

Kinetic Study of Supported Iron Oxide Reduction by Methane

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Abstract

The discovery and exploration of shale gas has provided the U.S. with abundant energy resources. Methane from shale gas has been widely considered a game-changing energy resource. However, the large quantity of CO₂ emissions associated with methane combustion raises environmental concerns. Chemical Looping Combustion (CLC) processes are widely considered to be transformative clean energy conversion technologies. These technologies utilize an oxygen carrier to efficiently oxidize the fuel to sequestrable CO₂ and steam. Thus, the performance of the oxygen carrier, i.e., supported iron oxides, is critical for these processes. In this study, iron oxides on different support materials are synthesized and compared. The reactivity for various supported iron oxides is investigated by Thermogravimetric Analyzer (TGA). The effect of varying the reducing gas composition (a mixture of methane and nitrogen) is also examined. Furthermore, a minimum gas flow rate of 100 mL/min with 66.67% methane gas composition is identified. Three supported iron oxides, namely MgAl₂O₄, MgO and Al₂O₃, are explicitly studied by thermogravimetric analysis experiments, which exhibited a similar two-stage reduction pattern. However, the distinct performances of each stage amongst these supported iron oxides indicate complex iron oxide-support interactions. Supported iron oxide at different stages are sampled and investigated by post-experimental solid characterization method. For instance, the surface area and total pore volume are determined by Brunauer-Emmett-Teller (BET) theory. This experiment illuminates the important mechanistic impacts of different supports on the iron oxide reduction by methane. Through the understanding of such interactions, the oxygen carrier can be optimized to facilitate the development of more efficient methane conversion in CLC processes.

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Introduction

A plentiful and cheap primary source of energy is the key to sustain higher living standards. In 2011, the United States consumed around 97.3 quadrillion BTUs, 82% of which came from fossil fuels¹. Shale gas is considered as the next abundant domestic energy resource. However, the large quantity of CO₂ emissions associated with methane combustion raises environmental concerns². Chemical Looping Combustion (CLC) processes have been widely recognized as a transformative clean energy conversion technology.³ The unique feature of this combustion technology is in its high energy conversion efficiency while CO₂ is fully captured with little parasitic energy requirement. Specifically, the CLC processes utilize the reduction-oxidation (redox) properties of metal oxides as an oxygen donor thereby avoiding direct fuel combustion with air, which yields a gaseous mixture of CO₂ and N₂ requiring costly separation. Thus, the metal oxide particles are the key to CLC success, and methane reduction by supported iron oxides are investigated in this study.

Shale Gas - New Sources of Natural Gas (Methane)

Shale gas is dramatically increasing as a new source of natural gas in the United States. Due to development of drilling and extraction technologies, methane from shale gas has been considered as a game-changing energy resource that can offset declines in production from conventional gas reservoirs. With the substantial amount of natural gas discovery in shale, U.S. natural gas reserves have increased approximately 35% from 2006 to 2008⁴. The economic success of shale gas in the United States has also spurred interest in development of shale gas extraction opportunities around the world, especially in Canada, Europe and Asian countries.

According to data from the U.S. Energy Information Administration (EIA) regarding new shale fields, i.e. Marcellus, Haynesville, and Eagle Ford, the recoverable shale gas reserves in the United States has more than doubled from 353 trillion cubic feet to 827 trillion cubic feet⁵.

The Syngas Chemical Looping (SCL)

The Syngas Chemical Looping (SCL) process developed at the Ohio State University (OSU) is an energy efficient method to transfer energy from coal combustion into electricity, hydrogen, and/or liquid fuel with zero net CO₂ emissions⁶. Through the assistance of a tailored iron-based composite particle, the SCL process simplifies the overall fuel conversion scheme while reducing pollutants in an indirect but highly effective manner, greatly reducing the cost for the hydrogen and electricity generated^{7,8}. Figure 1 demonstrates the simplified schematic flow diagram of the SCL process for hydrogen and electricity cogeneration.

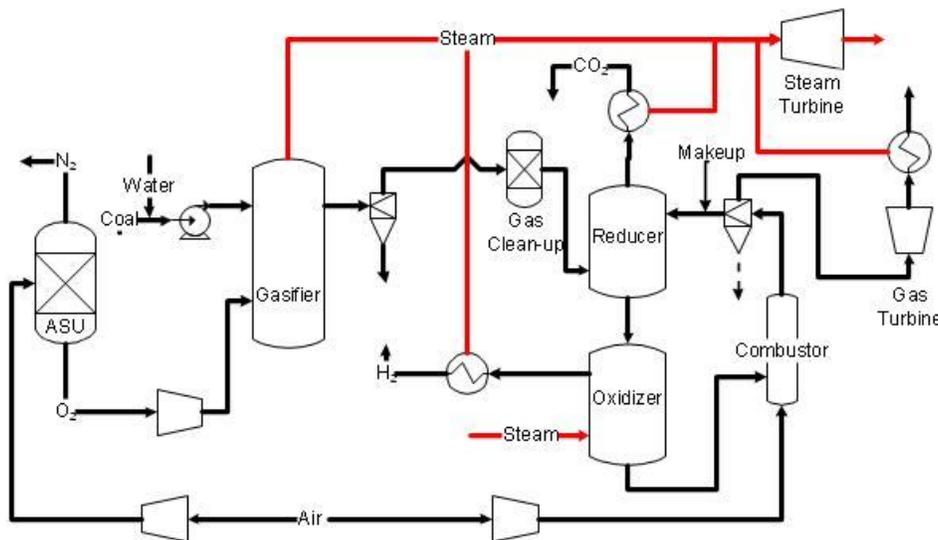


Figure 1. Syngas Chemical Looping Schematic from Hydrogen and Electricity Production

As illustrated in Figure 1, the feedstock of the SCL system is coal-derived syngas, steam and air. There are three main reactors in a chemical looping system: a reducer, an oxidizer and a combustor. In the reducer, Iron oxides (Fe_2O_3) are reduced by CO and H_2 to produce Fe/FeO in solid phase and $\text{CO}_2/\text{H}_2\text{O}$ in gas phase at high temperatures. By condensing the steam from the gaseous products, the CO_2 can be simply separated. The reduced form of iron oxide is sent into the oxidizer to react with steam to yield desired hydrogen. The solid particles, leaving for the reducer in the form of Fe_3O_4 , are to be further oxidized through combustor using compressed air. The hot spent gas containing N_2 and less O_2 with significant recoverable heat can drive gas turbines for power generation. The iron oxides are then recycled to reducer for next looping. The main reactions occurred in SCL system and designated operating conditions are listed in Table 1.

