the ability for electricity generation from supplemental O$_2$ oxidation. However, significant steam generation is required for full H$_2$O oxidation of CoFe$_2$O$_4$ and NiFe$_2$O$_4$, raising the concern that the energy required to generate steam for oxidation will detract from the overall system efficiency. A model of the CLH process with Fe$_2$O$_3$, CoFe$_2$O$_4$, and NiFe$_2$O$_4$ was developed to investigate the material conversion in the bed before breakthrough of CO and H$_2$, the product gas composition, the amount of H$_2$O necessary to fully oxidize the reduced material and steam-associated energy requirements, and the possibility of hybrid H$_2$O/O$_2$ oxidation for H$_2$ and electricity generation. The mixed metal spinel materials were found to be ideally suited for converting lower quality syngas (less than a 3:1 reducing gas/oxidizing gas ratio) to H$_2$ via lower temperature reactions.

6.2 Introduction

The CLH process allows the production of separate streams of pure H$_2$ and CO$_2$ from syngas without the use of energy intensive pressure swing adsorption or solvent-based gas
separation techniques. [1] The current state-of-the-art material for the CLH process, Fe$_2$O$_3$, allows the production of pure H$_2$ in addition to electricity, as a H$_2$O oxidation step is followed with an O$_2$ oxidation step that produces significant amounts of heat. [2] This O$_2$ oxidation is necessary for Fe$_2$O$_3$ regeneration and leads to decreased H$_2$ recovery from the CLH process. The Fe-based CLH process has been shown to produce H$_2$ from syngas with an overall process efficiency of 68% and electricity with an energy conversion efficiency of 43% with integrated carbon capture. [3] The same study shows the energy conversion efficiency of H$_2$ production from coal with the WGS reaction at 58%, and the energy conversion efficiency of electricity production with the IGCC-Selexol system at 35%. Technologies to further the capability of the CLH process are important in advancing this attractive option for future H$_2$ and electricity production with integrated CO$_2$ capture.

Previous laboratory experiments show that the mixed metal oxides CoFe$_2$O$_4$ and NiFe$_2$O$_4$ produce about four times more H$_2$ per mass than Fe-based materials, allowing complete recovery of the H$_2$ and CO used to reduce the metal oxide. This increased H$_2$ recovery could give the CLH process the flexibility to generate exclusively H$_2$, which Fe-based materials cannot do because of the necessary O$_2$ oxidation. Although the conversion of the solid in the bed has not been investigated for these materials, the increased H$_2$ production is assumed to be due to higher material conversions in the bed from the reduction of the Co and Ni cations to their metallic state, and the ability of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ to completely regenerate under H$_2$O oxidation. Experiments verify the necessity of complete regeneration of the mixed metal spinel for high syngas conversions in the subsequent reduction step. The additional H$_2$ recovery for the CoFe$_2$O$_4$ and NiFe$_2$O$_4$ involves steam oxidation for a significantly longer time than for Fe-based
materials and may require more energy for steam production than is recovered from the H₂ produced and the heats of reaction.

The CLH process energetics are bracketed on one side by the CLC reaction energetics and on the others side by the water-gas shift reaction. In the CLC process, syngas (or methane) is used to reduce a metal oxide, and the metal oxide is subsequently oxidized with O₂. As Eqns. 6.1a-c show, the total heat evolved in the reduction and oxidation reactions is equal to the heat released from conventional combustion of the syngas. [4, 5]

\[
mH_2 + nCO + MeO_x \leftrightarrow mH_2O + nCO_2 + MeO_{x-m-n} \quad \Delta H_r(1) \quad \text{Eq. 6.1a}
\]

\[
MeO_{x-m-n} + \frac{m + n}{2}O_2 \leftrightarrow MeO_x \quad \Delta H_r(2) \quad \text{Eq. 6.1b}
\]

\[
mH_2 + nCO + \frac{m + n}{2}O_2 \leftrightarrow mH_2O + nCO_2 \quad \Delta H_r(1) + \Delta H_r(2) \quad \text{Eq. 6.1c}
\]

The CLC process produces significant amounts of heat during the O₂ oxidation of the reduced metal oxides (>250 kJ/mol H₂/CO consumed), which is used to drive a steam turbine/gas turbine system for electricity generation. [3] The reduction of metal oxides with H₂, CO, and CH₄ can be endothermic or exothermic, and the magnitude depends greatly upon the syngas composition, the metal oxide material, and the reaction temperature. However, the heats of reaction for reduction are usually small in comparison to the heats of reaction of O₂ oxidation. [6]

The complete H₂O oxidation of the reduced metal oxide gives the energetics of the WGS reaction, as shown in Eqns. 6.2 a-c. [7]
\begin{align*}
mH_2 + nCO + MeO_x & \leftrightarrow mH_2O + nCO_2 + MeO_{x-m-n} \quad \Delta H_r (1) \quad \text{Eq. 6.2a} \\
MeO_{x-m-n} + (m + n) H_2O & \leftrightarrow MeO_x + (m + n)H_2 \quad \Delta H_r (2) \quad \text{Eq. 6.2b} \\
nH_2O + nCO & \leftrightarrow nH_2 + nCO_2 \quad \Delta H_r (WGS) \quad \text{Eq. 6.2c}
\end{align*}

The heat of reaction for the reduction of the metal oxide is the same as for the reduction step of the CLC process and depends greatly on the composition of the syngas. The H_2O oxidations of reduced metal oxides are usually slightly exothermic, and the overall WGS reaction has a value of about -30 kJ/mol in the CLH process temperature range. Since the desired product in this process is H_2 rather than heat, the lack of heat generation is only troubling when the energy to produce steam for oxidation is significantly greater than the energy content of the H_2 that is produced and the heat recovered from the reduction and oxidation reactions. For example, with the Fe-based system, the conversion of H_2O to H_2 is nearly 60% for the H_2O oxidation of Fe to FeO at 1073 K, making it a process that requires only moderate excess steam generation. [8]

Oxidation of Fe_3O_4 to the Fe_2O_3 phase with H_2O produces less than 1 x 10^{-7} moles of H_2 per mole of H_2O fed, so O_2 is used for re-oxidation because this reaction is not feasible for H_2 production. [1]

As shown in Chapter 3, the metal oxides CoFe_2O_4 and NiFe_2O_4 have a unique equilibrium value for each Fe-rich spinel composition rather than one H_2/H_2O ratio at which Co/Ni and Fe_3O_4 are oxidized to form the mixed metal spinel. The H_2/H_2O ratios range from 1 to 10^{-6} in this composition range at 873 K, which allows between 50% and 10^{-6}% conversion of the steam to H_2. The mixed metal oxides can be regenerated with supplementary O_2 when H_2 production is no longer efficient, as with the Fe-based system. This O_2 oxidation is predicted to be highly exothermic and would allow electricity generation in addition to H_2 generation. The overall energetics of this process will depend on the syngas composition, the metal oxide
material, the temperature of reaction, and the material conversion at which H\textsubscript{2}O oxidation is stopped and O\textsubscript{2} oxidation begins. Analyzing the balance between H\textsubscript{2}O and O\textsubscript{2} oxidation for these materials is requisite in determining how viable CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4} are for use in a CLH process.

Due to the complex nature of the reactions and the resulting conversion of the solid material in the reactor, a system model is necessary to evaluate the energy balances for the reduction and oxidation reactions in the CLH system. [8] In addition to modeling the H\textsubscript{2}O and O\textsubscript{2} oxidations of reduced material, the model must be capable of predicting the amounts of CO and H\textsubscript{2} that can be consumed before breakthrough during reduction to obtain the conversion of the material in the reactor at the beginning of the oxidation step. Such a model would allow an investigation of the effects of syngas composition, reaction temperature, metal oxide, and H\textsubscript{2}O and O\textsubscript{2} oxidations on the material conversion, H\textsubscript{2} production, and overall energy efficiency of the CLH process. Modeling the entire gasification and electricity generation system would provide more insight into the overall efficiency of the CLH process coupled with a gasifier; however, this study seeks only to examine the materials used in the CLH process. We believe a comparison of the mixed metal oxide performance with that of the widely accepted Fe\textsubscript{2}O\textsubscript{3} in the CLH reactor is sufficient to establish viability, assuming that all other system components remain the same between the Fe-based material and the mixed metal oxides.

This investigation seeks to develop and validate such a model of the CLH system, and then use the model to evaluate a range of operating conditions for the CLH process with Fe\textsubscript{2}O\textsubscript{3}, CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4}. The model will be validated against predictions from FactSage and experimental results from a laboratory packed bed reactor to ensure accuracy in approximating the CLH process. The investigation will allow us to probe the nature of solid conversion in the
reactor before breakthrough as a function of gas/solid ratio and its relationship to H₂ production, which is of interest due to the significantly higher H₂ production observed for mixed metal oxides than for Fe₂O₃. The model will allow investigation into the total amount of steam required to fully oxidize the solid material and the associated energy requirements to determine if complete H₂O oxidation is feasible. The possibility of hybrid H₂O/O₂ oxidation will be explored for combined H₂ and electricity production using the mixed metal oxides.

