ABSTRACT

YUSUF, SEIF MOMEN. Development of Redox Catalysts for the Oxidative Dehydrogenation of Ethane in a Cyclic Redox Scheme. (Under the direction of Dr. Fanxing Li).

In order to meet the growing demand for ethylene, the chemical looping oxidative dehydrogenation (CL-ODH) of ethane is being studied as a potential production route. CL-ODH is a two-step process where lattice oxygen from a metal oxide redox catalyst is used to oxidize hydrogen formed from the dehydrogenation of ethane. CL-ODH has the potential to increase ethylene yields, lower CO2/NOx emissions, and decrease energy consumption when compared to traditional steam cracking of ethane. This study focuses on the development of manganese based redox catalysts for the CL-ODH of ethane. The design of the redox catalyst is critical for the CL-ODH process: it must have a high oxygen capacity, oxygen mobility and be selective towards hydrocarbon products. Manganese oxides are particularly interesting candidates for the CL-ODH of ethane due to their low cost, relatively benign nature and long-term stability. The three base redox catalysts explored are Mg6MnO8, manganese silicates, and mixed iron-manganese oxides.

Mg6MnO8 was a redox catalyst that have been previously tested for the oxidative coupling of methane and oxidative dehydrogenation of ethane. While Mg6MnO8 had a sufficiently high oxygen capacity (4.1 wt%), it primarily formed CO2 in CL-ODH of ethane applications. After promotion with sodium tungstate, the ethylene yield increased from 12.9% to 68.2%. Both sodium and tungsten were necessary as promoters in order to maximize ethylene yields. The sodium tungsten promoter inhibited the activation of ethane by the redox catalyst and promoted the selective oxidation of hydrogen by lattice oxygen. X-ray photoelectron spectroscopy analysis of the sodium tungstate promoted Mg6MnO8 redox catalysts showed an enrichment of sodium and tungsten and a reduction in the amount of Mn4+ species and the
average oxidation state of manganese on the surface of the redox catalyst. Additional characterization of the sodium tungstate promoter revealed that the sodium tungstate promoter formed a shell around the Mg6MnO8 redox catalyst. The sodium tungstate shell was initially solid, but at reaction temperatures it entered a molten state. While solid, the sodium tungstate shell prevented the activation of carbon monoxide and hydrogen, but in a molten state hydrogen was oxidized by lattice oxygen from the redox catalyst. When methanol was used as a probe molecule, it was found that the sodium tungstate promoter reduces the number of basic sites on the surface of the redox catalyst and prevented the activation of reactant molecules. 18O-16O exchange studies showed that the sodium tungstate promoter decreased the mobility of lattice oxygen in Mg6MnO8, but not enough to prevent hydrogen oxidation at reaction temperatures. It was also found that the solubility of hydrogen in sodium tungstate was low, but sodium tungstate could be reduced by hydrogen indicating that the oxidation of hydrogen occurred at the gas phase-sodium tungstate shell interface. The proposed mechanism for the CL-ODH of ethane on sodium tungstate promoted Mg6MnO8 redox catalysts is: first ethane is thermally cracked in the gas phase and then hydrogen is oxidized to water by oxygen from sodium tungstate reducing the WO42- anion to WO3-. The WO42- anion is restored by lattice oxygen from Mg6MnO8 to allow the reaction to continue.

Manganese silicates are naturally abundant materials have been used in various applications including chemical looping combustion and hydrocarbon dehydrogenation. Un-promoted manganese silicate redox catalysts had higher ethylene yields un-promoted Mg6MnO8 due to the lack of Mn4+ species on the surface of the redox catalyst. However, a sodium tungstate promoter was necessary to achieve similar ethylene yields to the sodium tungstate promoted Mg6MnO8 redox catalyst. ASPEN Plus simulations showed that sodium tungstate
promoted manganese silicate redox catalysts had the potential to reduce emissions and energy consumption by 89% than the steam cracking of ethane process.

Mixed iron-manganese oxide catalysts were explored to develop a redox catalyst with high ethylene yields that could make the ODH reactor operate less endothermically and increase energy savings of the CL-ODH of ethane process. A less endothermic ODH reactor will allow for a lower circulation rate of the redox catalyst and temperature difference between the ODH and regenerator reactors. A sodium tungstate promoted iron-manganese redox catalyst with a molar ratio of 20-80 (Fe-Mn) had an exothermic heat of reduction and similar ethylene yields to sodium tungstate promoted Mg₆MnO₈ and manganese silicate redox catalysts. Traditional chemical looping combustion and CL-ODH with the sodium tungstate promoted 20-80 redox catalyst were compared using ASPEN Plus simulations. It was found that CL-ODH was able to have similar circulation rates to CLC while lowering the temperature of the regenerator reactor, resulting in additional energy savings for the CL-ODH process.
Development of Catalysts for the Oxidative Dehydrogenation of Ethane in a Cyclic Redox Scheme

by
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DEDICATION

To my mother, father, and sister: Selima Begum, Mohammed Yusuf and Sabrina Yusuf.

Without their support, I would not have been able to complete my PhD thesis.
Seif Yusuf was born in New Brunswick, NJ on October 28th, 1998. He grew up in Edison, NJ and after graduating high school, he attended Carnegie Mellon University where he completed a Bachelor of Science in chemical engineering with a minor in colloids, polymers and surfaces in May of 2010. He then attended the University of Delaware where he received a Master of Chemical Engineering in January of 2013. While there he completed a thesis titled “Development of Photocatalysts for Water Oxidation and Carbon Dioxide Reduction”. Next, he worked for MedImmune as a Manufacturing Technology Associate I/QC Analyst before entering the Ph.D program in the Chemical and Biomolecular Engineering Department at North Carolina State University in the August of 2014. Here he joined Dr. Fanxing Li’s research group where he has worked on the development of redox catalysts for the oxidative dehydrogenation of ethane in a chemical looping scheme.
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Chapter 1: Introduction

1.1 Ethylene and Natural Gas

Ethylene is a valuable commodity chemical that is used as a feedstock for a variety of products and chemical intermediates including polymers (polyethylene and polypropylene), ethylbenzene, ethylene glycol, propionaldehyde, ethylene oxide, and ethylene dichloride. Ethylene is currently the most produced organic chemical and worldwide production is expected to increase to 376 million tons/year by 2050.\textsuperscript{1,2} In the past 10 years, the US shale gas revolution has led to large increases in the supply of natural gas and significant growth in the US chemical industry: in March 2017 it was estimated that the “Golden Age of Natural Gas” had led to 294 capital projects with a total value of $179 billion, creating ~820,000 jobs.\textsuperscript{3} Ethane has become an attractive feedstock for the production of ethylene in the US for multiple reasons: 1) there is significant fraction of ethane in shale gas reserves that can be easily separated from other natural gas components,\textsuperscript{4} 2) the increase in ethane supply made it relatively cheaper than naphtha\textsuperscript{3} (Figure 1.1), and 3) high ethylene yields can be achieved when ethane is used as a feedstock when compared to naphtha as a feedstock.\textsuperscript{5}
The current industrial practice for the conversion of ethane to ethylene is the steam cracking of ethane. In this process, ethane is diluted with steam and then fed into reactor tubes. In the reactor tubes, ethane is converted to ethylene, hydrogen and other hydrocarbon products through a series of gas phase reactions. The residence time in the reactor tubes are between 0.1 and 0.5 seconds and the products have to be quenched within 0.1s after leaving the reactor tubes in order to prevent degradation. Despite the long history of this process, the steam cracking of ethane has multiple drawbacks. First, the temperature inside the reactors can reach 1100°C, which limits the choice of material for the construction of the reactors. Second, there is also a significant amount of coke that forms inside the reactors during the reaction. This leads to the intermittent shut down of reactors for the removal of coke through air or steam. Third, there is a thermodynamic equilibrium limitation on the conversion of ethane which restricts the single pass conversion.
yield of ethylene. Fourth, approximately 16GJ of energy is required for each ton of ethylene produced from the steam cracking of ethane because of the endothermic nature of the ethane cracking reaction (143 kJ/mol C₂H₆ at 850°C) and the separation costs of ethylene from other reaction products and unconverted ethane. The high energy demand of this process is met through the combustion of external fuel which leads to another important issue, i.e. high COₓ/NOₓ emissions. According to the US Energy Information Administration, when comparing the 18 most produced chemicals in the world, the production of ethylene has the second highest energy consumption and greenhouse gas emissions, only behind ammonia synthesis.

1.2 Oxidative Dehydrogenation of Ethane

To overcome the drawbacks of the steam cracking of ethane, the oxidative dehydrogenation (ODH) of ethane was studied as an alternative approach for the conversion of ethane to ethylene. In the ODH of ethane, oxygen is used to combust hydrogen that is formed during the conversion of ethane to ethylene (reaction 1)

\[ 2C₂H₆ + O₂ \rightarrow 2C₂H₄ + 2H₂O \quad (1) \]

The combustion of hydrogen makes the overall reaction exothermic (-105 kJ/mol C₂H₆ at 850°C), eliminating the need to combust fuel. The removal of hydrogen also has the potential to increase the single pass conversion of ethane. A variety of catalysts have been studied for their ability to promote the ODH of ethane reaction: including various metal oxides, and supported alkali chlorides. While some of these catalysts were able to achieve ethylene yields over 40%, they were achieved at lower ethane partial pressures (<40%) and were comprised of rare metals (tellurium, platinum, niobium, and dysprosium) or expensive and toxic metals such as vanadium. There are multiple hurdles the ODH of ethane reaction must overcome in order to be commercialized. In order to produce pure oxygen gas for the reaction, an expensive and
energy intensive air separation unit is required. The co-feed of ethane and gaseous oxygen leads to extra safety concerns and the exothermic nature of the ODH reaction makes it difficult to control the process. Finally, if the ethylene yield is not sufficiently high the downstream purification energy costs will be prohibitive.

1.3 Chemical Looping

1.3.1 Chemical Looping Combustion and Reforming

In order to address to concerns with the ODH of ethane, we propose a process similar to chemical looping combustion (CLC) and chemical looping reforming (CLR) which are both cyclic redox processes. There are multiple reactor configurations for that have been studied for chemical looping processes including circulating fluidized beds, alternating fixed-bed reactors, and a rotating reactor. In a circulating fluidized bed based chemical looping process (Figure 1.2), a metal oxide oxygen carrier donates it lattice oxygen in order to convert hydrocarbon species to oxidized products. The depleted oxygen carrier is transferred to a separate reactor where it is regenerated with air. The regeneration step also generates heat which is carried back to the first reactor by the oxygen carrier. In CLC, the oxygen carrier is used to combust various hydrocarbon fuels into a high concentration CO$_2$ stream for the generation of energy. The high concentration CO$_2$ stream allows for the efficient separation and capture of CO$_2$ and CLC also has lower NO$_x$ emissions. In CLR, the oxygen carrier donates its lattice oxygen in order to oxidize methane to CO and H$_2$. The oxygen carrier in a CLR process is also catalytically active for the conversion of methane to CO and H$_2$ and is sometimes referred to as a redox catalyst. In CLR, the heat from the re-oxidation of the oxygen carrier can offset the heat requirements of the conversion of methane to syngas leading to a more energy efficient process.
Figure 1.2: Simplified schematic of chemical looping processes.

1.3.2 Chemical Looping Oxidative Dehydrogenation of Ethane

The chemical looping oxidative dehydrogenation (CL-ODH) of ethane would be similar in design to CLC and CLR processes (Figure 1.3). In the ODH reactor, the oxygen carrier is a redox catalyst, that donates its lattice oxygen to convert ethane to ethylene and water. The reduced redox catalyst is then transferred to a separate reactor (regenerator) where it is re-oxidized with air through an exothermic reaction. The regenerated redox catalyst is then transferred back to the ODH reactor completing the cycle.
Figure 1.3: Simplified schematic of the CL-ODH process.

The CL-ODH process address multiple issues present in traditional ODH processes. Since the redox catalysts acts as the oxygen source, an air separation unit is not required to generate gaseous oxygen and it is possible to avoid co-feeding ethane and oxygen, making CL-ODH cheaper and safer. As in CLC and CLR processes, the redox catalyst carries heat from the regenerator to the ODH reactor improving heat integration reducing the need to supply energy to the CL-ODH process. Overall, the CL-ODH process has to potential to be have higher ethylene yields and lower energy costs than traditional steam cracking of ethane.

1.4 Redox Catalysts for the CL-ODH of ethane

The most studied redox catalysts for the CL-ODH of ethane have utilized vanadium and molybdenum. When operated in a CL-ODH scheme, the highest ethylene yield achieved by these redox catalysts was 38% while the majority of redox catalysts had an ethylene yield of less than 20%.\textsuperscript{27-31} Furthermore, vanadium is a toxic and expensive metal making it a non-ideal candidate
for the implementation in an industrial scale CL-ODH process. Manganese oxides are an alternative redox catalyst candidate for the CL-ODH of ethane. They are abundant, environmentally benign, and stable at high temperatures. These properties make them viable candidates for the CL-ODH of ethane. Manganese based redox catalysts have been used for CLC applications and have been shown to be active heterogeneous catalysts for the ODH of ethane and the oxidative coupling of methane (OCM),\textsuperscript{32-42} another route for the production of ethylene from shale gas reserves. When comparing CL-ODH of ethane to traditional steam cracking in ASPEN Plus,\textsuperscript{43} it was found that the CL-ODH process can lower energy demand and CO\textsubscript{2} emissions by up to 82\%. These savings are result of the high ethylene yield and H\textsubscript{2} conversion that simplifies downstream separation.

1.5 Redox Catalyst Design and Preliminary Studies

The ideal redox catalyst for the CL-ODH of ethane will have to be chosen carefully in order to maximize product yield, energy savings and emission reductions. First, it will need a sufficient oxygen capacity and be able to quickly donate its lattice oxygen so that it can significantly increase single pass conversion of ethane. While oxygen carriers for CLC applications are specifically selected to fully oxidize hydrocarbon species to CO\textsubscript{2}, the redox catalyst will have to inhibit the non-selective oxidation of hydrocarbon products. There are 2 types of redox catalysts that can be used in a CL-ODH process. Type I redox catalysts are selective hydrogen combustion (SHC) materials. Ethylene is produced from the dehydrogenation of ethane or the cracking of ethane without lattice oxygen from the redox catalyst. The lattice oxygen is instead utilized in the SHC reaction. The combustion of hydrogen generates heat for the overall CL-ODH process and helps to increase ethane conversion by pushing the ethane ODH equilibrium forward. Type II redox catalysts utilize their lattice oxygen to catalyze the
ODH of ethane reaction. In this work, the development of type I redox catalysts utilizing the ethane cracking and SHC reaction will be discussed. Previous simulations have determined that at least 70% of the hydrogen produced needs to be combusted in order to meet the heat balance requirements of the CL-ODH process.

In a preliminary study on manganese based redox catalysts for the CL-ODH of ethane, manganese oxides supported by SiO$_2$ and MgO were studied. As stated, earlier manganese oxides are active for the ODH of ethane and both SiO$_2$ and MgO supports have been used for OCM and ODH of ethane applications. Sodium and sodium tungstate were also used as promoters due to their previous effectiveness on Mn/SiO$_2$ and Mn/MgO redox catalysts for the OCM reaction.

XRD characterization of the Mn/SiO$_2$ and Mn/MgO redox catalysts can be seen in Figure 1.4. Initially on the Mn/SiO$_2$ redox catalyst, manganese oxides and largely amorphous silica were detected, but the addition of sodium converted the SiO$_2$ to the α-cristabolite phase. When sodium tungstate was added as a promoter, the α-cristabolite was formed again along with a separate sodium tungstate phase. On the Mn/MgO redox catalysts, manganese was incorporated into a mixed Mn-Mg oxide, Mg$_6$MnO$_8$. Unlike Mn/SiO$_2$ redox catalysts, the addition of sodium tungstate did not change the Mg$_6$MnO$_8$ phase.
In order to determine the oxygen capacity and stability of the redox catalysts, redox cycles were performed on the Mn/MgO and Na promoted Mn/SiO₂ redox catalysts (Figure 1.5). The Na promoted Mn/SiO₂ redox catalyst was chosen over the Mn/SiO₂ redox catalyst because of the formation of the α-cristabolite phase. 5 redox cycles were performed on each redox catalyst at 850°C and the reduction step was done with 10% hydrogen (to avoid the side reactions and the formation of coke) and the oxidation step was done with 10% oxygen. Both redox catalysts showed stable performance over 5 cycles, but the oxygen capacity of the Mn/MgO
redox catalyst was 4 times higher than the Na promoted Mn/SiO$_2$ redox catalyst (4.1 vs. 1.0 wt%). When the rate of the oxygen donation was calculated (Figure 1.6), it determined that the Mn/MgO redox catalyst was able to donate oxygen an order of magnitude faster than the Na promoted Mn/SiO$_2$. As the Mn/MgO redox catalyst had better oxygen transport properties and a higher oxygen capacity the Na promoted Mn/SiO$_2$ redox catalyst, the range of operating conditions would be much larger for Mn/MgO based redox catalysts making it very promising for CL-ODH applications.
Figure 1.5: TGA of redox cycles 1 through 5 for a). Na promoted Mn/SiO2 and b). Mn/MgO reduced in 10% H2 and oxidized in 10% O2.\textsuperscript{44}
Figure 1.6: TGA Weight loss/reduction rates in 10% hydrogen at 850 °C for a). Na promoted Mn/SiO2 and b). Mn/MgO

1.6 Summary

The design of the redox catalyst is the most critical factor for the success of the CL-ODH process. An ideal redox catalyst will have to meet multiple criteria: 1) The redox catalyst will be comprised of cheap and benign materials, 2) Have a sufficiently high oxygen capacity and facile oxygen donation, 3) have a high selectivity towards ethylene and other hydrocarbon products, and 4) have high selectivity towards the combustion of H₂. In this work, various manganese
based redox catalysts are investigated for CL-ODH of ethane. These redox catalysts were promoted with various sodium-based promoters in order to explore their effect on the activity of the base redox catalysts. Extensive characterization was also done on all redox catalysts in order to determine the nature of the redox catalyst. These results can be used to design of redox catalysts for the CL-ODH of ethane that can obtain high ethylene yields and reduce CO\textsubscript{x} emissions and energy consumption.

In chapter 2, Mg\textsubscript{6}MnO\textsubscript{8} based redox catalysts are explored for the CL-ODH of ethane. Base Mg\textsubscript{6}MnO\textsubscript{8} had a high oxygen capacity and oxygen donation rate, but had low selectivity towards ethylene, primarily producing CO\textsubscript{2}. In order to improve the ethylene yield of these redox catalysts, various sodium-based promoters were added to the base Mg\textsubscript{6}MnO\textsubscript{8} redox catalysts. The sodium tungstate promoter was the most effective, obtaining an ethylene selectivity of 89.2% and yield of 68.2%. This was significantly higher than the ethylene yield of thermal cracking (49.1%) and the base Mg\textsubscript{6}MnO\textsubscript{8} redox catalyst(14%). It was found that the sodium tungstate promoter inhibits the activation of hydrocarbon species, but still allows for the combustion of hydrogen. It was determined that the ethane ODH reaction mechanism over the sodium tungstate promoted Mg\textsubscript{6}MnO\textsubscript{8} redox catalyst were 2 parallel reactions: 1) Gas phase thermal cracking of ethane and 2) the selective combustion of hydrogen on the surface of the redox catalyst. X-ray Photoelectron Spectroscopy (XPS) showed that the sodium tungstate promoter was also enriched on the surface of the redox catalyst and lowered the average oxidation state of manganese. It was also found that tungsten and sodium work together to improve the ethylene yield of Mg\textsubscript{6}MnO\textsubscript{8} redox catalysts and both are necessary to maximize ethylene yield.
In chapter 3, the effect of sodium and tungsten promoters on \( \text{Mg}_6\text{MnO}_8 \) based redox catalysts for the CL-ODH of ethane is explored. The ratio of sodium to tungsten was varied and it was found that there is a balance between the amount of sodium and tungsten. Tungsten was required to retain sodium on the surface of the redox catalyst, but if the ratio of sodium to tungsten is significantly lower than 2:1, new mixed tungsten oxide phases formed, ethylene yield decreased, and \( \text{CO}_x \) selectivity increased. Surface characterization indicated that the sodium tungstate promoter forms a shell around the \( \text{Mg}_6\text{MnO}_8 \) redox catalyst, reduced the amount of basic sites on the surface of the redox catalyst and nonselective oxygen species and inhibited the activation of reactant molecules. The sodium tungstate promoter also lowered the rate of dissociative adsorption of oxygen and oxygen exchange. At reaction temperatures, the sodium tungstate shell became molten and prevented the activation of reactant molecules except for hydrogen. This selective combustion of hydrogen occurred at the gas-sodium tungstate molten shell interface with oxygen from the \( \text{Mg}_6\text{MnO}_8 \) redox catalyst. This detailed study can be used for the future design of redox catalysts for the CL-ODH of ethane.

In chapter 4, manganese silicate based redox catalysts are studied for the CL-ODH of ethane. Unlike previously studied manganese oxides supported by \( \text{SiO}_2 \), manganese silicates are single mixed oxide phase that had shown to be active in CLC and OCM applications. The synthesized redox catalysts were comprised of 2 distinct phases, \( \text{Mn}_7\text{SiO}_{12} \) and \( \text{SiO}_2 \). The redox catalyst with a \( \text{Mn}:\text{Si} \) molar ratio of 70:30 showed to highest oxygen capacity and \( \text{H}_2 \) conversion indicating that \( \text{Mn}_7\text{SiO}_{12} \) was the primary oxygen carrying phase. The base \( \text{Mn}:\text{Si} = 70:30 \) had a high \( \text{CO}_x \) selectivity so it was promoted with sodium tungstate, which improved the ethylene yield from 44.08% to 63.33% and decreased the \( \text{CO}_x \) selectivity from 36.52% to 2.96% (GHSV=3000hr\(^{-1}\) at 850°C). As seen on \( \text{Mg}_6\text{MnO}_8 \) based redox catalysts, sodium tungstate
inhibited the activation of ethane on the surface of the redox catalyst. XPS analysis showed a lack of Mn$^{4+}$ species on the surface of the redox catalyst, which were attributed to the low ethylene selectivity on the base Mg$_6$MnO$_8$ redox catalyst. ASPEN Plus simulations indicated that manganese silicate redox catalyst can lower CO$_2$/NO$_x$ emissions and energy demand by up to 89% when compared to traditional steam cracking.

In chapter 5, mixed iron-manganese oxide redox catalysts are explored for the CL-ODH of ethane. While the previously studied redox catalysts were able to achieve high ethylene yields, the reduction of those redox catalysts were endothermic. This had no effect on the exothermicity of the overall CL-ODH process, but it resulted in endothermic operation of the ODH reactor. In order to meet the heat demand of the ODH, redox catalyst particles carry sensible heat for the regenerator reactor which requires the regenerator to operate at a higher temperature than the ODH reactor (~100°C) and a high redox catalyst circulation rate. If the reduction of the redox catalyst were more exothermic, the temperature difference between the ODH and regenerator reactors and the redox catalyst circulation rate could be lowered, leading to additional savings for the CL-ODH process. Mixed iron-manganese redox catalysts are viable candidates because of their tunable heat of reductions and ability to produce high ethylene yields. The sodium tungstate promoted redox catalyst with a Fe-Mn molar ratio of 20-80 was the best candidate for the CL-ODH of ethane. The heat of reduction was exothermic at all stages of reduction and it was able to produce high ethylene yields (62.21%) and had a low CO$_x$ selectivity (3.15%) after promotion with sodium tungstate. ASPEN Plus simulations showed that the 20-80-Na$_2$WO$_4$ redox catalyst was able to maintain similar redox catalyst circulation rates to traditional CLC systems while decreasing the temperature difference between the ODH and regenerator reactors.
1.7 References


Chapter 2: Effect of Promoters on Manganese Containing Mixed Metal Oxides for Oxidative Dehydrogenation of Ethane via a Cyclic Redox Scheme

2.1 Abstract

Ethylene is an important building block in the chemical industry, state-of-the-art ethylene production (steam cracking) has multiple drawbacks including high energy consumption, coke formation, and significant CO₂ and NOₓ emissions. We proposed a chemical looping oxidative dehydrogenation (CL-ODH) process to convert ethane into ethylene in a two-step, cyclic redox scheme. In this process, lattice oxygen in a metal oxide based redox catalyst is used to combust the hydrogen formed in ethane dehydrogenation, thereby enhancing ethylene formation while retarding coke formation. The oxygen-deprived redox catalyst is subsequently regenerated with air, releasing heat to balance the overall heat requirement. CL-ODH can realize a reduction of over 80% in primary energy consumption and pollutant emissions. The key to this process is an efficient redox catalyst with high selectivity and facile oxygen transport. Previously we determined that oxides with an Mg₆MnO₈ structure allow high lattice oxygen mobility and satisfactory oxygen carrying capacity for the proposed redox reactions. However, un-promoted Mg₆MnO₈ exhibits poor ethylene selectivity, producing primarily CO₂. In the current study, we examine the effects of various sodium-containing promoters on Mg₆MnO₈ CL-ODH activity and mechanism. Sodium tungstate promoted Mg₆MnO₈ was the most effective redox catalyst, showing an ethylene selectivity of 89.2% and yield of 68.2%, a significant improvement of thermal cracking (38.9% yield). Temperature programmed reaction (TPR) experiments indicate that the reaction proceeds via gas phase ethane thermal cracking in parallel with selective hydrogen combustion on the redox catalyst surface. XPS analysis indicates that the decreased ethane/ethylene oxidation activity on the sodium tungstate promoted redox catalysts resulted
from the suppression of near surface Mn$^{4+}$. This is due to a combination of decreased surface manganese content and reduction in average Mn oxidation state. The suppression of Mn$^{4+}$ results in a decrease of electrophilic surface oxygen species, inhibition of ethylene combustion, and enhanced ethylene yield.

**Keywords:** oxidative dehydrogenation, chemical looping, ethane, ethylene, redox catalyst, oxygen carrier

### 2.2 Introduction

Ethylene is an important commodity chemical for a variety of products and chemical intermediates such as polyethylene, ethylene oxide, and ethylbenzene.\(^1\) Currently, the primary approach to produce ethylene is through the steam cracking of hydrocarbon feedstocks such as naphtha and ethane. Due to its abundant presence in natural gas, ethane is a particularly attractive feedstock for ethylene production in regions such as North America and the Middle East.\(^2\) In the ethane cracking process, ethane is first preheated and diluted with steam. This gaseous mixture is then introduced into externally heated reactor tubes, where it is converted to ethylene, hydrogen, and other light hydrocarbons via a complex network of homogeneous gas-phase reactions.\(^1\) Although ethane cracking is a well-established commercial process, there are multiple challenges from the standpoints of process efficiency, economics, and emission control. First, the highly endothermic cracking reactors are operated up to 1100 °C.\(^3\) This limits material selection for the reactors and requires robust heat-exchanging networks to recover heat. Second, the downstream recovery of ethylene from hydrogen, hydrocarbon byproducts, and unreacted ethane is highly energy intensive and is responsible for 50–55% of the total energy cost.\(^4,5\) Approximately 16 GJ of energy is required in order to produce each ton of ethylene.\(^1\) This energy demand is typically met through the combustion of natural gas, which leads to significant CO$_2$ and NO$_x$ emissions.
Other issues include equilibrium limitations for ethane conversion and the need for periodic reactor shutdowns for coke removal and maintenance.\(^6\)

To address the aforementioned limitations of steam cracking, oxidative dehydrogenation (ODH) was proposed as an alternative approach to produce ethylene from ethane.\(^3,7\text{-}10\) The desired overall ODH reaction is:

\[
2\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \quad \Delta H^{850°C} = -105 \text{ kJ/mol} \quad (1)
\]

In ODH, the oxidation of hydrogen shifts the reaction equilibrium toward ethylene formation. As a result, higher single-pass conversions of ethane can potentially be achieved. Unlike the endothermic steam cracking reaction, the ODH reaction is exothermic, eliminating the need for external fuel combustion. A number of promising catalysts for ethane ODH have been studied, including various metal oxides (vanadium,\(^11,12\) molybdenum,\(^13\text{-}15\) nickel–niobium,\(^2,16\) and lanthanum\(^17\)), platinum-group metals,\(^18\text{-}20\) and supported alkali chlorides.\(^21,22\) Despite extensive research and various potential advantages, the ethane ODH process has yet to be commercialized. One difficulty in commercial implementation is the tradeoff between ethane conversion and ethylene selectivity limiting per-pass yields. Although there are reports of ethylene yields up to 78\%\(^23\) and selectivity up to 90\%,\(^2\) the long-term stability of these catalysts under realistic operating conditions has yet to be demonstrated.\(^3\) To be attractive, high per-pass yields must be obtained due to high separation costs. For example, in a steam cracker operating at a typical 56.3\% per-pass yield, the downstream separation demand amounts to 8.32 GJ/ton of ethylene.\(^4\) The difficulty in safely controlling the process and efficiently recovering heat for a highly exothermic process in the presence of gaseous oxygen adds complexity and costs. Additionally, air separation to produce the oxygen feed is capital and energy intensive.
As an alternative to traditional cofeed ODH, we propose a chemical looping ODH (CL-ODH) scheme that eliminates the practical drawbacks of ODH while offering significant energy demand reduction over traditional steam cracking.4,24 In CL-ODH, a redox catalyst is used as an oxygen carrier, donating oxygen from its crystal lattice to convert ethane to ethylene and water. After reduction, the catalyst is reoxidized in air to complete the redox cycle. The reactions are shown by eqs 2 and 3, and a simplified schematic of the process is shown in Figure 2.1.

$$C_2H_6 + MeO_x \rightarrow C_2H_4 + MeO_{x-1} + 2H_2O \quad (2)$$

$$MeO_{x-1} + \frac{1}{2} O_2 (air) \rightarrow MeO_x + Heat \quad (3)$$

CL-ODH presents multiple advantages to conventional ODH processes: (i) oxygen in CL-ODH is provided from the lattice of the redox catalyst, making costly air separation unnecessary; (ii) the avoidance of oxygen cofeed with ethane makes the overall process safer and the selectivity easier to control; (iii) the inherent heat integration of a CL-ODH process allows for efficient recovery of process heat. The CLODH process is also advantageous in comparison to steam cracking.
Unlike gaseous oxygen based ODH, the CL-ODH concept is relatively new and has not been extensively studied to date. Vanadium oxide based redox catalysts have received the most attention for ethane CL-ODH. However, vanadium is toxic and expensive, and the reported yields of ethylene from these redox catalysts are typically below 15% due to the low ethane conversion (typically between 7 and 25%) and decreasing ethylene selectivity at higher ethane conversions (decreasing from 85% to 58%), making it difficult to be used in large-scale redox processes.

