Processing and evaluation of next generation oxygen carrier materials for chemical looping combustion

Mina Hamedi Rad

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A Thesis

Entitled

Processing and Evaluation of Next Generation Oxygen Carrier Materials for Chemical Looping Combustion

by

Mina Hamedi Rad

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Chemical Engineering

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May 2015
An Abstract of
Processing and evaluation of next generation oxygen carrier materials for Chemical Looping Combustion

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This study follows two methods to achieve a modified CaMnO$_{3-\delta}$ structure with higher oxygen capacity and stability. The first method is replacement of manganese with iron as a cheaper alternative and the second method is size effect investigations of A-site dopants on CaMn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ and its oxygen capacity and stability. Solid state reaction followed by mechanical extrusion is used as the preparation method. All synthesized perovskites are characterized by TGA and XRD analyses. The samples of highest oxygen capacity and stability are further characterized by SEM and BET analyses. Oxygen uncoupling behavior and reactivity of these samples are also examined using a fluidized bed reactor performing Chemical Looping Combustion. The temperature effect is also investigated during chemical looping process at temperatures of 800, 850, 900 and 950°C.

In the first method, since calcium could not be incorporated in the structure, strontium is used as the A-site cation. SrFeO$_{3-\delta}$ has shown to be more stable than CaMnO$_{3-\delta}$. However, because of low oxygen capacity, it is doped on the A-site (La and Ba) and B-site (Al, Ti, Mn, Co) by 10 mol% (Sr$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$, Sr$_{0.9}$Ba$_{0.1}$FeO$_{3-\delta}$, SrFe$_{0.9}$Al$_{0.1}$O$_{3-\delta}$,
SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$, SrFe$_{0.9}$Mn$_{0.1}$O$_{3-\delta}$, SrFe$_{0.9}$Co$_{0.1}$O$_{3-\delta}$). Results reveal that manganese doped structure (SrFe$_{0.9}$Mn$_{0.1}$O$_{3-\delta}$) has the highest oxygen capacity. Adding more manganese to the structure increases the oxygen capacity even further. The best iron-based structure has 30 mol% manganese, doped on the B-site, having 28% mass change in an inert atmosphere (SrFe$_{0.7}$Mn$_{0.3}$O$_{3-\delta}$, SFM73) and high stability.

Results of conducted experiments in second method demonstrated that Strontium doped perovskite (Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$, CS91MF91) is the best synthesized oxygen carrier among all synthesized manganese and iron-based perovskites. This material shows excellent oxygen uptake and release (1.78 wt. %) and high stability. The reactivity and oxygen uncoupling behavior experiments of SFM73 and CS91MF91 show no uncoupling behavior in the synthesized perovskites, nearly complete methane conversion for SFM73 and complete methane conversion for CS91MF91. The synthesized perovskites also possess high stability and no agglomeration tendency.
I dedicate my thesis work to my family and many friends. A special feeling of gratitude to my loving parents, whose unconditional encouragement and support have always helped me in every stage of my life; to my caring brother, Sam, whose guidance has always assisted me throughout every tough decision. I also dedicate my thesis to my friends who have had the confidence in me and to every other person who ever wished me good.
Acknowledgements

This thesis becomes a reality with the kind support of many individuals. I would like to extend my sincere appreciation to all of them. My sincere acknowledgment goes to my advisor and committee chair Dr. Arunan Nadarajah who has been very influential in ensuring my academic and professional well-being ever since I joined the graduate program. I am also thankful to Drs. Kim, and Lipscomb for serving on my supervisory committee and for their encouragement and timely support. It’s a great honor to have such outstanding researchers in the committee. Their constructive feedback at various levels has significantly helped me in shaping my thesis up to completion. I would like to express my special gratitude towards Dr. Mahammad Hassan Imanieh. He has been a great mentor, whose constructive feedback, unfailing support and constant encouragement always motivated me to excel in my research. It is my pleasure to extend my gratitude to Dr. Schall for her cheerful encouragement and Renee Norrils for being a great secretary. I would like to acknowledge the Chemical and Environmental Engineering department at the University of Toledo for providing me the support for completion of this endeavor. I would like to thank the US department of Energy for the Funding of the project.
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List of Abbreviations

BET............................Brunauer- Emmett- Teller
BFB............................Bubbling Fluidized Bed
CFB............................Circulating Fluidized Bed
CFC............................Chlorofluorocarbons
CLC............................Chemical Looping Combustion
CLOU..........................Chemical Looping Combustion with Oxygen Uncoupling
EDS............................Energy Dispersive Spectroscopy
SEM............................Scanning Electron Microscopy
TGA............................Thermogravimetry Analysis
XRD............................X-ray Diffraction
List of Symbols

δ.................................Oxygen Non-stoichiometry

t ..................................Tolerance factor

ra .............................Ionic radii of A-site cation
rb .............................Ionic radii of B-site cation
ro .............................Ionic radii of Oxygen anions
rcr .............................Critical radius for oxygen ion conduction

Å..................................Angstrom

R0 .............................Oxygen capacity
Chapter 1

1. Introduction

1.1. Greenhouse gases and Global warming

Global warming is one of the major crises that the modern world has faced during the last couple of decades. It has caused an increase in the earth’s surface temperature and has resulted in temperature fluctuations all over the world [1]. Anthropogenic emissions, heating, transportation and fossil fuel combustion are some known sources of greenhouse gas emissions, which are major contributors to the global warming effect. During the last decades, a drastic increase in energy consumption around the world has made civilization strongly dependent on fossil fuels (coal, petroleum and natural gas). Fossil fuels are the most significant contributors to anthropogenic carbon dioxide (CO₂) emissions, causing a serious challenge for industries and scientists [2].

As shown in figure 1.1, the earth is exposed to a large amount of solar radiation, particularly electromagnetic energy. Also, about half the radiation is visible short-wave.
Figure 1-1 A Schematic representation of global warming effect

These short length waves pass through the atmosphere and reach the Earth. This heats up the earth’s surface and as a result, long length waves are emitted, which will be absorbed by greenhouse gases, such as water vapor, CO$_2$, CH$_4$, N$_2$O, chlorofluorocarbons (CFC), SF$_6$, aerosols and nitrous oxides [3, 4].