6.3. Materials and Methods

6.3.1. Mathematical Model of the Chemical Looping Hydrogen Process

The mathematical model of the system was developed in MATLAB and encompasses the reduction reactions, oxidation reactions, and the steam generation for the oxidation. Energy balances for gas cooling for condensation of H₂O from the streams exiting the reduction and oxidation reactors have been calculated but are not reported due to their dependence on the type of equipment used and placement in a larger system. Figure 6.1 shows the CLH schematic with only H₂O oxidation, and Figure 6.2 shows the CLH schematic with a supplementary O₂ oxidation step.
Figure 6.1: Process schematic for the model operating with only H$_2$O oxidation.

Figure 6.2: Process schematic for the model operating with both H$_2$O and O$_2$ oxidation.
Key model assumptions are listed in Table 6.1. The packed bed reactor is modeled as a series of CSTR segments in which gas-solid equilibrium is reached between the H2/H2O and CO/CO2 systems and the solid phases in the reactor. The equilibrium conditions in each segment are a function of the reaction temperature, initial gas composition, and the conversion of the material in the bed and are discussed in section 6.3.2. [9]

<table>
<thead>
<tr>
<th>Model Assumptions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Clean, particulate- and tar-free syngas enters the reactor at the reaction temperature without any additional heating or cooling.</td>
</tr>
<tr>
<td>2) Both the reduction and oxidation reactions have sufficient heating or cooling to operate isothermally.</td>
</tr>
<tr>
<td>3) Reactions of H2 and CO with the solid proceed simultaneously and independently and reach equilibrium. The resulting gas then reacts to WGS equilibrium.</td>
</tr>
<tr>
<td>4) The forward reaction, reverse reaction, and the water-gas shift reactions are all considered in the reactor.</td>
</tr>
<tr>
<td>5) Equilibrium conditions are for H2, H2O, CO, CO2, and the solid phases only. No solid carbon or hydrocarbon formation is considered.</td>
</tr>
</tbody>
</table>

Table 6.1: List of key assumptions made in development of MATLAB model

6.3.2 FactSage Calculations

Temperature dependent equilibrium solid and gas compositions for the Fe-only, Fe-Co, and Fe-Ni CLH systems were investigated using FactSage (Version 6.2), which uses Gibbs free energy minimization calculations and extensive thermodynamic property databases for thermodynamic modeling. Multiple studies show the FactSage program correctly models the phase and composition of mixed metal spinels during thermal reduction and H2O oxidation. [10, 11] Including solution phases from the FactSage oxide solution database (version 5.3) in thermodynamic calculations, rather than only stoichiometric line compounds, significantly affects the accuracy of the thermodynamic calculations. [10] FactSage is able to reproduce thermodynamic properties, activities, M2+/M3+ ratios, solution sublattice cation distributions, and
partial pressures of equilibrium gases from compiled experimental data using these databases. [12]

In addition to pure solids and gases from the Fact 5.3 database, spinel, metal oxide and alloy solution phases were included for this study. The FactSage spinel solution phase uses the compound energy formalism model to describe the distribution of cations over spinel tetrahedral and octahedral sites. Vacancies in the octahedral sublattice allow oxygen non-stoichiometry and deviations from the ideal 2+/3+ cation ratio in the spinel phase model \((\text{Fe}^{2+}, \text{Fe}^{3+}, \text{M}^{2+}, \text{M}^{3+})^\text{Tr}\) \(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{M}^{2+}, \text{M}^{3+}, \text{Va}\)\(_2\text{O}_4\). [13] The metal oxide solution phase is modeled as a random solution of \(\text{M}^{2+}, \text{Fe}^{+2}, \text{Fe}^{+3}\) ions on cation sites. Vacancies associated with \(\text{Fe}^{+3}\) ions on cation sites allow for excess Fe cations in the wustite \((\text{Fe}_{1-x}\text{O})\) phase. [10, 14] These models allow the calculation of the Gibbs energy of each possible reaction product in the solution phase as a function of T, P and composition, and have been optimized over the temperatures and compositions examined in this chapter and validated by reproducing several thermodynamic datasets from literature. [12, 15]

FactSage uses a Gibbs energy minimization technique to identify the most probable reaction products at equilibrium given a set of constraints. The equation

\[
G = \sum_{\text{ideal gas}} n_i (g_i^0 + RT\ln P_i) + \sum_{\text{pure condensed phases}} n_i g_i^0 + \sum_{\text{solution}} n_i (g_i^0 + RT\ln X_i + RT\ln \gamma_i) + \cdots
\]

Eq. 6.3

where

\[n_i = \text{moles}\]
\[ P_i = \text{gas partial pressure} \]
\[ X_i = \text{mole fraction} \]
\[ \gamma_i = \text{activity coefficient} \]
\[ g_i^o = \text{standard molar Gibbs Energy} \]

is minimized by determining the combination of \( n_i, P_i, \) and \( X_i \) in the system. FactSage was used to construct phase diagrams for the Fe-O, Co-Fe-O, and Ni-Fe-O systems at temperatures between 673 K and 1173 K to identify the equilibrium solid composition as a function of the partial pressure of O\(_2\) (pO\(_2\)). The solid composition and pO\(_2\) data were then used in the model to determine the amount of oxygen exchange between the solid and gas phases to reach equilibrium, along with the resulting reaction products in each reactor segment.

6.3.2.1 Fe-O system

The gas-solid equilibrium for the binary Fe-O system as a function of temperature and pO\(_2\) is shown in Figure 6.3. The y axis, \( \log_{10} p(O_2) \), is the partial pressure of O\(_2\), which is related to the H\(_2\)/H\(_2\)O and CO/CO\(_2\) systems by the relationships:

\[ \text{CO}_2 \leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6.4a} \]
\[ \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6.4b} \]

If the amounts of CO\(_2\) and CO or H\(_2\)O and H\(_2\) in a gas mixture are known, then the pO\(_2\) can be calculated with knowledge of the temperature dependent equilibrium constant for the Eq. 6.4a or b, and the overall pressure, using Equation 6.5:

\[ K_{PO} = \exp \left( -\frac{\Delta G^o}{RT} \right) = \frac{p_{CO} p_{O_2}^{\frac{1}{2}}}{p_{CO_2}} \quad \text{Eq. 6.5} \]
The lines in Fig. 6.3 show the oxygen partial pressures at which the reactions in Eq. 6.6-6.9 take place:

\[
3 \text{Fe}_2\text{O}_3 \leftrightarrow 2 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6.6}
\]

\[
\text{Fe}_3\text{O}_4 \leftrightarrow 3 \text{FeO} + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6.7}
\]

\[
\text{Fe}_3\text{O}_4 \leftrightarrow 3 \text{Fe} + 2 \text{O}_2 \quad \text{Eq. 6.8}
\]

\[
\text{FeO} \leftrightarrow \text{Fe} + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6.9}
\]
Figure 6.3 is the same as Figure 6.4, which commonly appears in CLH literature. [1, 2] The pCO₂/pCO and pH₂/pH₂O values on the left and right axes correspond to the pO₂ values from Figure 6.3 using equation 6.5. For example, at 773 K (500°C), the pO₂ at equilibrium between Fe and Fe₃O₄ is 10⁻²⁹. From Figure 6.4, the equilibrium constant between Fe and Fe₃O₄ at 773 K is 0.3 for the H₂/H₂O system and 1.5 for the CO/CO₂ system. At 773 K, a gas with pH₂O/pH₂ ratio of 0.3 has an O₂ partial pressure of 2x10⁻²⁹, which is the log₁₀(pO₂) value predicted in Figure 6.3. A gas with a pCO₂/pCO value of 1.5 at 773 K has an O₂ partial pressure of 1.5x10⁻²⁹, which also correlates with the log₁₀(pO₂) predicted in Figure 6.3. Mixtures of H₂/H₂O and CO/CO₂ are commonly used to achieve the low pO₂ values necessary for oxidation of metals and metal oxides. [16]

![Figure 6.4](image1.png)

Figure 6.4: Equilibrium for the Fe-CO-CO₂ and Fe-H₂-H₂O system. From Muller et al. Chemical Engineering Journal; 2011:166 [17]
The lines in Figure 6.4 give the equilibrium constants (Kp) for the oxidation and reduction reaction in the Fe – H₂ – H₂O and Fe – CO – CO₂ systems. For example, a gas with a pCO₂/pCO ratio of 0.1 would reduce Fe₃O₄ at 700 K until either the gas composition reaches the composition shown by the line between the Fe and Fe₃O₄ phases (about 1) and would leave a mixture of Fe₃O₄ and Fe, or would reduce until only Fe remained if the solid was the limiting reactant. Using the data from Figure 6.3, the gas composition and solid composition in each reactor segment were evaluated to determine if a reaction was predicted, and, if so, the final composition was calculated based on the limiting reactant. In the Fe-O system, each component is a pure compound with an activity of 1, allowing the simplified equilibrium constant to be

\[ Kp = \frac{pCO_2}{pCO} \quad \text{or} \quad \frac{pH_2O}{pH_2} \]  