Unlike the previously mentioned oxide systems, manganese oxides are low-cost, environmentally benign materials that are stable at high temperatures. Mn-containing oxides have also been shown to be effective for the oxidative coupling of methane and chemical looping combustion (CLC) of methane and coal. We have previously reported proof of concept data showing that Mn-based redox catalysts can be effective for CL-ODH. ASPEN Plus modeling has shown that, in comparison to traditional steam cracking, the CL-ODH process
can result in up to 87% reduction in energy demand and CO$_2$ emissions.$^4$ The significant energy and CO$_2$ savings from CL-ODH primarily result from (i) the autothermal ethane conversion scheme, which is enabled by chemical looping without the needs for cryogenic air separation, and (ii) simplified downstream separations due to increased single-pass ethylene yield and effective conversion of the H$_2$ byproduct. Although these recent studies validate the feasibility and attractiveness of CL-ODH, thorough mechanistic understandings of the CL-ODH reactions facilitated by the redox catalysts, are highly desirable for redox catalyst development and optimizations.

This current study gains further insight into Mg$_6$MnO$_8$-based redox catalysts for the ODH of ethane. Previous work showed that Mg$_6$MnO$_8$ was selective toward deep oxidation of ethane. However, promotion with sodium tungstate leads to a very selective catalyst. To determine the mechanism of dopant effects, three alkali-based promoters (sodium, sodium pyrophosphate, and sodium tungstate) and two alkali-free promoters (phosphorus and tungsten) were characterized. Results indicate that sodium pyrophosphate and sodium tungstate promoters both improved the ethylene selectivity of the redox catalyst. Temperature-programmed reaction (TPR) and thermogravimetric analysis (TGA) indicate that the reaction follows a parallel gas phase (homogeneous) and surface (heterogeneous) reaction pathway: ethane is converted through a gas-phase cracking reaction, whereas H$_2$ produced from the cracking reaction is selectively combusted on the surface of the redox catalyst by its lattice oxygen. XPS analysis showed that the sodium pyrophosphate and tungstate promoters retain significant sodium on the surface, while sodium alone is leached off during redox reactions. Moreover, the presence of sodium salts significantly suppresses Mn$^{4+}$ on the surface and the associated electrophilic surface oxygen, thereby inhibiting nonselective ethylene combustion reactions.
2.3 Experimental Section

2.3.1 Redox Catalyst Synthesis

All redox catalysts were synthesized through incipient wetness impregnation. For the unpromoted redox catalyst, manganese(II) nitrate (SigmaAldrich, 98%) was dissolved in 4 mL of water and then mixed with magnesium oxide powder (Materion Advanced Chemicals, ≥99.5%) in order to create a 15 wt % manganese catalyst. The resulting slurry was stirred and then dried overnight at 80 °C. The catalyst was then calcined in air, first at 450 °C for 3 h and then at 900 °C for 8 h. The catalyst was then cooled in air. After cooling, the sample was ground and sieved.

The promoters in this study were sodium, sodium pyrophosphate, sodium tungstate, phosphorus, and tungsten. The promoter precursors were sodium nitrate (Fisher, ≥99%), sodium pyrophosphate tetrabasic (Sigma-Aldrich, ≥95%), sodium tungstate dihydrate (Sigma-Aldrich, ≥99%), ammonium phosphate monobasic (Sigma-Aldrich, ≥98%), and ammonium metatungstate (Sigma-Aldrich, ≥85% WO$_3$ basis), respectively. For the sodium-containing redox catalysts, the final sodium loading was 1.7 wt % and is within the range of alkali doping reported for similar systems$^{33,43}$ and corresponds to 5 wt % sodium pyrophosphate loading. The sodium-free promoted redox catalysts were loaded to the same weight percent of phosphorus (1.1%) or tungsten (6.8%) in the sodium phosphate and sodium tungstate samples, respectively. For the sodium-promoted catalyst, the sodium and manganese precursors were dissolved together in DI water and impregnated on the magnesium oxide powder as in the unpromoted catalyst. The sodium pyrophosphate promoted catalyst was produced in a similar manner, except that the precursors were dissolved together in a solution that was comprised of 4650 μL of DI water and 350 μL of nitric acid (Fisher, certified ACS plus). For the sodium tungstate and tungstate promoted catalysts, the impregnation procedure included two steps to prevent precipitation of the
tungsten precursor. First, manganese(II) nitrate was mixed with magnesium oxide powder as with the unpromoted catalyst. After drying at 80 °C overnight, the catalyst was heated to 200 °C to decompose the nitrates. Afterward, sodium tungstate dihydrate or ammonium metatungstate was dissolved in DI water and then mixed with the catalyst and dried overnight at 80 °C. All of the promoted catalyst were then calcined, ground, and sieved as with the unpromoted catalyst.

The redox catalysts in this study are referred to as unpromoted, Na (sodium)-promoted, NaP (sodium pyrophosphate)-promoted, NaW (sodium tungstate)-promoted, P (ammonium phosphate)-promoted, and W (ammonium metatungstate)-promoted redox catalysts.

2.3.2 Ethane ODH experiments

ODH of ethane was performed in a 1/4 in. o.d. × 1/8 in. i.d. U-tube reactor. The U-tube was loaded with 0.5 g of catalyst particles sieved between 425 and 850 μm. A 16 mesh white alumina grit was loaded on each side of the catalyst particles to hold the catalyst in place and reduce the gas volume of the heated reactor zone. For blank/thermal background tube runs, the entire tube was packed with inert alumina grit to maintain consistent gas residence times with ODH measurements. The quartz U-tube was heated by a tube furnace, and the gas composition and flow rate in the reactor were controlled with mass flow controllers and an automated valve manifold. In order to determine the catalyst activity for the ODH of ethane, redox cycle experiments were performed. During the reduction step, the reactor environment was comprised of 80% ethane/balance helium, and during the oxidation step it was changed to 17% oxygen/balance helium. After each reduction and oxidation step, 100% helium was flowed into the reactor to purge any remaining gases. The reactor gas manifold is configured such that the total flow rate into the reactor does not change between the purge and reduction steps. Before ODH testing, the redox catalysts were conditioned with two redox cycles comprising of a 3 min
reduction step and 3 min oxidation step at 900 °C to obtain a redox catalyst with stabilized redox properties. During ODH redox cycles, six different combinations of three different temperatures (800, 825, and 850 °C) and two different gas hourly space velocities (GHSV; 3000 and 4500 h⁻¹) were used. For all conditions, the oxidation step was 3 min and the purge steps were 5 min. During the reduction step, 5 mL of ethane was flowed into the reactor. The products from the reduction and oxidation steps were characterized using a quadrupole mass spectrometer (QMS), MKS Cirrus II. The products were calculated by integrating the signals for the characteristic peaks for each of these species. The products were also verified using a gas chromatograph (GC) after being collected in a gas sampling bag. An Agilent 7890 Series Fast RGA GC with two thermal conductivity detector (TCD) channels (He/TCD channel for CO/CO₂ analysis, Ar/ TCD channel for H₂ analysis) and a flame ionization detector (FID) channel for hydrocarbon analysis was used. The system was calibrated using a refinery gas calibration standard (Agilent Part # 5190-0519). As internal standard experiments indicated that no significant coking or tar formation occurred under the conditions tested, a mass balance was used to calculate the yields. The selectivities and conversions for carbonaceous species were calculated relative to the carbon mass balance. The total amount of hydrogen and water formed was calculated by hydrogen mass balance of all recovered species. The water selectivity was calculated relative to the amount of hydrogen recovered and the amount of total water and hydrogen expected by mass balance.

2.3.3 Redox Catalyst Characterization

Adsorption isotherms were collected on a Micromeritics ASAP 2010 instrument at 77 K using N₂ as the adsorbent gas. The surface areas were evaluated using Brunauer–Emmett–Teller (BET) theory. All of the samples were degassed at 473 K under vacuum before the measurements.
Phase identification of as-prepared redox catalysts was performed using powder X-ray diffraction (XRD). A Rigaku SmartLab X-ray diffractometer with Cu Kα (λ = 0.1542 nm) radiation operating at 40 kV and 44 mA was used. A scanning range of 10–80° (2θ) with a step size of 0.1° holding for 3.5 s at each step was used to generate XRD patterns.

In situ XRD studies were performed on an Empyrean X-ray diffractometer equipped with an Anton-Parr XRK-900 reactor chamber. Cu Kα (λ = 0.1542 nm) radiation operating at 45 kV and 40 mA and a scanning range of 10–80° (2θ) were used to generate XRD patterns. To determine if a phase change occurred in an inert environment for each redox catalyst, fresh catalyst was loaded into the reactor chamber and an initial XRD scan was taken at room temperature. The sample was heated in nitrogen at a rate of 5 °C/min. XRD scans were taken every 25 °C between 800 and 900 °C. The sample was then cooled to room temperature, and a final XRD scan was taken. To determine the phase behavior and stability of the catalyst during redox cycling, fresh catalyst was first heated to 850 °C under a flow of air and an initial XRD scan was taken. Next, the gas flow was switched to nitrogen for 15 min before a second XRD scan. The gas flow was then switched to a mixture of 3% hydrogen in nitrogen for 15 min prior to a third XRD scan. This redox catalyst was subsequently reoxidized in air for 15 min. The redox cycle was repeated three times.

X-ray photoelectron spectroscopy (XPS) was used to analyze surface compositions and oxidation states of fresh, reduced, and cycled variants of each of the four catalysts. The reduced samples were generated using a SETARAM SETSYS Evolution thermal gravimetric analyzer (TGA). The catalyst was heated to 900 °C in a helium environment, and then hydrogen was introduced (10%) until no mass loss was detected followed by cooling to room temperature. For the cycled samples, redox catalyst particles that had undergone over 50 redox cycles were used.
The catalysts were reoxidized at 850 °C and then purged in an inert environment at 850 °C. The XPS system consists of a Thermo-Fisher Alpha 110 hemispherical energy analyzer, a Thermo-Fischer XR3, 300 W dual-anode X-ray source, and a chamber with a base pressure of $1 \times 10^{-9}$ Torr. Survey spectra used a pass energy of 100 eV, and narrow scan spectra were taken with a pass energy of 20 eV. An Al anode was used for all analyses. The spectral energies were calibrated to an adventitious C 1s peak of 284.6 eV.

2.3.4 Temperature-Programmed Desorption/Reduction

$O_2$ temperature-programmed desorption (TPD) was performed on a TA Instruments SDT Q600 device to measure the oxygen desorption/uncoupling behavior of the redox catalysts. Fresh catalyst was loaded into the instrument and was then heated to 900 °C at a rate of 10 °C/min in a 10% oxygen/balance argon environment and held for 30 min to clean the surface of the catalyst. The sample was then cooled in oxygen to 100 °C, after which the oxygen flow was stopped. The sample was then heated in argon to 950 °C at a rate of 5 °C/min and held at 950 °C for 5 min before cooling back to room temperature.

Hydrogen and ethane temperature-programmed reduction (TPR) experiments were conducted using the quartz U-tube reactor as described previously and QMS MKS Cirrus II. A 0.3 g portion of the catalyst (particle size of 250–425 μm) was loaded into the U-tube, and the reactor was then heated to 900 °C for 30 min in a 10% oxygen/balance argon environment to clean the surface of the catalyst. After the catalyst was cooled to room temperature in 10% oxygen, the flow was changed to 5% $H_2$ or 5% ethane in argon. The reactor was then heated quickly to 500 °C and held to stabilize the temperature in the reactor. The catalyst was then heated to 900 °C at a rate of 2 °C/min and held for 5 min. All of the reactor effluent was analyzed by a QMS MKS Cirrus II instrument.
2.4 Results and Discussion

2.4.1 Redox Catalyst Characterization

XRD patterns of as-prepared redox catalysts are shown in Figure 2.2. For all redox catalysts, the characteristic peaks of the Mg$_6$MnO$_8$ phase (PDF# 01-074-1903) were observed. Promoted samples exhibited additional phases. For the Na-promoted catalyst, the Na$_{0.52}$MnO$_2$ (PDF# 04-016-8754) phase was present. Addition of sodium pyrophosphate led to an orthorhombic Na$_3$PO$_4$ phase (PDF# 00-027-0771), and sodium tungstate resulted in cubic Na$_2$WO$_4$ (PDF# 04-008-8508) and orthorhombic W$_8$O$_{21}$ phases (PDF# 04-005-5745). BET (Table 2.1) shows that the surface areas of the promoted redox catalysts are similar to that of the unpromoted redox catalyst.
Figure 2.2: XRD patterns of as-prepared redox catalysts, (a) un-promoted and Na promoted Mg₆MnO₈; (b) NaP and NaW promoted Mg₆MnO₈ [a]PDF# 01-074-1903 [b]PDF# 04-016-8754 [c]PDF# 00-027-0771 [d]PDF# 04-008-8508 [e]PDF# 04-005-5745
Table 2.1: BET surface areas for the as-prepared redox catalysts

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted</td>
<td>4.4</td>
</tr>
<tr>
<td>Na promoted</td>
<td>4.6</td>
</tr>
<tr>
<td>NaP promoted</td>
<td>5.3</td>
</tr>
<tr>
<td>NaW promoted</td>
<td>3.5</td>
</tr>
</tbody>
</table>

2.4.2 ODH Reaction Testing

Figure 2.3 summarizes ethane ODH results at varying temperatures and space velocities for the redox catalysts. Results from a blank case, i.e. thermal cracking, are also shown for comparison. It can be seen that the presence of redox catalysts significantly improves ethane conversions in comparison to thermal cracking (53.2% conversion and 49.1% yield at 850 °C and 3000 h⁻¹ GHSV). The NaW-promoted redox catalyst exhibited the highest ethylene yield (68.2%) followed by the NaP-promoted redox catalyst (42.1%, both yields at 850 °C and GHSV = 3000 h⁻¹). In comparison, the Na-promoted and unpromoted redox catalysts exhibited low ethylene yields (10.6% and 12.9%, respectively) despite high ethane conversions. This is due to the poor ethylene selectivity of these redox catalysts, with the primary product being CO₂. The reaction data indicate that the sodium pyrophosphate and sodium tungstate promoters are effective for inhibiting the overoxidation of ethylene. The underlying mechanisms of the various redox catalysts are further reported in later sections. In terms of ODH performance, a 38.9% increase in ethylene yield was observed for the sodium tungstate promoted redox catalyst in comparison to thermal cracking, indicating the effectiveness of the redox catalyst in promoting ethane dehydrogenation. We note that higher hydrocarbons such as butadiene and propylene were also formed along with ethylene. However, selectivity toward C₃⁺ were below 4% on a carbon basis in all cases on the basis of GC analysis. Coke formation was determined by
quantifying CO₂ species produced during the oxidation step. On the NaW-promoted redox catalyst, it was determined that coke formation accounted for less than 1% of the total carbon in the feed. Further details with respect to coke formation calculations are provided in Appendix A.

The effects of space velocity (Figure 2.3a) and reaction temperature (Figure 2.3b) were also investigated. As expected, an increase in reaction temperature leads to increased ethane conversion at the expense of ethylene selectivity for all redox catalysts. Among the redox catalysts investigated, the NaW promoted redox catalyst exhibited the smallest selectivity drop with increasing temperature, decreasing from 95.5% to 89.2% when the reaction temperature increased from 800 to 850 °C. In comparison, the ethylene selectivity of NaP-promoted redox catalyst dropped from 58.5% to 48.5%. An increase in GHSV leads to a decrease in ethane conversion and increase in ethylene selectivity. This is understandable, since an increase in gas residence time can promote the sequential combustion of ethylene products. The NaW-promoted redox catalyst again exhibited the smallest selectivity drop with increase in gas residence time. All of the redox catalysts in the present study exhibited excellent ability for lattice oxygen donation. The lattice oxygen released during ethane ODH ranged between 3.7 and 4.1 wt %.
Figure 2.3: Ethane ODH reaction data (a) at 850 °C with varying GHSV (blue, 3000 h$^{-1}$; red, 4500 h$^{-1}$) and (b) at varying temperatures (red, 800 °C; blue, 825 °C; green: 850 °C). Arrows point in the direction of decreasing GHSV or increasing temperature.
2.4.3 Redox Catalyst Characterizations under Cyclic Redox Environments

Since the proposed CL-ODH reactions involve bulk lattice oxygen, the structural properties and phases of the redox catalysts are likely to change during the redox cycles. To characterize such changes, in situ XRD measurements were performed. Figure 2.4 summarizes XRD patterns for each redox catalyst at different reaction stages, including heated in air (at 850 °C), decomposition under an inert atmosphere, H₂ reduction, and reoxidation in air. When they are heated to 850 °C in air, the redox catalysts, with the exception of the sodium tungstate promoted sample, remained unchanged except for slight peak shifts to lower angles due to an increase in lattice parameters resulting from thermal expansion. For the sodium tungstate promoted catalyst, peaks associated with the Na₂WO₄ phase disappear at approximately 650 °C. The disappearance of these peaks is consistent with the low melting temperature of Na₂WO₄, (698 °C) and indicates that the Na₂WO₄ phase is no longer in a crystalline state. This phenomenon has been observed for Na₂WO₄ in other catalyst systems.³⁰ This was confirmed by the reappearance of the Na₂WO₄ phase when the sample was cooled. To investigate the change in structural properties of the redox catalysts under low oxygen partial pressure (P_O₂) environments, the samples were heated under a nitrogen (5.0 grade) environment. As can be seen, the peak associated with the (111) plane (2θ = 18.3°) of Mg₆MnO₈ lost its intensity at high temperature. This peak corresponds to regularly spaced cation vacancies balancing the Mn⁴⁺ charge in the rock salt type structure, and the loss of its intensity indicates the elimination and randomization of some of these vacancies.⁴⁴ There were also shifts to lower angles as well as the formation of a new peak at 2θ = 30°. The change in (400) plane (2θ = 43.14°) is consistent with a shift toward a rock salt structure as vacancies become disordered, while the new peak at 30° can be attributed to the spinel Mg₂MnO₄ phase (PDF# 00-019-0773). Both phases were observed in
the Mg–Mn–O system under low-PO₂ environments. Under a reducing environment in H₂, the characteristic peaks of Mg₆MnO₈ shifted to even lower angles, which is consistent with the further elimination of lattice oxygen and cation vacancies. The Mg₂MnO₄ phase is also no longer present, which indicates a structure consistent with the MnO-MgO rock salt monoxide phase and the reduction of Mn to the 2+ state. Upon reoxidation in air, the structural properties of all the redox catalysts were restored to their original conditions. Further in situ XRD investigations indicate that the samples maintained good structural stability over multiple redox cycles (see Figure A.1 in Appendix A). The overall phase behavior of the Mg₆MnO₈ system offers insight into its excellent redox kinetics; it has the ability to maintain a rock salt structure with disordered cation vacancies over a wide range of its oxygen capacity without forming significant amounts of less reducible spinel structures.
Figure 2.4: In-situ XRD patterns for different stages of a redox cycle (a) Un-promoted (b) Na promoted (c) NaP promoted d) NaW promoted. Reactions are carried out at 850°C. Oxidation stages were operated under air, inert stage was operated under N2 (5.0 grade), reduction stages was under 3% H2 balance N2

In addition to structural stability, the proposed CL-ODH scheme requires that the redox catalysts remain stable for an extended number of redox cycles. A 25-cycle redox test indicates that the performance of the sodium tungstate promoted redox catalyst is stable, since no deactivation or loss in selectivity was observed (Figure 2.5).
2.5 Effects of Promoter Addition

Considering the significant effects after promoter addition, the roles of promoters were further investigated. To study the ODH reaction pathway, ethane TPR experiments were performed to analyze the production of the desirable ethylene and water and undesirable carbon dioxide byproducts as a function of reaction temperature under a constant ethane flow. The discussion below will focus on the thermal blank, unpromoted redox catalyst, and the NaW promoted redox catalyst. Mass spectral responses of the gaseous products from these TPR experiments are shown in Figure 2.6. It is noted that the onset temperatures for ethylene production (775 °C) were similar for thermal cracking and NaW-promoted redox catalyst. This indicates that ethylene production in the presence of NaW-promoted redox catalyst results from thermal cracking as opposed to catalytic activation of ethane on the oxide surface. The unpromoted catalyst shows activity for ethane conversion well below the onset temperature for
thermal cracking: carbon dioxide and water were produced from ethane deep oxidation starting at \( \sim 600 \, ^\circ\text{C} \) followed by a small ethylene peak at around 700 °C. It is also noted that no water or carbon dioxide is formed above 700 °C due to depletion of the active oxygen in the redox catalyst. Such findings indicate that the unpromoted redox catalyst contains highly active oxygen species that are capable of surface ethane activation. In addition, most if not all of the active oxygens in the unpromoted redox catalyst are nonselective. The NaW-promoted redox catalyst behaves differently: formation of carbon dioxide was nearly completely suppressed throughout the reaction temperature range tested, and no ethane oxidation activity was observed below the thermal cracking temperature. Moreover, water formation has an onset temperature similar to that of thermal cracking. These results indicate that the water formed on NaW-promoted redox catalyst is from the combustion of hydrogen from thermal cracking of ethane. The sodium tungstate promoter suppresses the overoxidation of ethylene on the catalyst surface and exhibits minimal activity for ethane/ethylene activation. Therefore, the likely ODH reaction scheme in the presence of NaW-promoted redox catalyst involves (homogeneous) gas-phase thermal cracking of ethane in parallel with (heterogeneous) selective combustion of \( \text{H}_2 \) products on the oxide surface. The oxidation of hydrogen drives the cracking reaction equilibrium toward the products, leading to higher ethylene yield. The unpromoted redox catalyst is active for \( \text{H}_2 \) combustion but also has high activity for deep oxidation of ethane/ethylene, leading to high ethane conversion and low ethylene selectivity.
Figure 2.6: Ethane TPR results for Mass 26(ethylene), Mass 18(water), and Mass 44 (carbon dioxide)

Since α-oxygen species, i.e. oxygen spontaneously released at temperatures between 300 and 700 °C, are often ascribed to nonselective oxygen species, TPD experiments were carried out (Figure 2.7). None of the redox catalysts exhibited significant weight loss at temperatures below 750 °C, showing few α-oxygen species. A peak for lattice oxygen release was observed for all redox catalysts between 880 and 900 °C (Figure 2.7a). The redox catalyst with the highest peak temperature was the unpromoted redox catalyst (896 °C), followed by the Na-promoted redox catalyst (895 °C), NaP-promoted redox catalyst (893 °C), and finally the NaW-promoted redox catalyst (892 °C). When this experiment was run in the in situ XRD analysis (Figure 2.7b), the same trend was seen, as indicated by the shift from the Mg₆MnO₈ crystal phase to the rock salt monoxide phase. Although our previous study has indicated that lattice oxygen can evolve into electrophilic surface oxygen species under reaction environments, we note that the lattice oxygen release at high temperatures may not directly
relate to such oxygen species under a reducing environment. This is confirmed by ethane TPR of the unpromoted redox catalyst, which shows carbon dioxide production at significantly lower temperatures (580−700 °C) in comparison to oxygen release temperatures in TPD.

Figure 2.7: a) Derivative weight (mg/°C) vs Temperature during O2 TPD and b) In-situ XRD plot of redox catalysts in inert environment (the shift in 2θ at around 42.8° indicates a phase transition from Mg6MnO8 phase to rock salt phase)
To explore the oxygen release properties of the redox catalyst under a reducing environment, H$_2$ TPR experiments were performed. On the basis of the results (Table 2.2), it can be seen that redox catalysts that are less reducible (higher peak temperatures) exhibit higher ethylene selectivity. Since decreased reducibility can correspond to inhibition of lattice oxygen evolution to surface oxygen species (O$^{2-}$ → O$^-$ → O$_2^{2-}$ → O$_2^-$), the relationship between catalyst reducibility and ethylene may indicate that electrophilic surface oxygen species evolved from O$^{2-}$ are responsible for the deep oxidation of ethylene products. To confirm these kinetics, the NaW catalyst was probed in via thermogravimetric (TGA) analysis and through an additional TPR with ethylene and hydrogen. Further information for these experiments can be found in the Appendix A. TGA data indicate that the reduction rate of the catalyst in the presence of ethane is consistent with the rate of reduction in the concentration of hydrogen produced by thermal cracking. The ethylene and hydrogen TPR showed that the NaW-promoted redox catalyst selectively oxidizes hydrogen instead of ethylene.

**Table 2.2:** Peak temperature for H$_2$ TPR of the un-promoted and Na-containing redox catalysts

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted</td>
<td>554</td>
</tr>
<tr>
<td>Na promoted</td>
<td>558</td>
</tr>
<tr>
<td>NaP promoted</td>
<td>616</td>
</tr>
<tr>
<td>NaW promoted</td>
<td>757</td>
</tr>
</tbody>
</table>

**2.5.1 XPS Analysis**

In addition to varying TPD and TPR spectra, promoters may change the distribution and oxidation states of near-surface manganese cations, and such effects can affect the catalytic properties of oxide catalysts.$^{54,55}$ XPS analysis was performed to determine the nature of surface manganese species on the redox catalysts. We focused on fresh (as-prepared) and cycled redox
catalysts (ending in oxidation and cooled under an inert environment). Additional data for the reduced redox catalysts are reported in Appendix A. XPS spectra for the O 1s peak can also be found in Appendix A.

The valence state of Mn is often determined by the magnitude of peak splitting of the Mn 3s peak. However, the Mg 2s peak overlaps with the Mn 3s peak, making such an analysis problematic. Therefore, the Mn 2p peak is used to obtain an understanding of the valence state of Mn. In Figure 2.8, the Mn 2p3/2 spectra are shown for the fresh (Figure 2.8a) and cycled (Figure 2.8b) redox catalysts. The various oxidation states of Mn 2p give rise to complicated multiplet patterns, making deconvolution and quantification difficult. However, literature on the Mn-MgO system indicates that the peaks assigned at 642.5, 641.7, and 640.5 eV are characteristic of Mn$^{4+}$, Mn$^{3+}$, and Mn$^{2+}$, respectively. The peak observed at 644.1 eV is assigned to the high binding energy 2p3/2 components of electrophilic Mn$^{4+}$ species (Mn$^{4+}$ HBE, Figure 2.8). Fitted peak positions and fwhm can be found in Appendix A. The relative areas of the 644.1 eV “Mn$^{4+}$ HBE” and 642.5 ev “Mn$^{4+}$” to the 641.7 and 640.5 eV (“Mn$^{2+}$” and “Mn$^{3+}$” characteristic) peaks are given in Table 2.3. For all of the as-prepared redox catalysts, the most abundant characteristic peak is at 642.5 eV, consistent with the 4+ oxidation state of manganese in Mg$\text{6}\text{MnO}_8$. On the promoted catalysts, the 642.5 eV peak comprises a smaller cross section of the Mn 2p3/2 peak and results in a lower binding energy for the Mn 2p3/2 maximum (642.2 vs 642.5 eV) (Table 2.4). This indicates a lower average oxidation in comparison to the unpromoted redox catalysts.

XPS spectra show a relative increase in the fraction of 641.7 and 640.5 eV peaks on the surface of the cycled redox catalysts in comparison to the as-prepared redox catalysts. As the fractions of these lower binding energy components increase, the ethylene selectivity of the
redox catalyst increased. The fractions of the Mn$^{4+}$ characteristic peaks (644.1 and 642.5 eV) of the cycled samples are significantly lower on the NaP-promoted (68.8%) and NaW-promoted (44.6%) redox catalysts in comparison to the unpromoted redox catalyst (89.9%). This is indicative of shifts toward the Mn$^{3+}$ state for NaP- and NaW-promoted samples. The full-width at half maximum (fwhm) values of the 2p3/2 peak of the cycled NaP- and NaW-promoted redox catalysts are larger than those of the unpromoted and Na-promoted redox catalysts (Table 2.4). This is indicative of a shift from the Mn$^{4+}$ to Mn$^{3+}$ oxidation state.61 For all cycled samples, as the fwhm increases and the Mn 2p3/2 peak binding energy decreases, the selectivity of the redox catalyst improves. This is consistent with literature reports that unpromoted Mn$^{4+}$ oxides are known to be very active for deep oxidation of hydrocarbons.28,29
Figure 2.8: XPS spectra of Manganese 2p$_{3/2}$ peaks of a) fresh redox catalyst b) cycled redox catalysts
Table 2.3: Fraction of (Mn$^{2+}$ + Mn$^{3+}$) and Mn$^{4+}$ on fresh and cycled redox catalysts

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>644.1 and 642.5 (”Mn$^{4+}$ HBE and Mn$^{4+}$”) surface %</th>
<th>641.7, and 640.5 eV (”Mn$^{2+}$ and Mn$^{3+}$”) surface %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted-as prepared</td>
<td>90.2</td>
<td>9.8</td>
</tr>
<tr>
<td>Na promoted- as prepared</td>
<td>80.2</td>
<td>19.8</td>
</tr>
<tr>
<td>NaP promoted – as prepared</td>
<td>83.7</td>
<td>16.3</td>
</tr>
<tr>
<td>NaW promoted – as prepared</td>
<td>84.9</td>
<td>15.1</td>
</tr>
<tr>
<td>Un-promoted-cycled</td>
<td>89.9</td>
<td>10.1</td>
</tr>
<tr>
<td>Na promoted-cycled</td>
<td>73.7</td>
<td>26.3</td>
</tr>
<tr>
<td>NaP promoted-cycled</td>
<td>68.8</td>
<td>31.2</td>
</tr>
<tr>
<td>NaW promoted-cycled</td>
<td>44.6</td>
<td>55.4</td>
</tr>
</tbody>
</table>

Table 2.4: Comparison of FWHM and position of Manganese 2p 3/2 peak for fresh and cycled redox catalysts

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>FWHM (eV)</th>
<th>Mn 2p 3/2 position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted-as prepared</td>
<td>2.64</td>
<td>642.5</td>
</tr>
<tr>
<td>Na promoted- as prepared</td>
<td>2.59</td>
<td>642.1</td>
</tr>
<tr>
<td>NaP promoted – as prepared</td>
<td>2.59</td>
<td>642.3</td>
</tr>
<tr>
<td>NaW promoted – as prepared</td>
<td>2.51</td>
<td>642.2</td>
</tr>
<tr>
<td>Un-promoted-cycled</td>
<td>2.9</td>
<td>642.3</td>
</tr>
<tr>
<td>Na promoted-cycled</td>
<td>2.8</td>
<td>642.2</td>
</tr>
<tr>
<td>NaP promoted-cycled</td>
<td>3.2</td>
<td>642.1</td>
</tr>
<tr>
<td>NaW promoted-cycled</td>
<td>3.23</td>
<td>641.8</td>
</tr>
</tbody>
</table>

When the XPS data are normalized to catalyst surface area and manganese surface percentage (see Appendix A), it can be seen that the addition of the sodium tungstate promoter results in a decrease in the overall amount of near-surface manganese for all oxidation states.
(Figure 2.9). This indicates that promotion both reduces the overall manganese oxidation state and decreases the amount of surface manganese sites.