An increase in the amount of greenhouse gases has been reported since the industrial revolution [5], (from a value of about 280 ppm to 390 ppm in 2010 [6]) which makes finding solutions to reduce it necessary. In recent years, there have been several introduced and experimented approaches for dealing with this crisis. One approach is using renewable resources for power generation in order to reduce CO$_2$ production. Renewable resources include bio-fuels, wind, solar power and many more. Although fossil fuels are going to be ruled over by renewable energy sources in the future, these technologies are at their early stages of evolution and cannot be considered as viable options, at least for use in the near future [7]. Another alternative is increasing the efficiency of current fuels and reducing their energy consumption. This is possible through mandated increases in vehicle fuel economy. This is also not practical for current use. Carbon capture and sequestration (CCS) technologies, on the other hand, are novel popular approaches for CO$_2$ capture. Oxy-fuel combustion, post combustion, and pre-combustion can be categorized as CCS
technologies. In oxy-fuel combustion, fuel is in contact with pure oxygen instead of air. Post combustion is known as separation of CO₂ from the fuel by chemical adsorption using amines, cryogenic nitrogen separation from air, and other available approaches. Pre-combustion is the process of fuel decarbonization before entering the reactor [6, 8-10]. In all CCS technologies, after CO₂ is captured, it is pressurized and transferred to storage facilities. All of CCS technologies have gone through a development path during the last few years and some of them are currently available at commercial scale[3]. Besides their advantages, these technologies are energy intensive and expensive which make them unfavorable candidates to further develop especially to an industrial scale[6]. In the effort to develop low cost CCS technologies, Chemical Looping Combustion (CLC), as a third generation CCS technology, was introduced and has attracted a great amount of attention due to its high efficiency, low price, and inherent CO₂ capture [1].

1.2. Chemical Looping Combustion (CLC) and Chemical Looping Combustion with Oxygen Uncoupling (CLOU)

Chemical Looping Combustion (CLC), also called unmixed combustion [11] was introduced for the first time in 1954 by Lewis et al. [12] for pure CO₂ production from fossil fuels by using two interconnected fluidized beds as the reactor system. Afterwards in 1983, Richter and Knoche [13] used CLC to increase thermal efficiency in power generation stations. Later on, Ishida et al. [14] presented the use of this technology for global warming effect mitigation and started laboratory experiments on oxygen carrier materials [15].

In a CLC process, a combustion reaction is composed of two separate consecutive oxidation and reduction reactions, which form a cycle. In this process, usually a metal
oxide, called oxygen carrier, is oxidized in presence of air and is reduced while in contact with the fuel [16]. This way, the combustion takes place in the presence of pure oxygen released from oxygen carriers during reduction, resulting in H\textsubscript{2}O vapor and CO\textsubscript{2} as the only combustion products. Having H\textsubscript{2}O vapor and CO\textsubscript{2} as the outlet stream represents the fact that no harmful undesired byproducts have been produced (such as NO\textsubscript{x} which is produced in a conventional combustion reaction). Using a simple water condensation unit, CO\textsubscript{2} can be separated from H\textsubscript{2}O vapor eliminating the need for additional expensive and energy intensive utilities and CO\textsubscript{2} can be easily packed and transferred to storage facilities.

The oxidation reaction is known to be always exothermic. However, the reduction reaction can be both endothermic and exothermic depending on the oxygen carrier and the utilized fuel [4]. The net released energy in these redox reactions is the same as combustion of the same fuel in the air, which demonstrates that CLC does not involve any additional energy consumption for CO\textsubscript{2} separation.

Figure 1.2 demonstrates a schematic of CLC. In this figure, two interconnected fluidized bed reactors are used as air and fuel reactor. This reactor type is the most common reactor used in CLC. The oxygen carrier is oxidized in the air reactor and is then transferred to the fuel reactor for reduction and oxygen release. Equation (1.1) and (1.2) occur in air and fuel reactor respectively.

\[
2Me_xO_y + O_2 \rightarrow 2Me_xO_{y+1} \quad (1.1)
\]

\[
(2n + m)Me_xO_{y+1} + C_nH_{2m} \rightarrow (2n + m)Me_xO_y + nCO_2 + mH_2O \quad (1.2)
\]
Chemical Looping Combustion with oxygen uncoupling (CLOU) is another CLC process that can be used for pure CO\textsubscript{2} production during fossil fuel combustion. This process is the same as CLC in terms of efficiency, combustion products, and energy production. However, it is different in combustion mechanism. The combustion mechanism is shown in reactions (1.3) and (1.4)

\[
2Me_xO_{y+1} \rightarrow 2Me_xO_y + O_2 \quad (1.3)
\]

\[
C_nH_{2m} + \left(n + \frac{m}{2}\right)O_2 \rightarrow nCO_2 + mH_2O \quad (1.4)
\]

During these reactions, the oxygen carrier will not be in direct contact with the fuel. Instead the released oxygen reacts directly with the fuel and returns to the air reactor for re-oxidation.

Gaseous, liquid and solid fuels can be used in CLC processes. The gaseous fuels, such as methane, are more common due to less complicated combustion mechanism.
Liquid fuels on the contrary, are not common types of fuels, especially in CLC and CLOU. These fuels have not been investigated in the literature for evaluation of their functionality and efficiency in a CLC process. These fuels can result in an efficient CLC if they are injected directly to the fuel reactor. Otherwise, they will evaporate prior to entering the reactor resulting in CO and H₂ formation. If injected directly to the reactor, the evaporation and oxidation occur simultaneously and CO₂ and H₂O vapor are the only products.

Solid fuels require a more complicated process for fuel combustion. There are two approaches dealing with these types of fuels. The first approach is prior gasification of the fuel. Afterwards, the fuel is combusted in a conventional gaseous CLC process. This approach is not economically viable due to use of energy intensive utilities. The second approach is the in situ gasification of the fuel in the fuel reactor. The existence of solid fuel in the fuel reactor causes the fuel to turn into charred and a volatile part. The volatile part reacts with oxygen and produces CO₂ and H₂O vapor. However, the charred part in contact with steam and CO₂ produces H₂ and CO, which are the reactants of an oxidation reaction having CO₂ and H₂O vapor as products. This can be done by use of a recycling stream of CO₂ and/or steam to increase the rate of gasification process (existence of H₂ and CO₂ can slow down the gasification process). This process can be time consuming and can result in parts of char to exit the reactor and decrease the efficiency of the process substantially. The other disadvantage of this process is the need to separate the unburnt fuel from the oxygen carrier prior to its re-oxidation [17-20].
1.3. Oxygen Carriers in CLC processes

For an effective CLC process, efficient oxygen carriers are necessary. Since metallic surfaces are able to catalyze the decarbonization process of carbonaceous fuels, metal oxides are usually used as oxygen carrier materials for CLC purposes [21]. Although recently introduced theoretical methods, such as the Microkinetic modeling, have accelerated the oxygen carrier design and selection, trial and error and heuristic methods are the most general approaches for these purposes[22]. Choice of the best oxygen carrier for a successful and efficient CLC process requires extensive knowledge of properties and intended application of the oxygen carrier. A promising candidate should possess the following characteristics:

High mechanical strength, resistance to attrition and agglomeration, stability, fast kinetics, high reactivity for oxidation and reduction processes, non-toxicity, recyclability, sufficient oxygen transport capacity, favorable thermodynamics regarding fuel conversion, negligible carbon deposition, good fluidization properties, environmentally benign characteristics and low cost (for the material to become commercially viable) [3, 6, 23-25]. In CLC processes these materials ought to release molecular oxygen at high operating temperatures (800°C-1200°C) [17].