Eq. 6.10

The following reactions involving only H₂, H₂O, CO, CO₂, and the solid metal oxide phases, are included in the model:

\[
3Fe_2O_3 + H_2/O \xleftrightarrow{kp} 2Fe_3O_4 + H_2O/CO_2 
\]

Eq. 6.11

\[
Fe_3O_4 + H_2/O \xleftrightarrow{kp} 3FeO + H_2O/CO_2 
\]

Eq. 6.12

\[
FeO + H_2/O \xleftrightarrow{kp} Fe + H_2O/CO_2 
\]

Eq. 6.13

\[
Fe_3O_4 + 4H_2/O \xleftrightarrow{kp} 3Fe + 4H_2O/CO_2 
\]

Eq. 6.14

6.3.2.2 Fe-Co-O and Fe-Ni-O systems

The ternary Co-Fe-O and Ni-Fe-O systems are more complex than the Fe – O system and contain two-phase regions of solid solutions of mixed metal spinels, metal oxides (MeO – FeO, CoO, NiO), metallic and alloy phases. The constant temperature and constant pressure
equilibrium distribution of solid phases for each Fe-Co-O composition, calculated from Gibbs free energy minimization, can be expressed in a phase diagram as shown in Figure 6.5. The dotted line marks the Fe/(Fe+Co) ratio for a material with a 2:1 Fe:Co, and an analysis at each point gives the equilibrium solid composition under the specified conditions. At low O mole fractions, a metal/alloy phase and a spinel phase are present. The composition transitions to spinel and Fe$_2$O$_3$ as the O mole fraction increases.

The relative amounts and compositions of the solid phases at equilibrium can be calculated along the 2:1 Fe:Co line using tie lines and the lever rule or, if available, software. For example, at point 1 in Figure 6.5, the overall system mole fractions are 0.28 O, 0.48 Fe and

![Figure 6.5: Phases present for the Fe-Co-O system under varying pO$_2$.](image)
0.24 Co. The equilibrium solid distribution at this composition is 0.25 moles Fe and 0.24 moles Co in the BCC phase, and 0.23 moles Fe and 0.28 moles O in the spinel phase. As before, the \( \log_{10} p(O_2) \) can be easily converted to \( p(CO_2)/p(CO) \) or \( pH_2O/pH_2 \), allowing the determination of the relationship between gas composition and the solid phases present in the material. These equilibrium solid compositions were calculated for each \( p(O_2) \) value along the 2:1 Fe:Co line shown in Figure 6.5. Resulting data describing the amount and composition of each solid phase were used in the model to determine the oxygen exchange between the gas and the solid phase and the equilibrium solid composition in each reactor segment.

For example, if 1 mole of solid with a composition at point 1 in Figure 6.5 was contacted with 1 mole of gas with a \( pH_2O /pH_2 \) value of 10 at 773 K, the \( \log_{10} p(O_2) \) value would be \( 10^{-26} \). The equilibrium solid phases under these conditions are FCC alloy and spinel, while the solid phase in the segment is a BCC alloy and spinel. The solid material would oxidize under these conditions, increasing the O in the solid phase while the Fe:Co ratio remained 2:1, and the \( \log_{10}(pO_2) \) value would decrease along with the amount of \( H_2O \) in the gas phase. An iterative approach was used to determine simultaneous small changes in both the gas and solid compositions. Iterations continued until the new gas composition was in equilibrium with the new solid composition. In these calculations the \( \log_{10}(pO_2) \) values are treated as pseudo-equilibrium constants, as they allow the determination of equilibrium solid phases present with a given gas composition but do not contain explicit information regarding the activity of the solid solutions in the material. The same process was applied to the Ni-Fe-O system to determine the applicable equilibrium conditions.
6.3.3 Model Development

Simultaneous solid reaction with CO and H\textsubscript{2} were modeled, with each component reaching equilibrium with the solid phase independently. Oxygen balances were performed for each segment using Equations 6.15a-c and 6.17a-c and conditions regarding the relevant equilibrium conditions based on the gas composition and the oxygen available in the solid.

\[
\frac{H_2O_i + x_H}{H_{2,i} - x_H} = K_{eq,H} \quad \text{Eq. 6.15a} \\
\frac{CO_{2,i} + x_C}{CO_{i} - x_C} = K_{eq,C} \quad \text{Eq. 6.16a}
\]

\[
H_2O_f = H_2O_i + x_H \quad \text{Eq. 6.15b} \\
CO_{2,f} = CO_{2,i} + x_C \quad \text{Eq. 6.16b}
\]

\[
H_{2,f} = H_{2,i} - x_H \quad \text{Eq. 6.15c} \\
CO_f = CO_i - x_C \quad \text{Eq. 6.16c}
\]

\[
O_{solid,f} = O_{solid,i} - x_H - x_C \quad \text{Eq. 6.17}
\]

The conversions of the H\textsubscript{2} (x\textsubscript{H}) and CO (x\textsubscript{C}) were determined from the conditions described in sections 6.3.2 and were used to calculate the equilibrium amounts of H\textsubscript{2}, CO, H\textsubscript{2}O, CO\textsubscript{2}, and oxygen in the solid.

All reactors shown schematically in Figure 6.1 and 6.2 are assumed to have sufficient heating or cooling to operate isothermally. Syngas entering the reactor was assumed to be at the temperature of reaction and free of any particulate matter or tars. The reduction reaction was assumed to reach equilibrium conditions; gas exiting a segment is in equilibrium with the solid material in the segment. For example, the reduction of Fe\textsubscript{3}O\textsubscript{4} to FeO with H\textsubscript{2} has an equilibrium constant of 0.97 at 923 K, meaning that gas with an H\textsubscript{2}O/H\textsubscript{2} ratio greater than 0.97 will reduce Fe\textsubscript{3}O\textsubscript{4} until the H\textsubscript{2}/H\textsubscript{2}O ratio is 0.97 or until the metal oxide is completely converted to FeO and no further O can be removed from the solid. Gas with an H\textsubscript{2}O/H\textsubscript{2} ratio greater than 0.97 will flow over the Fe\textsubscript{3}O\textsubscript{4} without changing the gas or solid composition. The assumption that the
materials reach equilibrium implies that the reactions have rapid enough kinetic rates that equilibrium is reached in the time that the gas is in contact with the solid. Based on the previous laboratory experiments showing nearly complete conversion of H₂ and CO for the Fe₂O₃, CoFe₂O₄, and NiFe₂O₄ materials during the first two to three minutes of reduction (detailed in Chapter 4), as well as analysis by other researchers showing near-equilibrium gas conversions during experiments, we believe this assumption is valid at low to moderate solid conversions.

[9]

The gas phase water-gas shift reaction was assumed to reach equilibrium in this model due to its relatively rapid kinetics at temperatures above 873 K and the propensity of Fe, Co, and Ni as WGS catalysts. [18] In a reactor, the gas-solid reactions and the WGS reactions would happen simultaneously; however, in this model the WGS reaction is considered after gas-solid equilibrium is reached. The CoFe₂O₄ and NiFe₂O₄ materials were assumed to reduce as FactSage predicts, first to Co/Ni and Fe₃O₄, then to reduce to Fe. We believe this assumption to be valid based on the XRD and Raman data from reacted samples, shown in Chapter 3. Equilibrium and enthalpy of reaction values for each reaction considered were obtained in the temperature range of 673-1273 K from the thermodynamic databases in FactSage.

During the oxidation reaction, the gas phase was also assumed to be in equilibrium with the solid phase; however, only the H₂/H₂O equilibrium is considered. In the reactor, the reverse reaction is also implemented since the H₂/H₂O may be high enough from oxidizing materials at the beginning of the reactor to reduce materials with lower conversions near the end of the reactor. For example, the equilibrium constant for oxidation of Fe to FeO at 973 K is 2.43. Steam in contact with Fe in the reactor will react until the H₂/H₂O ratio is 2.43, or until the Fe is fully oxidized to FeO; however, any Fe₃O₄ remaining in the bed will be reduced at H₂/H₂O ratios
greater than 1.1. The assumption of thermodynamic equilibrium during oxidation is made to allow us to analyze the “best case” scenario for the system since oxidation kinetics may depend greatly on the method of material preparation. Energy for steam generation was calculated using the standard temperature dependent heat capacities of liquid H₂O and steam, and heat of vaporization for H₂O that were obtained from the FactSage thermodynamic databases.

6.4 Sample Preparation and Reactor for Experimental Validation

Experiments in a packed bed reactor were used to validate the H₂ and CO conversions during the reduction reaction step and overall H₂ production during subsequent H₂O oxidation. The reactor and metal oxide sample preparation described here are addressed in detail in Chapter 4.