![XPS spectra of Manganese 2p 3/2 peaks of cycled redox catalysts normalized for surface area and surface manganese percentage](image)

**Figure 2.9:** XPS spectra of Manganese 2p 3/2 peaks of cycled redox catalysts normalized for surface area and surface manganese percentage

Previous literature has shown that alkali-metal promoters suppress active oxygen species and increase hydrocarbon selectivity.\(^{62}\) Therefore, the sodium surface percentage was analyzed for all the redox catalysts (Table 2.5). From these results, it can be seen that after cycling sodium is not retained on the Na-promoted redox catalyst. This is consistent with the similarity between the XPS spectra of the cycled Na promoted and unpromoted samples, and their similar ODH activities. The NaP-promoted redox catalyst is able to retain close to 50% of its original surface sodium over 25 redox cycles, while the NaW-promoted redox catalyst is slightly enriched in surface sodium after cycling. This indicates that phosphorus and tungsten species are able to
retain sodium on the surface of the catalyst. This is consistent with suggestions in the literature that tungsten can cooperate with alkali species to suppress deep oxidation of hydrocarbons.\textsuperscript{36,62,63}

**Table 2.5:** Mn and Na near-surface atomic % on fresh and cycled catalysts (oxygen and carbon free basis)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn%</th>
<th>Na%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted: as prepared</td>
<td>33.11</td>
<td>0</td>
</tr>
<tr>
<td>Un-promoted: cycled</td>
<td>23.01</td>
<td>0</td>
</tr>
<tr>
<td>Na promoted: as prepared</td>
<td>28.39</td>
<td>17.15</td>
</tr>
<tr>
<td>Na promoted: cycled</td>
<td>29.78</td>
<td>0.48</td>
</tr>
<tr>
<td>Na pyrophosphate promoted: as prepared</td>
<td>12.32</td>
<td>25.91</td>
</tr>
<tr>
<td>Na pyrophosphate promoted: cycled</td>
<td>17.32</td>
<td>11.99</td>
</tr>
<tr>
<td>Na tungstate promoted: fresh</td>
<td>17.73</td>
<td>24.26</td>
</tr>
<tr>
<td>Na tungstate promoted: cycled</td>
<td>6.90</td>
<td>27.86</td>
</tr>
</tbody>
</table>

To determine the promotion effects of phosphorus and tungsten oxides without alkali addition, sodium-free phosphate and sodium-free tungstate promoted redox catalysts were synthesized and tested (Table 2.6). It can be seen from these results that the tungstate and phosphate without alkali ions do improve the ethylene selectivity of the catalyst, but with lower ethylene yields and selectivity in comparison to the sodium tungstate and sodium phosphate promoters. These results confirm the cooperative effects of tungsten or phosphorus with sodium.

**Table 2.6:** Reaction data for P and W promoted redox catalysts at 850°C and GHSV= 4500hr-1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ethane Conversion</th>
<th>Ethylene Selectivity</th>
<th>Ethylene Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>45%</td>
<td>93%</td>
<td>42%</td>
</tr>
<tr>
<td>Un-promoted</td>
<td>87%</td>
<td>18%</td>
<td>16%</td>
</tr>
<tr>
<td>NaP Promoted</td>
<td>78%</td>
<td>57%</td>
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<tr>
<td>P Promoted</td>
<td>87%</td>
<td>32%</td>
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<tr>
<td>NaW Promoted</td>
<td>64%</td>
<td>87%</td>
<td>55%</td>
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<tr>
<td>W Promoted</td>
<td>82%</td>
<td>47%</td>
<td>39%</td>
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2.5.2 Conclusions

The present study has investigated the mechanisms of manganese-based redox catalysts for oxidative dehydrogenation of ethane under a chemical looping scheme (CL-ODH). As shown in this and previous work, Mg$_6$MnO$_8$ redox catalysts exhibit excellent oxygen-carrying characteristics but, without promoters, it is active as a deep oxidation catalyst. Sodium tungstate and sodium pyrophosphate promoters greatly enhance ethylene selectivity (48.5\% and 89.2\%, respectively, at 850 °C and 3000 h$^{-1}$ GHSV) in comparison to Mg$_6$MnO$_8$ (14\%), and sodium tungstate improves the ethylene yield (68.2\%) in comparison to thermal cracking (49.1\%). Ethane TPR experiments indicate that the sodium tungstate and sodium pyrophosphate promoters act by suppressing activation of ethane and ethylene on the oxide surface, while allowing facile oxidation of hydrogen. The reaction mechanism over these redox catalysts is parallel homogeneous gas-phase thermal cracking of and heterogeneous selective hydrogen combustion on the oxide surface.

The mechanism by which the sodium tungstate promoter suppresses the catalyst activity for deep oxidation of hydrocarbons while maintaining selective hydrogen combustion activity was probed by XPS. XPS results indicate that the addition of sodium tungstate inhibits the formation of nonselective, electrophilic oxygen species on the redox catalyst surfaces through the suppression of Mn$^{4+}$ and helps to retain surface Na cations. Moreover, cooperative effects between Na and W were observed in promoting the selectivity of the Mg$_6$MnO$_8$-based redox catalysts.

The results of this study can be used in the future design of selective ODH redox catalysts. The NaW-promoted redox catalyst serves as a selective hydrogen combustion catalyst under the same conditions of thermal ethane cracking. Such a redox catalyst system can be used
in a CL-ODH process to reduce energy consumption and greenhouse gas emissions from ethylene production.
2.6 References


36. Yoon, K. J.; Seo, S. W. The Catalyst for Oxidative Coupling of Methane Prepared from


Chapter 3: Effect of Sodium and Tungsten Promoters on Mg₆MnO₈-Based Core-Shell Redox Catalysts for Chemical Looping-Oxidative Dehydrogenation of Ethane

3.1 Abstract

The present study investigates the effect of sodium and tungsten promoters on Mg₆MnO₈-based redox catalysts in a chemical looping oxidative dehydrogenation (CL-ODH) scheme. CL-ODH has the potential to significantly lower energy consumption and CO₂/NOₓ emissions for ethylene production compared with conventional steam cracking. Sodium tungstate (Na₂WO₄) was previously shown to be an effective promoter for Mg₆MnO₈-based redox catalysts. Overall, the CL-ODH reaction proceeds via parallel gas-phase cracking of ethane and selective combustion of H₂ on the surface of the Na₂WO₄-promoted redox catalyst. Reaction testing indicates that both Na and W are necessary to form Na₂WO₄ and to achieve high ethylene selectivity. A Na:W ratio lower than 2:1 lead to significant formation of additional mixed tungsten oxide phases and decreases ethylene selectivity. Further characterizations based on low-energy ion scattering (LEIS) and differential scanning calorimetry (DSC) indicate that the NaW promoter forms a molten shell around the Mg₆MnO₈ redox catalyst. Methanol TPSR and in situ DRIFTS experiments indicate that the promoter significantly suppresses the number of basic sites on Mg₆MnO₈. ¹⁸O−¹⁶O exchange experiments reveal that the promoter decreases the rate of oxygen exchange. O₂ cofeed studies indicate that below the melting temperature of Na₂WO₄, H₂ and CO conversions are both inhibited, but above the melting temperature, H₂ combustion significantly increased while CO combustion is still inhibited. On the basis of extensive characterizations, it was determined that H₂ is primarily combusted at the gas−Na₂WO₄ molten shell interface via redox reactions of the tungsten salt, likely between the WO₄²⁻ (tungstate) and WO³⁻ (tungsten bronze).
3.2 Introduction

Ethylene is a valuable commodity chemical and an important building block for numerous compounds including oxygenates, polymers, and various chemical intermediates. Because of the significant fraction of ethane in shale gas (up to 20 vol %), ethane has become an abundant and economically attractive feedstock for ethylene production. Currently, ethane and other hydrocarbon feedstocks (e.g., naphtha and gas oil) are used to produce ethylene through steam cracking, a commercial process where ethane undergoes high temperature pyrolysis in the presence of diluting steam. In steam cracking of ethane, a mixture of ethane and steam is preheated and then fed into high-temperature reactor tubes for gas-phase cracking reactions. There are multiple challenges and drawbacks that this process faces: (1) the single pass conversion is equilibrium limited, (2) the formation of coke requires periodic shutdown of reactors, (3) there are significant amounts of both CO₂ and NOₓ emissions, and (4) there is a high energy demand for this process (16 GJ/ton of ethylene produced) due to the highly endothermic cracking reactions and complex downstream separations.

An alternative to steam cracking is the oxidative dehydrogenation (ODH) of ethane. In this reaction (reaction 1), oxygen is used to combust hydrogen, removing equilibrium constraints on ethane conversion, and making the overall reaction exothermic.

\[ 2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O \]  (1)

Despite its various potential advantages, ethane ODH faces a number of practical challenges including (i) the cofeeding of oxygen and ethane imposes potential safety hazards and hence significant inert gas dilution is required and (ii) oxygen generation via air separation can be
both capital and energy intensive.\textsuperscript{11} In addition, limited ethylene selectivity is often reported at high single-pass ethane conversions.

In order to address these challenges, we have previously proposed chemical looping-oxidative dehydrogenation (CL-ODH) (Figure 3.1).\textsuperscript{11−16} In some aspects, CL-ODH is similar to other chemical looping redox systems that have been used for various applications including oxygen uncoupling (CLOU),\textsuperscript{17−19} and the partial oxidation of methane.\textsuperscript{20−24} In CL-ODH, a redox catalyst, also known as oxygen carrier, donates oxygen from its lattice to convert ethane to ethylene and water in an ODH reactor. After the redox catalyst is reduced, it is transferred to an air reactor, where it is reoxidized in air and then transferred back to the ODH reactor to complete the redox cycle. This process removes the drawbacks from the ODH reaction as it does not require an air separation unit and eliminates the safety concerns from the cofeeding of oxygen and ethane. Additionally, process simulations have indicated that the CL-ODH process can reduce energy consumption and CO2 emissions by up to 82\% when compared to steam cracking.\textsuperscript{11}

![Figure 3.1: Simplified schematic of the CL-ODH process. ODH step is shown on the left and re-oxidation step is shown on the right.](image-url)
Vanadium-oxide-based redox catalysts have previously been studied for the CL-ODH of ethane, but the ethylene yields were typically below 15% due to the low conversion of ethane (between 7 and 25%) and a drop in ethylene selectivity at higher ethane conversions (from 85% to 58%). Iron-based perovskites were able to achieve significantly higher ethylene yields (up to 55%) but had low oxygen capacities (<0.7wt%) at 700 °C. The highest ethylene and light olefin selectivity (~92% total) with an ethane conversion of 76.2% were obtained from Na₂WO₄-promoted Mg₆MnO₈ redox catalysts in our previous study. Reaction testing also indicated that both sodium and tungsten need to be present on the surface of the redox catalyst in order to maximize ethylene yield. However, the exact nature and role of the Na₂WO₄ promoter on Mg₆MnO₈-based redox catalyst has still not been determined. This study focuses on the optimization of NaW based promoters on Mg₆MnO₈ redox catalysts and gaining further insight into the nature of the NaW promoter through comprehensive characterization of the redox catalysts.

3.3 Experimental

3.3.1 Redox Catalyst Synthesis

All the redox catalysts (unpromoted and NaW promoted) were synthesized through an incipient wetness impregnation method described in our previous study. Manganese(II) nitrate (Sigma-Aldrich, 98%) and magnesium oxide powder (Materion Advanced Chemicals, ≥ 99.5%) were used in all redox catalysts. For the NaW-promoted redox catalysts, the promoter precursors were sodium tungstate dihydrate (Sigma-Aldrich, ≥ 99%), sodium nitrate (Fisher, ≥ 99%), and ammonium meta tungstate (Sigma-Aldrich, ≥ 85% WO₃ basis). Sodium tungstate dihydrate was used for the 2:1 redox catalyst and a combination of sodium nitrate and ammonium meta tungstate was used for all other Na:W molar ratios of 4:1, 1:1 and 1:2. For all of the previously
listed Na:W ratios, the final sodium loading was 1.7 wt %. This loading is within the range of alkali doping on previously reported systems.\textsuperscript{27,28} An additional Na:W = 1:1 redox catalyst, where the tungsten loading was kept the same but the sodium loading was halved to 0.85 wt %, was also synthesized and is referred to as Na:W = 1:1 (0.5Na).

### 3.3.2 Ethane ODH Experiments

Reaction testing was performed using the same quartz U-tube reactor setup as described in our previous study.\textsuperscript{12} In order to determine the activity of the catalysts, redox cycle experiments were performed. During the reduction step, 80\% C\textsubscript{2}H\textsubscript{6} balance Ar was used, and during the reoxidation step, the gas was switched to 17\% O\textsubscript{2} balance Ar. After each reduction and oxidation step, 100\% Ar was flowed to purge the reactor. The reactor gas manifold is configured such that the total flow rate into the reactor does not change between the purge and reduction steps. Before ODH testing, the redox catalysts were pretreated with 3 redox cycles comprising a 3 min reduction step and a 3 min oxidation step at 900 °C to obtain a redox catalyst with stabilized chemical and physical properties. During ODH redox cycles, a GHSV of 4500 h\textsuperscript{−1} and temperature of 850 °C was used for initial testing of the redox catalysts. During the reduction step, 5 mL of ethane was flowed into the reactor, and the reoxidation step was 3 min. The purge step between the reduction and oxidation steps was 5 min.

The products from the reduction and oxidation steps were collected in a gas sampling bag and characterized using a gas chromatograph (GC). An Agilent 7890 Series Fast RGA GC with two thermal conductivity detector (TCD) channels (He/ TCD channel for CO/CO\textsubscript{2} analysis, Ar/TCD channel for H\textsubscript{2} analysis), and a flame ionization detector (FID) channel for hydrocarbon analysis was used. The system was calibrated using a refinery gas calibration standard (Agilent Part # 5190- 0519). The selectivity and conversion values for carbonaceous species were
calculated relative to the carbon mass balance. The total amounts of hydrogen formed and converted to water were calculated by hydrogen mass balance of all recovered species.

3.3.3 Redox Catalyst Characterizations

Phase identification of as-prepared redox catalysts was performed using Powder X-ray Diffraction (XRD). A Rigaku SmartLab X-ray Diffractometer with Cu Ka (λ = 0.1542 nm) radiation operating at 40 kV and 44 mA. A scanning range of 10−80° (2θ) with a step size of 0.1° holding for 3.5 s at each step was used to generate XRD patterns.

Low-energy ion scattering (LEIS) analysis was performed at the Surface Analysis Center at Lehigh on an ION_TOF Qtaz100 spectrometer to obtain surface compositional information. A 3 keV He+ (2 × 10^{14} ions cm^{-2}, 1.0 × 1.0 mm raster) primary ion beam was used at 3000 eV pass energy, while a 0.5 keV sputtering source (0.5 or 1.0 × 10^{15} cm^{-2} cyc^{-1}, 2.0 × 2.0 mm or 1.5 × 1.5 mm raster) was used at 30° angle to the sample surface for depth profiling; during spectra acquisition and sputtering, charge neutralization was invoked. Prior to analysis, sample powders were dispersed into a sample holder and compressed by 2000 psi.

Methanol temperature-programmed surface reaction (TPSR) experiments were performed to analyze the nature of the active sites of Mg₆MnO₈-based redox catalysts. Unpromoted and NaW promoted (Na:W = 2:1 and 1:2) redox catalysts were tested. One gram of redox catalyst was loaded into a quartz u-tube reactor and was cleaned in 10% O₂ balance He at 850 °C for 30 min and then cooled to room temperature. The gas flow was switched to 100% He and flown through a vessel with methanol at room temperature for 1 h. The flow was then switched to bypass the methanol vessel, and the reactor was heated up to 110 °C and held there for 2 h to remove physically adsorbed methanol. Next, the temperature was then ramped at 10 °C per minute to 600 °C and held at that temperature for 10 min. All products were analyzed using a
quadrapole mass spectrometer (QMS, MKS Cirrus II) and then a heated line was used to ensure that products stayed in the gas phase before being analyzed.

In situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) study was performed with methanol as a probe molecule to study the surface of Mg₆MnO₈-based redox catalysts. A Thermo Fisher Nicolet iS50 FT-IR with a Pike Technologies DiffusIR sample chamber/unit was used to take in situ spectra of the redox catalyst at different temperatures and conditions. The two redox catalysts studied were the unpromoted and Na:W = 2:1. After being loaded into the porous alumina crucible, the redox catalyst was heated to 750 °C in 10% O₂ balance Ar. The catalyst was then cooled in 50 °C increments, and background spectra were taken at each step. At 50 °C, the flow was switched to 100% Ar and flown through a vessel with methanol at room temperature for 2 h. The sample chamber was then purged for 1 h in 100% Ar. Afterward, a spectrum was taken at 50 °C, and then the temperature was raised in 50 °C increments, with a spectrum taken at each increment. Each spectrum taken after methanol adsorption was processed using the background spectrum at the corresponding temperature and the Kubelka–Munk model.

¹⁸O–¹⁶O isotope exchange experiments were performed on unpromoted and Na:W = 2:1 redox catalysts as described by Bouwmeester et al.²⁹,³⁰ 45 mg of redox catalyst was loaded into a 1/4 in. O.D. × 1/8 in. I.D quartz U-tube reactor and was heated to temperature under a 5% ¹⁶O₂ flow balance Ar. Once at temperature, 1 mL pulses of 5% ¹⁸O₂ was injected into the reactor. A total of 5 pulses 3 min apart were injected. m/z = 34 and 36 were measured on a QMS, to determine the amount of oxygen exchange in each pulse. Nitrogen (m/z = 28) was tracked in order to determine the integration limits for each pulse. A room-temperature pulse injection was used to determine a pulse where oxygen exchange did not occur. The initial temperature tested
was 650 °C, and the temperature was raised in 50 °C increments to 850 °C. The integrated QMS data was used to determine the exchange rate of oxygen and activation energies.

### 3.3.4 CO-O₂/H₂-O₂ Cofeed Experiments

The conversion of CO and H₂ were measured over the unpromoted and Na:W = 2:1 redox catalysts under O₂ cofeed conditions. The same quartz U-tubes used in ethane ODH reaction testing, including the blank were used for the cofeed experiments. For CO-O₂ cofeed experiments, each sample was initially cleaned in 10% O₂ balance Ar at 850 °C for 30 min. The temperature was then lowered to 600 °C, and the flow was switched to 10%CO/10% O₂ balance Ar. This flow was kept until a steady result was seen on the QMS. The flow was then switched back 10% O₂ balance Ar, and the temperature was adjusted. The other 2 temperatures tested was 700 and 800 °C. A QMS was used to determine the conversion of carbon monoxide. The same procedure was used for H₂-O₂ cofeed experiments except the flow during testing was 2% H₂, 2% O₂ balance argon, and the temperatures measured were 600 and 700 °C.

Details of several additional characterizations performed, such as in situ Raman experiments and the redox nature of Na₂WO₄, can be found in Appendix B.

### 3.4 Results and Discussion

#### 3.4.1 Redox Catalyst Characterization

XRD patterns of as-prepared redox catalysts are shown in Figure 3.2. For all the redox catalysts, the characteristic peaks of the Mg₆MnO₈ phase (PDF# 01-074-1903) were observed. The Na₂WO₄ (PDF#04- 008-8508) and Na₄MgW₃O₁₂ (PDF# 01-083-6809) phases were also observed in the promoted redox catalysts. The relative intensity of the Na₂WO₄ characteristic peaks initially increases as the Na:W ratio decreases form 4:1 to 2:1, but it then decreases as the Na:W ratio further decreases to 1:2. The strength of the characteristic peaks for Na₄MgW₃O₁₂
stayed the same, until Na:W = 1:2 redox catalyst where the relative intensity increased. The MgWO$_4$ (PDF# 04-006-9803) phase was also detected on the Na:W = 1:2 redox catalyst. On the Na:W= 1:1 (0.5 Na) redox catalyst, all four of the previously mentioned phases were detected. Na$_4$MgW$_3$O$_{12}$ and MgWO$_4$ phases were more significant on the Na:W = 1:1 (0.5 Na) redox catalyst when compared to the Na:W = 1:1 redox catalyst, indicating that a lack of sodium leads to formation of additional tungsten oxide phases.

In order to determine if the NaW promoter has an effect on the crystal structure of the base Mg$_6$MnO$_8$ redox catalyst, Rietveld refinement was performed on the unpromoted and the Na$_2$WO$_4$-promoted Mg$_6$MnO$_8$ redox catalysts. Information about XRD spectra and Rietveld refinement results can be found in the Appendix B (Figure B.1). There were no significant differences in the lattice parameters between the two redox catalysts, indicating that Na$_2$WO$_4$ and Mg$_6$MnO$_8$ are separate crystal phases in the redox catalyst.
Figure 3.2: XRD patterns of as-prepared redox catalysts (a) un-promoted, Na:W=4:1 and Na:W=2:1 redox catalysts. (b) Na:W=1:1, Na:W=1:2, and Na:W= 1:1 (0.5 Na) redox catalysts. [a]PDF# 01-074-1903 [b]PDF# 04-008-8508 [c]PDF#01-083-6809 [d]PDF# 04-006-8508

3.4.2 ODH Reaction Testing

Figure 3.3 summarizes ethane ODH testing at 850 °C and a GHSV of 4500 h⁻¹ for all the redox catalysts synthesized. When compared to the blank (thermal cracking), all the redox
catalysts show an increase in ethane conversion. Previous studies have determined that a H₂ conversion of 70% is desired for the CL-ODH process from a process energy balance standpoint, and all of the promoted catalysts show H₂ conversion well above 70%. While the unpromoted redox catalyst has the highest ethane conversion (94.60%), it has the lowest ethylene yield (13.29%) due to high CO₅ selectivity (83.48%). After the addition of sodium and tungsten at any ratio, there is a significant increase in the ethylene yield. This increase in ethylene yield occurs despite a decrease in ethane conversion because of the larger increase in ethylene selectivity and decrease in CO₅ selectivity. The two best performing redox catalysts were Na:W = 2:1 and 1:1 with ethylene yields of 62.17% and 62.91%, respectively.

The effect of sodium loading can be determined through testing of the Na:W = 1:1 (0.5Na) redox catalyst. When compared with the standard (1.7 wt % Na) Na:W = 1:1, the ethylene yield decreased slightly from 62.91% to 61.12%. The decrease in ethylene yield, which is primarily resulted from increased CO₅ selectivity, further confirms the importance of Na and W in suppressing CO₅ formation. In terms of the effect of Na and W ratio, our previous study indicates that a lack of W leads to loss of Na from the surface and increased CO₅ selectivity. The current study indicates that lowering the Na:W to less than 1:1 is also not desirable, as can be seen from the lowered ethylene yield for the Na:W = 1:2 sample. This decrease may have resulted from the formation of additional tungsten-containing phases other than Na₂WO₄.
Figure 3.3: ODH reaction data at 850 °C and GHSV=4500 hr⁻¹ for thermal cracking (blank) and all the redox catalysts

In Figure 3.4, the effects of reaction temperature on the performance of selected redox catalysts are shown. All of the promoted redox catalysts exhibited comparable ethane conversion and ethylene selectivity (Figure 3.4a). More noticeable differences can be seen between the COx selectivity values of the promoted redox catalysts (Figure 3.4b). At 850 °C, the Na:W = 2:1 and Na:W = 1:1 (0.5Na) redox catalysts showed similar COx selectivity (~8.3%) while the Na:W = 1:1 redox catalyst exhibited a lower COx selectivity of 5.52%. As the temperature decreases, the difference between the redox catalysts COx selectivity values decrease, but the Na:W = 1:1 (0.5Na) always exhibited the highest CO2 selectivity. Given the small differences in activity between the different promoted redox catalysts, further characterization in this study will primarily focus on the unpromoted and Na:W = 2:1 promoted redox catalyst because of its (i) high ethylene yield and (ii) better defined phase compositions; that is, Na2WO4 and Mg6MnO8 were the predominant phases with negligible amount of Na4MgW3O12 phase (Figure 3.2a).
Figure 3.4: ODH reaction data at varying temperatures a) Ethylene Selectivity vs ethane conversion and b) COx selectivity vs ethane conversion (Green: 800 °C, Blue: 825 °C, Red: 850 °C and GHSV=4500 hr⁻¹).
3.5 Surface Characterization of the Redox Catalyst

3.5.1 LEIS Analysis

Our previous XPS study on promoted Mg₆MnO₈-based redox catalysts showed an enrichment of sodium and tungsten on the surface of the Na:W = 2:1 promoted catalyst.¹² The Na₂WO₄ promoter also suppressed the amount of Mn atoms on the surface and lowered the average oxidation of Mn. While XPS can analyze the near-surface region of the catalyst, the penetration depth of this technique is greater than the first few atomic layers. As such, the true surface composition of the redox catalyst cannot be accurately determined by XPS. A more surface sensitive technique, LEIS was used to determine the surface elemental composition of the redox catalyst. For each catalyst, multiple sputtering cycles with a 0.5 keV Ar⁺ sputtering was done with 1 × 10¹⁵ Ar⁺ ions/cm² corresponding to one cycle and the removal of approximately one atomic layer. Figure 3.5 shows the spectra and integrated peak areas for the unpromoted and Na:W = 2:1 promoted redox catalysts. On the unpromoted catalyst, Mg and Mn are the primary elements detected after the first sputtering cycle. Additional sputtering shows increased amounts of Mg, but Mn remain relatively the same. A Ca impurity from the MgO powder used during synthesis was also observed. On the Na:W = 2:1 promoted catalyst, after one sputtering cycle, the primary elements detected were sodium/ magnesium (it is difficult to separate these 2 elements due to their similar atomic masses) and tungsten. Even after 10 sputtering cycles, there is significantly less manganese detected than sodium and tungsten. These results indicate that the outermost layers of the redox catalyst are likely to be composed of W and Na (as opposed to Mn). Since the activity of a catalyst is primarily determined by the first few atomic layers,³¹ it has been shown that the Na₂WO₄ is of significant importance for suppressed COₓ formation and increased ethylene yields.
Figure 3.5: LEIS spectra and peak area over sputter cycles for a, c) un-promoted and b, d) Na:W = 2:1 redox catalysts.

3.5.2 CO-O₂ Cofeed Study

Data presented in the previous section indicates that the outermost atomic layer of the redox catalyst is covered by Na₂WO₄. Differential scanning calorimetry (DSC) measurements of the promoted redox catalyst revealed that the Na₂WO₄ promoter melted at 684 °C, which was close to the melting point (698 °C) of bulk Na₂WO₄ (Figure B.2). This is also consistent with Rietveld refinement results, which indicated that Na₂WO₄ and Mg₆MnO₈ bulk phases were coexisting without solid-state reactions. It is therefore quite possible that the surface of the Mg₆MnO₈ redox catalyst is covered by a surface layer of Na₂WO₄. To further quantify the coverage of Na₂WO₄ promoter on the surface of Mg₆MnO₈, a series of CO combustion experiment were performed on both unpromoted and Na₂WO₄ promoted redox catalysts while
cofeeding gaseous O$_2$. The experiments were carried out at below, near, and above the melting point of Na$_2$WO$_4$ (i.e., 600, 700, and 800 °C). Figure 3.6 summarizes the CO combustion results for both unpromoted and NaW-promoted redox catalysts as well as the thermal blank.

The unpromoted redox catalyst was highly active for catalytic combustion of CO, showing complete conversion of CO at all measured temperatures and significantly higher than the thermal blank. In comparison, the Na:W = 2:1 redox catalyst showed CO conversions comparable to or lower than the thermal blank at all temperatures. These results indicate that (i) Na$_2$WO$_4$ inhibits CO combustion activity of Mg$_6$MnO$_8$ both in its solid and melted forms; (ii) consistent with LEIS results, Na$_2$WO$_4$ forms a shell to completely cover the surface of Mg$_6$MnO$_8$ since the promoted redox catalyst showed no increase in CO combustion activity compared to thermal blank.

![Figure 3.6](image-url)  
**Figure 3.6:** Summary of CO-O$_2$ co-feed study. The gas composition was CO/O$_2$/Ar in a 10/10/80 ratio (vol%).
3.5.3 Effect of the Sodium Tungstate Shell

In order to further investigate the effect of the \( \text{Na}_2\text{WO}_4 \) promoter shell on the redox catalyst, various surface characterizations and exchange studies were performed to determine the acid/base/redox properties, activity, and oxygen exchange behavior of the surface.