Table 1. SCL Reactors Summary

Reactor	Reactor Type	Reactions	Temperature	Pressure
Reducer	Moving Bed	$\text{Fe}_2\text{O}_3 + \text{CO}/\text{H}_2 \rightarrow 2\text{FeO} + \text{CO}_2/\text{H}_2\text{O}$ $\text{FeO} + \text{CO}/\text{H}_2 \rightarrow \text{Fe} + \text{CO}_2/\text{H}_2\text{O}$	750 - 900 °C	30atm
Oxidizer	Moving Bed	$\text{Fe} + \text{H}_2\text{O} (\text{g}) \rightarrow \text{FeO} + \text{H}_2$ $3\text{FeO} + \text{H}_2\text{O} (\text{g}) \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	500 – 750 °C	30atm
Combustor	Fluidized Bed	$4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3$	950 – 1150 °C	32atm

Oxygen Carriers and Reaction Mechanisms

The oxygen carrier particle circulates inside the chemical looping system and is involved in all the major chemical reactions. Therefore, the performance of oxygen carrier particle is critical to success for this novel technology. The clean coal research group at OSU has synthesized a patented iron-based composite oxygen carrier particle¹¹. The developed particles pertains several key advantages that make it the ideal choice for commercial applications. These advantages include: a. favorable thermodynamic properties; b. low raw material cost; c. high oxygen carrying capacity; d. high melting points for all oxidation states; e. excellent particle strength; f. less environmental and health concerns. Moreover, the composite particle is 10 times more reactive than commercially available Fe_2O_3 and can sustain more than 100 redox cycles according to TGA experiments. These essential achievements on oxygen carrier particles have established a solid foundation for further research on the SCL process.

The reduction of porous iron oxide particles is an important step in the SCL concept, and its reaction mechanism has been studied extensively. For example, in a series of publications, Turkdogan et al. studied the reduction of iron ores of different sizes at various temperatures and gas compositions^{9,10}. In this series of publications, they assumed that the reduction of iron oxide, similar to other non-catalytic gas-solid reactions, consists of the following general steps: 1) gas reactants diffusion across the gas film to the surface of the particle, 2) gas reactants diffusion through the solid, 3) gas reactants adsorption onto the reactive solid surface, 4) chemical reaction at the surface, 5) gas products desorption from the surface, 6) gas products diffusion out of the particle. Since all of these steps occur consecutively, the slowest step controls the overall reduction process. However, Turkdogan et al. found that the reduction of iron oxide does not

follow a single rate-limiting step. Instead, the reduction progressed from a reaction-controlled to a diffusion-controlled mechanism.

Experimental Methodology

Experimental Setup

A Setaram Setsys thermogravimetric analyzer (TGA) is used to characterize the reactivity and recyclability of different iron based composite particles. Figure 2 demonstrates the schematic of the experimental setup. The TGA is connected to a gas control panel through three Teflon tubes. This gas control panel can monitor the inlet gas flow composition, namely the inlet flow rate of three gas cylinders used in the experiment: nitrogen, methane and air. Nitrogen is introduced as an inert atmosphere in this experiment. Methane and air are used to perform the reduction and oxidation reaction. Moreover, the TGA is able to reach a desired temperature as high as 900 °C at atmosphere pressure.

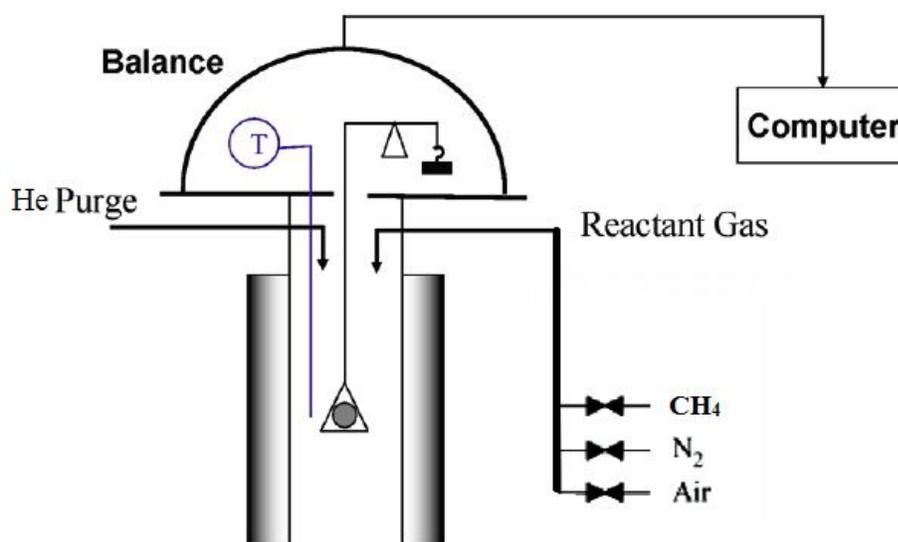


Figure 2. Experimental Setup for Particle Reactivity Studies

Computer software is used to control the furnace temperature and the three gas flow rates, and developed programs are used to execute the single-cycle and multiple-cycle redox reaction.

The weight change of the iron based composite particle is recorded as a function of time and temperature. Inside the furnace, the sample of powder or pellet can be placed inside a quartz sample holder suspended from the glass string of a balance that is accurate within 20 μg , and the reactant gases are injected through a 15 mm inner diameter glass tube. The furnace is protected from reaction by the inert gas Helium, and computer controls the heating of the glass tube to the desired temperature. The actual TGA setup is illustrated in Figure 3.

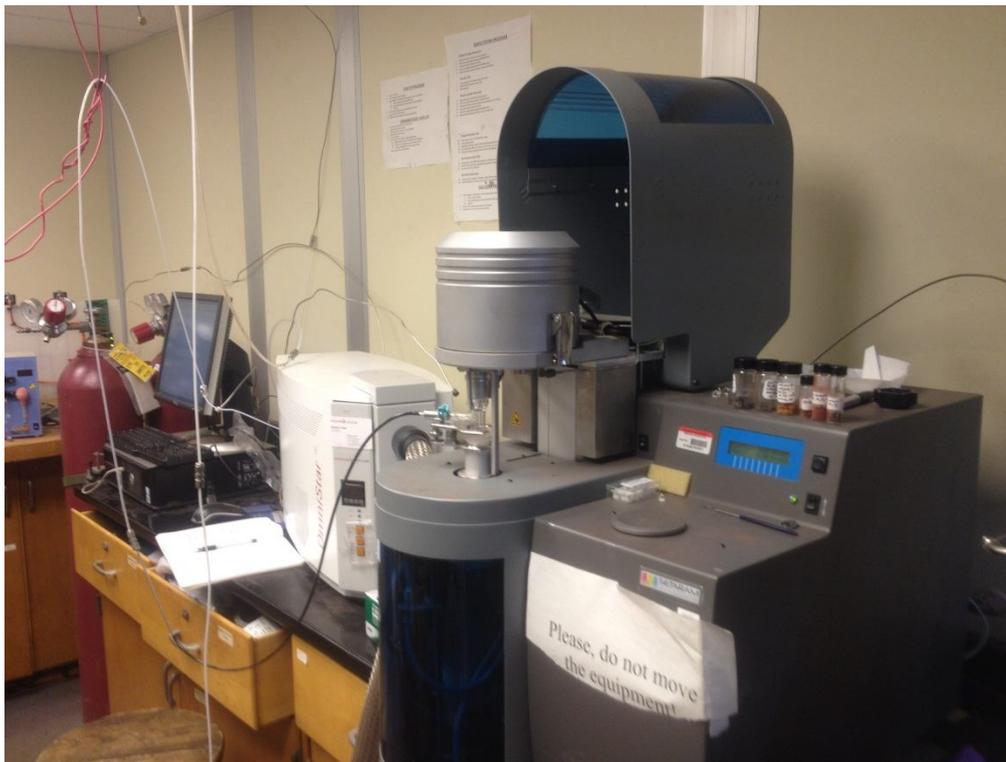


Figure 3. Thermogravimetric Analyzer (TGA)