As mentioned before, metal oxides are one of the promising materials in CLC processes because of their special characteristics. However, it has been proven that pure metal oxides do not fulfil the desired performance at CLC operating conditions and during numerous oxidation and reduction cycles. These materials show diminishing redox properties and reaction rates as the number of cycles increase [3, 26]. Hence using a
combination of metals oxides have been proven to demonstrate outstanding characteristics that make them good oxygen carriers. Adding metal oxides in a single material creates good synergic effects and results in having good qualities of each material in a single oxygen carrier [21]. Another alternative to enhance metal oxides performances is achieved by using an inert support associated with them.

1.3.1. Oxygen carriers History and Theoretical background

Until now, over 700 oxygen carriers have been developed and studied. Ni-based materials are one of the most extensively studied oxygen carriers in the literature. They show high reactivity, reversibility and good performance at high temperatures (900°C-1300°C). By using Ni-based materials, almost complete CH₄ conversion can be achieved. They have some of the best qualities and effectiveness during CLC processes from lab scale reactors to pilot plants up to 120 Kwh. Despite their advantages, Ni-based materials have some thermodynamic restrictions that result in traces of CO and H₂ at the reactor outlet. They are also toxic materials, causing the need for extra safety measures preventing environmental pollutions. NiO materials should be utilized using an inert support to eliminate their low reaction rates (because of their low porosity) and strong agglomeration tendency. For NiO, the widely used inert materials are Alumina, nickel Aluminate and Magnesium Aluminate, which have high thermal stability and mechanical strength [3, 27].

Cu-based materials are another group of investigated oxygen carriers. These materials have high reaction rates and high oxygen transfer capacities with no thermodynamic restrictions. They are also cheaper than nickel and have more environmentally friendly characteristics. Utilizing pure CuO as oxygen carrier, results in a decrease in oxidation reaction rates with an increase in cycle number. By adding inert
supports, such as Al₂O₃, bentonite, CuAl₂O₄, MgO, MgAl₂O₄, SiO₂, TiO₂ and ZrO₂, this problem will be solved. However, Cu-based materials show strong agglomeration tendency at low temperatures because of Cu melting point (1085°C). As a result, these materials are good candidates for CLC processes at temperatures lower than 800°C, which results in a less efficient CLC [3].

In spite of their weak redox properties (low oxygen transport capacity and CH₄ conversion), Fe-based oxygen carriers are attractive alternatives compared to the previous ones because of their low cost and environmental compatibility. These materials have high reactivity, especially for CO and H₂ fuels, and relatively lower reactivity for CH₄. Fe-based materials also have low tendency to carbon formation. In most cases, because of their weak oxygen transport properties they are used with a content of 60 wt% or higher in the oxygen carrier. Most common inert supports for these materials are Al₂O₃ (most usual), MgAl₂O₃, SiO₂, TiO₂ and Zr-based [3].

Mn-based materials, just like Fe-based materials, are attractive candidates because of the low cost and non-toxicity. Compared to iron compounds, they have higher oxygen transport capacities, which makes them attractive options. Like any other pure metal oxide, manganese oxide shows low reactivity with methane and coal. Inert supports, such as Al₂O₃, SiO₂, TiO₂ and MgAl₂O₄, cannot be associated with manganese oxide since they form highly irreversible unreactive phases. ZrO₂, as inert material, can show good reactivity and stability, but using it results in phase transformation and agglomeration. As a result, ZrO₂ becomes stabilized by using MgO, CaO and CuO, which results in a highly reactive oxygen carrier with CO and H₂ and a less reactive oxygen carrier with CH₄.
Cobalt oxides are another group of candidates as oxygen carriers due to their high oxygen transport capability. Considering their high cost and environmental hazards, still they have been considered as good candidates [3]. Ilmenite (FeTiO₃) is a material composed of (FeO.TiO), which is highly reactive with H₂ and has low reactivity with CO and CH₄. This material also has the advantage of low cost. However, at its highly reduced state, it shows defluidization properties. It also demonstrates structural changes after calcination process [28].

As mentioned before, using a combination of metal oxides can be an effective approach to oxygen carrier production with enhanced properties compared to pure metal oxides. The main outcome of this approach is improvement in conversion, mechanical strength, reactivity and stability, minimization of attrition rates, carbon deposition, preparation costs (by using cheaper metal oxides) and use of toxic metal oxides (such as nickel oxide) [3].

Ceramics are one of the few candidates for high temperature applications mostly in catalytic combustion processes, such as CLC [29]. Recently special kinds of ceramics, called perovskite oxides, have attracted great amount of attention due to their notable characteristics during redox reactions and CLC processes. Perovskites are attractive candidates because of their structure reversibility, thermal stability, and catalytic activity during redox cycles[29]. As stated by Pena et al. [30] most of these special properties are due to the fact that around 90% of metallic natural elements in the periodic table are stable in a perovskite structure as shown in figure 1.3.
1.3.2. Perovskite oxides

The general formula for an ideal perovskite structure is ABX₃, in which A and B are both cations, with A being a larger cation than B [32-34]. Multivalent transition metals will usually locate on the B-site, halides and oxides on the X-site and larger cations (such as Na⁺, K⁺, Ca²⁺, Sr²⁺, Ba²⁺) will be located on the A-site [34, 35]. The perovskites that have been synthesized have the formula of ABO₃ in most cases. The ideal perovskite, as shown in Figure 1.4, has a cubic crystal structure with octahedrons located at each edge of the cube. The A-site atoms are located at the center of the cube. The B-site atoms are located at the corners of the cubic structure, located at the center of the octahedron. Oxygen atoms are also located at the 8 corners of the octahedron. Perovskites are important for their diverse chemical and physical characteristics over a wide temperature range [34].
The properties of perovskite materials are highly dependent on their preparation method; as a result, several methods of synthesis have been introduced for perovskite production to date, which strongly influence their surface physicochemical properties, surface area, porosity, purity, stability and crystal size [36, 37]. Of all the proposed techniques, the solid state reaction, the sol-gel method, the combustion method, mechanical-chemical processing, the Pechini method and the microwave route are the most common [38]. Other common used methods are Spray-drying [39], Freeze granulation [40], Mechanical mixing [41], Extrusion [42], Co-precipitation [43] and Impregnation [41]. An important feature of the preparation method is the scale up capacity of it. Most of the preparation methods cited above are developed for laboratory scale production. Currently, the preparation methods planned for oxygen-carrier preparation at large-scale production are spray drying, impregnation [3] and extrusion. Extrusion is an important forming
technique in the ceramic industries owing to its ability to provide complex shapes and forms with dimensional accuracy, and to its flexibility for mass production [44].

The ideal perovskite oxide, which has a cubic crystal system, does not contain any distortions and deficiencies. However, perovskite oxides are adaptable and can obtain high oxygen ion conductivity if oxygen vacancies are incorporated into their structure. Oxygen vacancies are one of the most important requirements for oxide ion conduction.