Methanol TPSR experiments were performed to determine the change in the nature of the active sites on the surface of the redox catalyst after promotion. Previous studies have shown that products that desorb off the catalyst during the temperature ramp after methanol adsorption can be used to determine whether the active sites are basic, acidic, or redox in nature.\(^{32}\) The three potential products during TPSR runs were carbon dioxide (m/z = 44), dimethyl ether (m/z = 46), and formaldehyde (m/z = 29) for basic, acidic and redox sites, respectively. For these studies, the unpromoted, Na:W = 2:1 and Na:W = 1:2 promoted catalyst were tested.

Over all three tested catalysts, only two products were detected (i.e., carbon dioxide and formaldehyde). These products are expected as both magnesium and manganese are reported to have both basic and redox nature. While tungsten can be acidic, the mixed tungsten oxides that are present on these catalysts do not produce any measurable dimethyl ether even on the sample with W overexpressed (Na:W = 1:2). In Figure 3.7, a comparison of carbon dioxide and formaldehyde production from chemisorbed methanol over all three redox catalysts are presented. The unpromoted redox catalyst shows the highest production of carbon dioxide followed by the Na:W = 2:1 catalyst and then the Na:W = 1:2 redox catalyst which did not produce any significant amounts of carbon dioxide. On the Na:W = 2:1 redox catalyst, three separate peaks are observed for carbon dioxide at \(~384, 483, 600 \, ^\circ\text{C}\). These peaks can also be seen on the unpromoted catalyst, and all peaks are greater in magnitude than on the Na:W = 2:1 redox catalyst. On the unpromoted redox catalyst, a small amount of formaldehyde is detected.
with a peak at 258 °C. The Na:W = 2:1 and Na:W = 1:2 redox catalysts also produce formaldehyde with slightly decreased peak sizes. Overall, methanol TPSR results indicate that the NaW promoter significantly decreases the number of basic sites on the Mg$_6$MnO$_8$ surface by decreasing the amount of surface Mg and Mn cations on the redox catalyst as seen on previous XPS and LEIS measurements. It is also interesting to point out that redox sites are still observed on the NaW promoted redox catalysts with less significant inhibition, as shown in Figure 3.7b.
Figure 3.7: Production of a) carbon dioxide and b) formaldehyde from chemisorbed methanol during temperature ramp of methanol TPSR experiments.
In situ DRIFTS experiments were conducted in order to determine surface species formed after methanol adsorption over the unpromoted and Na:W = 2:1 promoted redox catalysts. The spectra are resulted from background subtraction (a fully oxidized catalyst surface) at the respective temperature and the Kubelka–Munk model was used so the observed peaks are proportional to their concentrations. Peaks at 1413, 1483, 1594, 2840, 2920, and 2950 cm$^{-1}$ were observed on the DRIFTS spectra from the redox catalysts. Peaks at 1413 and 1483 cm$^{-1}$ are associated with carbonate species,$^{33,34}$ and the peak at 1594 cm$^{-1}$ is associated with the formate ion that can be found in formic acid and formaldehyde,$^{35–39}$ both of which are possible products of methanol oxidation. The peaks at 2840 and 2950 cm$^{-1}$ are associated with molecularly adsorbed methanol while the peak at 2920 cm$^{-1}$ is associated with surface methoxy species.$^{40}$ Normalized DRIFTS spectra for both redox catalysts can be seen in Figure 3.8. On the unpromoted redox catalyst, molecularly adsorbed methanol, methoxy, and carbonate species are observed at 50 °C. As the temperature increases, the peaks associated with methanol and methoxy decrease in intensity (they are no longer significant at 250 °C and above), while the formate peak appears and grows. The formate peak is at its highest intensity at 250 °C, which is consistent with the peak temperature for formaldehyde observed during methanol TPSR experiments. While carbonate peaks disappeared at 250 °C, they re-emerged at 350 and 450 °C, indicating conversion of formates to carbonates. The presence of carbonate peaks at these temperatures matches with methanol TPSR data which shows significant CO$_2$ production within this temperature range. On the Na:W = 2:1 promoted redox catalyst, only carbonate, molecularly absorbed methanol and methoxy peaks were observed at 50 °C. The peaks associated with methanol and methoxy are stronger and peaks associated with carbonates are weaker when compared to the unpromoted redox catalyst. When the temperature is increased to 150 °C, peaks
associated with methanol and methoxy decreased significantly and the carbonate peaks grew in intensity. Unlike the unpromoted catalyst, the carbonate peaks were very weak at 250 °C and no longer present at higher temperatures. Also, no peak associated with formic acid and formaldehyde was observed at any temperatures. These DRIFTS results match with the methanol TPSR results; that is, the number of basic and redox sites on the surface of unpromoted redox catalyst were largely decreased after promotion with sodium tungstate. As such, in situ DRIFTS study further reinforces that the NaW surface layer inhibits interaction between reactant molecules and the surface of Mg6MnO8 while exhibiting negligible acid/base or redox properties.
Figure 3.8: In-Situ DRIFTS spectra after methanol exposure at 50°C on the a) un-promoted redox catalyst and b) Na:W=2:1 promoted redox catalyst. Adsorbed Methanol: 2950 cm\(^{-1}\) + 2840 cm\(^{-1}\), Methoxy: 2920 cm\(^{-1}\), Formate: 1594 cm\(^{-1}\), Carbonate: 1483 cm\(^{-1}\) + 1413 cm\(^{-1}\)
Since the CL-ODH process relies on cyclic donation and reincorporation of oxygen, rates of oxygen adsorption and incorporation can play an important role toward the following: (i) further understanding of the effect of the Na$_2$WO$_4$ surface layer and (ii) the redox activity of the catalyst. $^{18}$O$_2$-$^{16}$O$_2$ exchange experiments were performed to determine the oxygen surface exchange rates of the redox catalysts using the method previously reported by Bouwmeester et al.$^{29,30}$ The pulse isotope fractions for the three oxygen species ($^{16}$O$_2$, $^{18}$O$^{16}$O, $^{18}$O$_2$) were used to determine the overall oxygen exchange rate ($R_0$) at each tested temperature. It is further assumed that the oxygen exchange reaction occurs through a two-step mechanism as proposed by Boukamp et al.$^{41}$

\begin{align}
O^*_{2} & \leftrightarrow 2O^*_{ad} \quad (2) \\
2O^*_{ad} & \leftrightarrow O_{lattice} \quad (3)
\end{align}

Reaction 2 is the dissociative adsorption oxygen on the surface of the catalyst, and reaction 3 is the incorporation of adsorbed oxygen into the oxide lattice. The overall rate for reaction 2 is $R_a$ and for reaction 3 is $R_i$. $R_a$ and $R_i$ can be related to $R_0$ through the equation:

$$\frac{1}{R_0} = \frac{1}{R_a} + \frac{1}{R_i}$$

In Figure 3.9, the oxygen isotope fractions at different temperatures are plotted for each catalyst. m/z = 32, 34, and 36 corresponds to the three different oxygen species ($^{16}$O$_2$, $^{18}$O$^{16}$O, $^{18}$O$_2$, respectively) present in the pulse. At all temperatures, the unpromoted catalyst has a smaller m/z = 36 fraction than the Na:W = 2:1 redox catalyst, indicating a higher uptake and of $^{18}$O. As the temperature increases, the difference in m/z = 36 fraction becomes greater (97.5% vs 98.4% at 650 °C and 16.5% vs 69.2% at 850 °C). However, the two redox catalysts show opposite behavior with respect to m/z = 32 and 34. At temperatures of 750 °C and above, the unpromoted catalyst shows a higher fraction of m/z = 34 than m/z = 32. The increase in m/z = 34
is significant enough at 850 °C that it becomes greater than the m/z = 36 fraction. On the Na:W = 2:1 redox catalyst, the m/z= 32 fraction is higher than the m/z = 34 fraction at all temperatures, and both are always below the m/z= 36 fraction. This indicates high oxygen exchange activity and/or mobility on the unpromoted redox catalyst while the NaW promoter inhibits oxygen exchange.

![Graph showing isotope fractions over temperature](image)

**Figure 3.9:** Isotope fractions of oxygen species over the un-promoted (solid line) and Na:W = 2:1 (dashed line) redox catalysts at tested temperatures. M32, M34, and M36 correspond to $^{16}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$, $^{18}\text{O}_2$ respectively.

The calculated rates ($R_0$, $R_i$, and $R_a$) are plotted in Figure 3.10 for the unpromoted and Na:W = 2:1 redox catalysts. At 650 and 700 °C, $R_0$ is similar on both redox catalysts, but there is a significant increase on the unpromoted redox catalyst at 750 °C; however, there is no noticeable increase in $R_0$ on the Na:W = 2:1 redox catalyst until 800 °C. At all temperatures above 650 °C, $R_0$ is higher on the unpromoted redox catalyst than the Na:W = 2:1 redox catalyst.

When $R_0$ is further broken down into $R_a$ and $R_i$, significant differences between the unpromoted and Na:W = 2:1 redox catalysts can be observed. On the unpromoted catalyst, $R_a$ is initially less than $R_i$ and limits the value of $R_0$. As the temperature increases, $R_i$ increases at a
steady rate, but $R_a$ has a sharper increase at both 750 and 800 °C. At 800 °C, $R_a$ is approximately double the value of $R_i$, and is no longer the limiting factor for $R_0$. $R_a$ and $R_i$ at 850 °C cannot be solved, which is likely to be due to the accumulation of exchanged $^{18}$O in the near surface region considering the significantly higher activation energy for $R_a$ compared to $R_i$ (Table 3.1). Near surface accumulation of $^{18}$O would lead to violation of boundary condition in deriving the model.\textsuperscript{21,22}

On the Na:W = 2:1 redox catalyst, $R_a$ was lower than $R_i$ at all measured temperatures. Unlike the unpromoted catalyst, when the temperature was increased to 800 and 850 °C there were significant increases in $R_i$ instead of $R_a$. These increases in $R_i$ would make it more likely for any disassociated oxygen to be incorporated into the bulk and this is seen in the isotope fraction data which showed a higher fraction of m/z = 32 at these temperatures. It can also be seen that $R_a$ limits $R_0$ at all temperatures, keeping $R_0$ on the Na:W = 2:1 redox catalyst lower than $R_0$ on the unpromoted redox catalyst. These results indicate that the NaW promoter inhibits oxygen exchange activity on the redox catalyst.

![Figure 3.10](image)

**Figure 3.10:** $R_0$, $R_a$, and $R_i$ for the a) un-promoted redox catalyst, b) Na:W=2:1 redox catalyst. To maintain identical y-axis scales, $R_i$ for the Na:W = 2:1 redox catalyst at 800 °C($3.5*10^{-3}$ mol O m$^{-2}$ s$^{-1}$) and 850°C ($6.7*10^{-3}$ mol O m$^{-2}$ s$^{-1}$) were not shown in Figure 3.10b. Full plots can be found in Figure B.3
Figure 3.11 shows the Arrhenius Plots of the reaction rate data. To calculate the activation energies of $R_0$, $R_i$, and $R_a$, the entire temperature range was used for the unpromoted redox catalyst, but two separate temperature ranges (i.e., below and above 750 °C) were used for the Na:W = 2:1 redox catalyst. The change in slope on the Arrhenius plot is likely due to the melting of the Na2WO4 promoter. All calculated activation energies are summarized in Table 3.1. When comparing the unpromoted redox catalyst and the Na:W = 2:1 redox catalyst between 650 and 750 °C, it can be seen that the unpromoted redox catalyst has higher activation energies and higher or similar pre-exponential factors. At higher temperatures (750–850 °C), all three activation energies increased for the Na:W = 2:1 redox catalyst, along with significantly increased preexponential factors. When comparing the activation energies on the Na:W = 2:1 redox catalyst between 750 and 850 °C to the activation energies on the unpromoted redox catalyst, it can be seen that the activation energy for $R_a$ is similar, but $R_0$ and $R_i$ are higher on the Na:W = 2:1 redox catalyst. It is also noted that pre-exponential factor for $R_a$ is consistently lower on the Na:W = 2:1 redox catalyst than the unpromoted redox catalyst which may indicate fewer surface sites for the dissociative adsorption of oxygen. These oxygen exchange experiments show that the NaW surface layer inhibits the overall exchange activity on the redox catalyst by limiting the dissociative adsorption of O₂. However, the incorporation rate of adsorbed oxygen was promoted by the molten Na₂WO₄ surface layer. Since the typical CL-ODH reactions are carried out at above 800 °C, one would anticipate facile O²⁻ conduction through the molten Na₂WO₄ layer.
Table 3.1: Arrhenius Activation Energies for Un-promoted and Na:W=2:1 redox catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation Energy for R₀ (KJ/mol)</th>
<th>Pre-Exponential Factor for R₀</th>
<th>Activation Energy for Rᵢ (KJ/mol)</th>
<th>Pre-Exponential Factor for Rᵢ</th>
<th>Activation Energy for Rₐ (KJ/mol)</th>
<th>Pre-Exponential Factor for Rₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted</td>
<td>163.83</td>
<td>11.72</td>
<td>123.82</td>
<td>7.40</td>
<td>227.18</td>
<td>19.27</td>
</tr>
<tr>
<td>Na:W=2:1 (650-750°C)</td>
<td>94.94</td>
<td>1.60</td>
<td>143.11</td>
<td>9.93</td>
<td>89.80</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Figure 3.11: Arrhenius plots for a) $R_0$ and b) $R_a$ and $R_i$ for the un-promoted (red) and Na:W=2:1 (blue) redox catalysts. For the Na:W=2:1 redox catalyst, the solid line is for the 650-750°C range and the dashed line is for the 750-850°C range.
3.6 Probing the CL-ODH Reaction Scheme

To illustrate the overall reaction scheme for CL-ODH, TPR results on both the unpromoted and NaW promoted redox catalysts using a mixture of hydrogen and ethylene are shown in Figure 3.12.\textsuperscript{42} As can be seen, water formation from hydrogen combustion started at \(\sim 550^\circ\text{C}\) on the unpromoted redox catalyst. In comparison, the NaW promoted redox catalyst is significantly less reducible with an onset temperature of water formation at \(\sim 725^\circ\text{C}\). This temperature coincides with the onset temperature of ethane thermal cracking. More importantly, negligible CO\textsubscript{x} formation was observed. Therefore, the NaW promoted redox catalyst is capable of selectively combusting H\textsubscript{2} generated from thermal cracking of ethane without oxidizing the ethylene product. These results, consistent with our previous studies,\textsuperscript{12−14} indicate that CLODH proceeds via parallel reactions of (i) gaseous ethane cracking to ethylene and hydrogen and (ii) selective combustion of hydrogen by lattice oxygen of the NaW promoted redox catalyst.

In addition to the general reaction scheme illustrated above, it would be desirable to obtain additional mechanistic insights on the detailed reaction pathway in view of the redox catalyst’s unique Mg\textsubscript{6}MnO\textsubscript{8}-molten Na\textsubscript{2}WO\textsubscript{4} core–shell structure. Facile oxidation of the reduced redox catalyst and \(^{18}\text{O}_2-{^{16}\text{O}_2}\) exchange experiments clearly indicate that oxygen can migrate through the molten Na\textsubscript{2}WO\textsubscript{4} shell to facilitate the release and uptake of active lattice oxygen from/to the Mg\textsubscript{6}MnO\textsubscript{8} core in the cyclic redox scheme. The pathway for the oxidation reaction, which involves oxygen incorporation and migration through the molten Na\textsubscript{2}WO\textsubscript{4} layer to react with the reduced Mg\textsubscript{6}MnO\textsubscript{8} at the core/shell interface, is relatively straightforward. The selective H\textsubscript{2} combustion reaction in the CL-ODH step, however, can proceed via one of the following pathways: (i) H\textsubscript{2} reacts, on the outer surface of the redox catalyst, with oxygen diffused from the Mg\textsubscript{6}MnO\textsubscript{8} core through the molten Na\textsubscript{2}WO\textsubscript{4} layer; (ii) H\textsubscript{2} dissolves and
diffuses through the molten salt, getting combusted at the Na$_2$WO$_4$/Mg$_6$MnO$_8$ interface; and (iii) combustion of dissolved H$_2$ within the molten Na$_2$WO$_4$ phase. Additional characterizations were performed to determine the detailed mechanism.

**Figure 3.12:** 2.5%H$_2$/2.5%C$_2$H$_4$ TPR over un-promoted and NaW promoted Mg$_6$MnO$_8$ catalysts. Vertical dashed line represents the onset temperature for ethane thermal cracking. Total gas flow rate was 100 ml/min, H$_2$/C$_2$H$_4$/Ar = 2.5/2.5/95, ramp rate was 5 °C/min.

Previous sections have established that the NaW promoter forms a molten shell around the Mg$_6$MnO$_8$ redox catalyst that inhibits interaction between Mg$_6$MnO$_8$ and carbon containing fuels such as C$_2$H$_6$ and CO. In order to test if the oxygen species from the molten layer/redox catalyst are able to activate hydrogen, a H$_2$−O$_2$ cofeed study was performed at 600 and 700 °C. The results are summarized below in Figure 3.13.

As expected, the unpromoted redox catalyst shows significantly higher conversion of H$_2$ than the thermal blank sample, but more significant differences were observed for the Na:W = 2:1 redox catalyst. At 600 °C (below the melting temperature), the Na:W = 2:1 redox catalyst shows H$_2$ conversion similar to the thermal blank. However, at 700 °C (above the melting
temperature of Na$_2$WO$_4$), a significantly higher H$_2$ conversion than the thermal blank was observed. These results indicate that H$_2$ combustion is facilitated by the melting of the Na$_2$WO$_4$ shell whereas such effects were not observed with CO.

![Figure 3.13: Summary of H$_2$-O$_2$ co-feed study. The gas composition was H$_2$/O$_2$/Ar at a 2/2/96 ratio (vol%).](image)

3.6.1 Solubility of H$_2$ in the Molten NaW Promoter

Given the significantly increased H$_2$ combustion activity above the Na$_2$WO$_4$ melting temperature, it would be instructive to determine the solubility of H$_2$ in the molten promoter since a high solubility of H$_2$ in molten Na$_2$WO$_4$ would support pathways ii and iii. Gas switching experiments, similar to that reported by Gartner et. al.,$^{43}$ were conducted to probe the solubility of H$_2$. QMS data from this experiment is shown in Figure 3.14. The H$_2$ injection step clearly indicates water formation due to the reduction of Na$_2$WO$_4$. However, the rate of reduction is rather low ($4.79 \times 10^{-5}$ mmol O removed/ (min-gCatalyst)) compared with the average oxygen removal rate of 1.24 mmol O/(min-gCatalyst) for NaW promoted Mg$_6$MnO$_8$ in CL-ODH). This
confirms the low reducibility of the Na$_2$WO$_4$ shell, which was further confirmed by in situ Raman experiments (Figure B.4). After the H$_2$ flow was stopped, the water signal started to decrease, but the introduction of O$_2$ led to a small increase in the water signal before it continued the decreasing trend. Although the small peak indicates potential solubility of H$_2$, the rate of water formation from the “dissolved” H$_2$ was 43 times smaller than rate of water formation during H$_2$ flow ($1.10 \times 10^{-6}$ mmol O removed/(min-gCatalyst) vs $4.79 \times 10^{-5}$ mmol O removed/(min-gCatalyst)) indicating that the solubility of H$_2$ in molten Na$_2$WO$_4$ cannot be significant enough to support pathways ii and iii. As such, the likely reaction mechanism is that H$_2$ is combusted at the surface of the molten Na$_2$WO$_4$ layer by oxygen species from the Mg$_6$MnO$_8$ redox catalyst (pathway (i)).

Figure 3.14: Water signal (m/z=18) from 15% H$_2$/15% O$_2$ switching experiments over 20wt% Na$_2$WO$_4$/α-Al$_2$O$_3$ sample at 850 °C. Gas composition over time: 100%Ar(0-1min), 15% H$_2$/Ar(1-11min), 100%Ar(11-12min), 15%O$_2$/Ar(12-22min).
3.7 Proposed Mechanism

The extensive characterization results for the Na$_2$WO$_4$ promoted Mg$_6$MnO$_8$ redox catalyst presented in this paper support a potential CL-ODH mechanism illustrated in Figure 3.15. At CL-ODH reaction conditions, the Na$_2$WO$_4$ promoter forms a molten shell around the Mg$_6$MnO$_8$ redox catalyst. During the ethane ODH step, ethane undergoes thermal cracking in the gas phase to form ethylene and hydrogen. Next, the formed hydrogen is combusted to water at the gas−molten Na$_2$WO$_4$ interface. This combustion does not occur in the molten layer or at the molten Na$_2$WO$_4$−Mg$_6$MnO$_8$ interface as the solubility of hydrogen in molten Na$_2$WO$_4$ is too low to support such a reaction pathway. Rather, hydrogen is combusted by the molten Na$_2$WO$_4$ via a redox mechanism. During this reduction, the WO$_4^{2−}$ anion can be reduced to WO$_3^{−}$ anion (as reported in sodium tungsten bronze formation (Na$_x$WO$_3$, x ≤ 1$^{44}$)). The WO$_3^{−}$ anion is reoxidized to WO$_4^{2−}$ with lattice oxygen from the Mg$_6$MnO$_8$ redox catalyst so that further hydrogen combustion can occur. It is noted that such a redox mechanism would require electron conduction through the molten layer. Considering the high electronic conductivity well-documented for tungsten bronze,$^{45}$ such a pathway would be feasible. The redox nature of molten Na$_2$WO$_4$ was further validated in experiments utilizing sharp $^{18}$O$_2$ pulses during a broad H$_2$ pulse (see Appendix B). As such, the Na$_2$WO$_4$ promoter serves multiple functions in terms of the following: (i) forming a molten shell on Mg$_6$MnO$_8$ to inhibit hydrocarbon combustion; (ii) facilitating oxygen exchange at the interfaces of the gas-molten salt and molten salt-Mg$_6$MnO$_8$ via a redox mechanism (WO$_4^{2−} \rightleftharpoons$ WO$_3^{−}$); (iii) transporting the exchanged oxygen (and electrons) from/to the Mg$_6$MnO$_8$ core during the CL-ODH and reoxidation steps. A summary of the key findings on the properties of the redox catalysts before and after Na$_2$WO$_4$ promotion is provided in Table B.3.
3.8 Conclusion

The current study investigates the effect of sodium and tungsten promoters on Mg₆MnO₈-based redox catalysts for chemical looping-ODH of ethane. By varying the ratio of Na and W, it was determined that in order to optimize ethylene yield, there needs to be a balance between the relative amount of Na and W. W is important to retain Na on the surface of the redox catalyst. However, if the Na:W is lowered to significantly below 2:1 (the stoichiometric ratio of Na₂WO₄), mixed tungsten oxide phases other than Na₂WO₄ will form, resulting in increased COₓ formation. Surface characterization indicates that the NaW promoter forms a molten shell around the Mg₆MnO₈ redox catalyst under the CL-ODH operating conditions. Methanol TPSR and in situ DRIFTS experiments indicate that the NaW promoter inhibits the activation of reactant molecules on the surface of the catalyst by significantly suppressing the number of basic sites on redox catalyst. ¹⁸O−¹⁶O exchange experiments reveal that the NaW promoter also inhibits the dissociative adsorption of oxygen and decreases the rate of oxygen exchange. O₂ cofeed studies indicate that when the Na₂WO₄ promoter is in a solid phase, H₂ and CO conversions are both inhibited. Melting of the Na₂WO₄ shell at ~694 °C, however, led to significantly increased H₂ combustion activity, whereas combustion of CO and hydrocarbons are still inhibited. The ability to selectively combust H₂ is important since the CL-ODH reaction in the presence of Na₂WO₄ promoted Mg₆MnO₈ proceeds via gas-phase cracking in parallel with selective combustion of hydrogen by the redox catalyst. Further characterizations of H₂ solubility in Na₂WO₄, ¹⁸O₂ exchange behavior, and surface redox sites indicate that H₂ is primarily combusted at the gas-Na₂WO₄ molten shell interface via redox reactions of the tungsten salt, most likely between the WO₄²⁻ (tungstate) and WO₃⁻ (tungsten bronze). Therefore, the molten Na₂WO₄ layer plays critical roles in (i) decreasing the number of basic sites and nonselective oxygen species on
Mg₆MnO₈; (ii) facilitating the exchange and transport of lattice oxygen from/ to the Mg₆MnO₈ core for selective hydrogen combustion via redox reactions of tungsten salt. These detailed understandings of the functions of the Na₂WO₄ promoter and the reaction pathway can guide the design and further optimization of CL-ODH redox catalysts for ethylene production with significantly reduced energy consumptions and CO₂ emissions.
3.9 References


Chapter 4: Manganese silicate based redox catalysts for greener ethylene production via chemical looping- oxidative dehydrogenation of ethane

4.1 Abstract

The current study investigates manganese silicate based redox catalysts for ethane to ethylene conversion in a chemical looping oxidative dehydrogenation (CL-ODH) process. Facilitated by a two-step cyclic redox scheme, CL-ODH has the potential to overcome the drawbacks of traditional steam cracking including high energy consumption, coke formation, and significant CO\(_2\) and NO\(_x\) emissions. In CL-ODH, lattice oxygen in manganese silicate based redox catalysts is used to combust the hydrogen formed from ethane dehydrogenation, enhancing ethylene formation and suppressing coke formation. The oxygen-deprived redox catalyst is subsequently regenerated with air, releasing heat to balance the overall heat requirement. The key to this process is an efficient redox catalyst with high selectivity and facile oxygen transport. In this study, redox catalysts with combined manganese and silica phases were tested. We report that redox catalysts with high manganese content are more effective for CL-ODH due to their higher oxygen capacity at reaction temperatures. Sodium tungstate was used as a promoter due to its effectiveness to suppress CO\(_x\) formation. Among the redox catalysts investigated, sodium tungstate promoted (1.7 wt.% Na) manganese silicate (Mn:Si molar ratio = 70:30) was the most effective, showing an ethylene selectivity of 82.6% and yield of 63.3%. Temperature programmed reaction (TPR) experiments indicate that the sodium tungstate promoter inhibits ethane activation on the surface of the redox catalyst and is selective towards hydrogen combustion. XPS analysis indicates that the manganese silicate redox catalysts have a smaller amount of near surface Mn\(^{4+}\) than previously studied manganese containing redox catalysts, leading to higher ethylene selectivity on the un-promoted redox catalysts. XPS also indicates that
the reduction of the un-promoted redox catalysts leads to the consumption of silica and formation of inosilicate species. ASPEN Plus® simulations of the CL-ODH scheme using manganese silicate based redox catalysts indicate significant energy and emissions savings compared to traditional steam cracking: the overall energy consumption for ethylene production can potentially be reduced by 89% using the manganese silicate based redox catalyst in the CL-ODH process. Resulting from the significant energy savings, CO$_2$/NO$_x$ emissions can be reduced by nearly one order of magnitude when compared to traditional steam cracking.

### 4.2 Introduction

Ethylene is an important commodity chemical with an annual production projected to increase from 150 million tons/year (in 2013) to 376 million tons/year by 2050. Ethylene is primarily used to manufacture various chemical products and intermediates such as polyethylene, vinyl chloride, ethylene oxide, and ethyl benzene. Ethylene is almost exclusively produced through steam cracking, a commercial process where hydrocarbon feedstocks (ethane, propane, naphtha, or gas oil) undergo high temperature pyrolysis in the presence of diluting steam. Ethane steam cracking is becoming a more attractive approach for ethylene production with the increasing availability of shale gas in the U.S., since ethane is the second most abundant component in natural gas.

In ethane steam cracking, a mixed stream of ethane and steam is preheated and then fed into high temperature reactor tubes for gas-phase cracking reactions. Despite the widespread use of this process in industrial applications, there are a number of challenges it faces. First, the single pass conversion of ethane is limited due to thermodynamic equilibrium and coke formation. The latter requires periodic shutdown of steam crackers for coke removal and maintenance. Second, the cracking process is energy and pollutant intensive. Approximately 16
GJ of energy is required to produce each ton of ethylene due to the highly endothermic cracking reactions and the complexity in downstream separation of ethylene, hydrogen, hydrocarbon byproducts and unreacted ethane.\(^2\) This energy demand is met through the combustion of methane, leading to the emission of 1–1.2 ton CO\(_2\)/tonne ethylene and significant amounts of NO\(_x\).\(^3\)

The oxidative dehydrogenation (ODH) of ethane is an alternative to steam cracking for ethylene production.\(^5,7–10\) In ethane ODH (Reaction 1), gaseous oxygen is used to combust hydrogen to remove equilibrium constraints on ethane conversion and make the overall reaction exothermic \((\Delta H^{850 \degree C} = -105 \text{ kJ/mol})\).

\[
2\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \quad (1)
\]

Despite these potential advantages, ethane ODH has significant limitations: the need for oxygen gas requires an air separation unit (ASU) which is both capital and energy intensive (\(~26 \text{ kJ/mol of O}_2\)). The mixing ethane and gaseous oxygen also creates additional safety concerns. Additionally, in order to be an attractive process, high per pass yields of ethylene have to be obtained due to the high downstream separation/purification energy costs.\(^11\)

To address these challenges, we proposed a chemical looping ODH (CL-ODH) scheme (Fig. 4.1).\(^11–14\) In this two-step process, a redox catalyst, also known as oxygen carrier, donates oxygen from its lattice to convert ethane to ethylene and water in an ODH reactor. After the redox catalyst is reduced, it is transferred to an air reactor where it is reoxidized in air and then transferred back to the ODH reactor to complete the redox cycle. The CL-ODH process eliminates drawbacks of traditional ODH because an air separation unit is no longer needed, and the overall process is safer due to the avoidance of ethane-oxygen gas mixtures. Recent process simulations\(^11\) indicate that the CL-ODH process can reduce energy consumption and CO\(_2/\)NO\(_x\) emissions.
emissions in conventional steam cracking by as much as 87%. The significantly reduced energy consumption is largely due to the selective oxidation of hydrogen, providing energy needed for ethane dehydrogenation. Moreover, higher single-pass yield of ethylene and in-situ hydrogen oxidation reduces the load for the downstream purification steps. With proper design of redox catalysts to avoid over-oxidation of ethane or ethylene, the use of lattice oxygen in the redox catalyst instead of gaseous oxygen can also lead to higher ethylene selectivity.\textsuperscript{13,14}

A number of catalysts have been extensively studied for ethane ODH with oxygen co-feed\textsuperscript{15–22}, with some achieving ethylene yields over 40% when the ethane partial pressures were below 40%.\textsuperscript{23–29} However, these active catalysts are comprised of rare metals such as tellurium, niobium, platinum and dysprosium.