Experimental Procedure

Experiment 1: Effect of Different Support Materials and Composition in Composite Particles

In the first experiment, the effect of the supported iron oxide's composition on its single-reduction reactivity was investigated using the TGA. The powders of the various supports, with a mean particle diameter of 30 μm , were prepared for through mixing with Fe_2O_3 . Various supports studied in this experiment were Al_2O_3 , MgO , SiO_2 , TiO_2 , Bentonite, and Kaolinite. Specific compositions for each powder sample were tested for performance in the reduction. *(Due to the confidentiality agreement within the research group, the identification and composition of each tested sample will not be revealed.)*

For each experiment, the system was heated to the desired temperature of 900 $^\circ\text{C}$ under an inert gas stream of nitrogen at atmospheric pressure. Once the isothermal period begins at stabilized temperature, reducing gas mixture of CH_4 at 30 mL/min and N_2 at 50 mL/min was introduced from the top of the TGA, and the outlet gas stream was allowed to leave from the bottom. A single reduction reaction was programmed to proceed for 40 minutes with reduction reaction.

Experiment 2: Effect of Reducing Gas (Methane) Composition

In the second experiment, the effect of the reducing gas composition was investigated. This was accomplished by combining different inlet flow rates (volumetric) with a fixed flow rate of nitrogen. The pellets were made from the powders of supported iron oxides, which were prepared in three main steps, namely mixing, pelletization, and sintering. The reduction of the supported iron oxide was carried out isothermally at 900 $^\circ\text{C}$. Five different flow rates of methane

ranging from 50 mL/min to 150 mL/min in increments of 25 mL/min were combined with a fixed nitrogen flow rate of 50 mL/min. This experiment also investigated a single reduction.

Experiment 3: Two-stage Reduction Pattern

Based on the previous experiments of testing the effect in which different supports and reducing gas compositions were tested, a two-stage of reduction pattern for the supported iron oxides was observed. Solid samples were collected at different times for three kinds of composite pellets, each made with a different support material. The support materials tested were magnesium aluminate (MgAl_2O_4), magnesium oxide (MgO), and aluminum oxide (Al_2O_3). The samples were heated to 900°C in a gas flow consist of nitrogen at 50ml/min and helium at 100ml/min. Once the temperature stabilized at the desired value, methane at 50ml/min was introduced. Nitrogen was used as an inert gas throughout the reaction and to flush out the furnace between the reduction and oxidation reactions. This procedure was the pre-test for the experiment, and the data obtained was used for comparison later in the experiment.

The aim of the pre-test was to identify the basic shape of the curve for the tested sample during single redox reaction. As the temperature rose to 900°C , the TGA furnace was set to be flushed with N_2 for 30 minutes, followed by 1 hour of reduction reaction with the reducing mixture of CH_4 and N_2 . Once the reduction reaction was complete, the TGA furnace was again flushed with N_2 for 30 minutes and then oxidizes for 1 hour with air and N_2 . Figure 4 below demonstrates the basic curve of one redox cycle for Fe_2O_3 with MgAl_2O_4 support.

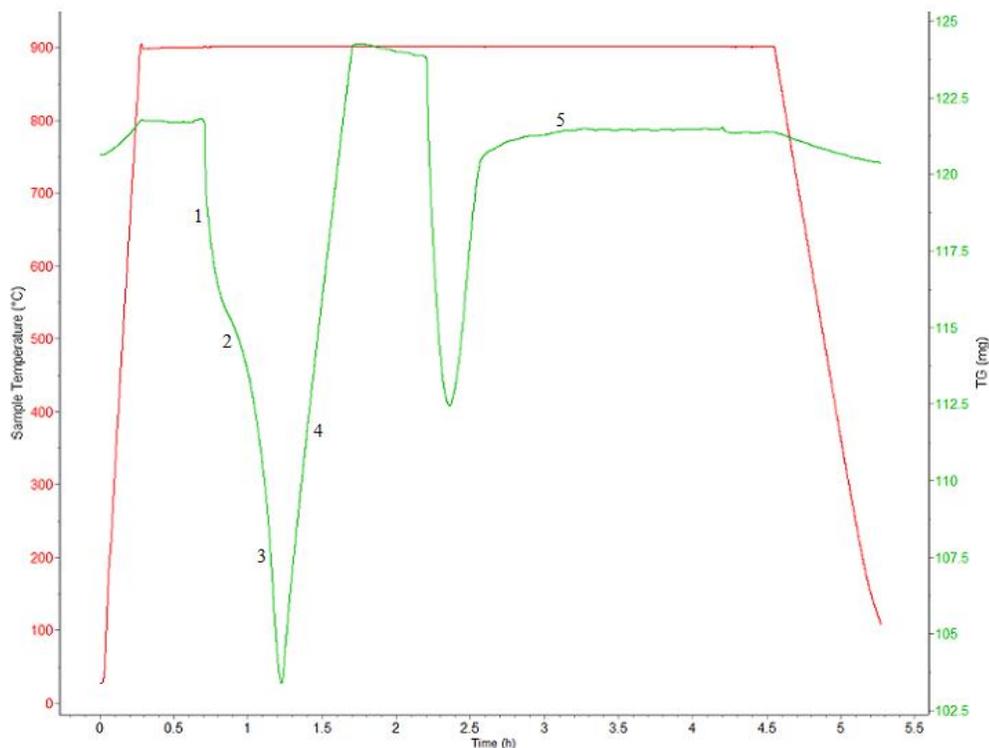


Figure 4. Two-stage Reduction of Fe_2O_3 with MgAl_2O_4 Support

The following experiments were tested based on the first test. Because the different reduction rates of weight change were observed from the pre-test, five samples from different stages from curve were determined to collect. Three were taken from each stage of downward sloping of the reduction; one was taken from carbon deposition period; the last one was taken from oxidation period. The first three testing point were determined by different slope observed through the reduction reaction. Each of the tests should follow the procedure below.

The temperature inside the furnace was raised to 900 °C. Once the temperature was stable for 10 minutes, CH_4 can be injected into furnace. Once the testing point was reached in Figure 4, where a different rate of weight decrease began, the injection of CH_4 was stopped. The sample was flushed for 10 minutes with nitrogen, and the experiment was terminated. The furnace was allowed to cool to room temperature. At room temperature, the sample pellet was collected from

the TGA and stored for further analysis. The collection points at the oxidation stage were determined using a similar procedure. The specific collecting time for each supported sample associated with the percentage of weight change is listed in the following table.