Although there are a few compounds that have a cubic crystal symmetry and are considered as ideal perovskites (ABO₃), many of these oxides are distorted and have lower symmetry than cubic crystal system. These distortions can happen to the rigid BO₆ octahedral, i.e., by changes in B–O bonds lengths. These types of distortions are induced by bond valence requirements, orbital degeneracies, polar distortions and/or valence fluctuations. Changes in B–O bond lengths, for example, are possible and expected in systems with d⁴ or d⁷ electronic configurations on the B atoms, leading to Jahn–Teller type anti-symmetric breathing of the BO₆ octahedral [45]. Numerous types of octahedral tilting are possible and the tilt system is typically described in terms of the BO₆ rotation about any of the three Cartesian axes (x,y,z). The resulting tilt angles are most accurately obtained from structural data, mainly atomic coordinates. Because of the intimate relationship between crystal structure and properties, these structural distortions often result in variations in the physical properties.

Deviations from the ideal structure with orthorhombic, rhombohedral, tetragonal, monoclinic, and triclinic symmetry are known, although the latter three ones are rare and poorly characterized. The distorted structure may exist at room temperature, but it transforms to the cubic structure at high temperatures. This transition may occur in several
steps through intermediate distorted phases. These deviations from the cubic perovskite structure may proceed from a simple distortion of the cubic unit cell or an enlargement of the cubic unit cell or a combination of both [46].

There are several other forms of oxygen deficient perovskites e.g., brownmillerite structure. Many of these perovskites have a rhombohedral lattice [31].

In contrast with distorted perovskite structures, Brownmillerite structures (also called double perovskites), contain ordered oxygen vacancies [47]. At low concentrations of oxygen vacancies, since vacancies do not interact with one another, they distribute randomly. However, when the vacancy concentration increases, the vacancies start to interact and can form ordered arrangements. Ordered vacancies cannot be promising for oxygen ion conduction since the oxygen diffusivity takes place in two dimensional planes that consist of oxygen vacancies, and oxygen ions cannot diffuse to adjacent layers. This obviously is not the case for ordered structures [48].

The main challenge dealing with perovskite oxides is the choice of A and B-site cations. A-site and B-site cations can have important roles on the final perovskite structure. Due to its larger ionic radii and consequently its lattice distorsional effects, the A-site cation has more influence on the vacancy concentration of the structure. The B-site cation, on the other hand, has less effect on vacancy concentration because of its lower ionic radii compared to A-site cation. However, since this cation is usually chosen from multivalent transition metals, its multivalent nature can determine the conductivity of vacancies and electrons across the structure [32].
In order for the perovskite oxides to act efficiently, A and B-site cations should be chosen based on the following criteria: ionic radii of A and B-site and electroneutrality of the structure [30].

Goldschmidt’s tolerance factor is one basis for choosing the right sized cations at A and B-sites.

\[
 t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}
\]  

(1.5)

If the tolerance factor is 0.9<t<1, the structure is cubic and ideal. If it is a lot larger than 1 (t >>1), it demonstrates the fact that B cation is too small to reside in the B-site and the structure changes completely. If the tolerance factor is 0.85<t<0.9, the structure distorts to enable the accommodation of the A-site cation into the structure. This will result in a distortion in the BO$_6$ octahedral. If the tolerance factor is less than 0.85, the distorted perovskite is not stable, and, consequently, the structure changes completely. As a result, using small enough A-site cations causes a distortion in BO$_6$ octahedral, and this distortion can change B-O-B bond angles (they are no longer 180°) and as a result form vacancies [34]. Due to existence of vacancies, these materials can represent the ion conduction ability making them suitable candidates for CLC technologies [29, 30].

Another criteria for determining the right size for A and B-site cations is by using the critical radius. While oxygen transfers through the structure, the oxygen ion has to pass through a saddle point which is built by two A-site and one B-site cation. As shown in figure 1.5, the size of A and B-site cations play a crucial role in the oxygen transport mechanism [32].
Figure 1-5 A schematic representation of saddle point during oxygen transport throughout the lattice of a perovskite structure [32]

An optimized size of A and B-site cations can be achieved by measuring a critical radius. The critical radius shown in equations (1.6) and (1.7) represents the maximum size of a mobile ion that can pass through the saddle point.

\[ r_{cr} (\text{Å}) = \frac{a_0 \left( \frac{2}{3}a_0 - \sqrt{2}r_B \right) + r_B^2 - r_A^2}{2(r_A - r_B) + \sqrt{2} a_0} \]  \hspace{1cm} (1.6)

\[ a_0 \approx V_{cell}^{\frac{1}{3}} = 2.37r_B + 2.47 - 2.00(t^{-1} - 1) \]  \hspace{1cm} (1.7)

Typical perovskite oxides have the critical radius of 1.05Å. However, an oxygen ion in its six fold coordination has the ionic radii of 1.40Å. So the only way for the oxygen ion migration is by an extensive outward relaxation of the cations (away from the mobile oxygen ion) which can result in a significant amount of repulsive overlap interactions of cations and anions. When the oxygen ion is passing the space shaped by two A-site cations and one B-site cation, it might take a three-fold coordination on a temporary basis. This can be due to the fact that the oxygen ion has a lower ionic radii when in a threefold coordination (1.36Å). But still in its threefold coordination, oxygen has larger ionic radii than the critical radius. Thermal vibrations of the cations are supposed to resolve the
existing problem. As a result, the higher the mass of the cations, the higher the thermal motions and more ionic conductivity can be the result [32].

Electroneutrality is another important factor that defines if the chosen A and B-site cations are suitable for the specific purpose. For an ideal perovskite to form, the sum of charges of A and B-site cations should be equal to oxygen anion charges in order for the structure to be neutral. If not, defective perovskites are the result. This can also happen by doping the structure at A and B-sites with cations of different charges. When the charge imbalance is introduced to the structure, for the structure to stay neutral, either the B-site cation changes its valence (electronic compensation) or vacancies form (Ionic compensation). Transition metals are interesting candidates as B-site cations because most have multiple valence states that can play an important role in electronic compensation and consequently the electron conductivity. Different valences of transition metals that coexist in a structure can act as hopping sites for electron/holes [32].

The formed defective perovskites are excellent candidates for CLC applications since they have oxygen vacancies in their structure that enables their oxygen storage and release abilities. Defective perovskites have the formula of $\text{ABO}_3 \delta$ in which $\delta$ is called the oxygen non-stoichiometry of the perovskite. The amount of oxygen non-stoichiometry in a perovskite is strongly influenced by the oxygen partial pressure [49].