\textbf{Figure 4.1:} Simplified Schematic of CL-ODH

A number of catalysts have been extensively studied for ethane ODH with oxygen co-feed\textsuperscript{15–22}, with some achieving ethylene yields over 40% when the ethane partial pressures were below 40%.\textsuperscript{23–29} However, these active catalysts are comprised of rare metals such as tellurium, niobium, platinum and dysprosium.
Comparatively, there have been far fewer studies for CL-ODH. Recent studies investigated vanadium and molybdenum oxides as redox catalysts for CL-ODH\textsuperscript{30–33}, but these redox catalysts demonstrated ethylene yields below 20% due to low ethane conversion (7–25%) and decreasing ethylene selectivity at higher conversions (85%–58%). Moreover, the toxicity and high cost of vanadium make it difficult for their utilization in large scale, circulating fluidized bed based CL-ODH processes.

Manganese oxides are an alternative redox catalysts that are stable at high temperatures, low-cost, and environmentally benign. Manganese based redox catalysts have been shown to be effective for chemical looping combustion (CLC) and chemical looping gasification (CLG) of methane and coal\textsuperscript{34–40} and we have previously reported on manganese based redox catalysts for the CL-ODH of ethane.\textsuperscript{12,14,41} In these CL-ODH studies, Mg$_6$MnO$_8$ and MnO$_x$/SiO$_2$ based redox catalysts were tested. When promoted with sodium tungstate, Mg$_6$MnO$_8$ based redox catalysts were able to achieve an ethylene yield of 68.2%, well above thermal cracking. However, MnO$_x$/SiO$_2$ based redox catalysts were not able to achieve significantly higher ethylene yields than thermal cracking. These redox catalysts were composed of distinct manganese oxide and SiO$_2$ phases. It is noted that manganese and silicon also form mixed oxides which may exhibit significantly different redox properties than the SiO$_2$ supported MnO$_x$ investigated. Mixed Mn and Si oxides are particularly interesting for CL-ODH due to the natural abundance of manganese silicates and their environmentally benign nature. It has been reported that mixed Mn and Si Oxides can release oxygen at high temperatures with satisfactory activity and stability for chemical looping combustion.\textsuperscript{42–44} Manganese silicates have been previously studied for the oxidative coupling of methane\textsuperscript{45} and been utilized in processes for hydrocarbon dehydrogenation.\textsuperscript{46}
This study focuses on the development of manganese silicate redox catalysts for the ODH of ethane in a CL-ODH scheme. The effect of a sodium tungstate precursor is also investigated as a promoter as previous studies have shown it to be effective for ODH of ethane when utilized with manganese based redox catalysts due to the suppression of CO\textsubscript{x} formation from the over oxidation of hydrocarbons.\textsuperscript{12,14} ASPEN Plus simulations are also performed in order to compare a CL-ODH process with manganese silicate based redox catalysts with traditional steam cracking.

4.3 Experimental

4.3.1 Redox Catalyst Synthesis

A solid state reaction (SSR) method was used to synthesize manganese silicate particles. First, Mn\textsubscript{3}O\textsubscript{4}(Noah Technologies, 99.5%) and SiO(Sigma-Aldrich, 10–20 nm, 99.5%) powders were mixed together in the desired ratio for 12 h in a planetary ball mill (XBM4X, Columbia International) at a rotation speed of 250 rpm. The mixture is then pressed into pellets by a hydraulic press (YJ-15T, MTI Corporation) at a pressure of 20 MPa. The pellets were then annealed in air in a tube furnace (GSL-1500-X50, MTI Corporation) at 1100 °C for 8 h. After annealing the particles, the particle were ground and sieved.

Three different molar ratios of Mn:Si were synthesized, 70:30, 30:70 and 05:95. A sodium tungstate promoter was added to the base redox catalyst through incipient wetness impregnation. Sodium tungstate dihydrate (Sigma Aldrich, 99.5%) was dissolved in water and then added on to the MnSiO\textsubscript{x} catalyst. Two different weight loadings were synthesized: 1.7wt.% and 0.85 wt.% sodium. After drying overnight at 80 °C, the promoted redox catalyst was annealed in air in a tube furnace at 1100 °C for 8 h.
4.3.2 Ethane ODH Experiments

Reaction testing was performed in a 1/4’’ O.D. × 1/8” I.D quartz U-tube reactor loaded with 0.5 g of catalyst particles sieved between 425 μm and 850 μm. To hold the catalyst particles in place and reduced the gas volume of the heated reactor zone, 16 mesh white alumina grit was loaded on each side of the catalyst particles. For blank tube runs, the entire tube was packed with the white alumina grit to maintain consistent gas residence times. The quartz U-tube was heated by a tube furnace and the gas composition and flow rate in the reactor was controlled with mass flow controllers with an automated valve manifold.

In order to determine the activity of the catalysts for the ODH of ethane, redox cycle experiments were performed. During the reduction step, the reactor environment was comprised of 80% ethane balance argon, and during the oxidation step it was changed to 17% oxygen balance argon. After each reduction and oxidation step, 100% argon was flowed into the reactor to purge any remaining gasses. The reactor gas manifold is configured such that the total flow rate into the reactor does not change between the purge and reduction steps. GHSV values were calculated assuming a 1mL catalyst bed volume. Before ODH testing, the redox catalysts were pretreated at a GHSV = 4500 h$^{-1}$ with 2 redox cycles comprising of a 3 min reduction step (in 80% ethane) and 3 min oxidation step (in 17% oxygen) at 900 °C to obtain a redox catalyst with stabilized chemical and physical properties. During ODH redox cycles, a GHSV of 4500 h$^{-1}$ or 3000 h$^{-1}$ and temperatures between 850 °C and 800 °C were used for testing of redox catalysts. During the reduction step, a total of 5 standard mL of ethane (with 1.25 ml argon dilution) was flown (5 s injection at GHSV = 4500 h$^{-1}$ and 7.5 s injection at GHSV = 3000 h$^{-1}$) into the reactor and the oxidation step was 3 min. The WHSV value for the reduction step was 9.64 h$^{-1}$ at
GHSV = 4500 h\(^{-1}\) and 6.43 h\(^{-1}\) at GHSV = 3000 h\(^{-1}\). The purge step between the reduction and oxidation steps was 5 min.

The products from the reduction and oxidation steps were collected in a gas sampling bag and characterized using a gas chromatograph (GC). An Agilent 7890 Series Fast RGA GC with two thermal conductivity detector (TCD) channels (He/TCD channel for CO/CO\(_2\) analysis, Ar/TCD channel for H\(_2\) analysis), and a flame ionization detector (FID) channel for hydrocarbon analysis was used. The system was calibrated using a refinery gas calibration standard (Agilent Part # 5190- 0519). As internal standard experiments indicated insignificant coking or tar formation under the conditions tested, a carbon mass balance was used to calculate the yields. The selectivity and conversion values for carbonaceous species were calculated relative to the carbon mass balance. The total amounts of hydrogen formed and converted to water were calculated by hydrogen mass balance of all recovered species. Additional information and formulas for selectivities, yields and hydrogen conversion calculations have been included in Appendix C.

### 4.3.3 Redox Catalyst Characterizations

Adsorption isotherms were collected on a Micromeritics ASAP 2010 at 77 K using N\(_2\) as the adsorbent gas. The surface areas were evaluated using Brunauer–Emmett–Teller (BET) theory. All of the samples were degassed at 473 K under vacuum before the measurements.

Phase identification of as-prepared redox catalysts was performed using Powder X-Ray Diffraction (XRD). A Rigaku SmartLab X-ray Diffractometer with Cu K\(\alpha\) (\(\lambda = 0.1542\) nm) radiation operating at 40 kV and 44 mA. A scanning range of 10–70° (2\(\Theta\)) with a step size of 0.1° holding for 3.5 s at each step was used to generate XRD patterns.
To determine the oxygen capacity, redox catalysts underwent redox cycles on a Thermal Gravimetric Analyzer (TGA, SETARAM SETSYS Evolution). As prepared catalysts were loaded into the instrument and then heated to 850 °C in a 10% O\textsubscript{2}/90% He environment to maintain an oxidized catalyst. Next, the flow is switched to 100% He to purge oxygen and then to a 10% H\textsubscript{2}/90% He environment to reduce the catalyst. The hydrogen is then purged and the environment is switched back to 10% O\textsubscript{2}/90% He to re-oxidize the catalyst. A total of 20 cycles were performed and the oxygen capacity was determined from the last 3 redox cycles.

X-ray photoelectron spectroscopy (XPS) was used to analyze surface compositions and oxidation states of fresh, reduced, and cycled variants of each of the four catalysts. For the cycled samples, redox catalyst particles that had undergone over 50 redox cycles were used. The catalysts were re-oxidized at 850 °C and then purged in an inert environment at 850 °C. The XPS system consists of a Thermo-Fisher Alpha 110 hemispherical energy analyzer, a Thermo-Fischer XR3, 300 W dual anode X-Ray source, and an Al anode was used for all the analyses. The spectra energies were calibrated to an adventitious C1s peak of 284.6 eV.

Ethane temperature programmed reduction (TPR) experiments were conducted using the quartz U-tube reactor as described previously and QMS MKS Cirrus II. 0.5 g of catalysts (particle size of 425–850 μm) was loaded into the U-tube and then heated to 900 °C for 30 min in a 10% oxygen balance argon environment to clean and fully oxidize catalyst. After the catalyst was cooled down to room temperature in 10% oxygen, the flow was changed to 5% ethane in argon. The reactor was then heated quickly to 500 °C and held to stabilize the temperature in the reactor. The catalyst was then heated to 900 °C at a rate of 2 °C/min and held for 5 min. All of the reactor effluent was analyzed by a QMS MKS Cirrus II.
4.3.4 Process Evaluations

ASPEN Plus® simulation was carried out using a CL-ODH model published previously. Ethane conversion and product distributions from 1.7 wt.% Na promoted redox catalyst (Mn:Si = 70:30) were used in the model to estimate the process performance using the promoted Si-Mn redox catalyst. The performance of the CL-ODH process was then compared with that of a reference steam-cracking process. Further details with respect to the ASPEN model and simulation can be found in the reference and Appendix C.

4.4 Results and Discussion

4.4.1 Redox Catalyst Characterization

XRD patterns of the as prepared manganese silicate redox catalysts are show in Fig. 4.2. For all the redox catalysts, characteristic peaks of the Mn$_7$SiO$_{12}$ phase (PDF# 04-008-9539) and the $\alpha$-cristobalite phase (PDF# 04-008-7641) were detected. Promoted redox catalysts also showed the cubic Na$_2$WO$_4$ phase (PDF# 04-008-8508). It can be seen that as the Mn content increases, the intensity of peaks associated with Mn$_7$SiO$_{12}$ increases and peaks associated with SiO$_2$ decrease in intensity. The $\alpha$-cristobalite phase that is detected by XRD is likely to be excess $\alpha$-cristobalite that is not converted into Mn$_7$SiO$_{12}$. XRD patterns of redox catalysts after reaction testing can be found in Appendix C (Fig. C.5). BET analysis indicated that the surface areas for all the base redox catalysts were less than 1 m$^2$/g.
Figure 4.2: XRD patterns of as-prepared redox catalysts (a) un-promoted redox catalysts at three different Mn:Si ratios: 05:95, 30:70 and 70:30; (b) un-promoted and promoted (1.7wt%, 0.57wt% Na) redox catalysts with Mn:Si = 70:30. [a]PDF# 04-008-9539 [b]PDF# 04-008-7641 [c]PDF#04-008-8508
Oxygen capacity values, determined from the % of mass lost during H\textsubscript{2} – O\textsubscript{2} redox cycling in the TGA, are summarized in Table 4.1. As the ratio of Mn:Si increased, the oxygen capacity of the redox catalyst also increased. These results indicate that the Mn\textsubscript{7}SiO\textsubscript{12} phase is primarily responsible for oxygen donation during the reduction step. When the rate of oxygen loss/donation was calculated as in a previous study\textsuperscript{12}, the rate of oxygen loss of the Mn:Si = 70:30 redox catalyst (Fig. C.1) was lower than Mg\textsubscript{6}MnO\textsubscript{8} redox catalysts, but higher than Mn/SiO\textsubscript{2} redox catalysts. The maximum oxygen donation rate for Mn:Si = 70:30 was \(~3\%\)/min (Fig. C.1), 0.8\%\)/min for Mn/SiO\textsubscript{2} and 7\%/min for Mg\textsubscript{6}MnO\textsubscript{8} (reported in our previous study).

### Table 4.1: Reaction data for P and W promoted redox catalysts at 850°C and GHSV= 4500hr\textsuperscript{-1}

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Oxygen Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:Si = 70:30</td>
<td>5.84%</td>
</tr>
<tr>
<td>Mn:Si = 30:70</td>
<td>1.94%</td>
</tr>
<tr>
<td>Mn:Si = 05:95</td>
<td>0.41%</td>
</tr>
</tbody>
</table>

#### 4.4.2 ODH reaction testing

In order to determine the ODH performance of the un-promoted redox catalysts, they were tested at 850 °C under a GHSV of 4500 h\textsuperscript{-1}. A blank (thermal cracking) experiment was also performed for comparison (Table 4.2). A more detailed product breakdown can be found in Appendix C. Reaction testing indicates that the presence of a redox catalyst improves ethane conversion when compared to thermal cracking for all Mn:Si ratios. While the Mn:Si = 70:30 redox catalyst exhibit the lowest ethylene yield (45.97\%) and highest CO\textsubscript{x} selectivity (33.70\%) of all the un-promoted redox catalysts, it has a significantly higher H\textsubscript{2} conversion (95.29\% vs. 52.95\% and 22.77\%). The conversion of H\textsubscript{2} to water helps push the equilibrium of ethane ODH forward as well as generate heat for the overall CL-ODH process. Previous studies have determined that a H\textsubscript{2} conversion of 70\% is desired for the CL-ODH process from a heat balance.
standpoint and the addition of Na$_2$WO$_4$ as a promoter has been previously shown to lower H$_2$ conversion. Therefore, we chose the Mn:Si = 70:30 redox catalyst to be promoted with Na$_2$WO$_4$ as it has the highest H$_2$ conversion value and the highest oxygen carrying capacity.

After promotion with Na$_2$WO$_4$ at two different loadings (1.7% and 0.57 wt.% Na), the CO$_x$ selectivity decreased significantly. The 1.7 wt.% Na promoted redox catalyst had a lower CO$_x$ selectivity (1.93% vs. 3.73%) and H$_2$ conversion (74.06% vs. 88.16%) and a slightly higher ethylene yield (58.2% vs. 58.1%). These results indicate that the 1.7 wt. % Na promoted redox catalyst is superior due to its higher ethylene yield, lower CO$_x$ selectivity while still converting more than 70% of the hydrogen produced during the ODH reaction.

Table 4.2: ODH reaction data at 850°C and GHSV=4500hr$^{-1}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ethane Conversion</th>
<th>Ethylene Selectivity</th>
<th>CO$_x$ selectivity</th>
<th>H$_2$ conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>62.87%</td>
<td>89.95%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Mn:Si = 70:30</td>
<td>80.51%</td>
<td>57.10%</td>
<td>33.70%</td>
<td>95.29%</td>
</tr>
<tr>
<td>Mn:Si = 30:70</td>
<td>66.57%</td>
<td>84.91%</td>
<td>4.09%</td>
<td>52.95%</td>
</tr>
<tr>
<td>Mn:Si = 05:95</td>
<td>64.19%</td>
<td>88.07%</td>
<td>1.36%</td>
<td>24.11%</td>
</tr>
<tr>
<td>Mn:Si = 70:30 – Na$_2$WO$_4$ (1.7wt% Na)</td>
<td>67.15%</td>
<td>86.66%</td>
<td>1.93%</td>
<td>74.06%</td>
</tr>
<tr>
<td>Mn:Si = 70:30 – Na$_2$WO$_4$ (0.57wt% Na)</td>
<td>69.41%</td>
<td>83.68%</td>
<td>3.73%</td>
<td>88.16%</td>
</tr>
</tbody>
</table>

Further reaction testing was done on the un-promoted and 1.7 wt.% Na promoted Mn:Si = 70:30 redox catalyst to test the effects of GHSV (Fig. 4.3a) and temperature (Fig. 4.3b). A more detailed product breakdown can be found in Appendix C. It can be seen that the promoted
redox catalyst has a higher ethylene yield than the un-promoted redox catalyst and thermal cracking under all the tested conditions. As expected, a decrease in GHSV led to an increase in ethane conversion and a decrease in ethylene selectivity. The 1.7 wt.% Na promoted redox catalysts had the smaller drop in ethylene selectivity (86.66%–82.64%) than the un-promoted redox catalysts (57.10%–51.35%) when the GHSV was decreased from 4500 h$^{-1}$ to 3000 h$^{-1}$. A decrease in GHSV leads to an increase in gas residence time, which can promote the sequential combustion of ethylene products. With decreasing reaction temperature, the ethane conversion also decreases while the ethylene selectivity increases. The 1.7wt% Na promoted redox catalyst exhibited a smaller selectivity drop (91.64%–82.64%) than the un-promoted redox catalyst (76.1%–51.35%) as the temperature increased from 800 °C to 850 °C. At all temperature and GHSV conditions, the 1.7 wt.% Na promoted redox catalyst had a higher ethylene yield than the un-promoted redox catalysts and thermal blank.
Figure 4.3: ODH reaction data (a) at varying GHSV (Blue: 3000hr$^{-1}$, Red: 4500hr$^{-1}$ and 850°C) b) at varying temperatures (Green: 800°C, Blue: 825°C, Red: 850°C and GHSV=3000hr$^{-1}$). Arrows point in direction of increasing GHSV or temperature.
While there is a large increase in the ethylene yield between the unpromoted and 1.7 wt.% Na promoted redox catalyst (30.4% at 850 °C and GHSV of 3000 h$^{-1}$), the ethylene yield of the blank sample is only slightly less than the 1.7 wt.% Na promoted redox catalyst (1.4% at 850 °C and GHSV of 3000 h$^{-1}$). However there is a significant difference in the overall heat of reaction between the blank, un-promoted and 1.7 wt.% Na promoted redox catalyst (Fig. 4.4). The blank sample has an endothermic heat of reaction (94.9 kJ/mol ethane each pass), both redox catalysts lead to exothermic overall heats of reaction $[-258.5$ (un-promoted) and -29.2 (1.7 wt.% Na promoted) kJ/mol ethane each pass]. The exothermicity for both redox catalysts is due to the combustion of hydrogen and hydrocarbons ($CO_x$ formation). This means that in the blank (thermal cracking) case, heat would need to be provided to maintain the temperature for thermal cracking. In comparison, CL-ODH using these redox catalysts can allow autothermal operations. Further details with respect to the benefit of the autothermal CL-ODH reactions are provided in the ASPEN Plus® simulation section.
Figure 4.4: Comparison of a) ethylene yield and b) Overall heat of reaction. (Temperature = 850°C, GHSV of 3000hr⁻¹)
It is important for a redox catalyst in the proposed CL-ODH scheme to remain stable for an extended number of redox cycles. A 25 cycled redox test shows no deactivation or loss in selectivity for the 1.7 wt.% Na promoted redox catalyst, indicating that its performance is stable over these 25 redox cycles (Fig. 4.5).

![Figure 4.5: 25 cycle Ethane ODH data for 1.7wt% Na promoted redox catalyst](image)

4.4.3 Ethane Temperature Programmed Reaction

In order to study the ODH reaction pathway over the manganese silicate redox catalysts, ethane TPR were performed. The discussion below will focus on the blank, un-promoted and 1.7 wt.% Na promoted Mn:Si = 70:30 redox catalysts. Mass spectra of mass 26 (ethylene), 44 (carbon dioxide), and 18 (water) from the TPR experiments are shown in Fig. 4.6. Mass spectra of Mass 30 (ethane) can be found in Fig. C.2. For the thermal blank, the only mass detected during the TPR experiment was mass 26, due to the lack of available oxygen in the sample. The onset temperature for ethylene production was 775 °C, which corresponds with thermal cracking
temperatures of ethane. The un-promoted redox catalyst showed an ethane conversion onset temperature of \( \sim 625 \, ^\circ\text{C} \), well below thermal cracking temperatures. The deep oxidation of ethane led to the production of carbon dioxide and water which was followed by ethylene production (onset temperature of 700 \( ^\circ\text{C} \)). On the 1.7 wt.% Na promoted redox catalyst, the onset temperature for carbon dioxide, water, and ethylene were all similar to thermal cracking. As reported in previous work on sodium tungstate promoted manganese based redox catalysts\(^\text{14}\), the sodium tungstate promoter suppresses the over oxidation of ethane/ethylene through the inhibition of ethane activation on the surface. While both redox catalysts are active for hydrogen combustion, the un-promoted redox catalyst is also active for the deep oxidation of ethane and ethylene, leading to higher ethane conversion and lower ethylene selectivity.

**Figure 4.6:** Ethane TPR results for Mass 26(ethylene), Mass 18(water), and Mass 44 (carbon dioxide)
4.4.4 Surface Characterization

XPS analysis was performed to determine the nature of surface manganese and silicon species on the redox catalysts. The three redox catalysts studied were the un-promoted, 1.7 wt.% Na, and 0.57 wt.% Na redox catalysts (Mn:Si = 70:30). For each of these redox catalysts, we analyzed two different variations: as-prepared and cycled redox catalysts (undergone more than 50 redox cycles ending in oxidation and cooled under an inert environment). In Table 4.3, the near-surface atomic composition (normalized, carbon and oxygen free basis) for all the redox catalysts analyzed are summarized. On both as-prepared un-promoted and promoted redox catalysts, it can be seen that there is a significant enrichment of Si as compared to Mn:Si ratio of the bulk base redox catalyst. There is also an enrichment of sodium on the promoted redox catalysts similar to the enrichment found on sodium tungstate promoted Mg₆MnO₈. The as-prepared Na enrichment factor (observed surface Na% divided by the bulk Na%) is 3.69 for the 1.7 wt.% Na promoted redox catalyst and 4.75 for the 0.57 wt.% Na promoted redox catalyst. The ratio of Na to W on the as-prepared promoted redox catalysts is about 2, as found in sodium tungstate. After cycling, there is a slight enrichment of Mn and loss of Si on the near-surface of both unpromoted and promoted redox catalysts. For the 1.7 wt.% Na promoted redox catalyst, there is a small decrease of both Na and W after cycling, decreasing the Na enrichment factor to 2.75. However, on the 0.57 wt.% Na promoted redox catalyst there is a slight enrichment of both Na and W increasing its Na enrichment factor to 5.70. These results indicate that i) tungsten is able to retain sodium on the surface of the catalyst and can cooperate with alkali species to suppress deep oxidation of hydrocarbons and ii) there is an enrichment of sodium tungstate on the surface of the redox catalyst. DSC runs on the 1.7 wt.% Na promoted redox catalyst show a melting behavior at 650 °C, likely corresponding to the melting of Na₂WO₄ which has a bulk
melting temperature of 698 °C. These results along with XPS surface analysis indicate that the Na₂WO₄ forms a physical layer on the near surface of the catalyst and this layer may be molten at the reaction conditions.

### Table 4.3 Near-surface atomic % on as-prepared and cycled catalysts (oxygen and carbon free basis)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn%</th>
<th>Si%</th>
<th>Na%</th>
<th>W%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted: as-prepared</td>
<td>27.57</td>
<td>72.43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Un-promoted: cycled</td>
<td>33.84</td>
<td>66.16</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.7wt% Na promoted: as-prepared</td>
<td>21.00</td>
<td>51.47</td>
<td>18.35</td>
<td>9.19</td>
</tr>
<tr>
<td>1.7wt% Na promoted: cycled</td>
<td>35.49</td>
<td>43.94</td>
<td>13.65</td>
<td>6.92</td>
</tr>
<tr>
<td>0.57wt% Na promoted: as-prepared</td>
<td>27.73</td>
<td>60.80</td>
<td>8.27</td>
<td>3.21</td>
</tr>
<tr>
<td>0.57wt% Na promoted: cycled</td>
<td>29.66</td>
<td>56.47</td>
<td>9.91</td>
<td>3.96</td>
</tr>
</tbody>
</table>

Analysis of the Si 2p peak on both the fresh and cycled redox catalysts can be seen in Fig. 4.7. On all as-prepared redox catalysts (Fig. 4.7a), peaks associated with SiO₂ species (cristobalite and/or quartz)⁵⁰ and the orthosilicate([SiO₄]⁻⁴) mixed oxides⁵⁰,⁵¹ were found. The SiO₂ type species is consistent with the α-cristobalite phase observed in XRD (Fig. 4.2) and/or an amorphous silica phase. The ortho-silicate type species is completely consistent with Mn₇SiO₁₂, although the presence of XRD insensitive Mn₂SiO₄ surface species cannot be entirely dismissed. On the cycled redox catalysts (Fig. 4.7b), it can be seen that there was decrease in the overall Si 2p peak binding energy from 103.2 eV to 101.9 eV. Peaks associated with SiO₂ species were found again, but their relative intensity decreased. The orthosilicate type peak is still present consistent with unreduced Mn₇SiO₁₂. There is also a new peak consistent with the [SiO₃]⁻² ions.⁵¹ XRD of the cycled samples (Fig. C.5) support assignment of this peak to MnSiO₃. This is consistent with reports that during oxygen is released from Mn₇SiO₁₂, SiO₂ is consumed to form MnSiO₃.⁵²
Figure 4.7: XPS spectra of Si 2p peaks of a) as-prepared and b) cycled redox catalysts
The Mn 3s spectrum has been previously used to distinguish manganese oxidation states.\textsuperscript{53} The Mn 3s spectrum has two multiplet peaks caused by the coupling of non-ionized 3s electrons with 3d valence band electrons. The ΔeV between the two peaks on the Mn 3s spectrum can be used to estimate the average oxidation state of manganese. As the average oxidation state decreases, the ΔeV increases. This value for each of the tested redox catalysts can be found in Table 4.4. For all of the as-prepared redox catalysts, the ΔeV between the two multiplet peaks are all \( \sim 5.4 \) eV which corresponds to an average oxidation state between 2+ and 3+.\textsuperscript{54} After cycling, the ΔeV value increases to \( \sim 6.0 \) eV for all redox catalysts, indicating decreasing oxidation state. Spectra on the Mn 3s peaks can be found in Appendix C (Figs. C.3 and C.4).

\textbf{Table 4.4} ΔeV of Mn 3s multiplet peaks for as-prepared and cycled redox catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn 3s ΔeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-promoted: as-prepared</td>
<td>5.3</td>
</tr>
<tr>
<td>Un-promoted: cycled</td>
<td>5.9</td>
</tr>
<tr>
<td>1.7wt% Na promoted: as-prepared</td>
<td>5.4</td>
</tr>
<tr>
<td>1.7wt% Na promoted: cycled</td>
<td>5.8</td>
</tr>
<tr>
<td>0.57wt% Na promoted: as-prepared</td>
<td>5.4</td>
</tr>
<tr>
<td>0.57wt% Na promoted: cycled</td>
<td>6.2</td>
</tr>
</tbody>
</table>

While it is difficult to distinguish between the Mn2+ and Mn3+ oxidation states from the Mn 2p spectra due to their similar peak positions\textsuperscript{55}, the Mn 2p peak can also be used in addition to the Mn 3s peak to gain insight into the valence state of manganese. In Fig. 4.8, the Mn 2p spectra are shown for all of the as-prepared and cycled redox catalysts. There were no significant differences in the peaks between the different redox catalysts; the overall Mn 2p 3/2 peak position was between 641.3 and 641.4 eV. However there is a small feature on the cycled redox catalysts at \( \sim 647 \) eV that is not present of the as-prepared catalysts. This is consistent with a satellite peak for Mn\textsuperscript{2+} \textsuperscript{55} and the presence of MnSiO\textsubscript{3}. In contrast to the to the previously studied
Mg₆MnO₈ redox catalysts, the lack of a high binding energy shoulder for the Mn 2p 3/2 peak indicates a lack of near surface Mn⁴⁺ species on the manganese silicate redox catalysts. On Mg₆MnO₈ redox catalysts, as the presence of Mn⁴⁺ on the near surface of the redox catalyst was associated with deep oxidation. Its absence on the unpromoted manganese silicate redox catalyst is consistent with the improved ethylene selectivity of the un-promoted manganese silicate as compared to un-promoted Mg₆MnO₈ (51.4% vs. 17.9%). However, since all cycled manganese silicate redox catalysts have similar oxidation states, the average oxidation state was not the primary factor in determine the selectivity of the catalyst. Instead, the sodium tungstate promoter is likely to act as a physical blocker, suppressing the surface activation of ethane and ethylene and the over oxidation to COₓ species.