6.4.1 Sample Preparation

Samples of Fe₂O₃, NiFe₂O₄, and CoFe₂O₄ were prepared via the incipient wetness method from iron nitrate (Fe(NO₃)₃ · 9H₂O, Sigma Aldrich, 98%), nickel nitrate (Ni(NO₃)₂·6H₂O, Alfa Aesar, 98%), and cobalt nitrate (Co(NO₃)₂·6H₂O, Alfa Aesar, 98%). [19, 20] Crushed catalyst pellets made of approximately 20 nm sintered ZrO₂ spheres (Alfa Aesar, 99%, 0.31 cm³/g, 50 m²/g), were sieved to 110 – 175 μm diameter particle size and subsequently mixed with the aqueous metal nitrate solutions of the desired stoichiometry. Samples were calcined at 873 K in air for eight hours once 30% by mass of metal oxide was reached. Sample mass loadings and deposited cation ratios were confirmed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and phase identification was performed using X-Ray diffraction (XRD, Scintag PAD5 Powder Diffractometer, CuKα1 radiation, λ=0.15406 nm, scan rate 0.5°/min, step size 0.02°).
6.4.2 Packed Bed Reactor

Approximately 250 mg of sample material were placed on top of ZrO$_2$ spheres inside an alumina reactor tube to form a bed of active material. The tube was placed in a horizontal furnace constructed using a 1.27 cm OD/0.95 cm ID (0.5” OD/0.375” ID) Al$_2$O$_3$ tube wrapped in nichrome wire secured using a high temperature ceramic epoxy and wrapped in insulation. An Omega CNi16 process controller module was used to control the temperature of the reactor, which was monitored using a thermocouple placed between the furnace tube and the Al$_2$O$_3$ reactor tube.

Calibrated MKS 1179A mass flow controllers delivered gases to the system. A New Era NE-1000 syringe pump delivered water to heated coils and a stream of Ar carrier gas to generate steam for the oxidation step. A constant stream of Ar purged the reactor before and after delivery of reactant gases. The reducing syngas mixture and oxidizing steam mixture equilibrated on a separate pressure controlled reactor bypass line for fifteen minutes prior to introduction contact with the sample. Upon completion of each reaction step, the Ar purge immediately resumed. A column of drierite removed H$_2$O from the gas stream before the mass spectrometer. Pressure controllers and a vacuum pump maintained a constant pressure on the bypass and reactor lines, and the bypass line pressure controller monitored the upstream pressure during the reactions.

A downstream absolute pressure of 81.3 ± 0.03 kPa (610 ± 0.2 Torr) was maintained during reduction and oxidation of the sample. A flowrate of 24 sccm of syngas and steam in argon created a 13 - 20 kPa (100-150 Torr) pressure drop across the reactor. Reduction and oxidation reactions were performed at a furnace temperature of 873 ± 1.5 K. Steam production
occurred at 383 K by injecting 0.006 mL/min of H₂O into 20 sccm of Ar in heated coils. The resulting mixture was 30% steam in Ar. All gas lines were maintained at a temperature of 293 K to avoid condensation of H₂O before the drierite column. Oxidations continued until H₂ levels returned to their baseline as measured before reaction.

6.4.2 Gas Composition and Analysis

A Stanford Research Systems QMS 200 mass spectrometer monitored reaction products in each experiment. Five point calibrations, performed each day for H₂, CO, and CO₂, covered the gas parts-per-million (ppm) ranges observed in reactor operation. Two different syngas compositions were used in reduction; a 10% H₂, 10% CO, 13% CO₂ in Argon mixture and an 8% H₂, 8% CO, 30% CO₂ in Argon mixture.

6.5 Results and Discussion

6.5.1 Model Validation

Model results were compared with FactSage predictions to verify correctness of calculations, and then with laboratory experiments to confirm accurate approximation of the CLH system.

First, to ensure model results were in accord with thermodynamic predictions from FactSage, the same conditions were evaluated in both the MATLAB model and with FactSage predictions. The FactSage Equilibrium module functions as a batch reactor, in which solid and gas are in direct contact and change composition until gas-solid equilibrium is reached without any material leaving the reactor. A batch reactor predicts significantly lower conversions than would be observed in a packed bed, because in a packed bed gasses that inhibit the forward reaction are swept away and replaced with gasses that are farther away from equilibrium. As
with the MATLAB model, in FactSage a packed bed reactor can be simulated with a series of reactor “segments” in which small amounts of solid and gas are allowed to reach equilibrium, after which the gas is moved to the next segment and the solid is contacted with the gas from the previous segment. [8]

For both FactSage and the model, total moles of metal oxide were divided into five segments for the calculation to simulate five reactors in series (see Figure 6.3). A model with a higher number of segments was tested, but gave results equivalent to the five-segment model. An amount of syngas equal to the moles of metal oxide was contacted with the solid in each segment, but divided into five portions, or “time steps”, to simulate the flow over a period of time. FactSage calculations were completed in the Equilibrium module, and solid streams were recycled for each timestep to carry the products from the previous timestep to the subsequent one. The CLH MATLAB model was run in a similar manner, but solid recycle was not necessary due to the ability to store the solid phase products at each timestep. Results from the model for timesteps 1 through 3, before breakthrough of H$_2$ and CO was observed for Fe$_2$O$_3$, are shown with results from FactSage in Figure 6.6. Conversions of H$_2$ and CO

\[
X_H = 1 - \frac{H_2}{H_2 + H_2O} \quad \text{Eq. 6.18}
\]

\[
X_C = 1 - \frac{CO}{CO + CO_2} \quad \text{Eq. 6.19}
\]

in each segment are shown at timesteps 1 through 3, and illustrate the decreased ability of reacted solid to convert CO to CO$_2$ and H$_2$ to H$_2$O. Nearly identical values were calculated using FactSage and the CLH MATLAB model. Similarly, the solid conversion

\[
X_M = 1 - \frac{\text{Moles}_\text{final}}{\text{Moles}_\text{initial}} \quad \text{Eq. 6.20}
\]
at timestep 5 showed nearly identical predictions from both FactSage and the CLH MATLAB model.
Figure 6.6: Model predictions for gas and solid conversions in the packed bed in comparison to FactSage predictions.
To verify the heats of reaction from the model, the total heats of reaction associated with syngas reduction and O$_2$ or H$_2$O oxidations were calculated. In the case of O$_2$ oxidation, the heat of reaction was compared with the energy of combustion for the syngas, as shown in Eq. 6.1. The heat of reaction for the complete oxidation with H$_2$O was compared with the WGS reaction, as shown in Eq. 6.2. In all cases, the heats of reaction from the model were within 3% of the calculated combustion and WGS reaction energies.

Packed bed reactor experiments were conducted using the same total moles of metal oxide, syngas composition, and temperature as modeled in both FactSage and MATLAB. Reductions lasted for three minutes, followed by a reactor purge and H$_2$O oxidation. Breakthrough of H$_2$ and CO was not observed during the reduction step for CoFe$_2$O$_4$ and NiFe$_2$O$_4$, but was seen for the Fe$_2$O$_3$ material between two and three minutes of reduction. Model predictions under the same material conditions showed no breakthrough during three minute reductions of CoFe$_2$O$_4$ and NiFe$_2$O$_4$, but breakthrough occurred in the last minute of the Fe$_2$O$_3$ reduction. Measured H$_2$ production during H$_2$O oxidation matched the predicted H$_2$ production closely, as shown in Figure 6.7. Equivalent H$_2$ production from the reactor and the model, in combination with nearly 100% conversion of the H$_2$ and CO in the syngas observed in experiments during the reduction step, confirm that the assumption of equilibrium during the reduction step is reasonable under these conditions.
6.5.2. Model Results and Analysis

6.5.2.1. Solid Conversion

The packed bed reactor experiments in Chapter 4 showed significantly higher H\textsubscript{2} production from CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4} materials than from Fe\textsubscript{2}O\textsubscript{3} under the same conditions. We proposed this additional H\textsubscript{2} generation to result from a combination of the ability of the mixed metal ferrites to be reduced under lower H\textsubscript{2}/H\textsubscript{2}O and CO/CO\textsubscript{2} ratios, and the recovery of all the H\textsubscript{2} and CO used in the reduction step as H\textsubscript{2} during H\textsubscript{2}O oxidation using the mixed metal ferrites. An examination of the predicted metal oxide conversion in the reactor from the model allowed us to investigate the solid conversion for each material and the resulting H\textsubscript{2} production.
Figures 6.8 and 6.9 show the conversion of the material in the bed at syngas breakthrough for two different syngas compositions (1:1 reducing gas to oxidizing gas and 3:1 reducing gas to oxidizing gas, referred to as “1:1 syngas” and “3:1 syngas”) at 873 K and 1073 K. The total moles of oxygen in the metal oxide materials were the same for each test (135 mol O). These simulations investigated material behavior normalized by available O in the solid, but in a pilot or test-scale system, a mass- or volume-based metric would be more applicable. The conversion of the solid is calculated as before

\[ X_M = 1 - \frac{\text{Moles } O_{\text{final}}}{\text{Moles } O_{\text{initial}}} \]  

Eq. 6.21

where moles \( O_{\text{final}} \) is moles of oxygen in the solid and moles \( O_{\text{initial}} \) is moles of O initially in the solid. For Fe\(_2\)O\(_3\), a conversion of 11% gives Fe\(_3\)O\(_4\), a conversion of 33% gives FeO, and a conversion of 100% gives Fe metal. For NiFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\), a conversion of 33% gives a mixture of Co or Ni metal and Fe\(_3\)O\(_4\), while a conversion of 50% gives a mixture of Co or Ni metal and FeO. A conversion of 100% gives metallic Fe and Co or Fe and Ni. The metal oxide’s capacity for oxidizing H\(_2\) and CO to H\(_2\)O and CO\(_2\) before H\(_2\) and CO breakthrough, R, is expressed as

\[ R = \frac{M_{\text{Solid,T}}}{M_{\text{Gas,B}}} \]  

Eq. 6.22

where \( M_{\text{Solid,T}} \) is the total moles of Fe\(_2\)O\(_3\), NiFe\(_2\)O\(_4\) or CoFe\(_2\)O\(_4\) in the reactor and \( M_{\text{Gas,B}} \) is the total moles of syngas through the reactor at breakthrough. A lower R value translates to fewer moles of solid necessary per mole of syngas reacted, and would likely require smaller reactor sizes for the same syngas throughput.
Figure 6.8: Conversion of solid materials at syngas breakthrough at 873 K for each metal oxide type under two different syngas compositions. X values are material conversion and R-values are the ratio of moles of solid in the bed to moles of syngas through the reactor at breakthrough.