Perovskites in the air reactor capture oxygen, release the captured oxygen into the fuel reactor and the released oxygen can be measured via Eq. (1.5).

$$\text{ABO}_{(3-\delta)A} \leftrightarrow \text{ABO}_{(3-\delta)F} + 1/2(\delta \text{F} - \delta \text{A}) \quad (1.5)$$
The term $\delta$ calculates the degree of oxygen non-stoichiometry. A and F refer to the air and the fuel reactor, respectively, hence $(\delta F - \delta A)$ represents the amount of gaseous oxygen released. Calculating the enthalpy of the oxidation/reduction of the perovskites can clarify the oxygen partial pressure at which $\delta$ starts to grow and for the number of oxygen atoms to start to deviate from 3. Oxygen non-stoichiometry can be calculated using coulometric titration and thermogravimetry [50].

1.3.2.1. Ionic motion mechanism

A complete comprehension of ionic motion mechanism in oxygen carriers, and specifically perovskites, will be a useful tool to speed up the oxygen carrier design and selection process. There are three commonly introduced mechanisms that can describe the oxygen ion motion in oxides. The first mechanism is called vacancy mechanism which describes jump of an atom or oxygen ion between oxygen vacancies. The second mechanism is called interstitial mechanism in which the motion of smaller atoms from and interstitial site to another neighboring interstitial site takes place. The third mechanism is a combination of vacancy and interstitial mechanisms simultaneously. Due to oxygen vacancy existence in perovskite structures, oxygen ion transportation occurs by vacancy mechanism [51]. In perovskites the ionic motion depends on presence and concentration of vacancies and geometrical factors. Since the oxygen ion performs a diffusive jump from one vacancy to another adjacent vacancy, it is obvious that existence and concentration of vacancies plays an important role in oxygen transport properties of the material. It has been proven that at higher symmetries better ionic motion is possible [32].

A common belief is that the oxygen ion performs a diffusive jump along $\langle110\rangle$ edge of BO$_6$ octahedral to a proximate vacancy. The saddle point is believed to be between
the two anion sites. Despite that, calculations proved otherwise. Based on calculations done by Cherry et al. and shown in figure 1.6 [52], the oxygen ions go through a curved path with the saddle point being away from the neighboring B-site cation. Considering such fact, there is much less energy barrier for an oxygen ion to migrate to an adjacent vacancy.

![Diagram of oxygen vacancy migration](image)

*Figure 1-6 A representation of curved rout for oxygen vacancy migration along BO$_6$ octahedral edge[52]*

1.3.2.2. CaMnO$_{3-\delta}$ family of perovskites

In recent years, several studies have been conducted into synthesizing efficient perovskites applicable to CLC as oxygen carriers [29]. CaMnO$_3$ perovskite as is shown in figure 1.7, has been extensively studied in the literature, especially in solid state inorganic chemistry[53], and has proven to be a promising candidate for CLC processes.

The extensive research done on this material shows that it is able to capture and release oxygen at different oxygen partial pressures. Bakken et al. [49] has reported the ability of CaMnO$_3$ material to lose oxygen continuously during oxygen partial pressure reduction in the fuel reactor by reducing Mn$^{4+}$ to Mn$^{3+}$. The special interest in this material is because of the simultaneous existence of manganese cations with different valences in
the structure, and that their ratio can be chemically adjusted. This phenomena occurs in response to oxygen loss in reducing atmospheres or heterovalent doping of A and B-site cations with different cations in various sizes and charges. Perovskite compounds can be synthesized by doping the A and B-sites with different cations changing the formula to $A_{1-x}A'B_{1-x}B'O_3$ ($0 < x < 1$). The substituted cations on the A-site and the B-site should have the appropriate charge and size for the structure to stay stable [30]. Doping different cations on A and B-sites allows for fine tuning of the properties and characteristics of the product to better suit its intended application [53].

![Calcium Manganite Perovskite Structure](image)

**Figure 1-7 A schematic preview of calcium Manganite perovskite structure**

The sum of reaction heat in the fuel reactor is slightly exothermic while using calcium manganite as the oxygen carrier. This is another reason why this material is an attractive candidate. The $O_2$ release reaction enthalpy is extensively discussed by Romark et al. [54]. This structure, on the other hand, is subject to change to $Ca_2MnO_4$ and $CaMn_2O_4$.
at high temperatures which results in a substantial decrease in oxygen release efficiency during redox cycles [55].

According to the literature doping A and B-site cations with transition metals and alkaline earth metals leads to a more stable structure during CLC processes. Till now there have been several articles reporting different dopants on CaMnO$_3$ structure on the A and B-sites and their effects on the oxygen carrier performance. Titanium doped calcium manganite was proposed as highly reactive material during oxidation reduction reactions by Leion et al. [55]. The general proposed formula for this structure was CaMn$_{1-x}$Ti$_x$O$_3$ which after Ti content optimization became CaMn$_{0.875}$Ti$_{0.125}$O$_3$. This material showed small reactivity and capacity variations by changes in Ti content. The material’s reactivity was investigated using TGA (Thermogravimetry Analysis) and a batch fluidized bed reactor using both solid (petroleum coke) and gaseous (methane) fuels. High reaction rates during reduction and no CO formation were observed. This material proved to be stable during numerous oxidation and reduction cycles after releasing 8-9wt. % oxygen in the fuel reactor (this number should be compared to the total of 33.8 wt. % which is the amount of oxygen in the structure). Ryden et al. [56] studied the oxygen transport properties of this material in a continuously operating system using natural gas as the fuel and showed high reactivity and was proven to be a promising candidate as oxygen carrier in CLC processes. It was concluded from XRD analysis (shown in figure 1.8) that the particles maintained most of their physical properties and underwent some compositional changes (formation of CaMn$_2$O$_4$). No coke formation was observed during the experiments. In these studies the material was synthesized using spray pyrolysis. In another experimental study
conducted by Sundqvist et al. [57] CaMn$_{0.875}$Ti$_{0.125}$O$_3$ was proven to be highly reactive and stable during oxidation and reduction.

![XRD data for CaMn$_{0.875}$Ti$_{0.125}$O$_3$-δ particles. Peaks at 24, 34, 40, 49, 55 and 61 corresponds to CaMn0.875Ti0.125O3−δ (identified as CaMnO2.8 and CaMnO2.65). Peaks at 26, 30, 31, 33, 35, 36, 39, 41, 44, 55, 56, 57, 58, 59, 62 and 63 are CaMn$_2$O$_4$.](image)

Figure 1-8 XRD data for CaMn$_{0.875}$Ti$_{0.125}$O$_3$-δ particles. Peaks at 24, 34, 40, 49, 55 and 61 corresponds to CaMn0.875Ti0.125O3−δ (identified as CaMnO2.8 and CaMnO2.65). Peaks at 26, 30, 31, 33, 35, 36, 39, 41, 44, 55, 56, 57, 58, 59, 62 and 63 are CaMn$_2$O$_4$.