Table 2. Sampling Time Associated with Percentage of Weight Change for Each Supported Pellet

Supports:	Al ₂ O ₃		MgO		Al ₂ MgO ₄	
	Sampling Time(min)	Weight Change %	Sampling Time(min)	Weight Change %	Sampling Time(min)	Weight Change %
P1	6	2.85	6	7.00	6	2.77
p2	10	4.95	12	14.38	13	6.03
p3	15	8.64	NA	NA	17	7.37
p4	24	4.14	18	11.66	36	13.08
p5	216	0.46	252	0.87	228	0.17

Results & Discussion

Experiment 1: Effect of Different Support Materials and Composition in Composite Particles

Reactivity of each different iron-based composite particle was investigated for a single reduction reaction. The TGA was used to measure the weight change of each particle as a function of time and temperature. In the reduction reaction, this weight change is primarily associated with the loss of the oxygen from the iron oxide in the composite particle, based on the assumption that the support materials does not react with methane and serves only as a catalyst. Specifically, the lost oxygen from iron oxide is used to achieve indirect combustion of the carbonaceous fuel in the chemical looping process. The oxygen carrier capacity can be defined as the percentage of weight of oxygen in the iron oxide of the composite particle. The change in its weigh can thus be used to quantify the reactivity of the particle. Specifically, the oxygen capacity is calculated by the following equation.

Equation 1. Oxygen Carrier Capacity Change of Iron-based Composite Particle

$$\text{OC}\% = \frac{\Delta M_o}{M_{total,O}} \times 100\%$$

Based on previous study in which the oxygen capacity of pure iron oxide particle decreased immediately within a few of reaction cycles, the support materials need to be added in order to enhance the reactivity and recyclability of the particle¹¹. In order for chemical looping combustion to be economically feasible, the composite particles are expected to maintain over 100 reaction cycles without exceeding limits of reactivity decrease.

In these experiments, powder mixtures of iron oxide and various metal oxide supports (Al_2O_3 , MgO , SiO_2 , TiO_2 , Bentonite, and Kaolinite) were investigated, and the oxygen carrier capacities were calculated for each sample based on its unique composition of iron oxide and supports. First, the actual weight change from oxygen loss in the iron oxide can be obtained via the experimental data from the TGA. The theoretical maximum value of oxygen reduced by methane can be determined from the amount of iron oxide in the powder sample mixtures. Then, the oxygen capacity can be calculated as the ratio of actual weight change as obtained from the TGA to the theoretical maximum weight. However, several assumptions have been made in this oxygen carrier capacity calculation.

First of all, the supports are considered to be as catalysts and assumed to be unreactive with methane through the entire reaction. However, this assumption is not completely valid because some of the supports undergo complicated reactions with iron oxide, which the chemical and physical properties of the original composite particle may change.

Second, the decomposition of methane to carbon and hydrogen can take place at the temperature of 900 °C. The carbon can deposit on the iron oxide and support materials. This leads to the TGA readings that may not represent reactivity accurately, because it is assumed that weight loss accounts only for oxygen consumption.

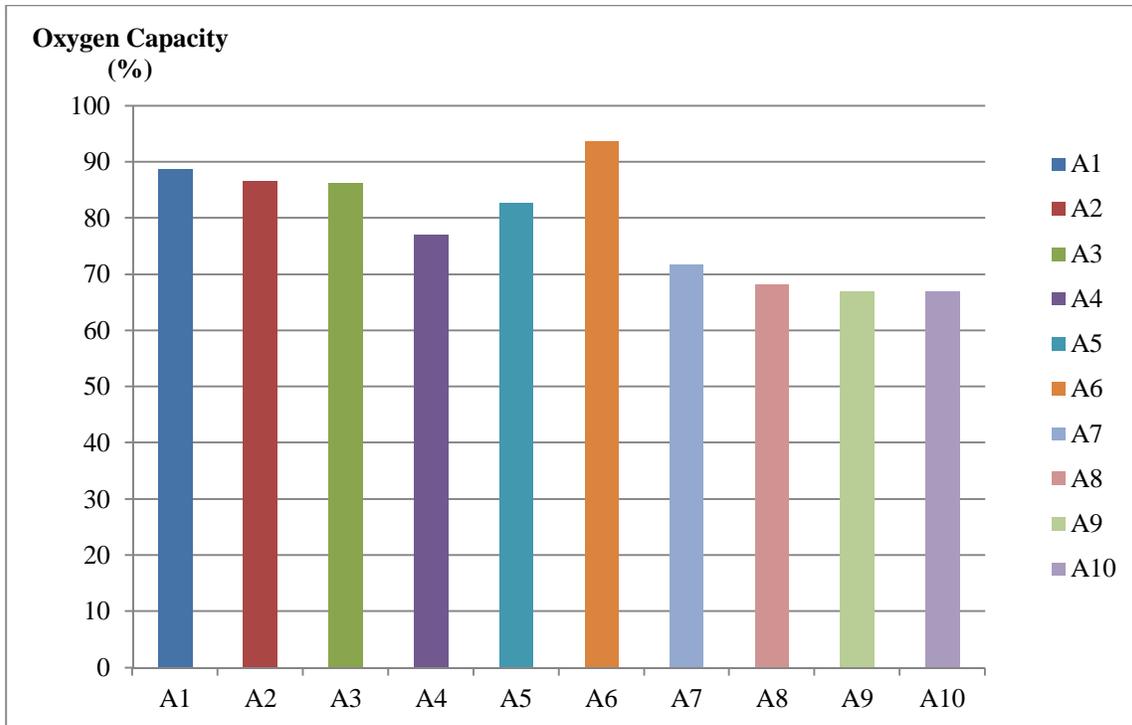


Figure 5. Oxygen Carrier Capacity of Iron-based Powder with Different Support Materials

Figure 5 illustrates the oxygen capacity of each iron-based powder sample is affected by the composition of different support materials. We can easily see from the histogram that some powder sample mixtures, namely, A1, A2, A3, A5, and A6 demonstrate relatively good oxygen carrier capacities that achieve 80% for reduction reaction. A6 exhibits the highest oxygen carrier capacity among the samples (93.71%). However, the other powder samples: A4, A7, A8, A9, and A10, have relatively low oxygen capacities ranging from 68.12% to 77.13%. These mixtures do not satisfy the reactivity requirement to perform as a suitable oxygen carrier.

Figure 6 illustrates the oxygen carrier capacity of the supported iron based composite particle as a function of time for five mixtures: A4, A7, A8, A9, and A10. It is clear from Figure 6 that the reactions occur at different reducing rate across different mixture samples.

Compared to other samples included in Figure 6, A8 is reduced at relatively consistent reaction rate; while this may be desirable in certain scenarios, here it is an indicator of its poor reactivity. Furthermore, two-stage of reaction is identified for rest of the samples, namely A4, A7, A9, and A10. Their reaction rates rise rapidly in the first three minutes until reaching an oxygen carrier capacity level between 30% and 35%. However, the reaction rates slow down afterwards, and reach at the same level as sample A8. Although a relatively high reaction rate occurs in the first stage of reaction, the disadvantage of low oxygen carrier capacity in latter stage lead to further investigation of other supports.