Figure 6.8 shows the pre-breakthrough solid conversion for $\text{Fe}_2\text{O}_3$ is much lower than for the mixed metal oxides at 873 K. The 1:1 syngas composition and the 3:1 syngas composition both form $\text{Fe}_3\text{O}_4$ (solid conversion = 0.11) throughout the bed before breakthrough. The 1:1 syngas forms a small amount of $\text{FeO}$ at the bed entrance, while the higher quality 3:1 syngas
forms slightly more FeO at the bed entrance before breakthrough. Since the material reduced to Fe$_3$O$_4$ cannot be regenerated with H$_2$O, the predicted H$_2$ output of the Fe$_2$O$_3$ at these temperatures is less than 0.1 moles of H$_2$ per mole of metal oxide after reduction with either syngas composition.

CoFe$_2$O$_4$ and NiFe$_2$O$_4$ are also reduced to Fe$_3$O$_4$ at 873 K; however, the Co and Ni are reduced as well, giving the material a conversion of at least 33% (representative of solid products Fe$_3$O$_4$ and Co or Ni) throughout the bed before breakthrough. As with the Fe$_2$O$_3$ material, a small amount of FeO forms during reduction with the 1:1 syngas. Reduction with the 3:1 syngas forms Fe in the first 10% of the bed, which was not seen with the Fe$_2$O$_3$. For these materials at 873 K, the H$_2$ production per mole of metal oxide was 1.25 after reduction with 1:1 syngas, and 1.5 after reduction with the 3:1 syngas. The R value for the Fe$_2$O$_3$ was nearly three times the value of R for the mixed metal ferrites, meaning that over three times the Fe$_2$O$_3$ would be needed in a reactor to react with the same amount of syngas as the CoFe$_2$O$_4$ and NiFe$_2$O$_4$.

At 1073 K (Figure 6.9), the 1:1 syngas reduced about one third of the Fe$_2$O$_3$ in the bed to FeO (solid conversion = 33%), a direct result of the increase in H$_2$O/H$_2$ equilibrium constant as the temperature increases, which allows formation of Fe and FeO at higher H$_2$O/H$_2$ ratios. The rest of the material is reduced to Fe$_3$O$_4$. The 3:1 syngas reduced nearly half of the Fe$_2$O$_3$ to FeO, and formed a small amount of Fe in the first 5% of the reactor. At these higher temperatures, the H$_2$ produced per mole of metal oxide is 0.52 after reduction with 1:1 syngas and 0.78 after reduction with 3:1 syngas.
The CoFe₂O₄ and NiFe₂O₄ were also reduced to FeO and Co or FeO and Ni (solid conversion = 0.5) in the majority of the bed under both syngas compositions at 1073 K. The 3:1
syngas formed Fe in the first 10% of the reactor, and the materials had an H₂ production per mole of metal oxide of 2.1. After reduction with 1:1 syngas, the H₂ production per mole of metal oxide was 1.65. The R values for Fe₂O₃ under these conditions are nearly twice those of the mixed metal ferrites, meaning that twice as much Fe₂O₃ as CoFe₂O₄ or NiFe₂O₄ is necessary to fully react with the same amount of syngas.

For both materials, higher temperatures resulted in higher overall conversions due to the increase in the equilibrium constant, which allows access to more of the O in the solid under the same gas compositions. Although the higher temperature is attractive for the reduction step, in the oxidation step, the result is lower conversions of H₂ to H₂O during the H₂O oxidation.

6.5.2.2. Complete Steam Oxidations

Simulations for complete H₂O oxidation following syngas reduction allowed the calculation of the energy requirement for steam generation. Reduction simulations were performed with 1:1 and 3:1 syngas compositions at 873 K and 1073 K until the point of breakthrough, and then complete H₂O oxidation was simulated at the same temperature. The ratio of total H₂ generated/total H₂O fed and the HHV of produced H₂/steam generation energy for these oxidations are shown in Table 6.2, and indicate significant energy requirements to generate enough steam for complete H₂O oxidation of mixed metal oxides. For Fe₂O₃, the ratio of H₂/H₂O ranges from 0.35 to 0.57, indicating an overall high conversion of the H₂O to H₂ as expected. For the 1:1 syngas, the H₂/H₂O ratio decreases at higher temperatures due to the decrease in the equilibrium for H₂O oxidation at higher temperatures; however, the 3:1 gas composition shows an increase in conversion. This is due to the formation of Fe metal at the higher temperature, which has a higher H₂O to H₂ conversion during oxidation.
For CoFe$_2$O$_4$, the amount of energy required to generate steam for complete oxidation was more than double the energy gained from the H$_2$ produced at 673 K, and the overall conversion of H$_2$O to H$_2$ was less than 10%. At higher temperatures these values decrease due to the decrease in the oxidation equilibrium constant. The energy necessary to produce steam for the NiFe$_2$O$_4$ oxidation was nearly ten times the energy recovered from the H$_2$, and overall H$_2$O conversion to H$_2$ during oxidation was less than 5% under all conditions. These results indicate that full oxidation with H$_2$O is not feasible for CoFe$_2$O$_4$ and NiFe$_2$O$_4$, and that an O$_2$ oxidation
step is necessary for efficient full regeneration in a CLH reactor. The combined H$_2$O/O$_2$ oxidation is investigated in the next section.

6.5.2.3. Hybrid steam/O$_2$ Oxidations

The point at which H$_2$O oxidation should be terminated and O$_2$ oxidation begun is system specific, but depends on the amount of H$_2$ recovered, the amount of H$_2$O necessary to produce the H$_2$, and the heats of reaction for both the reduction and oxidation reactions. Two parameters were calculated in this analysis to compare the benefit of the H$_2$ recovery to the energy cost of the additional steam generation. The first was called the CLH efficiency, and was defined as

$$\eta_{CLH} = \frac{\Delta H_r[-] + \Delta H_{C,H_2}[-] + \Delta H_{steam}[+]}{\Delta H_{C,syngas}[-]} \quad \text{Eq. 6.23}$$

where $\Delta H_{C,H_2}$ is the heat of combustion of the generated H$_2$, $\Delta H_{C,syngas}$ is the heat of combustion of the syngas used in the reduction, and $\Delta H_r$ is the sum of all heats of reaction in the system:

$$\Delta H_r = \Delta H_{\text{reduction}} + \Delta H_{H_2O \text{ oxidation}} + \Delta H_{O_2 \text{ oxidation}} \quad \text{Eq. 6.24}$$

This parameter penalized the process for the energy required to generate steam, $\Delta H_{\text{steam}}$. The bracketed signs indicate the sign expected for each $\Delta H$ value. The total $\Delta H_r$ should always be negative, as should the $\Delta H_{C,H_2}$ and the $\Delta H_{C,syngas}$. The $\Delta H_{steam}$ will always be positive; therefore, when the energy required to generate steam for the oxidation is more than can be recovered from the H$_2$ combustion, and the reduction and oxidation reactions combined, the $\eta_{CLH}$ becomes negative. A value of 1 represents the combustion of the syngas and is the CLC limit. The second parameter was the syngas conversion efficiency, as defined in Chapter 3:
\[ \eta_{\text{syngas conversion}} = \frac{\text{Moles } H_2 \text{ generated}}{\text{Moles } H_2/CO \text{ consumed in reduction}} \quad \text{Eq. 6.25} \]

and was a measure of the H₂ recovered from the process.

Two syngas compositions were tested for each material at temperatures 873 K and 1073 K, and the CLH efficiency and conversion efficiency were calculated for each. Reduction until breakthrough was modeled for each condition, and different ratios of H₂O oxidation followed by O₂ oxidation were modeled for each reduction condition at the same temperature. Results are plotted in Figure 6.10.