A more general experiment was carried out by Hallberg et al. [58] evaluating CaMn$_{1-x}$M$_x$O$_3$-δ (M = Ti, Fe, Mg) using a batch fluidized-bed reactor. The particles were synthesized using spray-drying and all exhibited a significant O$_2$ release and good reactivity with methane and syngas. However, an undesired phase (CaMn$_2$O$_4$) was observed for every single one of these perovskites, even though not affecting their efficiency. Fe and Ti were shown to be incorporated into the perovskite structure. However, this was not the case for Mg, since a separate phase of MgO was observed. The structure doped with MgO exhibited the best fuel conversion, superseding the strength and fluidization behavior of all. The XRD results also confirmed this observation, showing MgO as a separate phase, not incorporated into the structure, which is due to its small ionic radius. They suggested that MgO had better properties than Ti- and Fe-doped manganese oxides, stating that “MgO might be an active component in the oxidation reaction with
methane, for instance, it may have a role as reforming catalyst on the particle exterior.”

Further experiments are needed to understand the effect of this separate phase [59-61].

In addition to Ti, Fe and Mg as B-site dopants, Arjmand et al. [62] also investigated Cu as a B-site dopant and La as an A-site dopant for oxygen carriers used in CLOU. Ca$_x$La$_{1-x}$Mn$_{1-y}$M$_y$O$_{3-\delta}$ (M = Mg, Ti, Fe, Cu), using mechanical homogenization followed by extrusion as the method of synthesis, were characterized and examined (using a laboratory-scale fluidized-bed reactor). Methane, synthesis gas and devolatilized wood char were used as fuels. As observed in other articles, perovskites doped with Mg, Ti and Fe exhibited promising features for use in CLOU, such as high reactivity, high oxygen release, almost complete gas yields, stability and no agglomeration. However, the Cu-doped perovskite exhibited defluidization behavior while in contact with methane, hence a complete gas yield was not achieved. On the other hand, while using synthesis gas as fuel, all the synthesized particles achieved a complete gas yield. Devolatized wood char was also used for measuring their oxygen release rate and all of them exhibited a reasonable amount of oxygen release during reduction. In this study lanthanum has been chosen as the A-site dopant since according to the literature, there have been excellent behavior observed by addition of aliovalent dopants in this group of perovskites, and it is well known that it is a promising strategy to increase the amount of oxygen non-stoichiometry in the structure [62].

As mentioned before the main reason of adding dopants to calcium manganite structure is to evaluate the changes in reactivity, stability oxygen capacity and performance of oxygen carriers. The oxygen uncoupling results achieved by Arjmand et al. as shown in figure 1.9 reveals the amount of released oxygen in an inert environment after going
through several oxidation and reduction cycles. It can be observed from the results that CaMnO$_{3.6}$ (CM) has the highest amount of oxygen non-stoichiometry among all samples and doping the A-site, has a negative effect on the amount of oxygen non-stoichiometry of the structure. Double doped structures depending on the B-site dopant have different amounts of oxygen release. It is shown that Cu has the highest oxygen release even compared to CM. In comparison with the test conducted by inert material it is obvious that all synthesized materials show oxygen release properties. According to these results doping La at the A-site and Cu at the B-site revealed the best results for the oxygen carrier. However, this material does not result in full fuel conversion when methane is used as the fuel and as mentioned previously showed defluidization behavior.

![Oxygen release profiles](image)

*Figure 1-9 Oxygen release profiles for various carriers investigated by Arjmand et al. [62] during inert gas purge for 360 s at temperature 900°C.*
The iron doped perovskite has shown the highest oxygen concentration after the Cu doped structure in the outlet representing its oxygen transport abilities.

Due to favorable thermodynamics, environmental compatibility, low cost and abundant availability [6, 63], iron-based oxygen carriers have also been studied extensively in the literature.

1.3.2.3. Iron-based family of perovskites

A family of perovskites with La at the A-site and Fe at the B-site were doped at the A and B-sites in various studies. La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.1, 0.3, 0.5$ and $0.9$) synthesized by combustion method are single perovskites that were investigated for methane partial oxidation using a fixed-bed reactor [64]. The X-ray diffraction (XRD) results of fresh samples demonstrated monophasic crystalline structures (orthorhombic). These results also demonstrated that, as the degree of Sr substitution increased, there would be more distinct peak shifts along the $2\theta$ axis. As more La$^{3+}$ is substituted by Sr$^{2+}$, more Fe$^{3+}$ changes to Fe$^{4+}$ and/or more oxygen vacancies are formed. As Fe$^{4+}$ has a smaller ionic radius than Fe$^{3+}$, the XRD results are justified (in accordance with Bragg’s law). Hence, as the results demonstrated, Sr substitution can increase the amount of oxygen vacancies in the perovskite structure. It was proved that this substitution had an optimal amount ($x = 0.3–0.5$). However, doping the A-site with Sr decreases the oxygen carrier’s selectivity towards carbon monoxide (CO)/H$_2$ and its reactivity with methane [64]. This perovskite structure was also examined in two-step steam-reforming of methane towards the simultaneous production of syngas and pure hydrogen and was shown to be a promising oxygen carrier [65]. Hydrogen can be produced as a by-product of chemical looping processes during the
steam-reforming of carbonaceous fuels via the water-splitting reaction discussed extensively by Thursfield et al. [66].

La_{0.8}Sr_{0.2}Fe_{0.9}Co_{0.1}O_3 was also introduced as an oxygen carrier for methane partial oxidation to produce syngas. This perovskite structure was synthesized using the sol–gel method. Experiments were conducted in a fixed-bed quartz micro-reactor and resulted in an average methane conversion of 85 % and CO selectivity of 93.1 %. These materials exhibited the potential for use in methane partial oxidation. However, the XRD results demonstrated that the samples after several oxidation and reduction cycles did not have a perovskite structure. This observation showed a lack of structural stability for these perovskites over several consecutive oxidation and reduction cycles. Structural instability occurs when, at high temperatures and in a reductive atmosphere, the perovskite loses its lattice oxygen which results in structural collapse. The results demonstrated a notable increase in the oxygen carrier’s activity after the B-site doping with Co (x = 0.1) [67]. Doping of the B-site with the equal amounts of Co and Fe resulted in having La_{0.8}Sr_{0.2}Fe_{0.5}Co_{0.5}O_3 as an oxygen carrier in the partial oxidation of methane. The citrate method was used for this material’s synthesis. During experiments in a packed-bed reactor, it was observed that both cracking and combustion occurred along with partial oxidation. However, this material exhibited high methane conversion (more than 85 %) and high selectivity towards H_2 and CO (over H_2O and CO_2) [68].

Ryden et al. [21] proposed materials applicable to methane combustion (CLC) and methane partial oxidation to produce syngas (La_{x}Sr_{1-x}Fe_yCo_{1-y}O_{3-δ}). The study stated La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_3 (synthesized by the glycine nitrate combustion method and the spray drying method) to be a viable option for use in CLC. The results showed it to have high
selectivity towards water vapor and CO₂ production and high reactivity with methane. XRD analysis confirmed that this material maintained its perovskite structure. Samples without Co as a dopant were also investigated. It was shown that these materials underwent three stages, the first stage being combustion resulting in H₂O and CO₂ as products. The duration of this stage for LaFeO₃₋δ, La₀.₈Sr₀.₂FeO₃₋δ and La₀.₅Sr₀.₅FeO₃₋δ was shortest to longest, respectively. The second stage was the methane partial oxidation which is of interest for these materials, which exhibited high selectivity towards CO and H₂ without the formation of solid carbon. The final stage was solid carbon formation. These materials also exhibited the ability to maintain their perovskite structure. As stated previously they can be used in methane partial oxidation.