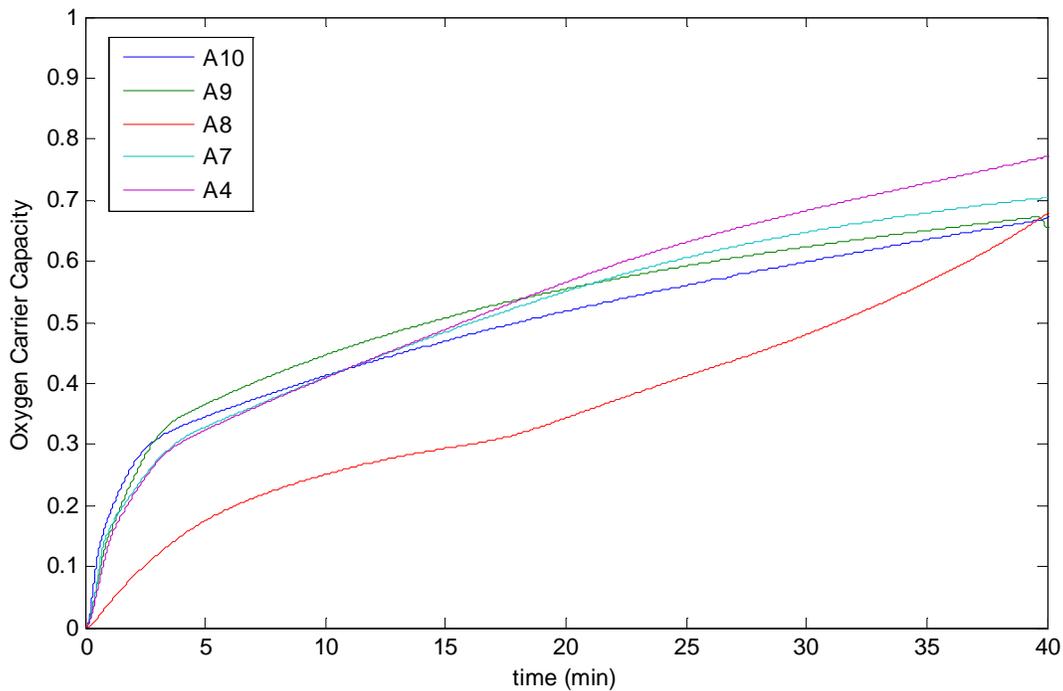


Figure 6. Oxygen Carrier Capacity over Time (A4, A7, A8, A9, A10)

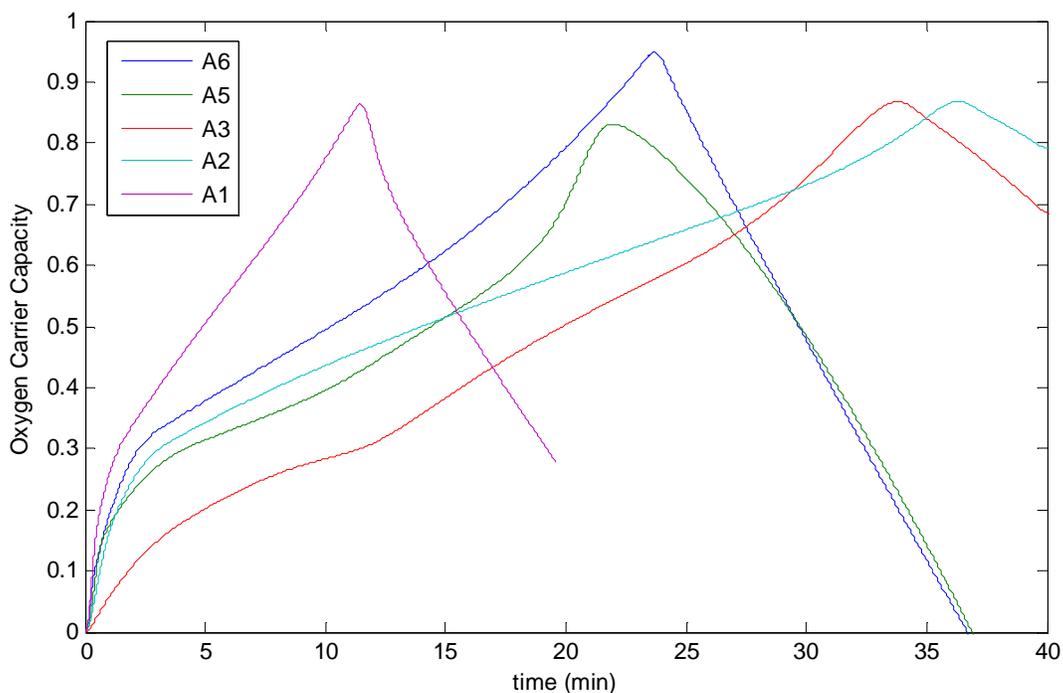


Figure 7. Oxygen Carrier Capacity over Time (A1, A2, A3, A5, A6)

The oxygen carrier capacities of powder samples, A1, A2, A3, A5 and A6 in Figure 7 exhibit distinguishing patterns from those of powder samples in Figure 6. Specifically, the oxygen capacity rises as the reaction occurs, but then decreases once a peak is reached. Compared to the powder samples with relatively slowly and steadily overall reaction rates, the mixtures in Figure 7 demonstrate comparatively fast reaction rates. This is especially true for samples A1, A5, and A6, in which oxygen carrier capacity peaks over 80% are reached in less than 25 minutes of beginning the methane reduction. More importantly, A6 climbs at a fast rate and reaches its peak oxygen capacity of 93.71% around 24 minutes, and A1 rises dramatically to reach its peak of oxygen capacity 88.65% within 12 minutes. Therefore, compared with other samples, A1 is proven to be the best support material for specific iron oxide's composition. It is not only for a suitable oxygen carrier powder to demonstrate excellent reactivity, but also need to

be examined in recyclability test. It is suggested that a suitable supported iron based particle should sustain its level of reactivity through 100 cycles¹¹. Furthermore, it was also noticed that same sample in pelletized form sample may exhibit behavior that is different from its powder form. Based on previous work in my research group, the powder form particles show higher reactivity and recyclability than those of pellet form¹². The advantages of using powder are primarily caused by the following reasons. First, the powder form has a larger surface area to volume ratio than the pellet form, which allows larger reaction area for a given mass of a sample to reduce the oxygen in the iron oxides. Second, volume of the pellet sample has been found to expand during the redox reaction, which may indicate its internal structure being varied. This may cause the reaction to be carried out at different rate. However, for the actual chemical looping system, the powder can cause clogging in the reactors¹². Such clogging issues in the reactor and pipeline may result in potential failure in continuous operation of CLC technology. This is significantly reduced by using the pelletized form, but still remains an issue due to particle attrition. This necessitates the removal of fines and solids makeup during the process.

As indicated earlier, different oxygen carrier capacity patterns are observed in Figure 7. Most notably, there is a decrease in oxygen carrier capacity once the maximum is reached. This decreasing trend is primarily caused by the deposition of carbon on the surface of the reduced particle. Based on the thermodynamics of methane, as the supported Fe_2O_3 particle reduced by CH_4 at a relative high temperature, the methane was decomposed into C and H_2 , and the carbon deposition on reduced Fe_2O_3 is also carried out. Therefore, it has been proposed that the overall reaction rate, when using methane as the reducing agent at elevated temperature such as 900 °C, is affected by the decomposition of methane accompanied by carbon deposition. The carbon deposition on the surface of particle will lead to blockage of pores in the iron oxide particle, and

a decreasing trend of reduction rate is expected. Such phenomena can be observed in Figure 7, the reduction rate for each powder sample also varies as the reaction is carried out, which this two-stage reaction pattern will be explicitly described and investigated in experiment 3.