At 873 K, the CLH conversion value was greater than 80% under all conditions for Fe₂O₃; however, the syngas conversion was limited to under 25% due to the inability to oxidize Fe₃O₄ to Fe₂O₃. This was especially evident with the 1:1 syngas, as less than 10% of the H₂ was recovered from the process. For the 1:1 syngas reduction at 873 K, the performance of the mixed metal ferrites was superior to that of the Fe₂O₃ material due to this low conversion.

For the 3:1 syngas reductions at 873 K, the CoFe₂O₃ and NiFe₂O₄ CLH conversion values follow those of the Fe₂O₃ up until syngas conversion is nearly 30%. Then, the slope of the CLH conversion curves for NiFe₂O₄ and CoFe₂O₄ change to follow the slope of the 1:1 syngas reduction values. These trends make clear the dependence of the oxidation properties on the reduction state of the materials in the bed prior to oxidation. As shown in Figure 6.9, mixed metal ferrites reduced with 3:1 syngas form FeO and Fe near the entrance of the reactor. The oxidation thermodynamics of Fe and FeO in the mixed metal ferrites bed follow those of the Fe-only material during the initial oxidation of the Fe to Fe₃O₄, as shown in Figure 6.10. Then, they follow a characteristic curve for the formation of the mixed metal spinel from Fe₃O₄ and Co or Fe₃O₄ and Ni. The response is non-linear due to the non-linear relationship between H₂O
generated and H₂ produced as the reaction proceeds. The H₂ recovered along this curve does add significantly to the total H₂ recovered from the process; however, it does so at the expense of the CLH efficiency value.

Figure 6.10: CLH efficiency vs. the conversion efficiency of the materials at 873 K and 1073 K after reduction with two different syngas compositions
At 1073 K, the syngas conversions for the Fe$_2$O$_3$ material double from their values at 873 K. This H$_2$ recovery is due to the Fe and FeO formed in the reactor during reduction, which allow significantly more H$_2$ recovery than the Fe$_3$O$_4$ and FeO formed at 873 K do. The mixed metal ferrites show higher syngas conversions than Fe$_2$O$_3$ up to about 60%, at which point the CLH efficiency drops to zero with a 5-10% increase in syngas conversion. This sharp decrease is in CLH efficiency is due to the decrease in oxidation equilibrium constant at the higher temperatures for the regeneration of the mixed metal ferrite.

Results show that these materials can operate as efficiently as Fe$_2$O$_3$ in the lower syngas conversion region of the plot at both temperatures under each reduction condition. At 873 K, the mixed metal ferrites, especially CoFe$_2$O$_4$, can have a significantly higher syngas conversion at lower CLH efficiency values. The NiFe$_2$O$_4$ can only offer modest H$_2$ recovery gains at lower CLH efficiency values. At 1073 K, both mixed metal ferrites offer significant H$_2$ recovery compared to Fe$_2$O$_3$ after reduction with the 1:1 syngas; however, the H$_2$ recovery gain is modest after the 3:1 syngas reduction. Under all conditions, use of the mixed metal ferrites would require less material in the bed for the same syngas throughput, thereby decreasing the size of reactor for the CLH process.

Mixed metal ferrites would offer significant advantage over conventional Fe$_2$O$_3$ materials for systems with lower quality syngas and/or lower operating temperatures. For example, much of the syngas produced from gasification of biomass, such as wood products, has reducing gas to oxidizing gas ratios between 1:1 and 2:1, which are lower ratios than much of the syngas produced from coal gasification. [21] In this composition range, the mixed metal ferrites would allow higher metal oxide conversions than Fe$_2$O$_3$, and would give the CLH process more flexibility with the amounts of H$_2$ produced without sacrificing the ability to efficiently generate...
electricity with integrated CO₂ capture. Depending on efficiency requirements of the system, up to 80% of the H₂ could be recovered from the process.

### 6.6 Conclusions

First, this study showed that the reduction step for the CLH process with Fe₂O₃, CoFe₂O₄, and NiFe₂O₄ in a packed bed reactor can be reasonably approximated in a model as reaching thermodynamic equilibrium at low to moderate solid conversions. The developed model was used to investigate the conversion of Fe₂O₃, CoFe₂O₄, and NiFe₂O₄ during syngas reduction in a packed bed reactor prior to H₂ and CO breakthrough. The conversion in the bed was shown to be significantly higher for mixed metal ferrites before breakthrough than for Fe₂O₃, offering the advantage of a smaller reactor for the same syngas throughput and conversion with these mixed metal materials. Higher solid conversion, combined with the ability of CoFe₂O₄ and NiFe₂O₄ to fully re-oxidize with H₂O, lead to more than three times greater H₂ production from the mixed metal ferrites than from Fe₂O₃. When the reaction energetics are considered, full recovery of H₂ from mixed metal ferrites is not favorable; however, the materials offer increased flexibility over the Fe₂O₃ materials in the ratio of H₂/electricity generation possible due to the low recovery of H₂ using Fe₂O₃. Thus, the greatest advantage in using the mixed metal ferrites is observed at the lower conversions obtained at lower reduction temperatures and from reduction with weaker syngas, making them an ideal material choice for syngas from various biomass materials like wood products. At higher temperatures, the CoFe₂O₄ still offers slightly greater H₂ recovery than Fe₂O₃, but the advantage is less due to higher H₂ recovery from the Fe-based materials at these temperatures. Under all conditions, the mixed metal ferrites still consume significantly more syngas per cycle than Fe₂O₃.
6.7 References


Chapter 7: Conclusions and Future Work

7.1 Conclusions

The purpose of this thesis was to investigate the materials CoFe$_2$O$_4$ and NiFe$_2$O$_4$ for use in the CLH system. These materials have been proposed as alternatives to Fe$_2$O$_3$ as metal oxides for the CLH process and the limited experimental data in literature regarding their use looks promising; however, no comprehensive investigation involving cyclability with phase analysis or their performance meeting the criteria for CLH materials in a packed bed reactor has been published.

Both CoFe$_2$O$_4$ and NiFe$_2$O$_4$ cycled under CLH conditions, and both reduced materials were highly reactive with steam in the CLH temperature range. Raman spectroscopy showed the mixed metal spinel phase was regenerated during H$_2$O oxidation, an important finding due to the concerns of metal segregation during H$_2$O oxidation. The use of a high surface area inert m-ZrO$_2$ support substrate resulted in materials that were stable in chemical redox at temperature below 873 K. Interactions between the metal oxide and support were not detected with Raman spectroscopy or XRD analysis. The oxidation rates of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ were shown to be sensitive to both temperature and H$_2$O concentration.

To justify the use of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ in a CLH system, the conversion of H$_2$ to H$_2$O and CO to CO$_2$ during the CLH reduction step must be high to both limit the amount of chemical energy lost, and limit the amount of impurities in the CO$_2$ for sequestration. The FactSage$^\text{TM}$ thermodynamic software and associated databases were used to investigate the predicted equilibrium conditions between the metal oxides and the H$_2$/H$_2$O and CO/CO$_2$ systems. Calculations predicted high conversions during the reduction step for each material, and showed
the formation of a Fe-rich spinel and metallic Co or Ni phase during the initial stage of spinel reduction. Experiments with NiFe$_2$O$_4$ and CoFe$_2$O$_4$ confirmed the high conversion of CO and H$_2$ during the reduction step, and XRD and Raman analysis of the material showed formation of a Fe-rich spinel and a metallic phase during reduction. Additionally, the H$_2$ produced during full H$_2$O oxidation was over 90% of the quantity of H$_2$/CO used to reduce the material when the reduction step was stopped at breakthrough. In contrast, the H$_2$ produced from the Fe$_2$O$_3$ material was only 20% of the H$_2$/CO used in the reduction step, a consequence of the inability of Fe$_2$O$_3$ to be regenerated with just H$_2$O oxidation. The H$_2$O oxidation was observed to be slower for the mixed metal ferrites than for the Fe-only material, prompting a kinetic investigation into the oxidation mechanism for the mixed metal spinels.

A kinetic investigation of the H$_2$O oxidation of Fe-only materials and mixed metal spinels, conducted in a stagnation flow reactor, showed the oxidation of reduced Fe$_3$O$_4$ to be limited by an order of reaction model that is believed to represent a surface reaction limitation. The mixed metal materials also showed order of reaction behavior during the first 100-200 seconds of reaction, followed by a slower H$_2$ production tail modeled as a diffusion limitation. This limitation was hypothesized to be in the spinel phase, since cation migration in Fe$_3$O$_4$ has been shown to slow as a secondary cation is incorporated into the lattice. Reaction models were fit with an error minimization technique that took into account all data points from all temperatures and H$_2$O concentrations for each material, resulting in a globally optimized fit over all the data.