Figure 4.8: XPS spectra of Mn 2p peaks of as-prepared and cycled of all redox catalysts
4.4.5 Process Analysis and practical implications

The performance of the CL-ODH process is determined using the ASPEN Plus® simulator and is compared with traditional steam cracking, based on the models developed in our previous work.\textsuperscript{11} The product distribution for CL-ODH, based on the results from the 1.7 wt.% Na promoted redox catalyst (see Table C.2) is used for the simulation, whereas data from literature is used for steam cracking.\textsuperscript{2} The ASPEN Plus® modules, property methods, and physical property databanks are summarized in Table C.3 and the flowsheet for the CL-ODH process is shown in Fig. C.6. Owing to the selective combustion of H\textsubscript{2} product, the reactor-regenerator scheme of the CL-ODH is net exothermic, unlike the steam cracking process, which requires all overall energy input of 15.2 GJTh/tonne ethylene. Overall, the CL-ODH with the promoted Mn-Si redox catalyst requires 1.7 GJTh of energy for each tonne of ethylene produced. This corresponds to 89% less energy demand compared to steam cracking. The primary energy saving is resulted from the ethane conversion step, which is net exothermic as compared to the highly endothermic cracking process. In addition, 38% decrease in compression work is projected for downstream separations. Comparisons for the energy distributions of the two processes are depicted in Fig. 4.9. Compared to steam cracking, the CL-ODH can result in 89% reduction in the CO\textsubscript{2} and NO\textsubscript{x} emissions, which is proportional to its energy savings. As shown in Fig. C.7, the cracking process has an energy deficiency of 1.42 GJth/tonne ethylene even after all the fuel gas produced in the process (CO, H\textsubscript{2} and CH\textsubscript{4}) are combusted. The CL-ODH, on the other hand, has an excess fuel equivalent to roughly 5 GJth/tonne ethylene. These results highlight the potential advantages and benefits of CL-ODH using the Mn-Si based redox catalysts.
The current study investigated manganese silicates as redox catalysts for the oxidative dehydrogenation of ethane in a chemical looping scheme. Redox catalysts with different molar ratios of Mn:Si were synthesized. Characterization of the redox catalysts indicated the presence of Mn$_7$SiO$_{12}$ and SiO$_2$ phases. The Mn:Si = 70:30 redox catalyst was the preferred base redox catalyst due its high oxygen carrying capacity and H$_2$ conversion, despite its relatively high CO$_x$ selectivity (36.52% at 3000 h$^{-1}$ GHSV and 850 °C). When promoted with sodium tungstate, the ethylene yield increased significantly (44.08%–63.33%) while CO$_x$ selectivity decreased (36.52%–2.96% at 3000 h$^{-1}$ GHSV and 850 °C). Ethane TPR indicated that the sodium tungstate promoter suppresses the over oxidation of ethane and ethylene and decreases the redox catalyst’s ability to activate ethane.

The current study investigated manganese silicates as redox catalysts for the oxidative dehydrogenation of ethane in a chemical looping scheme. Redox catalysts with different molar ratios of Mn:Si were synthesized. Characterization of the redox catalysts indicated the presence
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(36.52%–2.96% at 3000 h$^{-1}$ GHSV and 850 °C). Ethane TPR indicated that the sodium tungstate
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ability to activate ethane.
4.6 References


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Chapter 5: Mixed Iron-Manganese as Redox Catalysts for Chemical Looping-Oxidative Dehydrogenation of Ethane with Tailorable Heat of Reactions

5.1 Abstract

The chemical looping-oxidative dehydrogenation (CL-ODH) of ethane is explored in this study. In CL-ODH, a redox catalyst donates lattice oxygen to combust hydrogen formed from ethane dehydrogenation (ODH reactor) and is then transferred to a separate reactor (regenerator) where it is re-oxidized with air. Typically, the ODH reactor is endothermic because of the reduction of the redox catalyst. This energy demand is met through sensible heat carried by the redox catalyst from the regenerator, which operates at a higher temperature than the ODH reactor. This temperature difference leads to exergy losses. An Fe-Mn redox catalyst (molar ratio = 20-80) had a tunable exothermic heat of reduction and promotion with Na$_2$WO$_4$ resulted in high ethylene yields due to the suppression of surface Fe/Mn. ASPEN Plus® simulations indicated that Fe-Mn redox catalysts can lower the temperature difference between the two reactors with reasonable solids circulation rates, which can lead to efficiency improvements for CL-ODH.

5.2 Introduction

Ethylene is a heavily utilized commodity chemical for the production of important compounds such as polyethylene, ethylene oxide, dichloroethane, ethylbenzene, and acetaldehyde.$^1$ Worldwide production of ethylene is projected to more than triple by the year 2050 relative to the 2013 production level of 150 million tonnes/year.$^2$ Due to the recent increase in shale gas production, ethylene production from ethane, the second most abundant component in shale gas, has become particularly attractive.$^3$ The predominant production route for ethylene is the steam cracking of ethane, in which ethane is pyrolyzed at elevated temperature in the
presence of steam diluent.\textsuperscript{1} This endothermic process requires fired heaters to supply the necessary high heating rates, resulting in substantial CO\textsubscript{2} and NO\textsubscript{x} emissions from the combustion of carbonaceous fuels such as methane.\textsuperscript{4} Additional energy demands arise from downstream compression and separation units such that, in total, more than 16 GJ of energy is required to produce one ton of ethylene through steam cracking.\textsuperscript{1} Thermodynamic equilibrium limitations on ethane conversion and coke formation in steam crackers also limit the performance of steam crackers.\textsuperscript{5}

Ethylene production through direct oxidative dehydrogenation (ODH) of ethane has been explored to replace steam cracking.\textsuperscript{6–10} ODH utilizes a co-feed of ethane and oxygen, the latter of which combusts hydrogen and removes equilibrium limitations. The resulting reaction is exothermic (\(\Delta H = -105\text{ kJ/mol at } 850^\circ C\)):

\[
\text{C}_2\text{H}_6 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}
\]

Ethane ODH with oxygen co-feed has been extensively studied in terms of both catalyst development and mechanistic investigations.\textsuperscript{11–19} Satisfactory ethylene yields (>40%) were reported in numerous studies,\textsuperscript{20–29} with a MoVTeNbO catalyst showing an ethylene selectivity of 81\% and ethylene yield of 75\%.\textsuperscript{30} Although these results are highly promising, conventional ODH faces a few practical challenges. For instance, this method introduces the potential safety hazard of mixing ethane and gaseous oxygen, and air separation units upstream of the ODH reactor are costly and energy-intensive to build and operate. Downstream separation and purification of the ethylene product stream is also complex and energy intensive.\textsuperscript{31} To overcome the challenges of co-feeding ethane ODH, we investigated a two-step chemical looping ODH (CL-ODH) scheme, which addresses many of the challenges facing catalytic ethane ODH.\textsuperscript{31–35} In CL-ODH, a redox catalyst donates oxygen from its crystal lattice to convert ethane to ethylene
and water. Subsequently, the reduced catalyst is transferred to the regenerator where it is re-oxidized in air and sent back to the ODH reactor, completing the redox cycle. Acting as an oxygen carrier, the redox catalyst can be repeatedly reduced and oxidized.

\[
\text{C}_2\text{H}_6 + \text{MeO}_x \rightarrow \text{C}_2\text{H}_4 + \text{MeO}_{x-1} + \text{H}_2\text{O} \text{ (ODH reactor)}
\]

\[
\text{MeO}_{x-1} + \frac{1}{2}\text{O}_2 \text{ (air)} \rightarrow \text{MeO}_x + \text{heat} \text{ (Regenerator)}
\]

There are several potential benefits of CL-ODH over traditional ODH: (i) CL-ODH avoids the safety issues inherent to co-feeding ethane and oxygen; and (ii) the use of an oxygen carrier eliminates the need for costly air separation units. In CL-ODH, process heat integration between the two reactors is accomplished through the direct heat transfer of the sensible heat in the oxygen carrier particles, resulting in reduced energy requirements. Experimental studies indicated that CL-ODH can result in higher single-pass yield of ethylene compared to thermal cracking.\textsuperscript{33–37} ASPEN Plus\textsuperscript{®} simulations further indicated that the CL-ODH scheme can reduce energy consumption and emissions by up to 82% compared to traditional steam cracking because of the selective combustion of hydrogen and lower demand for downstream separation.\textsuperscript{31}

Compared to conventional ODH in the presence of a heterogeneous catalyst, CL-ODH is comparatively less developed. Previous CL-ODH studies have examined redox catalysts containing vanadium and molybdenum,\textsuperscript{38–42} but the highest obtained ethylene yield was 38% with the majority of catalysts showing ethylene yields below 20%. Further concerns with toxicity, high material cost, and potential stability/sublimation issues may limit and attractiveness of V and Mo based redox catalysts. Manganese and iron oxides are alternative redox catalysts that are abundant, low-cost and relatively benign and each have been studied for chemical looping applications.\textsuperscript{43–49} Mn oxides have been studied as oxygen carriers for chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) of methane.
We have previously reported Mn-containing oxides such as mixed Mn-Mg and Mn-Si oxides for CL-ODH. For instance, Mg₆MnO₈ exhibited a low ethylene selectivity of 14% at 850°C and 3000hr⁻¹ GHSV, but the selectivity was increased to 48.5% with a sodium pyrophosphate promoter and to 89.2% with a sodium tungstate (Na₂WO₄) promoter. A manganese silicate oxygen carrier showed ethylene selectivity of 44.08% at 850°C and 3000hr⁻¹ GHSV, which increased to 63.33% with the addition of sodium tungstate. The primary effect of Na₂WO₄ promotion was to decrease the COₓ selectivity, which was the primary undesired byproduct in CL-ODH. For instance, COₓ selectivity dropped from 36.52% to 2.96% for manganese silicate redox catalysts and from 78.04% to 2.23% for Mg₆MnO₈ redox catalysts. Alkali metal oxide promotion also improved the selectivity of redox catalysts composed of Fe-containing perovskites. Overall, alkali metal containing promoters, especially Na₂WO₄, have shown promise to improve the ethylene selectivity on various redox catalysts containing Mn and/or Fe oxides in CL-ODH.

It is noted that CL-ODH reactions carried out using the redox catalysts mentioned above are generally endothermic, with Mn₃O₄ redox catalysts showing an estimated heat of reaction of 118 kJ/mol C₂H₆, which is comparable to thermal cracking (143 kJ/mol C₂H₆). Although this endothermicity would not affect the overall exothermicity of the two-step CL-ODH cycle, the energy demand in the ODH step does need to be satisfied by the sensible heat carried by the redox catalyst particles from the regenerator. Such heat integration requirements would dictate: (i) a large temperature difference between the ODH reactor and regenerator; and/or (ii) a high solids circulation rate. As such, CL-ODH operation can potentially be further optimized by developing CL-ODH redox catalysts with lower endothermicity for CL-ODH (Figure 5.1). In this aspect, mixed Fe-Mn oxides are promising candidates considering their abilities for tunable
and spontaneous oxygen release. The present study investigates mixed Fe-Mn oxides as redox catalysts for the CL-ODH of ethane. Specifically, focuses were placed on the development of redox catalysts with less endothermic and potentially tunable CL-ODH heat of reactions while maintaining high activity and selectivity. It was determined that the best performing redox catalyst had a Fe-Mn molar ratio of 20-80. This heat of reduction of this catalyst was exothermic at all stages of reduction, and after promotion with Na$_2$WO$_4$, it was able to achieve an ethylene yield of 62.21% and a CO$_x$ selectivity of 3.15%. ASPEN Plus® simulations indicate that Fe-Mn redox catalysts can decrease the temperature difference between the ODH and regenerator reactors and while having similar solid circulation rates as traditional coal chemical looping combustion (CLC) systems. The properties of this redox catalyst will allow for the further optimization of the CL-ODH process through additional energy savings.

**Figure 5.1:** CL-ODH scheme with Mn$_3$O$_4$ (left) and Fe-Mn redox catalysts (right)
5.3 Experimental

5.3.1 Redox Catalyst Synthesis

All redox catalysts were synthesized through a sol-gel procedure in order to obtain a redox catalyst with higher homogeneity. In this procedure, metal precursors (iron (III) nitrate nonahydrate (Sigma-Aldrich ACS reagent, ≥ 98%) and manganese (II) nitrate tetrahydrate (Sigma-Aldrich, ≥ 97.0%) and citric acid (Sigma Aldrich ≥ 99.5%) were dissolved in DI water. The citric acid to total cation molar ratio was 2.5 and the mixture was stirred at 50°C for 30 minutes. Afterwards, ethylene glycol (Sigma Aldrich, anhydrous 99.8%) was added (ethylene glycol to citric acid molar ratio = 1.5) and the temperature was raised to 80°C to complete the gelation process. The resulting mixture was dried overnight at 80°C and then calcined in air at 450°C for 3 hours to decompose any nitrates and remove citric acid. Then the temperature was raised to 900°C for 8 hours in order to obtain the desired crystal phases. After calcination, the synthesized redox catalyst was sieved into 3 particles sizes: 850-425 μm, 425-250 μm, and < 250 μm. A total of three Fe-Mn molar ratios were synthesized: 20-80, 50-50 and 60-40.

Each of the base redox catalysts were promoted with sodium tungstate. The sieved redox catalyst particles were mixed with a water solution containing sodium tungstate dihydrate (Sigma Aldrich, 99.5%). The weight loading of sodium tungstate for all redox catalysts was 1.7wt% on an Na basis. The promoted particles were then dried overnight at 80°C, and then calcined in air at 900°C for an additional 8 hours. In this paper, un-promoted redox catalysts are designated by the Fe-Mn molar ratio (20-80, 50-50, and 60-40) and promoted redox catalysts are designated using the Fe-Mn molar ratio and Na2WO4 (20-80-Na2WO4, 50-50-Na2WO4, and 60-40-Na2WO4).
5.3.2 Ethane ODH Experiments

The activity of the synthesized redox catalysts for the ODH of ethane was determined using a previously described reactor setup and gas chromatography analysis. A U-tube reactor made of quartz with a 1/4” O.D and 1/8” I.D. was used for reaction testing. 0.5g of redox catalyst particles was loaded into the bottom of the reactor and alumina grit (16 mesh) was used on both sides of the U-tube to prevent loss of redox catalyst particles and to reduce the gas residence time inside the heated reactor. In order to obtain thermal cracking (blank) measurements, a U-tube with only alumina grit was used.

The gas composition and flow rate inside the quartz U-tube reactor were controlled with mass flow controllers and a valve manifold. The overall GHSV during all pretreatment steps and reaction testing was 4500hr⁻¹. During the pretreatment step, the redox catalysts underwent 2 redox cycles which were comprised of a 3 minute reduction step (80%/20% H₂/Ar) and a 3 minute oxidation step (17%/83% O₂/Ar) at 900°C. The pretreatment step resulted in a redox catalyst with stable chemical and physical properties. For ethane ODH reaction testing, the oxidation remained unchanged, but the reduction step was altered: a total of 5 mL of ethane was flown into the reactor (5 second injection of 80%/20% C₂H₆/Ar). In between each reduction and oxidation step during the pretreatment and ethane ODH reaction testing, 100% Ar was flown into the reactor for 5 minutes. Ethane ODH reaction testing was performed at 850, 825, and 800°C for all redox catalysts.

The products from the reduction step were collected in a gas bag and injected into a gas chromatograph (GC) for analysis. The GC was an Agilent 7890 Fast RGA with a flame ionization detector (FID) for hydrocarbon analysis and two thermal conductivity detectors for CO, CO₂, and H₂ analysis. A refinery gas standard (Agilent Part # 5190-0519) was used to
calibrate the GC. Mass Spectroscopy analysis of the oxidation step did not show significant
coking or tar formation, so a carbon mass balance was used to calculate ethane conversion and
hydrocarbon product selectivity and yields. The product distribution was also used to calculate
the amount of hydrogen formed during the reduction step and the amount of hydrogen converted
to water. Formulas for product selectivity, yield and hydrogen conversion can be found below
(n(x) refers to the total amount of carbon in species x measured by GC).

\[
\text{Ethane Conversion} = 1 - \frac{n(\text{Ethane})}{n(All \text{ carbon species})}
\]
\[
\text{Selectivity (species x)} = \frac{n(x)}{n(All \text{ carbon species}) - n(ethane)}
\]
\[
\text{Ethylene yield} = \text{Ethane Conversion} \times \text{Selectivity(Ethylene)}
\]
\[
H_2 \text{ combustion} = 1 - \frac{(H_2)_{out}}{(H_2)_{gen}}
\]

5.3.3 Surface Area Measurements

A Micromeritics ASAP 2020 was used to collect N\textsubscript{2} adsorption isotherms at 77K. Before
adsorption isotherms were generated, all redox catalysts were degassed at 473K. Brunauer-
Emmett-Teller (BET) theory was used to calculate surface areas from the measured adsorption
isotherms.

5.3.4 TGA/DSC Measurements

The heat of reduction of each of the redox catalysts was measured on a TA Instruments
SDT Q600 Dual Thermogravimetric Analysis (TGA)/Differential Scanning Calorimetry (DSC)
unit. First, fresh redox catalyst was loaded into the sample crucible and heated to 850°C in a 10%
O\textsubscript{2}/Ar environment to clean the redox catalyst. Then, the 5 H\textsubscript{2}/O\textsubscript{2} redox cycles were performed
on the redox catalyst. In each cycle, the initial gas flow was 10% O\textsubscript{2}/Ar. After 10 minutes, the
gas flow was switched to 100% Ar for 10 minutes and then to 10% H\textsubscript{2}/Ar for 10 minutes to
reduce the redox catalyst. After another 10 minute 100% Ar purge, the gas flow was switched to
its initial conditions (10% O₂/Ar). This completed the redox cycle and allowed the redox catalyst to be re-oxidized. The heat flow curve was integrated using TA Instruments TRIOS software in order to determine the heat of reduction of each redox catalyst. A detailed explanation of the integration process can be found in Appendix D.

5.3.5 XPS Analysis

Fresh (as-synthesized) and cycled (more than 30 C₂H₆/O₂ redox cycles, cleaned in 17% O₂/Ar at 850 °C, held at 850°C in a 100% Ar atmosphere for 1 hour, and then cooled to room temperature in 100% Ar atmosphere) redox catalysts were analyzed using X-ray photoelectron spectroscopy (XPS). Both the near-surface atomic composition and the oxidation states of manganese and iron were determined for all measured redox catalysts. All analysis was performed using an Al anode and the XPS system was comprised of a Thermo-Fisher Alpha 110 hemispherical energy analyzer and a Thermo-Fischer XR3, 300W dual-anode X-Ray source. The C₁s peak (284.6eV) was used to calibrate all spectra.

5.3.6 Process Simulation

ASPEN Plus® is used to simulate the ODH reactor and analyze the effect of obtained heat flow in the Fe-Mn system on the solid circulation rates. The ODH reactor is represented by an RStoic reactor model, using the product distribution obtained in the ethane ODH experiments. A sequential modular approach is used. The ODH reactor is operated at 850°C. Fe₂O₃ is used as a representative solid with pure ethane as the feed. The heat of the reaction is balanced so that it matches the experimentally obtained ΔH values. Additional information is provided in the Appendix D. The circulation rates of the CL-ODH system are compared with coal CLC systems, which are well studied.
5.4 Results and Discussion

5.4.1 Redox Catalyst Characterization

Figure 5.2 shows the XRD patterns for the freshly synthesized redox catalysts. The characteristic peaks for a bixbyite phase [(Fe,Mn)$_2$O$_3$ (PDF# 01-075-0894)] were observed on all un-promoted and promoted redox catalysts. The Na$_2$WO$_4$ (PDF#04-008-8508) phase was also seen on all of the promoted redox catalysts. No (Fe,Mn)$_3$O$_4$ spinel oxide phases, which represent a reduced form of mixed Fe-Mn oxides, were identified on any of the redox catalysts. The measured surface areas(Table 5.1) of the as-synthesized un-promoted redox catalysts are similar and after promotion with Na$_2$WO$_4$, the surface area for all redox catalysts decreases by around 50% in all cases.
Figure 5.2: XRD patterns of as-synthesized redox catalysts (a) un-promoted and (b) Na2WO4 promoted Fe:Mn oxide catalysts. [a]PDF# 01-075-0894 [b]PDF# 04-008-8508
Table 5.1: BET surface areas for the as-synthesized redox catalysts

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Surface Area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-80</td>
<td>3.48</td>
</tr>
<tr>
<td>50-50</td>
<td>4.10</td>
</tr>
<tr>
<td>60-40</td>
<td>3.17</td>
</tr>
<tr>
<td>20-80-$\text{Na}_2\text{WO}_4$</td>
<td>1.75</td>
</tr>
<tr>
<td>50-50-$\text{Na}_2\text{WO}_4$</td>
<td>1.28</td>
</tr>
<tr>
<td>60-40-$\text{Na}_2\text{WO}_4$</td>
<td>1.47</td>
</tr>
</tbody>
</table>

5.4.2 ODH Reaction Testing

Ethane ODH results at 850°C and a GHSV of 4500hr$^{-1}$ for all synthesized redox catalysts are summarized in Figure 5.3. All of the redox catalysts exhibited higher ethane conversions than thermal cracking (75.7-83.3% vs 62.9%) and had a H$_2$ conversion higher than 70% (which is desirable for the CL-ODH from an energy balance standpoint). When comparing the un-promoted redox catalysts, the 20-80 redox catalyst showed the highest CO$_X$ selectivity (50.7%) while the 50-50 and 60-40 redox catalysts had lower CO$_X$ selectivity values (35.2 and 37.5% respectively). These results matched with previous literature, which have shown that Mn$^{3+}$ oxides are active for the deep oxidation of hydrocarbons. In previous studies, promotion with Na$_2$WO$_4$ caused a decrease in ethane and H$_2$ conversion, but the significant increase in ethylene selectivity led to an increase in ethylene yield. For all redox catalysts, the ethylene yields significantly increased after promotion with Na$_2$WO$_4$. The largest increase in ethylene yield was observed on the 20-80 redox catalyst (33.5% to 62.2%) and the 60-40-Na$_2$WO$_4$ redox catalyst demonstrated the highest ethylene yield (64.5%). H$_2$ conversion also decreased for all promoted redox catalysts, but ethane conversion only decreased for the 20-80-Na$_2$WO$_4$ redox catalyst (78.5% to 75.9%). The increase in ethane conversion on the 50-50-
Na$_2$WO$_4$ and 60-40-Na$_2$WO$_4$ redox catalysts (75.9% to 79.6% and 75.7% to 83.3% respectively) is likely to be due to the densification of the promoted redox catalysts during reaction testing. This densification increased the effective gas residence time in the U-tube reactor, allowing for additional ethane conversion. In Figure 4, the effect of reaction temperature on ethylene and CO$_x$ selectivity is shown. As expected, a decrease in reaction temperature caused a decrease in ethane conversion and increase in ethylene selectivity (Figure 5.4a). With respect to ethylene yield, the 60-40-Na$_2$WO$_4$ redox catalyst was the best performing at all temperatures, but the yield differences are relatively small as can be seen from Figure 4a. The small differences between the promoted redox catalysts decreased as the reaction temperature decreased. A slightly different trend is seen in CO$_x$ selectivity values on the promoted redox catalysts (Figure 5.4b). At 850°C, the 20-80-Na$_2$WO$_4$ redox catalyst showed the lowest CO$_x$ selectivity (3.2%) followed by the 50-50-Na$_2$WO$_4$ redox catalyst (4.8%) and finally the 60-40-Na$_2$WO$_4$ redox catalyst (5.8%). At all temperatures, the 20:80-Na$_2$WO$_4$ redox catalyst exhibited the lowest CO$_x$ selectivity. Due to the similar ethylene yield and lower CO$_x$ selectivity, the 20-80-Na$_2$WO$_4$ redox catalyst was determined to be the best performing redox catalyst. Detailed reaction data for the 20-80-Na$_2$WO$_4$ redox catalyst at all reaction temperatures can be found in Appendix D (Table D.1)
Figure 5.3: Ethane ODH reaction data at 850°C and GHSV=4500hr⁻¹ for thermal cracking (blank) and CL-ODH in the presence of the redox catalysts.
Figure 5.4: Ethane ODH reaction data at varying temperatures a) Ethylene Selectivity vs ethane conversion and b) CO$_x$ selectivity vs ethane conversion (Green: 800°C, Blue: 825°C, Red: 850°C and GHSV=4500hr$^{-1}$).
The proposed CL-ODH scheme requires that the redox catalysts demonstrate a long lifetime. Therefore, extended redox cycling was performed on the 20-80-Na$_2$WO$_4$ redox catalyst (Figure 5.5). As the redox catalyst undergoes additional redox cycles, the ethane conversion increased until reaching a steady value at cycle 35 (80.1% to 90.0%). Over the first 35 cycles, there was also a decrease in ethylene selectivity (80.7% to 72.2%), but the ethylene yield was relatively stable (64.6% to 65.1%). There was also an increase in C3+ selectivity (8.5% to 12.2%) and CO$_x$ selectivity (3.3% to 7.5%) while the methane selectivity was relatively stable (6.9% to 7.1%). The overall C2+ selectivity, which represents the formation of value-added products, decreased by 4.8% over extended redox cycle testing (89.0% to 84.2%). After cycle 35, no significant changes in these values were observed. These results indicated that the 20-80-Na$_2$WO$_4$ redox catalyst is potentially suitable for CL-ODH applications in terms of redox stability.

Figure 5.5: Extended redox cycle testing on 20-80-Na2WO4 redox catalyst at 850°C and GHSV=4500hr⁻¹
5.4.3 XPS Analysis

XPS analysis was performed to determine the near surface atomic composition and oxidation states of iron and manganese species on the 20-80 and 20-80-Na$_2$WO$_4$ redox catalysts. As described earlier in the experimental section, 2 versions of each redox catalysts were analyzed: fresh and cycled. The near surface atomic percentages (normalized to a carbon and oxygen free basis), for all analyzed redox catalysts are shown in Table 2. On the fresh 20-80 redox catalyst, the surface atomic percentages were similar to the bulk molar ratio and after cycling there were no significant changes in the surface composition. On the fresh 20-80-Na$_2$WO$_4$ redox catalyst, both Na and W are enriched as seen on previously studied Mg$_6$MnO$_8$ and manganese silicates based redox catalysts.$^{34,35}$ The as-synthesized Na and W enrichment factor (observed surface % divided by bulk %) were 4.92 and 4.87 respectively. Also, there were twice as many Na atoms observed as W atoms on the near surface of the fresh 20-80-Na$_2$WO$_4$ redox catalyst. The is the same ratio of Na to W in sodium tungstate. When comparing the fresh and cycled 20-80 redox catalysts there were no substantial differences. The cycled 20-80-Na$_2$WO$_4$ redox catalyst had slightly lower Na and Fe surface atomic percentages when compared to the fresh 20-80-Na$_2$WO$_4$ redox catalyst, but there was a significant enrichment of W and loss of Mn which led to a decrease in the Na to W atomic surface ratio (~2 to 0.7). The decrease in this ratio is due to the loss of the Na$_2$WO$_4$ phase which was confirmed through XRD analysis of the cycled 20-80-Na$_2$WO$_4$ redox catalyst (Figure D.1). After ethane ODH reaction testing, the Na$_2$WO$_4$ phase was replaced by and (Fe,Mn)WO$_4$, NaFe(WO$_4$)$_2$ and NaFeO$_2$ phases. Unlike previously studied redox catalysts,$^{34,35,53}$ the increase in ethylene yield was not due to the formation of a physical layer of Na$_2$WO$_4$ around the base redox catalyst. Instead, the primary reason for increased selectivity of the promoted redox catalysts was likely to be the suppression
of Mn and Fe cations, and hence nonselective oxygen species, through the enrichment of Na and W on the surface of the redox catalyst. Further analysis of the XPS spectra, as discussed below, provides additional insights on the change in redox catalyst selectivity before and after Na₂WO₄ promotion.

**Table 5.2:** Near-surface atomic % on fresh and cycled catalysts (oxygen and carbon free basis)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fe%</th>
<th>Mn%</th>
<th>Na%</th>
<th>W%</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-80: fresh</td>
<td>13.21</td>
<td>86.79</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20-80: cycled</td>
<td>16.05</td>
<td>83.95</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20-80-Na₂WO₄: fresh</td>
<td>7.88</td>
<td>52.53</td>
<td>26.47</td>
<td>13.11</td>
</tr>
<tr>
<td>20-80-Na₂WO₄: cycled</td>
<td>5.79</td>
<td>37.98</td>
<td>23.09</td>
<td>33.14</td>
</tr>
</tbody>
</table>

The Mn 2p₃/₂ peak for the fresh and cycled redox catalysts can be seen in Figure 5.6a. For the fresh redox catalysts, both the 20-80 and 20-80-Na₂WO₄ had an overall Mn 2p₃/₂ peak position of 641.2 eV which is consistent with Mn³⁺. The cycled 20-80 redox catalyst had the same peak position as the fresh 20-80 redox catalyst, but the peak position shifted down by 0.5 eV for the cycled 20-80-Na₂WO₄ redox catalyst, indicating a slight decrease in the oxidation state for the near surface Mn cation. This shift was also seen on previously studied Mg₆MnO₈ redox catalysts. Figure 5.6b compares the Fe 2p₃/₂ spectra for the fresh and cycled redox catalysts. On fresh 20-80 redox catalyst, the Fe 2p₃/₂ peak was at 710.9 eV which corresponds to Fe³⁺ and promotion with Na₂WO₄, caused the Fe 2p₃/₂ peak to shift down by 0.5 eV. When comparing the fresh and cycled redox catalysts, there were no changes observed in the Fe 2p₃/₂ peak positions. While small differences in the Fe and Mn oxidation states were observed on the Na₂WO₄ promoted redox catalysts, the primary effect of the Na₂WO₄ promoter is the decrease in Fe and Mn and enrichment of Na and W species on the surface of the redox catalyst leading to increases in ethylene yield. This matches with previously observed results which indicated that
the over oxidation of methane, ethane and other hydrocarbon species can be suppressed when both sodium and tungsten are present on the surface of the redox catalyst.\textsuperscript{14,15,40,47–49}

**Figure 5.6:** XPS spectra of a) Mn 2p\text{3/2} peak and b) Fe 2p\text{3/2} of fresh and cycled redox catalysts

\textbf{Figure 5.6:} XPS spectra of a) Mn 2p\text{3/2} peak and b) Fe 2p\text{3/2} of fresh and cycled redox catalysts
5.4.4 Heat of Reaction Analysis

A potential challenge for CL-ODH is the endothermic reaction that occurs in the ODH reactor.\textsuperscript{11} Our previous studies indicate that ethane ODH on Na$_2$WO$_4$ promoted Mn oxide redox catalysts proceeds via ethane cracking in parallel with selective hydrogen combustion.\textsuperscript{14} Even though the overall two-step CL-ODH process is exothermic, the endothermic reduction of the redox catalyst with H$_2$ in the ethane conversion step makes the ODH reactor endothermic for all the redox catalysts reported to date. The necessary heat for the ODH reactor is supplied from the circulation of the redox catalysts through the regenerator. In one potential configuration with Mg$_6$MnO$_8$ based redox catalyst, the operating temperature of the regenerator needs to be 100°C higher than the ODH reactor. Since the re-oxidation of the redox catalysts is exothermic, this temperature difference allows thermal energy to be carried back to the ODH reactor through sensible heat of the redox catalysts. If the heat of reaction in the ODH reactor was less endothermic, the heat requirements of the ODH reactor would be easier to meet. This can lead to (i) decreased redox catalyst circulation rate; and/or (ii) decreased temperature differences between the two reactors. Both can result in additional capital and energy savings for CL-ODH. With this in mind, dual TGA/DSC measurements were performed to determine the heat of reduction of the mixed Fe-Mn oxides to assist the identification of redox catalysts with decreased endothermicity for ethane conversion. The average heat of reduction determined by dual TGA/DSC measurements are summarized in Table 5.3.