LaₓSrₓCo₁₋ₓFeₓO₃₋δ synthesized by the citric acid method was also investigated for its applicability to the CLC of natural gas. The in-situ powder XRD method was used to investigate the structural properties of perovskites during the reaction. The experiments revealed that structures with high amounts of Co exhibited decomposition to La₂O₃, cobalt metals and at least one unknown phase during reduction. However, La₀.₈Sr₀.₂Co₀.₂Fe₀.₈O₃₋δ was revealed as a promising material with the appropriate amount of Co for CLC processes since it did not undergo structural changes during the oxidation and reduction cycles. This perovskite has a low oxygen capacity, hence a high-speed gas switching system is required [69]. A comparison between the above structures was also made [70]. LaFeO₃, La₀.₈Sr₀.₂FeO₃ and La₀.₈Sr₀.₂Fe₀.₉Co₀.₁O₃ (synthesized by the sol–gel method) were made in terms of methane partial oxidation activity. It was proven that A-site substitution or a combination of A and B-site substitutions resulted in an increase in catalytic activity and oxygen availability of the structures during the reduction period, as
previously concluded. However, A and B-site doping decreased selectivity towards CO. La$_{0.8}$Sr$_{0.2}$Fe$_{0.9}$Co$_{0.1}$O$_3$ showed less structural stability during reduction than the other two perovskite oxides because of Co as a B-site dopant [70]. The reactivity and performance of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$, La$_{0.7}$Sr$_{0.3}$FeO$_3$, co-precipitated iron oxide (60%; Fe$_2$O$_3$/Al$_2$O$_3$) and supported nickel oxide (20%; NiO/Al$_2$O$_3$) were also evaluated and compared in the chemical looping water-gas shift process. A decline in H$_2$ production and carbon deposition for co-precipitated iron oxide and supported nickel oxide was observed. La$_{0.7}$Sr$_{0.3}$FeO$_3$ was shown to have the best performance over a large number of cycles [71].

Nalbandian et al. [72] took a more general approach to investigate these materials by including Ni, Cr and Cu in addition to the Co-doped materials previously investigated, resulting in La$_{1-x}$Sr$_x$M$_y$Fe$_{1-y}$O$_3$ (M = Ni, Co, Cr, Cu). These materials were used for syngas generation from methane, and the citrate method was used as the production method. No impurities or unreacted species were identified in the course of the experiments. The results reveal that the addition of a small amount of NiO by mechanical mixing (Ni cannot be incorporated into the structure) leads to increased reactivity and selectivity of the particles towards CO and H$_2$. All samples were shown as good for use in methane partial oxidation. However, the best performance was observed for La$_{0.7}$Sr$_{0.3}$Cr$_{0.05}$Fe$_{0.95}$O$_3$ associated with 5% NiO which resulted in H$_2$ yields of up to 90% and good stability. LaCoO$_3$ perovskite was doped with Cu (LaCo$_{0.8}$Cu$_{0.2}$O$_3$) by [73]. These materials were produced by a polymerisable complex route and were investigated for methane partial oxidation. The results proved the existence of a single phase for both perovskites, which means that no additional or undesired phase was formed. High activity to syngas was observed for LaCoO$_3$ but a considerable amount of carbon deposition occurred during the reaction,
which might result in catalyst deactivation. By copper substitution on the B-site, the structure acquired the ability to be resistant to carbon deposition. An increase in reducibility and decrease in temperature to produce syngas were other results of copper substitution. In another study by Ksepko et al. [74], instead of a fraction of La and Sr on the A-site, Sr was used as the A-site cation and Fe and Cu were the B-site cations. SrFe$_{1-x}$Cu$_x$O$_{3-n}$ ($0 < n < 1$) was synthesized by sintering the raw material at 700 °C for 20 h. Thermogravimetric analysis (TGA) experiments on these samples revealed their high oxygen mobility. The results also showed an increase in the oxygen mobility with increasing the Cu content in the structure.

An overview of the research groups investigating chemical looping reactors and oxygen carriers used in chemical looping combustion is shown in table 1.1.

Table 1.1 overall representation of research groups investigating CLC [75, 76]

<table>
<thead>
<tr>
<th>Groups</th>
<th>Reactor</th>
<th>Fuel</th>
<th>Oxygen Carrier</th>
<th>CO$_2$ Capture efficiency</th>
<th>Operation time</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALSTOM (USA)</td>
<td>3MW$_{th}$ CFB-CFB</td>
<td>Coal</td>
<td>CaSO$_4$</td>
<td>N/A</td>
<td>N/A</td>
<td>2010</td>
</tr>
<tr>
<td>Chalmers University of Technology (Sweden)</td>
<td>10 kW$_{th}$ CFB-BFB</td>
<td>CH$_4$, Natural gas</td>
<td>NiO</td>
<td>94.5-99%</td>
<td>&gt;1000 hr</td>
<td>2008, 2009, 2011</td>
</tr>
<tr>
<td>Darmstadt University of technology (Germany)</td>
<td>1 MW$_{th}$ CFB-CFB</td>
<td>Coal</td>
<td>Ilmenite</td>
<td>N/A</td>
<td>N/A</td>
<td>2010</td>
</tr>
<tr>
<td>Institution</td>
<td>Power, kWth</td>
<td>Fuel</td>
<td>Catalyst</td>
<td>Fe2O3</td>
<td>Syngas</td>
<td>NiO, CoO</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>-------------</td>
<td>----------------</td>
<td>----------</td>
<td>-------</td>
<td>--------</td>
<td>----------</td>
</tr>
<tr>
<td>Institute of Carboquimica, CSIC, Spain</td>
<td>10</td>
<td>CFB, BFB, CH₄, CuO</td>
<td>~100%</td>
<td>200 hr</td>
<td>2007</td>
<td></td>
</tr>
<tr>
<td>Korean Institute of Energy Research, KIER, Korea</td>
<td>50</td>
<td>CFB, BFB, CH₄, Syngas, NiO, CoO</td>
<td>&gt;98%</td>
<td>300 hr</td>
<td>2010</td>
<td></td>
</tr>
<tr>
<td>South East U., China</td>
<td>10</td>
<td>CFB, Coal, Biomass, Fe₂O₃</td>
<td>95%</td>
<td>230 hr</td>
<td>2009</td>
<td></td>
</tr>
<tr>
<td>Ohio State University</td>
<td>2.5</td>
<td>moving bed</td>
<td>&gt;97%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>Coal</td>
<td>N/A</td>
<td></td>
<td>2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>Fe₂O₃</td>
<td>99.8%</td>
<td>N/A</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Technical University of Vienna, Austria</td>
<td>120</td>
<td>CFB, Syngas</td>
<td>NiO</td>
<td>~95%</td>
<td>390</td>
<td>2009</td>
</tr>
<tr>
<td>University of Kentucky</td>
<td>200</td>
<td>Coal</td>
<td>Iron-based oxygen carriers</td>
<td>N/A</td>
<td>N/A</td>
<td>2012-2013</td>
</tr>
<tr>
<td>Babcock &amp; Wilcox</td>
<td>15</td>
<td>Coal</td>
<td>Iron-based</td>
<td>N/A</td>
<td>N/A</td>
<td>2012-2013</td>
</tr>
<tr>
<td>University of Florida</td>
<td>Fluidized and magnetically stabilized bed</td>
<td>Coal derived syngas</td>
<td>Fe, Fe/Zr, Fe/MgO, Fe and alloyed Fe-metal oxides</td>
<td>N/A</td>
<td>N/A</td>
<td>2009-2013</td>
</tr>
<tr>
<td>University of Utah</td>
<td>Simulation-based</td>
<td>Cu-based</td>
<td>N/A</td>
<td>N/A</td>
<td>2008-2013</td>
<td></td>
</tr>
<tr>
<td>Western Kentucky University</td>
<td>10</td>
<td>coal</td>
<td>Cu-based</td>
<td>8hrs/day for 3 days</td>
<td>2009-2012</td>
<td></td>
</tr>
</tbody>
</table>
1.4. Scope of Study