The full H$_2$O re-oxidation of the mixed metal ferrites in a packed bed reactor required excess steam generation for hours, requiring significant energy for steam production while generating small amounts of H$_2$. Since the CoFe$_2$O$_4$ and NiFe$_2$O$_4$ must be fully regenerated for
the subsequent reduction cycle, a secondary O$_2$ oxidation is proposed to fully oxidize the metal oxide and generate heat. The reduction reaction in a packed bed was shown to have rapid enough kinetics to be approximated with an equilibrium model, which predicted the conversion of solid material in the bed prior to H$_2$O oxidation. The mixed metal ferrites have higher material conversions than Fe$_2$O$_3$ under all reduction conditions due to the reduction of the Co$^{2+}$ and Ni$^{2+}$ to their metallic states. When the H$_2$O oxidation is also approximated as an equilibrium-limited reaction, as a “best-case” scenario, complete steam oxidation of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ is not a feasible option. However, when H$_2$O oxidation is followed by O$_2$ oxidation, the mixed metal ferrites are equally as efficient as Fe$_2$O$_3$ materials, and offer superior and efficient H$_2$ production after lower temperature reductions and when reduced with lower quality syngas.

7.2 Future Work

Ultimately, these metal oxides are for use in large, industrial scale CLH reactors. Since these mixed metal ferrites have proven successful in a laboratory scale reactor, the next step is to test them in a larger system with more realistic operating conditions. New synthesis techniques would need to be investigated and tested for CoFe$_2$O$_4$ and NiFe$_2$O$_4$, as typical metal oxide mass loadings for industrial scale CLH reactors are in excess of 60%. [1] Since most large-scale CLH reactors include physical movement of particles from one reactor to the next, particle attrition would also need to be studied.

The initial stage of H$_2$O oxidation of reduced CoFe$_2$O$_4$ and NiFe$_2$O$_4$ appears to be limited by a surface reaction, modeled in this study by an order of reaction model. If a surface reaction is indeed limiting, then the rates of oxidation may be improved by the incorporation of a catalyst that is active for the rate-limiting step. Samples prepared using ALD are ideal for this test, as a
catalyst deposited over the total area of the film could provide superior metal oxide–catalyst contact. Additionally, use of DFT to examine the H2O surface reaction could help to identify the exact mechanism of limitation.

This study focused on CoFe2O4 and NiFe2O4, but preliminary studies show Cu/Fe, Zn/Fe, and Mn/Fe materials to be capable of redox cycling with syngas.[2, 3] A more comprehensive study of these ferrite materials may identify them as potential CLH materials as well. Investigations would need to include packed bed reactor studies to determine the H2 and CO conversion during syngas reduction and the H2 production capacity of the material in comparison to other CLH materials.

The chemical looping process with the highest projected H2 production efficiency is the Coal-Direct Chemical Looping (CDCL) scheme. [1] This process directly contacts coal or biomass with metal oxides at high temperatures, significantly decreasing the complexity of the overall system. The oxygen from the metal oxide that is used to produce CO2 and H2O from the solid material decreases the O2 necessary from an air separation unit during gasification, thereby decreasing the expense of the gasification process. The CDCL process is receiving an increased level of interest from researchers worldwide, and an investigation of CoFe2O4 or NiFe2O4 for use in this system would directly contribute to this growing field.

7.3 References


Bibliography


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Appendix A: Diffusion in Metals and Spinels

A.1 Diffusion in metal and spinel lattices

Rates of solid state diffusion processes are controlled by the migration of atoms through the lattice and are dependent upon the energy it takes to move the atom, as well as the number of adjacent sites into which the atom can move. [1] Atoms may move to a neighboring unoccupied site, or vacancy, or may move to occupy an interstitial site located between normally occupied sites. A vacancy site or an atom occupying an interstitial site are called point defects and exist in pairs to preserve electrical neutrality. The combination of an anion vacancy with a cation vacancy is called a Schottky defect, and a cation interstitial paired with a cation vacancy is called a Frenkel defect. [2] Unpaired defects do occur and exist in non-stoichiometric materials. Perfect crystal lattices at 0 K contain no point defects; however, as the temperature increases atoms in the lattice gain vibrational energy and defects form. Point defects increase both the internal energy and entropy of the crystal, thus an equilibrium defect concentration exists when the free energy is minimized. [2] The equilibrium concentration of defects at a given temperature can be calculated using statistical thermodynamics with a knowledge of the energies required to form the defects.

Similarly, in a perfect crystal lattice at 0 K, atoms do not migrate. As atoms gain vibrational energy, they can translate into a defect, either forming an interstitial (called an interstitial diffusion mechanism) or hopping to a vacancy where the atom and vacancy move in opposite directions through the lattice (called a vacancy diffusion mechanism). [2] This movement requires passing through a higher energy intermediate site, where adjacent atoms are pushed from their lattice positions into higher energy states. [3] The critical point on the energy
surface during atomic migration is called the transition state, and is the highest energy state between the initial and final location of the migrating atom. [3] Enthalpy change between the material with a defect, and the material with a defect in the transition state, is called the migration barrier, or migration enthalpy ($\Delta H_m$). In the ideal limit, the temperature dependent diffusion coefficient can be calculated from knowing both the enthalpy of vacancy formation and the enthalpy of the transition state:

$$D = D_0 \exp\left(\frac{Q}{RT}\right)$$  \hspace{1cm} \text{Eq. A.1}$$

where $Q = \Delta H_{\text{vacancy formation}} + \Delta H_m$, and $D_0$ is a function of the neighboring atom distance and concentration, and the frequency with which the atoms are vibrating. [2] The vibration frequency of the atoms in the lattice, which is the Debye frequency for pure metals, is the jump attempt frequency, and the probability of an atom successfully completing a jump along with the attempt frequency determine the atomic jump rate. [1]

**A.2 Diffusion in Fe, Co and Ni Metals**

The metals examined in this study are arranged in the face-centered cubic (FCC) or body centered cubic (BCC) structures. [4, 5] The FCC structure is the most tightly packed structure, with each atom touching its neighboring atom on all sides. [6] In metals with an FCC structure, the energy of an interstitial defect formation is much greater than the energy for a vacancy formation due to this close packing. The dominating diffusion in these materials is most often found to be through vacancies. In a BCC lattice, more space exists between atoms and the energies of vacancy formation and interstitial formation are similar.
Iron arranges into a BCC structure at temperatures below 1173 K. [4] Diffusion studies indicate that Fe self-diffusion occurs through a vacancy mediated process rather than an interstitial mechanism due to the higher concentration of vacancies in the lattice at all temperatures. [7] Cobalt and Ni exist in the FCC structure in the CLH temperature range and in accord with the defect formation energies the diffusion mechanism is vacancy mediated for each of these metals. [4]

A.3. Diffusion in Spinels

The spinel structure is a close packed FCC arrangement of oxygen anions with cations on the interstitial sites in two types of positions. The tetrahedral site is coordinated with four oxygen anions and the octahedral site is coordinated with six oxygen anions. [8] Each oxygen anion is tetrahedrally coordinated with one tetrahedral and three octahedral cations. [9] The terms “octahedral sublattice” and “tetrahedral sublattice” refer to the cations on the octahedral and tetrahedral sites, respectively. The distances between atoms in the lattice depend on the cation valency and cation ionic radius. Cations are able to migrate from tetrahedral sites to tetrahedral vacancies, from octahedral sites to octahedral vacancies, or between the two types of cation sites. [8]

Oxygen activity dependence of the rate limiting cation migration mechanism has been observed in Fe$_3$O$_4$ between the temperatures of 773 K and 1473 K in several studies. [10-12] The dominant defect at low O$_2$ activity is cation interstitials, while at high O$_2$ activities cation vacancies become dominant; however, the mechanism of cation vacancy diffusion remains ambiguous. [12] Computer simulations of the defect formation and migration energies in Fe$_3$O$_4$ identified the energies associated with vacancy formation and migration on the tetrahedral
sublattice as having higher energies and concluded that vacancy migration must take place through the octahedral sublattice. [10]

Studies of vacancy formation and migration in CoFe$_2$O$_4$ at high temperatures similarly show that cation migration through cation vacancies is the dominant diffusion mechanism at high oxygen activities, and cation migration through cation interstitials is the dominant diffusion mechanism at low oxygen activities. [13] Additionally, as the Co content of the spinel increases (as the spinel becomes less Fe-rich) at the same O$_2$ activity, the overall defect concentration decreases. The measured tracer diffusion decreases two orders of magnitude as the spinel composition is changed from Fe$_3$O$_4$ to CoFe$_2$O$_4$ at 1473 K.