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Dual TGA/DSC (kJ/mol O)</th>
<th>HSC Chemistry (kJ/mol O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-80</td>
<td>-14.26</td>
<td>-14.53</td>
</tr>
<tr>
<td>50-50</td>
<td>2.40</td>
<td>1.74</td>
</tr>
<tr>
<td>60-40</td>
<td>4.75</td>
<td>7.16</td>
</tr>
</tbody>
</table>
Table 3 also included the estimated heat of reduction calculated from HSC Chemistry assuming the redox catalyst was reduced from the spinel phase to the monoxide phase. This assumption was based of TGA measurements, which indicated that the reduction of the bixbyite to the spinel phase was irreversible and the sample primarily cycled between spinel and monoxide phases (Figure D.2). The transition from the bixbyite to the spinel phase was also seen on XRD spectra of the redox catalysts after the TGA/DSC measurements (Figure D.3).

As can be seen from Table 5.3, there was good agreement between the DSC results and HSC calculations. As the iron content of the redox catalysts increases, the heat of reduction became more endothermic. This was because the reduction of Fe$_3$O$_4$ to FeO with H$_2$ is endothermic (28.85 kJ/mol O) while the reduction of Mn$_3$O$_4$ to MnO is exothermic (-25.38 kJ/mol O). Only the 20-80 redox catalyst had the desired exothermic heat of reduction, but for CL-ODH applications, it would be better to compare how the heat of reduction changes as the catalyst is reduced. In Figure 5.7, the cumulative average heat flow per mol of O released is plotted versus the weight of O donated normalized by the initial redox catalyst weight (see Appendix D). All of the redox catalysts initially had a highly exothermic heat flow. As additional lattice oxygen was donated, the cumulative average heat flow became less exothermic (Figure 6a). The 60-40 redox catalyst had the highest exothermic peak, which is likely due to the hematite phase that was detected from XRD measurements (Figure D.3). As expected from the previous heat flow data, the average heat flow for the 20-80 redox catalyst was exothermic regardless of the amount of oxygen donated while the average heat flows for the 50-50 and 60-40 redox catalysts become endothermic after extensive oxygen donation. All redox catalysts were initially able to offset the endothermicity for ethane cracking (143 kJ/mol C$_2$H$_6$ at 850 °C) at low oxygen donation. Therefore, we focused on the initial reduction of each of the redox catalysts
(Figure 5.7b). Here it was seen that the 60-40 redox catalyst was able to donate the most amount of lattice oxygen (0.16 wt%) while maintaining exothermic or heat neutral during the CL-ODH step. This is followed with 20-80 (0.14 wt%) and 50-50 (0.12 wt%) redox catalysts. Despite the higher exothermicity during the initial reduction, the 60-40 redox catalyst was a less desirable candidate than the 20-80 redox catalyst from a process development standpoint.
Figure 5.7: Cumulative average heat flow per mol of O donated for the un-promoted redox catalysts. a) The complete integrated range for each redox catalyst. b) The first weight percent donated for each the redox catalysts. Positive average heat flow is exothermic and negative average heat flow is endothermic.
Since CL-ODH in principle just decouples an overall exothermic ODH reaction into two-steps, the regenerator reactor would supply the heat, if necessary, to offset the endothermic reaction in the ODH reactor. In Figure 5.8, the heat of reaction in the ODH and regenerator reactors utilizing the 20-80 redox catalyst are plotted versus the oxygen capacity of the 20-80 redox catalysts. For the first 0.14% of the oxygen capacity, the heat of reaction in the ODH reactor was exothermic, so all of the heat from the regenerator could be used to generate low pressure steam. Additional oxygen donation leads to an overall endothermic ODH reactor, but at 1% oxygen capacity donated, only 30.8% of the heat from the regenerator reactor is needed for the ODH reactor (111 kJ/mol O vs 360 kJ/mol O). As such, both the heat of reaction and ethane ODH results indicate that the 20-80-Na$_2$WO$_4$ is promising for a CL-ODH process. It is therefore further studied in an ASPEN Plus® model.

**Figure 5.8:** Average heat flow for the ODH and regenerator reactor for the 20-80 redox catalyst. Positive average heat flow is exothermic and negative average heat flow is endothermic.
5.4.5 Process Analysis

The CL-ODH system is proposed to be operated in a circulating fluidized bed (CFB) scheme, where the redox catalyst circulation rate ($R_{cat}$) is crucial as the redox catalyst supplies the necessary heat to offset the endothermicity of the ODH reactor. There are two important factors which govern the circulation rate of redox catalyst in the system: 1) oxygen release from the redox catalyst supplying the heat via selective hydrogen combustion ($\Delta H_{SHC}$) and 2) $\Delta T$ between the ODH reactor and regenerator providing sensible heat. Optimization of these factors can allow for adiabatic operation of the ODH reactor, providing a more efficient operation, which adds to the energy savings for the process.

The Fe-Mn system provides an exothermic SHC, as shown in Figures 5.7 and 5.8, which can reduce the overall $\Delta H$ of the ODH reactor. This can lower the required $R_{cat}$ values (mass of redox catalyst circulated/hr). To analyze the effects of the observed heat flows, the ODH reactor is simulated using ASPEN Plus®. For the ODH reactor, with a fixed $\Delta H_{SHC}$ and oxygen capacity, the temperature of the regenerator (or redox catalyst feed) is varied, till the ODH reactor reaches 850°C. This leads to a data set of projected solids circulation rate ($R_{cat}$) vs $\Delta T$ (between the regenerator and ODH reactor).
**Figure 5.9:** Projected solid circulation rates of the Fe-Mn redox catalyst system (20-80) for CL-ODH and the corresponding reactor temperature differences (at 1500 MW\textsubscript{th} feedstock processing capacity). Corresponding data on coal chemical looping combustion (CLC) system are also shown as references.\textsuperscript{50}

\(R_{\text{cat}}\) values (ktonne/hr) are calculated for a 1500 MW\textsubscript{Th} ethylene production plant which corresponds to an annual ethylene production of approximately 1 million tonnes. The selected points are mapped on Figure 5.9, plotted as \(R_{\text{cat}}\) vs \(\Delta T\). CLC of coal has been well documented in literature and is used as a reference.\textsuperscript{42,50–53} Ilmenite is chosen as the reference oxygen carrier for the CLC systems. Based on the available literature, circulation rates for a 1500 MW\textsubscript{Th} capacity CLC system are also plotted in Figure 5.9.

As one would anticipate, low oxygen release (or oxygen capacity utilized) for CL-ODH would correspond to large solids circulation rates mainly due to the needs to supply adequate lattice oxygen for ethane conversion. This leads to high circulation rates and low temperature difference between reactors. Increasing oxygen release from the Fe-Mn oxides can lower solids circulation from an oxygen supply standpoint. However, this leads to increased endothermicity in the CL-
ODH reactor and hence requires a higher reactor temperature difference. Overall, the tunable heat of reaction for mixed Fe-Mn oxide redox catalysts, as a function of oxygen release, allows the flexibility of adjusting reactor temperature differences and solids circulating rates. Moreover, under a similar reactor temperature difference, the projected solids circulation rate for CL-ODH is comparable or slightly lower than that required for CLC of coal, indicating its potential technical feasibility.

5.5 Conclusion

This study explored mixed iron manganese redox catalysts for the CL-ODH of ethane. Three molar ratios (Fe-Mn) were studied: 20-80, 50-50, and 60-40. XRD analysis indicated that all as-synthesized redox catalysts contained a mixed (Fe,Mn)$_2$O$_3$ phase. Ethane ODH reaction testing showed that after promotion with Na$_2$WO$_4$, the 20-80 redox catalyst achieved high ethylene yields (62.21%) and a low selectivity towards CO$_x$ species (3.15%). XPS results showed that both sodium and tungsten were enriched on the surface of the 20-80-Na$_2$WO$_4$ redox catalyst. Continuous redox cycling induced the formation of (Fe,Mn)WO$_4$, NaFe(WO$_4$)$_2$ and NaFeO$_2$ phases in addition to the mixed Fe-Mn oxides which acted as the oxygen carrying phases. These results indicated that near surface tungsten and sodium synergistically suppressed the deep oxidation of hydrocarbons. Dual TGA/DSC measurements indicated that a 20-80 redox catalyst had an exothermic heat flow during reduction indicating that it can help offset the endothermic nature of ethane cracking. ASPEN Plus® simulations indicate that the Fe-Mn redox catalyst can significantly lower the solids solid circulation rate when compared to traditional coal CLC processes. Moreover, the circulation rate and reactor temperature difference is tunable by varying the amount of oxygen extraction from the redox catalyst. Overall, the 20-80-Na$_2$WO$_4$
redox catalyst is a promising oxygen carrier for a CL-ODH process and can lead to reductions in energy consumption and emissions from ethylene production.
5.6 References


37. Gao, Y.; Haeri, F.; He, F.; Li, F. Alkali Metal-Promoted La x Sr 2–x FeO 4–δ Redox


48. Mishra, A.; Galinsky, N.; He, F.; Santiso, E. E.; Li, F. Perovskite-Structured AMn x B


60. Ji, S. Surface WO4 Tetrahedron: The Essence of the Oxidative Coupling of Methane over


Chapter 6: Conclusions and Future Work

6.1 Conclusions

The chemical looping oxidative dehydrogenation (CL-ODH) of ethane is a two-step cyclic redox process for the conversion of ethane to ethylene. A metal oxide redox catalyst donates its lattice oxygen in order to combust the hydrogen formed from the dehydrogenation of ethane. The reduced redox catalyst is transferred to a separate reactor where it is regenerated with air and generates heat. The redox catalyst is then transferred back to the original reactor, carrying the generated heat to balance the CL-ODH heat requirement and complete the redox cycle. When compared to the traditional steam cracking of ethane, the current industrial practice for the production of ethylene, CL-ODH provides multiple advantages: the combustion of hydrogen can increase ethylene yields and decrease the production of coke, CO$_2$/NO$_x$ emissions, and energy consumption. The most crucial component of the CL-ODH process is the redox catalyst. The redox catalyst must be specifically designed so that it has a large enough oxygen capacity, high oxygen mobility, and have high selectivity towards oxidation of hydrogen instead of hydrocarbon species in order to maximize product yield. The most studied redox catalysts for CL-ODH of ethane to date are vanadium oxides, but they were only able to achieve ethylene yields up to 20%. Moreover, vanadium is a toxic and expensive metal further making it a non-ideal candidate for the CL-ODH of ethane. Manganese oxides are a promising candidate due to their high stability, low-cost, benign nature. In particular, silica and magnesium oxide supported manganese oxide redox catalysts have been used for the ODH of ethane. Magnesium oxide supported manganese oxides formed the Mg$_6$MnO$_8$ phase which had shown a sufficiently high oxygen capacity (4.1wt%) and oxygen mobility but had low hydrocarbon yields. The lattice oxygen from Mg$_6$MnO$_8$ was not selective and oxidized hydrogen and hydrocarbon products.
In order to improve the performance of Mg₆MnO₈, three sodium-based promoters were added: sodium, sodium pyrophosphate and sodium tungstate. While the sodium promoted Mg₆MnO₈ redox catalyst performed similarly to un-promoted Mg₆MnO₈, sodium pyrophosphate and sodium tungstate promoted Mg₆MnO₈ had significantly increased ethylene yields. The improved performance of these redox catalysts was due to the ability of phosphorous and tungsten to retain sodium on the surface of the redox catalyst. When phosphorous and tungsten were added as promoters on the Mg₆MnO₈ redox catalyst, there were improvements in ethylene yield, but they still underperformed their sodium containing counterparts. The sodium tungstate promoted Mg₆MnO₈ had the highest ethylene yield and ethane temperature programmed reactions showed that sodium tungstate hindered the ability of the redox catalyst to activate ethane but allowed lattice oxygen to selectively combust hydrogen produced from thermal cracking of ethane. Both sodium and tungsten were enriched on the surface of the redox catalyst and the addition of the sodium tungstate led to a decrease on Mn⁴⁺ surface species and a reduction in the average oxidation state of manganese. Further exploration of sodium and tungsten promoters indicated that the balance between sodium and tungsten is important to the overall performance of the redox catalyst. While the addition of sodium and tungsten improved ethylene regardless of the sodium:tungsten ratio, the ethylene yield was highest at a ratio of 2:1. When the ratio was increased the 4:1 or decreased to 1:2, the ethylene yield decreased and COₓ selectivity increased. The 4:1 redox catalyst did not have enough tungsten on the surface and the 1:2 redox catalyst had additional mixed sodium, magnesium and tungsten oxide phases. The sodium tungstate promoter formed a shell around the Mg₆MnO₈ redox catalyst and at reaction temperatures, the sodium tungstate shell was in a molten state. CO/H₂-O₂ co-feed studies revealed that when sodium tungstate was solid, it prevented to activation of either carbon
monoxide or hydrogen, but once molten it allowed for the combustion of hydrogen. Experiments utilizing methanol as a probe molecule indicated that the sodium tungstate promoter decreased the number of basic sites on the surface of the redox catalyst and prevented the activation of reactant molecules. The sodium tungstate promoter also lowered the mobility of lattice oxidation, inhibiting the oxidation of hydrocarbon species. Despite this decrease, the mobility was still high enough at reaction temperatures to allow for the combustion of hydrogen. It was determined that molten sodium tungstate could be reduced by hydrogen, but the solubility of hydrogen in molten sodium tungstate was insignificant, so the combustion of hydrogen by lattice oxygen could not occur in molten sodium tungstate or at the molten sodium tungstate-Mg$_6$MnO$_8$ interface. These findings allow for the proposal of a potential CL-ODH mechanism. During the ODH of ethane step, the thermal cracking of ethane in the gas phase occurs, forming ethylene, hydrogen, and other hydrocarbon products. Then hydrogen is oxidized to water and the gas phase-molten sodium tungstate interface by oxygen species from molten sodium tungstate. The WO$_4^{2-}$ is reduced to the WO$_3^-$ anion found in sodium tungsten bronze. Then lattice oxygen from Mg$_6$MnO$_8$ restores the WO$_3^-$ anion back to WO$_4^{2-}$ to allow for further hydrogen combustion.

Manganese silicates were also studied as redox catalyst candidates for the CL-ODH of ethane. These materials have been used in chemical looping combustion, oxidative coupling of methane and hydrocarbon dehydrogenation applications. These materials are also naturally abundant and stable and benign like other manganese oxides. The un-promoted manganese silicate redox catalysts performed better than un-promoted Mg$_6$MnO$_8$, but had lower ethylene yields than sodium tungstate promoted Mg$_6$MnO$_8$. The addition of sodium tungstate to manganese silicate redox catalysts increased ethylene yields to slightly below those obtained by sodium tungstate promoted Mg$_6$MnO$_8$. XPS showed a lack of surface Mn$^{4+}$ species on the un-
promoted manganese silicate particles. Mn$^{4+}$ was associated with non-selective oxygen species in Mg$_6$MnO$_8$ redox catalysts and the lack of them would lead to lower CO$_x$ selectivity. The enrichment of the sodium tungstate promoter on the surface of the redox catalyst was seen again and ASPEN Plus simulations showed reductions in energy demand and CO$_2$/NO$_x$ emissions up to 89% when compared to the steam cracking of ethane.

In order to decrease the endothermicity of the ODH reactor and gain additional energy savings, mixed iron manganese oxide redox catalysts were studied for the CL-ODH of ethane. These additional energy savings will come through lowering the circulation rate of the redox catalyst and the temperature difference between the ODH and regenerator reactors. A redox catalyst with an iron-manganese molar ratio of 20-80 was found to have an exothermic heat of reduction at all degrees of reduction and promotion with sodium tungstate increased its ethylene yields so to similar levels achieved by Mg$_6$MnO$_8$ and manganese silicate redox catalysts. ASPEN Plus simulations comparing a traditional CLC system and CL-ODH with mixed iron-manganese redox catalysts determined that CL-ODH was able to have similar circulation rates to CLC while lowering the temperature of the regenerator reactor.

6.2 Future Work

The work in this study has established the effectiveness of Na$_2$WO$_4$ as a promoter on manganese based redox catalysts for the CL-ODH of ethane. The Na$_2$WO$_4$ promoter inhibits the activation of hydrocarbon species on the surface of the redox catalyst but allows for the oxidation of hydrogen at thermal cracking temperatures. The high activity towards the selective combustion of hydrogen formed from the thermal cracking of ethane, lead the significant increases in ethylene yield when compared to their un-promoted versions. The mixed Fe-Mn redox catalysts are particularly interesting compared to Mg$_6$MnO$_8$ and manganese silicate based
redox catalysts. Na$_2$WO$_4$ promoted mixed Fe-Mn oxide redox catalysts are able to similar ethylene yields to Mg$_6$MnO$_8$ and manganese silicate based redox catalysts, but they also can potentially lead to additional energy savings for the CL-ODH process through decreasing the temperature difference between the ODH and regenerator reactor and the redox catalyst circulation rate. It was also found the Na$_2$WO$_4$ is not a separate phase from the mixed Fe-Mn oxide redox catalyst as found with Na$_2$WO$_4$ promoted Mg$_6$MnO$_8$ and manganese silicate redox catalysts. Further investigations can focus on the development of redox catalysts with more favorable heats of reaction and the interactions between Na$_2$WO$_4$ and the newly developed redox catalysts. Specifically, perovskite supported mixed Fe-Mn oxide redox catalysts and mixed Cu-Mn oxide redox catalysts can be explored.

6.2.1 Perovskite supports for mixed iron-manganese oxide redox catalysts

While mixed iron-manganese oxide catalysts were able generate additional energy savings for the CL-ODH process, the full oxygen capacity of the redox catalysts was not utilized. Despite the as-synthesized being primarily composed of the bixbyite phase, the redox catalyst could only be restored back to the spinel phase after the first redox cycle (Figure D.3). This irreversible phase change worsens the performance of the mixed iron-manganese redox catalyst in 2 ways. First, it lowers the effective oxygen capacity of the redox catalyst. If there was more usable lattice oxygen, less redox catalyst would be needed to achieve the same conversion of ethane. Second, the reduction of the redox catalyst is more endothermic when the bixbyite phase cannot be regenerated. For both iron and manganese oxides, the reduction from the bixbyite/hematite phase to the spinel phase is more exothermic than the reduction from the spinel phase to the monoxide phase (Table 6.1). If the bixbyite/hematite phases can be regenerated, the reduction of the redox catalyst would be more exothermic. This would lead to further reductions
in the temperature difference between the ODH and regenerator reactors and the redox catalyst circulation rate. Both of these improvements would lead to additional energy and capital savings for the CL-ODH process.

**Table 6.1:** Heat of reduction for iron and manganese oxides calculated from HSC Chemistry

<table>
<thead>
<tr>
<th>Phase Transition</th>
<th>Heat of reduction (kJ/mol O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃ → Fe₃O₄</td>
<td>8.159</td>
</tr>
<tr>
<td>Fe₃O₄ → FeO</td>
<td>28.851</td>
</tr>
<tr>
<td>Mn₂O₃ → Mn₃O₄</td>
<td>-143.697</td>
</tr>
<tr>
<td>Mn₃O₄ → MnO</td>
<td>-25.377</td>
</tr>
</tbody>
</table>

Perovskites are a group of materials that can act as a support in order to improve the regeneration of the mixed iron-manganese oxide redox catalyst. The general formula for perovskite materials is ABO₃. A and B are both cations with A being a larger cation than B. There are a wide variety of perovskite materials as all elements in groups IA to IVB can be in the A or the B site of the material. Perovskites had been previously shown to have high mixed ionic-electronic conductivities and have improved the performance of metal oxide redox catalysts

and it is possible to have Fe and Mn in the B site of the perovskite material. This allows for the support material to have high phase stability and for the iron and manganese content to be similar in both the redox catalyst and support materials.

The general formula for the perovskite support material will be La₀.₈Sr₀.₂FeₓMn₁₋ₓ. Strontium is doped into the A site of the perovskite support in order to improve the conductivity of the perovskite material and the B site will have the same Fe-Mn molar ratio as the base redox catalyst that it is supporting. The support material will be synthesized along with the base redox catalyst in a one-pot sol-gel synthesis. The synthesis will be the same as previously described in Chapter 5 except nitrate precursors for the perovskite support will be added. Additional citric
acid and ethylene glycol will also be added to the sol-gel synthesis to maintain the molar ratio between cations and citric acid/ethylene glycol. The molar ratios of iron and manganese that will be synthesized are 20-80 and 60-40. The 20-80 redox catalyst showed in the best performance in the study performed in Chapter 5 and the 60-40 redox catalyst had shown high activity in previous studies. As with the base mixed iron-manganese redox catalyst, the perovskite supported catalyst will be calcined in air at 900°C. Dual TGA/DSC measurements as described in Chapter 5 will be performed in order to determine if the addition of the perovskite improves the heat of reduction of mixed iron-manganese redox catalysts. From previous results, it is expected that the addition of the perovskite support will improve the effective oxygen capacity of the redox catalyst and from thermodynamic calculations it is expected that the heat of reductions will become more exothermic. If these expected results are confirmed, the supported redox catalysts will be promoted with sodium tungstate and CL-ODH of ethane reaction testing will be performed in order to ensure that high ethylene yields are maintained. XRD and XPS characterization will also be performed on the perovskite supported catalysts before and after undergoing CL-ODH reaction testing and dual TGA/DSC measurements in order to determine any changes in crystal structure and surface composition. 

6.2.2 Mixed Copper Manganese Oxides for CL-ODH of ethane

An additional redox catalyst candidate for the CL-ODH of ethane are mixed copper manganese oxides. Copper oxide materials have been used as oxygen carriers in chemical looping oxygen uncoupling (CLOU) and chemical looping combustion (CLC) applications for multiple reasons: 1) they have a high oxygen capacity, 2) they have a high oxygen donation rate, 3) the reduction and oxidation of copper oxides are exothermic, 4) they are highly reactive towards to the conversion of hydrocarbons and 5) they are relatively cheap when compared to
other redox catalysts/oxygen carriers. These properties can make the overall chemical looping processes more efficient because less material is needed to meet the decreased energy demands. However, copper oxides have issues operating in high temperature chemical looping processes: copper oxides can be reduced to metallic copper which has a relatively low melting point (1085°C) and this can lead to agglomeration and defluidization of copper particles. In order to improve the stability of copper oxides, various support materials including Al$_2$O$_3$, SiO$_2$ and TiO$_2$ have been utilized.$^{8,9}$ In particular, Al$_2$O$_3$ interacts with copper oxide and leads to the formation of a mixed spinel CuAl$_2$O$_4$ phase.$^{10}$ This material is able to maintain the high oxygen donation rate of pure copper oxides for CLC applications. Another candidate for improving the stability of copper oxides are manganese oxides. Like Al$_2$O$_3$, manganese oxides can lead to the formation of a mixed spinel oxide phase- CuMn$_2$O$_4$. This mixed phase can combine the high activity of copper oxides and high stability of manganese oxides in order to have superior performance than either of the single metal oxide materials. Mixed copper manganese oxides have been used for the CLC of methane and have shown high activity and stable performance at high temperatures.$^{11}$

These properties also make further improvements to the CL-ODH of ethane process than mixed iron-manganese catalysts. If the reduction of the redox catalyst is more exothermic, it will be possible to utilize more lattice oxygen while offsetting the endothermic thermal cracking of ethane. As with the perovskite support, this can lead a lower redox catalyst circulation rate and temperature difference between the ODH and regenerator reactors which will lower the capital and energy costs of the CL-ODH process. For the initial screen of redox catalysts, four different molar ratios of Cu-Mn will be synthesized: 1-4, 1-2 1-1, and 2-1. All catalysts will be synthesized through a sol-gel method as with the mixed iron-manganese oxide redox catalysts.
Copper oxide redox catalysts previously shown high selectivity towards CO$_2$, which is ideal for CLC applications but not for CL-ODH of ethane, so all synthesized redox catalysts will be promoted with sodium tungstate in order to inhibit the oxidation of hydrocarbon products. Dual TGA/DSC measurements as described in Chapter 5 will be performed on the base redox catalyst so that heat of reduction can be determined as a function the amount of oxygen donated by the redox catalyst and CL-ODH of ethane reaction testing will be performed to ensure that high yields of hydrocarbon products are obtained. As with all previously studied manganese based redox catalysts, characterization will be performed in order to determine any bulk and surface changes in the redox catalysts after dual TGA/DSC measurements and CL-ODH of ethane reaction testing.
6.3 References


APPENDICES
Appendix A. Supplementary Information for Chapter 2

Table A.1: Product Distribution Data from GC analysis (Temperature=850°C, GHSV= 4500hr\(^{-1}\))

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Ethane Conversion</th>
<th>Ethylene Selectivity</th>
<th>Methane Selectivity</th>
<th>CO(_x) Selectivity</th>
<th>C3 Selectivity</th>
<th>C4+ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>45.30%</td>
<td>93.09%</td>
<td>3.23%</td>
<td>0.00%</td>
<td>1.26%</td>
<td>2.20%</td>
</tr>
<tr>
<td>Un-promoted</td>
<td>87.13%</td>
<td>17.93%</td>
<td>3.69%</td>
<td>78.04%</td>
<td>0.08%</td>
<td>0.14%</td>
</tr>
<tr>
<td>Na Promoted</td>
<td>85.37%</td>
<td>18.33%</td>
<td>3.31%</td>
<td>78.08%</td>
<td>0.21%</td>
<td>0.07%</td>
</tr>
<tr>
<td>NaP Promoted</td>
<td>78.16%</td>
<td>56.66%</td>
<td>4.10%</td>
<td>34.62%</td>
<td>0.95%</td>
<td>3.18%</td>
</tr>
<tr>
<td>NaW Promoted</td>
<td>63.59%</td>
<td>86.36%</td>
<td>4.48%</td>
<td>2.23%</td>
<td>1.73%</td>
<td>4.58%</td>
</tr>
<tr>
<td>W Promoted</td>
<td>86.83%</td>
<td>32.15%</td>
<td>3.21%</td>
<td>63.48%</td>
<td>0.23%</td>
<td>0.74%</td>
</tr>
</tbody>
</table>

Table A.2: Detailed Product Breakdown (selectivity) for Blank, Un-promoted, and NaW Promoted Samples

<table>
<thead>
<tr>
<th>Product</th>
<th>Blank</th>
<th>Un-promoted</th>
<th>NaW Promoted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>3.23%</td>
<td>3.69%</td>
<td>4.48%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.00%</td>
<td>78.04%</td>
<td>0.86%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.37%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>93.09%</td>
<td>17.93%</td>
<td>86.36%</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.23%</td>
<td>0.12%</td>
<td>0.62%</td>
</tr>
<tr>
<td>Propane</td>
<td>0.19%</td>
<td>0.03%</td>
<td>0.22%</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.06%</td>
<td>0.05%</td>
<td>1.46%</td>
</tr>
<tr>
<td>Methyl Acetylene</td>
<td>0.02%</td>
<td>0.00%</td>
<td>0.06%</td>
</tr>
<tr>
<td>Propadiene</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Butanes</td>
<td>0.56%</td>
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<tr>
<td>Butenes</td>
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<td>0.00%</td>
<td>0.19%</td>
</tr>
<tr>
<td>1,3 butadiene</td>
<td>1.39%</td>
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<td>3.63%</td>
</tr>
<tr>
<td>C6+</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.44%</td>
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Table A.3: Effect of Alumina Grit Packing on Product Distribution (Temperature=800°C, Total Flow Rate = 75 mL/min)

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Ethane Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-tube with Alumina Grit Packing</td>
<td>32.20%</td>
</tr>
<tr>
<td>U-tube without Alumina Grit Packing</td>
<td>55.0%</td>
</tr>
</tbody>
</table>
Figure A.1: In-situ XRD patterns for 2\textsuperscript{nd} and 3\textsuperscript{rd} cycles of un-promoted and NaW promoted redox catalyst after a) oxidation in air, b) uncoupling in nitrogen c) 3\% hydrogen reduction at 850\degree C
Figure A.2: XPS spectra of Manganese 2p 3/2 peaks of reduced redox catalyst
Figure A.3: XPS spectra of Manganese 2p peaks of a) fresh redox catalyst and b) cycled redox catalysts
Figure A.4: XPS spectra of Oxygen 1s peaks of a) fresh redox catalyst and b) cycled redox catalysts
Table A.4: Mn Fitted Characteristic Peak Positions and Full Width Half Maximum (FWHM) values.