Experiment 2: Effect of Reducing Gas (Methane) Composition

The effect of varying the reducing gas composition (mixture of methane and nitrogen) was investigated at 900 °C. The reaction rates and the oxygen carrier capacities were compared for combination of varied reducing gas flow rates with a fixed nitrogen flow rate of 50 ml/min N₂ within 54 minutes. These different combinations had the methane gas compositions ranging from 50% by volume to 75% by volume. As can be seen from Figure 8, the supported iron oxide pellet is reduced at a relatively slow reaction rate when the flow rate of methane is at 50 mL/min, and its oxygen carrier capacity nearly reaches 30%. However, the reaction rate can be greatly improved by increasing the methane gas composition to 60% (75 mL/min), which leads the oxygen carrier capacity to achieve nearly 70% within 54 minutes. Based on gas-solid reaction theory, as the reducing gas volumetric flow rate increases, it becomes more rapid that the gas reactants cross the gas film to the surface of the particle. However, with multiple gas-solid reactions occur consecutively, only the slowest step controls the reduction process of iron oxides. As the flow rate of reducing gas reaches a level that is adequate to eliminate the external mass transfer resistance, the reduction of iron oxide will progress from a reaction-controlled to a diffusion-controlled mechanism. Therefore, the minimum gas flow rate to reach this limit is defined as the minimum gas flow. From Figure 8, it can be observed that the overall reaction pattern becomes similar once methane gas flow rate reaches above 100 mL/min. Therefore, it is

determined that the minimum gas flow rate of 100 mL/min, or 66.67% methane gas composition by volume.

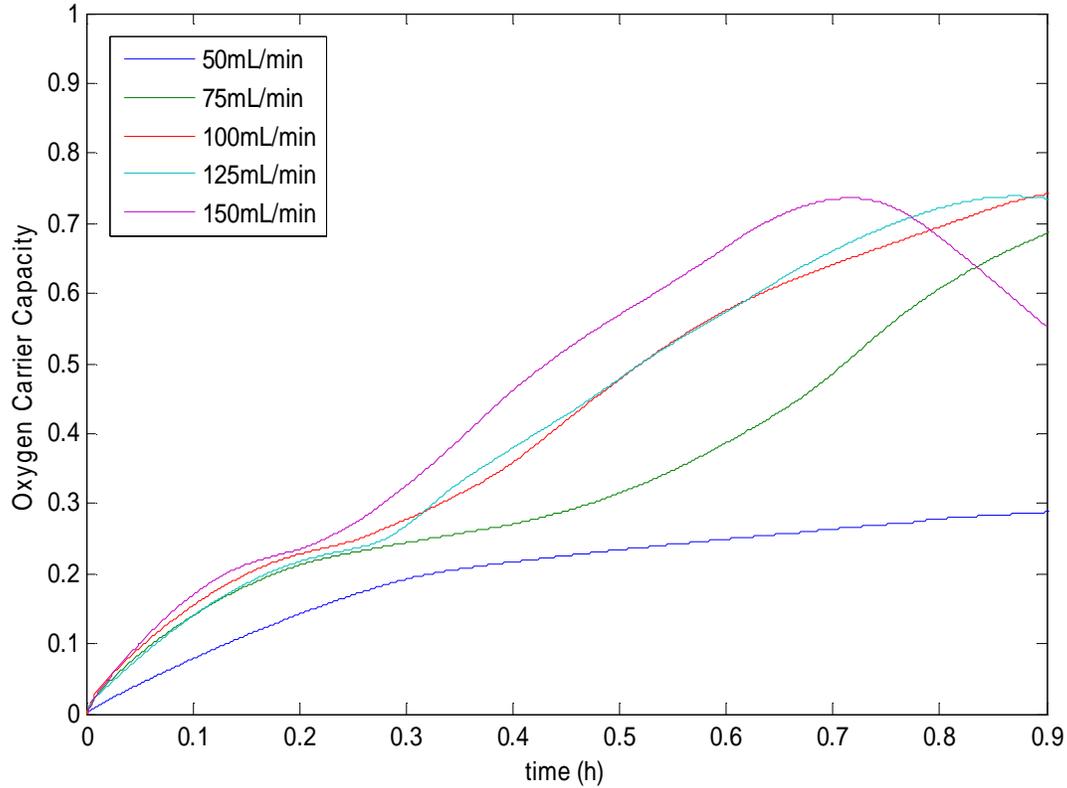


Figure 8. Oxygen Carrier Capacity over Time for Various Methane Flow Rate

Experiment 3: Two-stage Reduction Pattern

It was observed from the previous experiments that the reduction of each supported iron-oxide pellets showed a similar two-stage reduction pattern. This two-stage pattern was revealed based on the TGA experiments for three different support materials, specifically magnesium aluminate (MgAl_2O_4), magnesium oxide (MgO), and aluminum oxide (Al_2O_3). Experimental conditions are as follows:

Pellet weight : 0.057g to 0.121g

Pellet diameter : 4 mm to 5 mm

Temperature : 1173 K

Gas flow rate : 50 mL/min for methane

: 50 mL/min for air

Flushing gas flow rate: 50 mL/min for nitrogen

Similar size and weight pellets of the different supports were tested under the same conditions in order to make comparisons in their reduction behaviors. Figure 9 demonstrates the weight changes, in the percentage of the original weight, over time for the three different supported iron oxide pellets during the methane reduction reaction. The weight of each sample is decreased once the methane reduction is taking place. The duration of reduction reaction and reduction reaction rates in the decreasing portions of the curves vary with the supports. The rates of weight change are calculated numerically and plotted as a function of time in Figure 10. The three different rates of reaction are easily observed from the iron oxide samples with different supports. Among these three oxygen carriers, the MgO-supported sample shows the fastest reaction rate. Additionally, the Al₂O₃-supported sample exhibits a similar behavior as the MgAl₂O₄-supported sample at the initial stage. As shown in Figure 10, all three samples share a similar behavior at the start; the rate of weight change is initially high, but decreasing sharply. After reaching a minimum rate of weight change, rate of weight change begins to increase until a sharp drop appears at the end of the reduction phase.