Little information is available in the literature detailing migration barriers and vacancy formation enthalpies for spinel materials, and existing data is summarized in Table A.1. The migration enthalpies in NiFe$_2$O$_4$ are unavailable, along with vacancy formation enthalpies for CoFe$_2$O$_4$. The values that are not readily available in the literature must be measured experimentally or calculated using ab-initio methods. Our goal is to investigate the migration barriers and vacancy formation enthalpies in Fe$_3$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, and in the Fe, Co, and Ni metallic states using ab-initio methods to identify the phase in which the diffusion process is likely to limit the oxidation kinetics.
<table>
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<th></th>
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<th>Tetrahedral vacancy formation (kJ/mol (eV))</th>
<th>Octahedral-octahedral migration barrier (kJ/mol (eV))</th>
<th>Tetrahedral-tetrahedral migration barrier (kJ/mol (eV))</th>
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<td>Tetrahedral vacancy formation for Fe (kJ/mol (eV))</td>
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<td>368 (3.8)</td>
<td>262 (2.7)</td>
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<tr>
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<td>Cation vacancy migration barrier (Fe) (kJ/mol (eV))</td>
<td>Cation vacancy migration barrier (Co) (kJ/mol (eV))</td>
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<td></td>
<td>139 (1.4)</td>
<td>145 (1.5)</td>
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</table>

Table A.1: Defect migration and formation enthalpies found in the literature

**A.4 Diffusion Studies by Atomistic Computer Simulations**

Diffusion coefficients are difficult to accurately determine experimentally and involve precise measurement of tracer concentrations in the lattice at discrete timesteps. The measurements are expensive and difficult to complete without error. [7] An alternative method for determining diffusion coefficients is through ab-initio computer simulations which have the benefit of providing insight into the mechanism of specific diffusion and the rate limiting steps through calculations of the vacancy formation enthalpy and migration barriers. Density functional theory (DFT) is a technique used to calculate the ground state electron density of a many-body system by minimizing electron density functionals through iteratively solving the Kohn-Sham Equations. [3] Accurate ground state properties can be calculated for solid state materials using DFT, from which temperature dependent vacancy formation enthalpy and migration barriers can be calculated.
A.5 Computational Details

Vacancy formation enthalpies, lattice constants, and migration barriers in metallic and spinel systems were calculated using Periodic Boundary Condition (PBC) DFT as implemented in the Vienna Ab initio Simulation Program (VASP). [16, 17] DFT computations were performed using the Perdew-Burke-Ernzerhof (PBE) Generalized Gradient Approximation (GGA) exchange-correlation functional coupled with Projector Augmented Wave (PAW) pseudopotentials. [18] [19, 20] PAWs treated Fe’s 4s²3d⁶ electrons, Co’s 4s²3d⁷ electrons, Ni’s 4s²3d⁸ electrons, and O’s 2s²2p⁴ electrons explicitly with a plane wave expansion.

The calculations for metallic systems were performed with a 125(-1) atom periodic simulation supercell. After geometric relaxation, the cell volume was fixed while relaxations were allowed within the cell. An examination of the effect of cut off energies on the metallic cells found less than a 0.001 eV/atom difference in total cell energy for plane wave expansions with 500 and 600 eV cut off energies; therefore, we utilized the less computationally expensive 500 eV cut off energy. Vacancy formation enthalpies were calculated with a 64(-1), a 125(-1) and a 216(-1) periodic supercell to ensure adequate defect spacing. [21] The vacancy formation enthalpy difference was less than 0.05 eV between the 125 atom, 6x6x6 Γ-point centered Monkhorst-Pack k point mesh calculations and the 216 atom 2x2x2 Γ-point centered Monkhorst-Pack k point mesh calculations. The less computationally expensive 125 cell and 6x6x6 kpoint mesh was used. Calculations were spin polarized to account for magnetic ordering.

The calculations for spinel systems were performed with a 140(-1) atom periodic simulation cell. Studies regarding k-point mesh and cutoff energy showed an optimized 2x2x2 Γ-point centered Monkhorst-Pack k point mesh and 500 eV cutoff energy. A DFT+U correction term
was used for each transition metal in the spinel calculation to account for non-cancelling overbinding errors, and the calculations were spin polarized to account for magnetic ordering. (Citation here)

The Nudged Elastic Band (NEB) method was utilized to calculate migration barriers for the diffusion of a single cation atom through each type of cell and calculations were converged to forces under at least 0.03 eV/Å unless otherwise noted. [22] Vacancy formation energies were calculated from

\[ E_f(\text{defect}) = E_c(\text{defect}) + E_{\text{atom}} - E_c(\text{no defect}) \]  \hspace{1cm} \text{Eq. A.2}  

where \( E_f(\text{defect}) \) is the defect formation energy, \( E_c(\text{no defect}) \) is the total energy of the complete cell, \( E_c(\text{defect}) \) is the total energy of the cell with a defect, and \( E_{\text{atom}} \) is the cohesive energy per atom.

**A.6. Calculation Results**

Based on literature reports indicating that the vacancy mechanism dominates diffusion in BCC and FCC metals, only the vacancy migration was investigated for the metals. [1, 7, 23] The process under investigation is oxidation, which takes place under high oxygen activity conditions; therefore, only the cation vacancy diffusion mechanism is considered in the spinel material. Calculations were performed in this dilute limit, such that only one defect and one foreign atom are introduced into the lattice. Due to the small size of DFT calculations, and the periodic boundary conditions, this minimizes the interaction between vacancies and tracer atoms. [3]
Results from the calculations with metallic supercells are shown in Table A.3, along with values from literature. Calculated values are in accord with the accepted literature values.

<table>
<thead>
<tr>
<th></th>
<th>This Study</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ni (FCC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>3.52</td>
<td>3.52</td>
</tr>
<tr>
<td>(H_{\text{vf}}) (kJ/mol(eV))</td>
<td>137 (1.63)</td>
<td>150-157 (1.55-1.63) [24]</td>
</tr>
<tr>
<td><strong>Co (FCC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>3.52</td>
<td>3.42-3.55</td>
</tr>
<tr>
<td>(H_{\text{vf}}) (kJ/mol(eV))</td>
<td>175 (1.81)</td>
<td>178-184 (1.84-1.91) [5, 26]</td>
</tr>
<tr>
<td><strong>Fe (BCC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>2.83</td>
<td>2.83-2.87</td>
</tr>
<tr>
<td>(H_{\text{vf}}) (kJ/mol(eV))</td>
<td>211 (2.18)</td>
<td>208-236 (2.15-2.44) [27]</td>
</tr>
</tbody>
</table>

Table A.2: Lattice structures and vacancy formation in metals

The self-migration enthalpies and tracer atom migration enthalpies calculated using the NEB method are shown in Table A.3.

<table>
<thead>
<tr>
<th></th>
<th>This Study</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H_{\text{mig}}) (Fe bulk) kJ/mole (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe in Fe</td>
<td>-</td>
<td>57.9 (0.60) [7]</td>
</tr>
<tr>
<td>Co in Fe</td>
<td>68.4 (0.71)</td>
<td></td>
</tr>
<tr>
<td>Ni in Fe</td>
<td>58.7 (0.61)</td>
<td>65.6 (0.68) (?)</td>
</tr>
<tr>
<td>(\Delta H_{\text{mig}}) (Co bulk) kJ/mol (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co in Co</td>
<td>98.7 (1.02)</td>
<td></td>
</tr>
<tr>
<td>Fe in Co</td>
<td>68.4 (0.71)</td>
<td></td>
</tr>
<tr>
<td>(\Delta H_{\text{mig}}) (Ni bulk) kJ/mol (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni in Ni</td>
<td>-</td>
<td>100.4 (1.1) [28]</td>
</tr>
<tr>
<td>Fe in Ni</td>
<td>90.9 (0.94)</td>
<td>93.6 (0.97) [28]</td>
</tr>
</tbody>
</table>

Table A.3: Migration enthalpies in metals calculated in this study and from literature
Due to a lack of proper convergence, the values for Fe self-migration and for Ni self migration were not determined. Values from literature correlate well with the calculated values in this study.

As shown with previous spinel studies, the values calculated for octahedral vacancy formation enthalpy in the spinels were at least 50 kJ/mole (0.5 eV) less than those calculated for tetrahedral vacancy formation, making tetrahedral - to - tetrahedral and octahedral - to - tetrahedral site jumps unlikely pathways for cation migration. [13-15] In this study, only octahedral – to - octahedral site migration barriers were investigated. Calculated migration barriers are shown in Table A.4. The Fe through CoFe$_2$O$_4$ migration barrier was not reported due to lack of proper convergence.

<table>
<thead>
<tr>
<th>Bulk</th>
<th>$\Delta H_{mig}$ (kJ/mol (eV))</th>
<th>Migrating atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>68.3 (0.71)</td>
<td>74.1 (0.77)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>95.8 (0.99)</td>
<td></td>
</tr>
</tbody>
</table>

Table A.4: Migration barriers for octahedral-octahedral migration in Fe$_3$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$.

The lowest barrier in the spinels is for Fe migration through Fe$_3$O$_4$. A previous study calculated this barrier to be 125.5 kJ/mol (1.3 eV), but the calculations for migration barrier were conducted using fixed points in a direct line between octahedral sites, a method that often overestimates the migration barrier because it does not account for perpendicular motion of the atom to reach the transition state. [14] For all mixed metal oxide systems, the migration barrier
is greater through the spinel phase than through the metallic phase. The most important diffusion processes in the metallic material are migration of Fe through Ni and migration of Fe through Co, as these could inhibit the migration of Fe to the alloy/Fe$_3$O$_4$ interface. In both cases, these values are smaller than the migration barriers for each cation in the spinel. This investigation identifies diffusion in the spinel as the likely limiting mechanism during oxidation of CoFe$_2$O$_4$ and NiFe$_2$O$_4$.

A.7 References