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Peak</th>
<th>Position (eV)</th>
<th>FWHM</th>
<th>Relative Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Un-promoted as prepared</strong></td>
<td>“Mn 4+ HBE”</td>
<td>643.9</td>
<td>2.42</td>
<td>19.03</td>
</tr>
<tr>
<td></td>
<td>“Mn 4+”</td>
<td>642.6</td>
<td>2.26</td>
<td>71.17</td>
</tr>
<tr>
<td></td>
<td>“Mn 3+”</td>
<td>641.9</td>
<td>1.37</td>
<td>6.60</td>
</tr>
<tr>
<td></td>
<td>“Mn 2+”</td>
<td>640.6</td>
<td>1.14</td>
<td>3.20</td>
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<tr>
<td><strong>Un-promoted cycled</strong></td>
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<td>643.9</td>
<td>2.32</td>
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<td>642.41</td>
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<td>1.59</td>
<td>5.18</td>
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<tr>
<td></td>
<td>“Mn 2+”</td>
<td>640.7</td>
<td>1.31</td>
<td>4.96</td>
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<tr>
<td><strong>Na promoted as prepared</strong></td>
<td>“Mn 4+ HBE”</td>
<td>644.3</td>
<td>2.49</td>
<td>6.44</td>
</tr>
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<td>2.41</td>
<td>73.81</td>
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<tr>
<td></td>
<td>“Mn 3+”</td>
<td>641.7</td>
<td>1.32</td>
<td>15.09</td>
</tr>
<tr>
<td></td>
<td>“Mn 2+”</td>
<td>640.5</td>
<td>1.63548</td>
<td>4.96</td>
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<tr>
<td><strong>Na promoted cycled</strong></td>
<td>“Mn 4+ HBE”</td>
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<td></td>
<td>“Mn 3+”</td>
<td>641.6</td>
<td>1.7</td>
<td>20.07</td>
</tr>
<tr>
<td></td>
<td>“Mn 2+”</td>
<td>640.3</td>
<td>1.31</td>
<td>6.22</td>
</tr>
<tr>
<td><strong>NaP promoted as prepared</strong></td>
<td>“Mn 4+ HBE”</td>
<td>643.9</td>
<td>3.00</td>
<td>14.87</td>
</tr>
<tr>
<td></td>
<td>“Mn 4+”</td>
<td>642.5</td>
<td>2.31</td>
<td>68.91</td>
</tr>
<tr>
<td></td>
<td>“Mn 3+”</td>
<td>641.9</td>
<td>1.26</td>
<td>9.45</td>
</tr>
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<td></td>
<td>“Mn 2+”</td>
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<td>1.75</td>
<td>6.76</td>
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<td><strong>NaP promoted cycled</strong></td>
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<td>3.00</td>
<td>13.03</td>
</tr>
<tr>
<td></td>
<td>“Mn 4+”</td>
<td>642.3</td>
<td>2.58</td>
<td>55.77</td>
</tr>
<tr>
<td></td>
<td>“Mn 3+”</td>
<td>641.8</td>
<td>2.38</td>
<td>18.41</td>
</tr>
<tr>
<td></td>
<td>“Mn 2+”</td>
<td>640.6</td>
<td>1.9</td>
<td>12.78</td>
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</table>
Table A.4 (continued)

<table>
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<th>NaW promoted as prepared</th>
<th>“Mn 4+ HBE”</th>
<th>644</th>
<th>2.62</th>
<th>6.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Mn 4+”</td>
<td>642.5</td>
<td>2.38</td>
<td>78.10</td>
<td></td>
</tr>
<tr>
<td>“Mn 3+”</td>
<td>641.8</td>
<td>1.16</td>
<td>12.70</td>
<td></td>
</tr>
<tr>
<td>“Mn 2+”</td>
<td>640.3</td>
<td>1.54</td>
<td>2.32</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaW promoted cycled</th>
<th>Mn 4+ HBE</th>
<th>643.9</th>
<th>0.90</th>
<th>2.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn 4+</td>
<td>642.7</td>
<td>1.87</td>
<td>42.32</td>
<td></td>
</tr>
<tr>
<td>Mn 3+</td>
<td>641.6</td>
<td>1.35</td>
<td>20.37</td>
<td></td>
</tr>
<tr>
<td>Mn 2+</td>
<td>640.5</td>
<td>2.33</td>
<td>35.05</td>
<td></td>
</tr>
</tbody>
</table>

Surface normalization of XPS data

The surface normalization was done by taking the XPS that had been normalized to 1 and then multiplying a ratio of (Surface area of un-promoted redox catalyst *surface Mn% percentage of un-promoted catalyst) / (Surface area of NaW promoted redox catalyst *surface Mn% percentage of NaW promoted catalyst)

Isothermal redox cycling with Ethylene and Hydrogen

Isothermal redox cycling was carried out at 800°C and 850°C under a cyclic redox scheme. For the reduction step, 40% H₂, 40% C₂H₄ and 20% Ar was used (100 ml/min total flow rate, 10 seconds reduction time). The oxidation step used 16.7% O₂ in Ar to fully re-oxidize the redox catalysts. An argon purge for five minutes between reduction and oxidation steps was implemented to avoid the mixing of combustible gases and O₂. Results were analyzed by gas chromatography.

The H₂ combustion and SHC metrics are defined below and can be seen in Figure A.5. At 850 °C, sodium tungstate promoter improves the hydrogen combustion selectivity of Mg₆MnO₈ from 45.4% (un-promoted) to 91.6% (promoted with 20 wt.% sodium tungstate loading).
\[
H_2 \text{ combustion} = 1 - \frac{(H_2)_{\text{out}}}{(H_2)_{\text{in}} + (H_2)_{\text{gen}}} 
\]

\[
\text{SHC selectivity} = \frac{(H_2O)_{\text{out}}}{(H_2O)_{\text{out}} + (CO)_{\text{out}} + 2 \times (CO_2)_{\text{out}}}
\]

**Figure A.5:** SHC and H₂ combustion values from isothermal redox cycles.

**Coke Formation Calculations**

Coke formation calculations were performed using QMS data. The amount of carbon in both the reduction step \((C_2H_6, C_2H_4, CO_x)\) and the oxidation step \((CO_x)\) were determined. \(CO_x\) species detected during the oxidation step can be attributed to coke and therefore can be used to determine the percentage of total carbon that is due to coke.
Appendix B. Supplementary Information for Chapter 3

Rietveld Refinement

The XRD pattern for Rietveld refinement was collected on a PANalytical Empyrean diffractometer under CuKα radiation from a sealed tube generator at 45kV and 40mA, with PIXcel1D detector at room temperature. Measurement was taken under Bragg-Brentano configuration using a spinning sample stage at 0.01° step size and 4.5s per step. Data was analyzed and refined using GSAS-II software package\(^1\).

![Reitveld Refinement fits of a) un-promoted Mg₆MnO₈ and b) Na:W=2:1 promoted Mg₆MnO₈ redox catalysts](image)

**Figure B.1:** Reitveld Refinement fits of a) un-promoted Mg₆MnO₈ and b) Na:W=2:1 promoted Mg₆MnO₈ redox catalysts
Table B.1: Refinement Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg$_6$MnO$_8$</th>
<th>Na$_2$WO$_4$·Mg$_6$MnO$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Mg$_6$MnO$_8$</td>
<td>Mg$_6$MnO$_8$</td>
</tr>
<tr>
<td>Phase Fraction</td>
<td>1</td>
<td>0.9588</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm-3m</td>
<td>Fm-3m</td>
</tr>
<tr>
<td>a</td>
<td>8.38337</td>
<td>8.383307</td>
</tr>
<tr>
<td>V</td>
<td>589.191</td>
<td>589.127</td>
</tr>
<tr>
<td>wR</td>
<td>0.033</td>
<td>0.052</td>
</tr>
</tbody>
</table>

DSC Measurement

Figure B.2: DSC measurements over Na:W=2:1 redox catalyst
Figure B.3: Full plots of $R_0$, $R_a$, and $R_i$ for the a) un-promoted redox catalyst, b) Na:W=2:1 redox catalyst.
**In-situ Raman Spectroscopy**

**Experimental Details**

*In-situ* Raman spectroscopy measurements were performed at Oak Ridge National Laboratory on the a 20wt% Na$_2$WO$_4$/α-Al$_2$O$_3$ sample in a Linkam CCR1000 reactor using excitation from a HeCd laser (Melles Griot) at 442 nm (5 mW at sample position). After the sample was loaded into the sample chamber, it was heated to 850°C in 10% O$_2$/Ar (30mL/min). The temperature was held at 850°C throughout the following steps. Next, the sample chamber was purged with 100% Ar for 10 minutes and then the flow was switched to 4% H$_2$/Ar. After 1 hour, the sample chamber was purged with 100% Ar and then the flow was switched back to 10%O$_2$ for 10 minutes before the sample chamber was cooled. Raman spectra were taken throughout the experiment and the results are summarized in Figure B.4.

The Raman spectra were normalized to the highest peak at ~ 400 cm$^{-1}$ and no significant changes can be seen during the experiment in both O$_2$ and H$_2$ atmosphere. This indicates that there is no bulk reduction of Na$_2$WO$_4$ by H$_2$ at the typical reaction temperature of 850°C.
Redox Nature of Na$_2$WO$_4$

Experimental Details

In order to test the redox nature of Na$_2$WO$_4$, a 20wt% Na$_2$WO$_4$/α-Al$_2$O$_3$ sample was synthesized. The synthesis was done with the same procedure as described for the redox catalysts. Sodium tungstate dihydrate was used as the precursor for Na$_2$WO$_4$ and the Al grit used to pack reactor U-tubes was used as the α-Al$_2$O$_3$ material. After mixing sodium tungstate dihydrate dissolved in water with α-Al$_2$O$_3$, the sample was dried overnight at 80°C and calcined in air at 450°C for 3 hours and then at 900°C for 8 hours.

The test to determine the redox nature of Na$_2$WO$_4$ utilized a broad pulse of H$_2$ and a sharp pulse $^{18}$O with helium as a carrier gas. 5g of the 20 wt% Na$_2$WO$_4$/α-Al$_2$O$_3$ sample (1g of Na$_2$WO$_4$ total) was then loaded into a quartz U-tube reactor and packed with un-promoted Al grit.

![Figure B.4: Raman spectra of 20wt%Na$_2$WO$_4$/Al$_2$O$_3$ during in-situ experiments at 850°C. All spectra were collected at 850 °C and normalized from 0 to 1.](image-url)
on either side. The U-tube was then loaded into the reactor and 60 sccm of He was flown to
purge any oxygen. Then a six-way valve was used to inject a 1ml pulse of 100% H₂ into the
reactor. Before entering the reactor, the pulse was broadened by flowing through an empty
vessel. When the peak of the H₂ pulse was reached, a sharp 0.1mL of ¹⁸O (33% in He) was
injected into the reactor. A QMS was used to analyze the products formed during the experiment.
For comparison, experiments with an Ar pulse instead of ¹⁸O and an experiment with only a
broad H₂ pulse were run. The experiment took place at 850°C and a room temperature run was
used for reference. A blank sample (only Al grit) was also run for comparison at the same
conditions as the 20 wt% Na₂WO₄/α-Al₂O₃ sample.

Results

In Figure B.5, a comparison of the blank and the 20 wt% Na₂WO₄/α-Al₂O₃ at 850°C with
a broad H₂ pulse and a sharp ¹⁸O₂ pulses can be seen. On m/z= 18 of the 20 wt% Na₂WO₄/α-
Al₂O₃ sample, a sharp peak followed by a broad peak can be seen. The sharp peak is due to
injection of ¹⁸O₂ (¹⁸O fragment) as no sharp pulse can be seen of m/z= 17, which would have
been solely associated with H₂¹⁶O. The broad peak is associated with ¹⁶O displaced from
Na₂WO₄ by ¹⁸O reacting with H₂. This broad pulse is not seen on the blank sample indicating
that the peak is only generated by the oxygen in Na₂WO₄. The broad peak is also not observed
when only a broad pulse of H₂ is injected or when a sharp pulse of Ar is used instead of ¹⁸O₂
confirming that the additional water production is due to redox behavior of Na₂WO₄.
Figure B.5: Broadened pulse of H$_2$ with sharp pulse $^{18}$O$_2$ at 850°C over a) blank and b) 20wt% Na$_2$WO$_4$/α-Al$_2$O$_3$
C₂H₄-O₂ co-feed

C₂H₄-O₂ co-feed experiments were performed the same way as CO-O₂ and H₂-O₂ co-feed experiments. Unlike the previous co-feed experiments, we used the production rate of CO₂ to compare the thermal blank and Na₂WO₄ promoted redox catalyst. This was because gas phase ethylene reactions make direct quantification of ethylene conversion with mass spec difficult.

We did not test the un-promoted redox catalyst because of its high ethane conversion (81.1%) and COx selectivity (75%) during ODH reaction testing at 800 °C. In a co-feed environment, we would expect an even higher CO₂ production due to the presence of gaseous oxygen.

Table B.2: CO₂ production rate during C₂H₄-O₂ co-feed study.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Un-promoted</th>
<th>Na₂WO₄ promoted</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>5.8*10⁻³ mL/min</td>
<td>1*10⁻² mL/min</td>
</tr>
<tr>
<td>700</td>
<td>2.6*10⁻² mL/min</td>
<td>2.7*10⁻² mL/min</td>
</tr>
<tr>
<td>800</td>
<td>0.16 mL/min</td>
<td>0.17 mL/min</td>
</tr>
</tbody>
</table>
Table B.3: Comparison of un-promoted and Na$_2$WO$_4$ promoted redox catalysts

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Un-promoted</th>
<th>Na$_2$W = 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEIS</td>
<td>Mg and Mn primary elements on surface of redox catalyst</td>
<td>Na$_2$WO$_4$ forms a shell around the Mg$_6$MnO$_8$ redox catalyst</td>
</tr>
<tr>
<td>Methanol TPSR</td>
<td>Basic and redox sites detected</td>
<td>Na$_2$WO$_4$ significantly reduces the amount of basic sites</td>
</tr>
<tr>
<td>In-situ DRIFTS</td>
<td>Formate and carbonate species detected. Species still</td>
<td>Only carbonate species detected. No species present at 250°C. Na$_2$WO$_4$ inhibits</td>
</tr>
<tr>
<td></td>
<td>present at 450°C</td>
<td>surface activity for oxidation</td>
</tr>
<tr>
<td>CO-O$_2$ co-feed</td>
<td>Complete conversion of CO at all temperatures</td>
<td>No additional conversion of CO over the thermal blank, Mg$_6$MnO$_8$ is fully covered by Na$_2$WO$_4$</td>
</tr>
<tr>
<td>H$_2$-O$_2$ co-feed</td>
<td>Significantly higher H$_2$ conversion than thermal</td>
<td>Solid Na$_2$WO$_4$: H$_2$ conversion similar to thermal blank</td>
</tr>
<tr>
<td></td>
<td>blank at all temperatures</td>
<td>Molten Na$_2$WO$_4$: H$_2$ conversion higher than thermal blank, molten</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na$_2$WO$_4$ promotes H$_2$ combustion</td>
</tr>
<tr>
<td>$^{18}$O-$^{16}$O exchange</td>
<td>Significant uptake of $^{18}$O and isotopic randomization</td>
<td>Isotopic randomization is suppressed, Na$_2$WO$_4$ shell inhibits O$_2$ dissociative adsorption</td>
</tr>
<tr>
<td>$\text{Na}_2\text{WO}_4$ reduction and gas switching experiments</td>
<td>n/a</td>
<td>$\text{Na}_2\text{WO}_4$ is reducible (albeit slow) and the sample combusts hydrogen by shuttling oxygen from Mg$_6$MnO$_8$</td>
</tr>
<tr>
<td>ODH Reaction testing (850°C)</td>
<td>Ethylene Yield: 13.29%</td>
<td>Ethylene Yield: 62.17%</td>
</tr>
</tbody>
</table>
References


https://doi.org/10.1107/S0021889813003531.
Appendix C. Supplementary Information for Chapter 4

Formulas for Selectivity, Yield and H₂ Conversion

\[
\text{Ethane Conversion} = 1 - \frac{n(\text{Ethane})}{n(\text{All carbon species})}
\]

\[
\text{Selectivity (species } x) = \frac{n(x)}{n(\text{All carbon species}) - n(\text{ethane})}
\]

\[
\text{Ethylene yield} = \text{Ethane Conversion} \times \text{Selectivity(Ethyelene)}
\]

\[
H_2 \text{ combustion} = 1 - \frac{(H_2)_{out}}{(H_2)_{gen}}
\]

n(x) refers to the total amount of carbon in species x measured by GC. For hydrocarbon species, GC measurements were performed by an FID and COₓ species were measured using a TCD. Therefore, n(x) for any hydrocarbon or COₓ species is directly proportional to the peak area.

Formula for Oxygen Capacity

\[
\text{Oxygen Capacity} = 1 - \frac{\text{Mass after } H_2 \text{ reduction}}{\text{Mass after oxidation}}
\]
Table C.1: Product Distribution Data from GC analysis (Temperature=850°C, GHSV= 4500hr\(^{-1}\))

<table>
<thead>
<tr>
<th>Redox Catalyst</th>
<th>Ethane Conversion</th>
<th>Ethylene Selectivity</th>
<th>Methane Selectivity</th>
<th>CO(_x) Selectivity</th>
<th>C3 Selectivity</th>
<th>C4+ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>62.87%</td>
<td>89.95%</td>
<td>4.43%</td>
<td>0.00%</td>
<td>1.52%</td>
<td>3.56%</td>
</tr>
<tr>
<td>Mn:Si = 70:30</td>
<td>80.51%</td>
<td>57.10%</td>
<td>4.13%</td>
<td>33.70%</td>
<td>0.95%</td>
<td>3.17%</td>
</tr>
<tr>
<td>Mn:Si= 30:70</td>
<td>66.05%</td>
<td>85.29%</td>
<td>4.50%</td>
<td>3.85%</td>
<td>1.51%</td>
<td>4.09%</td>
</tr>
<tr>
<td>Mn:Si= 05:95</td>
<td>64.19%</td>
<td>88.07%</td>
<td>4.58%</td>
<td>1.36%</td>
<td>1.50%</td>
<td>3.58%</td>
</tr>
<tr>
<td>Mn:Si= 70:30 – Na(_2)WO(_4) (1.7wt% Na)</td>
<td>67.15%</td>
<td>86.66%</td>
<td>4.25%</td>
<td>1.93%</td>
<td>1.66%</td>
<td>4.91%</td>
</tr>
<tr>
<td>Mn:Si= 70:30 – Na(_2)WO(_4) (0.57wt% Na)</td>
<td>69.41%</td>
<td>83.68%</td>
<td>4.03%</td>
<td>3.73%</td>
<td>1.85%</td>
<td>6.09%</td>
</tr>
</tbody>
</table>

Table C.2: Detailed Product Breakdown (selectivity) for Blank, Un-promoted, and NaW Promoted Samples

<table>
<thead>
<tr>
<th>Product</th>
<th>Blank</th>
<th>Mn:Si = 70:30</th>
<th>Mn:Si= 70:30 – Na(_2)WO(_4) (1.7wt% Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>4.43%</td>
<td>4.13%</td>
<td>4.25%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.00%</td>
<td>6.19%</td>
<td>0.85%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.00%</td>
<td>27.51%</td>
<td>1.08%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>89.95%</td>
<td>57.10%</td>
<td>86.66%</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.54%</td>
<td>0.95%</td>
<td>0.59%</td>
</tr>
<tr>
<td>Propane</td>
<td>0.16%</td>
<td>0.14%</td>
<td>0.18%</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.31%</td>
<td>0.77%</td>
<td>1.47%</td>
</tr>
<tr>
<td>Methyl Acetylene</td>
<td>0.05%</td>
<td>0.04%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Propadiene</td>
<td>0.02%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Butanes</td>
<td>0.27%</td>
<td>0.06%</td>
<td>0.19%</td>
</tr>
<tr>
<td>Butenes</td>
<td>0.23%</td>
<td>0.05%</td>
<td>0.22%</td>
</tr>
<tr>
<td>1,3 butadiene</td>
<td>2.66%</td>
<td>2.42%</td>
<td>3.64%</td>
</tr>
<tr>
<td>C6+</td>
<td>0.33%</td>
<td>0.55%</td>
<td>0.61%</td>
</tr>
</tbody>
</table>
**Figure C.1:** TGA weight loss rate for Mn:Si=70:30 redox catalysts

**Figure C.2:** Ethane TPR results for Mass 30
Figure C.3: XPS spectra of Mn 3s peaks of as-prepared redox catalysts

Figure C.4: XPS spectra of Mn 3s peaks of as-prepared redox catalysts
Figure C.5: XRD patterns of cycled redox catalysts: un-promoted and promoted (1.7wt%, 0.57wt% Na) redox catalysts with Mn:Si = 70:30. [a]PDF# 04-008-9539 [b]PDF# 04-008-7641 [c]PDF#00-029-0895

**ASPEN Plus® Model**

ASPEN Plus® simulator is used to determine the process performances. The solids used in the simulation include Mn$_3$O$_4$ and MnO with SiO$_2$ added as an inert to mimic the actual catalyst. The key operating assumptions and parameters used in the simulations are listed in Table C.3. The feed is considered at a preheated temperature of 650°C. In the case of cracking, steam is also fed at 650°C. The Mn$_3$O$_4$ particles are initially fed into the reactor, from the exit of which they are transported to the regenerator. There is a ΔT of 100°C, between the reactor and regenerator, with the regenerator being higher at 950°C. In the regenerator, the reduced oxygen carrier is fully oxidized in 10% excess air, preheated to 650°C prior to the recirculation to the reactor for another redox loop. The unreacted ethane is completely recycled to the reactor at 650°C. Since the process consumes different forms of energy such as thermal energy, steam, and electricity, it is helpful to convert them into a same thermal basis for process comparison.
### Table C.3: Simulation conditions and assumptions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient condition</td>
<td>$T = 25^\circ\text{C}, P = 1\text{ atm}$</td>
</tr>
<tr>
<td>Reaction assumptions</td>
<td>As per the carbon yield distribution in Table 4.2</td>
</tr>
<tr>
<td>Heat loss in chemical looping reactors</td>
<td>1% of the total thermal output</td>
</tr>
<tr>
<td>Chemical looping reactor operating pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Deacetylenizer operating pressure</td>
<td>42 atm</td>
</tr>
<tr>
<td>Compressor specifications</td>
<td>4 stage with intercooler at $25^\circ\text{C}$</td>
</tr>
<tr>
<td>Air feed (to the regenerator)</td>
<td>10% excess</td>
</tr>
<tr>
<td>Discharge temperatures to the environment</td>
<td>Temperature: $25^\circ\text{C}$</td>
</tr>
<tr>
<td>Thermal energy to steam efficiency</td>
<td>85%</td>
</tr>
<tr>
<td>Thermal energy to electric energy efficiency</td>
<td>40%</td>
</tr>
</tbody>
</table>

![Figure C.6: ASPEN Plus flowsheet of the CL-ODH process](image-url)
Figure C.7: Energy demand and surplus (GJ/tonne ethylene)
Appendix D. Supplementary Information for Chapter 5

Figure D.1: XRD pattern of cycled 20-80-Na$_2$WO$_4$ redox catalyst (a) PDF# 01-077-9278 (b) PDF# 00-012-0727 (c) PDF# 00-025-0838 (d) PDF# 04-002-2541

Table D.1: Ethane ODH reaction data for 20-80-Na$_2$WO$_4$ redox catalyst (GHSV = 4500 hr$^{-1}$)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ethane Conversion</th>
<th>Methane Selectivity</th>
<th>Ethylene Selectivity</th>
<th>C3 Selectivity</th>
<th>C4+ Selectivity</th>
<th>CO$_x$ Selectivity</th>
<th>H$_2$ Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>850°C</td>
<td>75.9%</td>
<td>6.1%</td>
<td>82.0%</td>
<td>2.1%</td>
<td>6.3%</td>
<td>3.2%</td>
<td>90.5%</td>
</tr>
<tr>
<td>825°C</td>
<td>62.5%</td>
<td>4.6%</td>
<td>87.3%</td>
<td>1.8%</td>
<td>4.4%</td>
<td>1.6%</td>
<td>83.9%</td>
</tr>
<tr>
<td>800°C</td>
<td>43.6%</td>
<td>3.6%</td>
<td>91.1%</td>
<td>1.5%</td>
<td>2.60%</td>
<td>1.1%</td>
<td>74.9%</td>
</tr>
</tbody>
</table>

Dual TGA/DSC Measurements

As there were no significant changes observed between the 2$^{nd}$ and 5$^{th}$ redox cycles, so heats of reduction were calculated using data from the 2$^{nd}$ redox cycle. For heat of reduction measurements, the heat flow from the entire reduction step was not integrated. Instead the heat
flow from the start of the reduction until the first and second derivative of the heat flow had reached a steady value of zero. After this point, there were no significant changes in the measured heat flow.

In order to calculate the cumulative average heat of reduction, we started with the heat flow values [mW] obtained from the TA Instruments SDT Q600 unit in the chosen integration range, which will be referred to as the “initial heat flow”. The first point in the “initial heat flow” was then set to zero and this value was subtracted from all points making the “zeroed heat flow”. Then a linear baseline between the two endpoints of the integration was calculated and then subtracted from the “zeroed heat flow” to calculate “final heat flow” values for integration.

The “final heat flow” was then integrated using the trapezoid rule in order to obtain a heat flow in Joules. The SDT Q600 collected reported the heat flow every 0.5 seconds in order to increase the number of partitions and accuracy of the integration. The sum of the integrated heat flow was then calculated at each time point collected. Finally, the sum of the integrated heat flow was divided by the total mol of O released at that time point (e.g. at 2 seconds into the reduction, the sum of the integrated heat flow at 2 seconds was divided by the mol of O donated 2 seconds after the start of reduction). This value was then plotted against the oxygen capacity of the redox catalyst which was represented by the amount of O donated (mg) divided by the redox catalyst weight at the start of reduction (mg).

For HSC Chemistry, a reduction of the spinel to the monoxide phase by H$_2$ for both iron and manganese oxides were calculated and then were weighted by the molar ratio of Fe to Mn in the redox catalyst in order to calculate the heat of reduction per mol of O. Then the weight loss during dual TGA/DSC measurements was calculated in order to obtain heat of reduction for comparison.
Figure D.2: TGA curves for (a) 20-80 (b) 50-50 (c) 60-40 redox catalysts
Process Simulation using AspenPlus

The 20-80 Fe-Mn ratio is chosen as a representative composition. Different points from Figure 5.7 (from main text) are selected along the 20:80 curve, denoting varying oxygen capacities and corresponding $\Delta H_{\text{SHC}}$ (heat of the selective hydrogen combustion reaction) values. In the AspenPlus® model, each of these points is utilized by maintaining the oxygen capacity and corresponding $\Delta H$ of the ODH reactor (based on the obtained $\Delta H_{\text{SHC}}$).
Table D.2: AspenPlus modules, property methods and databanks

<table>
<thead>
<tr>
<th>Stream class</th>
<th>MIXCISLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Databank</td>
<td>PURE, AQUEOUS, SOLIDS, INORGANIC</td>
</tr>
<tr>
<td>Solid components</td>
<td>Fe₂O₃, FeO</td>
</tr>
<tr>
<td>Property method</td>
<td>PR-BM and STEAM –TA for steam cycles</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unit operation models</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODH Reactor</td>
</tr>
<tr>
<td>Heat exchangers</td>
</tr>
<tr>
<td>Separators</td>
</tr>
<tr>
<td>Ambient condition</td>
</tr>
<tr>
<td>Reaction assumptions</td>
</tr>
<tr>
<td>Reactor operating pressure</td>
</tr>
<tr>
<td>Thermal to steam efficiency</td>
</tr>
<tr>
<td>Thermal to electric efficiency</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>% C yield</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>62.220</td>
<td>ETHANE --&gt; ETHYLENE(MIXED) + H₂(MIXED)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.332</td>
<td>ETHANE --&gt; ACETYLEN(MIXED) + 2 H₂(MIXED)</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.375</td>
<td>3 ETHANE --&gt; 2 PROPYLEN(MIXED) + 3 H₂(MIXED)</td>
</tr>
<tr>
<td>Propane</td>
<td>0.135</td>
<td>3 ETHANE --&gt; 2 PROPANE(MIXED) + H₂(MIXED)</td>
</tr>
<tr>
<td>Butadiene</td>
<td>3.397</td>
<td>2 ETHANE --&gt; 1:1-B-01(MIXED) + 3 H₂(MIXED)</td>
</tr>
<tr>
<td>Butene</td>
<td>0.145</td>
<td>2 ETHANE --&gt; ISOBU-01(MIXED) + 2 H₂(MIXED)</td>
</tr>
<tr>
<td>Butane</td>
<td>0.061</td>
<td>2 ETHANE --&gt; ISOBU-02(MIXED) + H₂(MIXED)</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.944</td>
<td>3 ETHANE --&gt; BENZENE(MIXED) + 6 H₂(MIXED)</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.000</td>
<td>7 ETHANE --&gt; 2 TOLUENE(MIXED) + 13 H₂(MIXED)</td>
</tr>
<tr>
<td>CO</td>
<td>0.934</td>
<td>ETHANE + 5 HEMAT-01(CISOLID) --&gt; 2 CO(MIXED) + 3 H₂O(MIXED) + 10 FERRO-01(CISOLID)</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.629</td>
<td>ETHANE + 7 HEMAT-01(CISOLID) --&gt; 2 CO₂(MIXED) + 3 H₂O(MIXED) + 14 FERRO-01(CISOLID)</td>
</tr>
<tr>
<td>Methane</td>
<td>4.591</td>
<td>ETHANE + H₂ --&gt; 2 METHANE(MIXED)</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.030</td>
<td>5 ETHANE --&gt; 2 N-PEN-01(MIXED) + 3 H₂(MIXED)</td>
</tr>
<tr>
<td>Propadiene</td>
<td>0.109</td>
<td>3 ETHANE --&gt; 2 PROPA-01(MIXED) + 5 H₂(MIXED)</td>
</tr>
<tr>
<td>Ethane</td>
<td>24.098</td>
<td>H₂ + HEMAT-01(CISOLID) --&gt; H₂O(MIXED) + 2 FERRO-01(CISOLID)</td>
</tr>
</tbody>
</table>

Figure D.4: Product distribution (with 90% H₂ combustion to H₂O) and AspenPlus flow diagram
Figure D.5: Approach used to obtain the circulation rates at various oxygen release capacities

For each selected point from Figure 7:
- Fixed oxygen capacity (mol O/mol redox catalyst)
- Fixed reactor Net Q (GJ/hr)
- Solved for the temperature of the feed redox catalyst such that the reactor temperature is 850°C
- Corresponding solid circulation rate and temperature difference noted