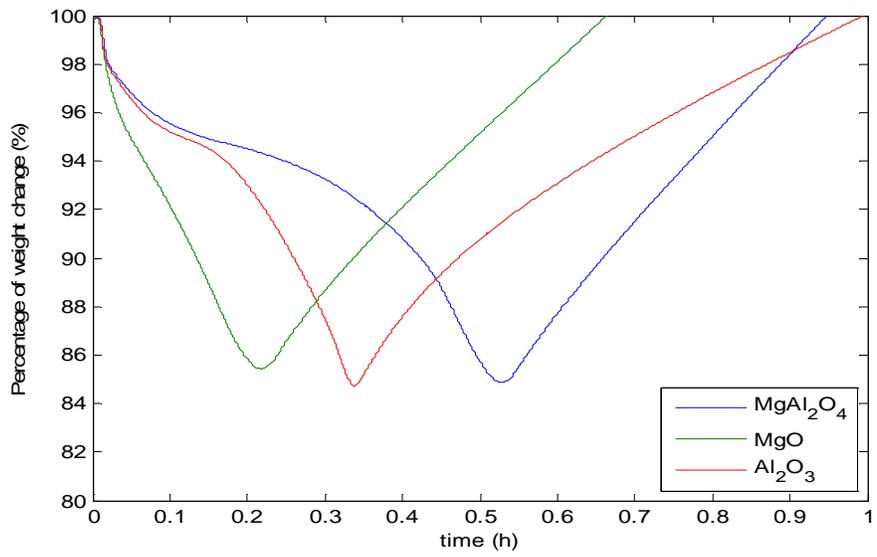


Figure 9. Percentage of Original Weight for Composite Pellets during Reduction over Time

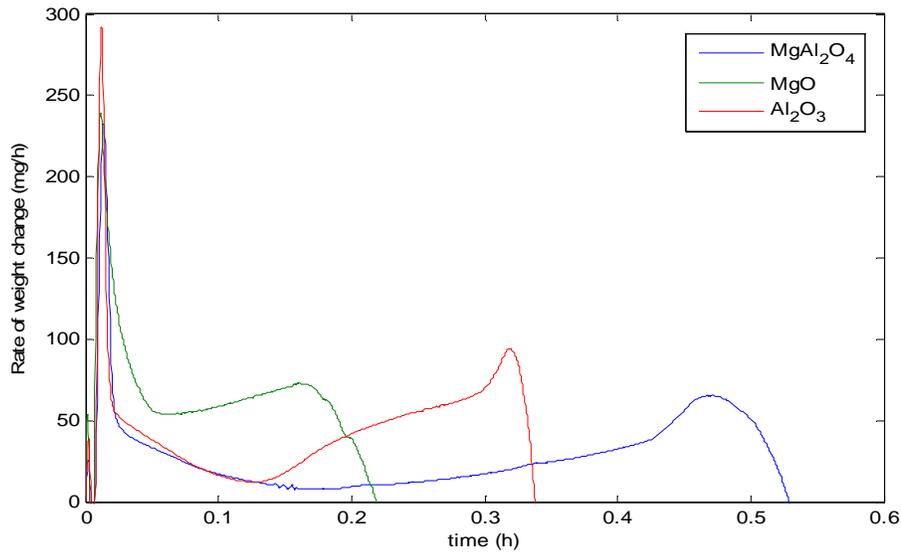
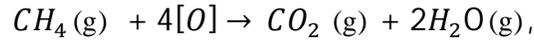


Figure 10. Rate of Percentage Weight Changes for Composite Pellets during Reduction over Time

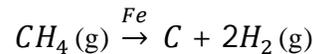
As can be seen from Figure 9 and 10, once each curve reaches the bottom, the weight of each supported iron oxide starts to increase with time. The interesting shape of curves in Figure 9

can be attributed to the following two stages reaction mechanisms: 1. reduction reaction of iron oxides by methane (weight losing); 2. carbon deposition from the decomposition of methane (weight gaining)¹³. The solid sample loses weight in the 1st phase as iron oxide is reduced:



Where [O] is from iron oxides

As oxygen in the sample is depleted, metallic iron dominates the surface, and reactions of the 1st phase are superseded by that of the 2nd:



The weights of samples increase in the 2nd stage because carbon resulting from the decomposition of methane was deposited on the surface of the samples without being further oxidized.

As proposed, the overall reaction rate is determined by the interaction between these two reactions. At the same time as the oxygen ion in iron oxides is reduced by methane at 900 °C, the carbon decomposed from methane accumulates on the surface of pellets and block pores, which reduces the rate of the intraparticle diffusion. Once this intraparticle diffusion rate is lower than the rate of carbon deposition on the surface of the solid, the decomposition of methane will dominate the overall reaction rate, leads to an increasing trend of the weight of the pellets.

The “transition point”, as shown in Figure 9, refers to the point where the rate of weight losing reaction equals the weight gaining reaction. This point is very important in CLC combustion using methane as feedstock since oxygen carrier no longer functions as an oxygen transfer material after this point and the fuel efficiency deteriorates due to methane

decomposition. A “transition point” taking place at the more reduced form of iron oxides is desirable since it indicates a higher oxygen carrying capacity in CLC, which means that more oxygen could be transferred to fuel by a fixed amount of oxygen carrier. As shown in Figure 9, the transition point occurred when the sample is reduced to a mixture of 75% Fe and 25% FeO by calculation for MgO, Al₂O₃, and MgAl₂O₄ supported iron oxides.

In order to obtain a detailed understanding on how these three types of supported iron oxides behaved during reduction reactions, solid samples were collected at different points as shown in Figure 4, 11, and 12. These samples were then analyzed using a series of analytical methods including Brunauer–Emmett–Teller (BET), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and carbon analyzer to investigate how the solid evolved during the reaction.

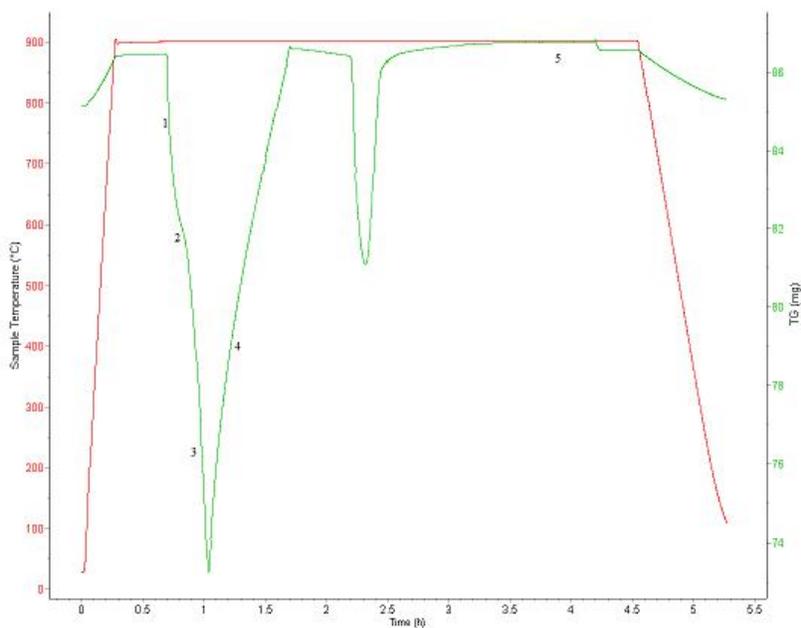


Figure 11: Two-stage Reduction of Fe₂O₃ with Support Al₂O₃

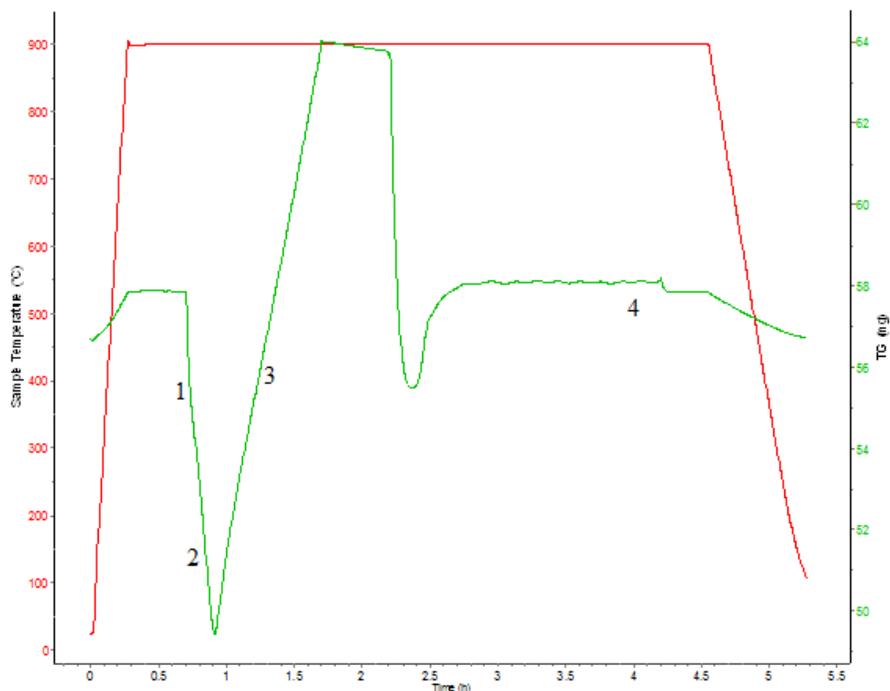


Figure 12: Two-stage Reduction of Fe_2O_3 with Support MgO

The morphological properties of three supported iron oxides were tested in a NOVA 4200e analyzer (Quantachrome Co.). The surface area and pore volume were measured by BET method at $-193\text{ }^\circ\text{C}$ using liquid N_2 as adsorbent.

As shown in Figure 13 and Figure 14, all three supported pellets have the largest surface area and pore volume at Point 4, where significant methane decomposition had taken place for a while. The huge surface area and pore volume are largely attributed to the deposited carbon on solid samples. During this stage of reduction reaction, the MgO -supported oxygen carrier performs distinctly from the Al_2O_3 - and MgAl_2O_4 -supported pellets demonstrating much higher experimental values for surface area and pore volume. As for Al_2O_3 - and MgAl_2O_4 -supported oxygen carriers, there are little changes for the surface and pore volume. Thus, the morphologic properties cannot fully explain the difference on the reaction rate and “transition point” among

the three oxygen carriers. Therefore, to further the understanding of the complex iron oxides-support relationship, the sampled supported iron oxides at different stages will be investigated by the post-experimental solid characterization methods, such as analyzing surface chemistry by XPS, examining surface morphology by SEM and identifying the metal complex by XRD.

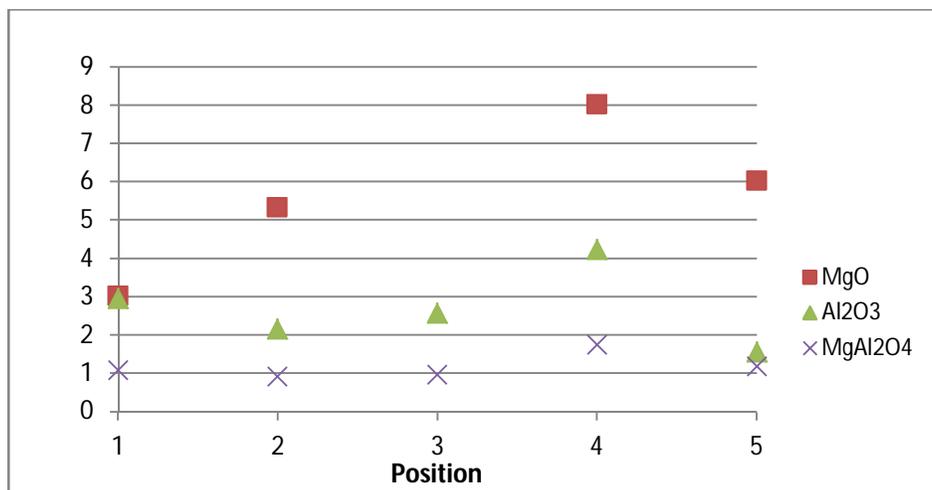


Figure 13: Surface Area for Supported Iron Oxide Pellets at Different Points

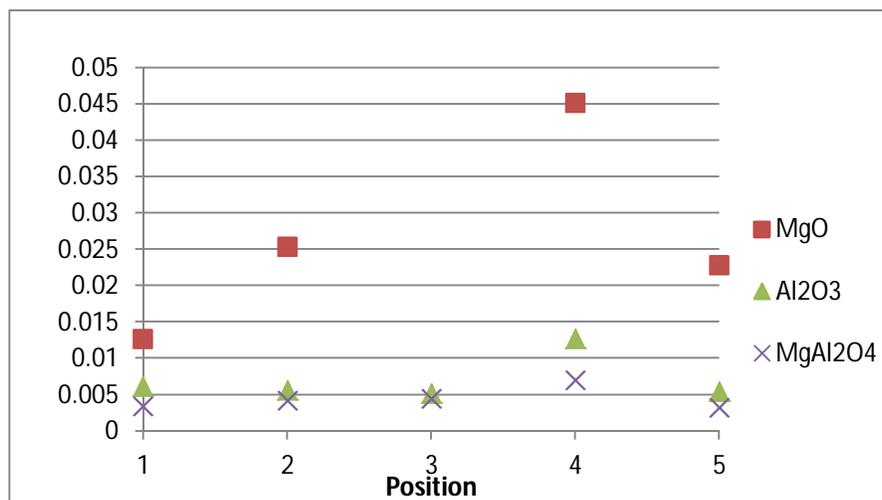


Figure 14: Total Pore Volume for Supported Iron Oxide Pellets at Different Points

Conclusions & Recommendations

Iron oxides on different support materials are synthesized and compared. The reactivity for various supported iron oxides is investigated by thermogravimetric analyzer. Al is proven to be the best support materials for specific iron oxides' composition. The effect of varying the reducing gas composition (mixture of methane and nitrogen) is also examined. Furthermore, the minimum gas flow rate of 100 mL/min, or 66.67% methane gas composition is identified. The MgAl₂O₄-, MgO-, and Al₂O₃-supported iron oxides, are synthesized and explicitly studied by thermogravimetric analysis experiments. TGA experiments show that iron oxides on all three different support materials exhibited a similar two-stage reduction pattern. Supported iron oxide at different stages are sampled and investigated by post-experimental solid characterization methods such as determining pore density by BET. The largest surface area and pore volume where significant methane decomposition occurred, which are largely attributed to the deposited carbon on solid samples. The MgO-supported iron oxides perform distinctly reduction behavior from the other synthesized particles. The reasons for the different behaviors may be attributed to the crystal structure change in the particles during methane reduction. Therefore, to further the understanding of the complex iron oxides-support relationship, and the proposed mechanism for carbon deposition reduction, the sampled supported iron oxides at different stages will be investigated by the post-experimental solid characterization methods, such as analyzing surface chemistry by XPS, examining surface morphology by SEM and identifying the metal complex by XRD. These results provide important fundamental knowledge about the reduction mechanism in CLC with methane.

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