As stated previously a good oxygen carrier is a key factor to an efficient CLC process. Good oxygen transport properties, high stability, recyclability, mechanical strength, environmental compatibility, low cost, high reactivity, no agglomeration tendency, fast kinetics and good fluidization properties. Although CaMnO$_{3.8}$ has shown to undergo decomposition with variations in ambient oxygen partial pressures and temperatures, it was proven that this material possesses most of these properties which make it a good base material for further modifications. The main objective of this thesis is to propose a better substitution for CaMnO$_{3.8}$ with enhanced reactivity, stability, and oxygen transport properties. To achieve this objective two approaches have been followed. As shown previously, one way to overcome the decomposition problem is by doping the A and B-site cations with different cations with various charges and sizes. As proven by Arjmand et al. [42] CLMF is one of the best oxygen carriers in the combustion of methane in terms of stability and oxygen capacity (it has the highest oxygen release in an inert atmosphere and is the closest to CaMnO$_{3.8}$). In most of the conducted studies, dopants are of a different charge compared to the A-site (La$^{3+}$ has been used mostly as the A-site dopant). Here, the main objective is evaluating the size of the dopant on the A-site of CLMF to further investigate the variations in oxygen release properties of the material. Hence, Ba$^{2+}$ and Sr$^{2+}$ are being evaluated as A-site dopants to produce Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$ (CS91MF91) and Ca$_{0.9}$Ba$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$ (CB91MF91).

Manganese is an environmentally benign material and has a low cost compared to Ni, Co and Cu. However, compared to iron, it is more expensive, and if used in an industrial
scale, it will cost a lot more than iron. For this reason producing iron-based materials can be of economic interest in CLC processes. Nonetheless, iron has weak redox properties compared to manganese which make it less special as a B-site cation in perovskites. This is mainly because Mn$^{4+}$ and Mn$^{3+}$ are easily transferable to one another in oxidation and reduction respectively and Fe$^{4+}$ and Fe$^{3+}$ are not. The main reason is due to the differences in electronic configurations of each of these atoms and their cations as shown below.

\[
\text{Mn}_{25}: \text{[Ar]} 3d^5 4s^2 \\
\text{Fe}_{26}: \text{[Ar]} 3d^6 4s^2
\]

These materials also show the tendency for agglomeration and sintering at temperatures higher than 800°C which is the temperature range in which CLC processes are operated [63].

Considering this, doing some modifications on the structure might make iron a better B-site cation than manganese which results in a more cost effective process and more viability for scale up and industrial applications. These modifications can also be done by doping the A and B-site of the structure to enhance the redox properties of the oxygen carrier material.
Chapter 2

2. Materials and Methods

2.1. Preparation and Fabrication of the oxygen carriers

The perovskite-based oxygen carrier particles, which were investigated in this study, are listed in Table 2.1. They were synthesized using solid state reaction followed by mechanical extrusion. The preparation steps are as follows:

\[
\begin{align*}
\text{Ca(OH)}_2 & \text{ (Alfa-Aesar, 95 wt %), MnCO}_3 & \text{ (Alfa-Aesar, 99 wt %), SrCO}_3 & \text{ (Alfa-Aesar, 99 wt\%), Fe}_2\text{O}_3 & \text{ (Alfa-Aesar, 99 wt %), BaO & (Strem Chemicals, 99.5 wt\%), CoO & (Alfa-Aesar, 99.99 wt\%), TiO}_2 & \text{ (Acros Organics, 99 wt \%), nano Al}_2\text{O}_3 & \text{ (Alfa-Aesar, 99 wt \%) and La}_2\text{O}_3 & \text{ (Alfa-Aesar, 99.9 wt \%) powders with an average particle size of } \sim 46 \mu\text{m (325 mesh) were}}
\end{align*}
\]

mixed in an appropriate weight ratio to make 10 g batches of the final product in each case. The numbers in the formulas represent the amount of each element used for production of the compound (SFM73 is the short form of SrFe$_{0.7}$Mn$_{0.3}$O$_3$ and SL91F is the short form of Sr$_{0.9}$La$_{0.1}$FeO$_3$)
Table 2.1. Single perovskite formulations investigated in this work, number shown in the table are in grams

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ca(OH)₂</th>
<th>MnCO₃</th>
<th>La₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>BaO</th>
<th>Al₂O₃</th>
<th>CoO</th>
<th>SrCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>4.842</td>
<td>5.158</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CF</td>
<td>4.81</td>
<td>-</td>
<td>-</td>
<td>5.187</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.424</td>
<td>-</td>
<td>6.546</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.510</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.489</td>
</tr>
<tr>
<td>SL91F</td>
<td>-</td>
<td>-</td>
<td>0.711</td>
<td>3.487</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.802</td>
</tr>
<tr>
<td>SB91F</td>
<td>-</td>
<td>-</td>
<td>3.501</td>
<td>-</td>
<td>0.672</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.826</td>
</tr>
<tr>
<td>SFT91</td>
<td>-</td>
<td>-</td>
<td>3.159</td>
<td>0.351</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.489</td>
</tr>
<tr>
<td>SFA91</td>
<td>-</td>
<td>-</td>
<td>3.199</td>
<td>-</td>
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<td>-</td>
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<td>6.573</td>
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<td>-</td>
<td>3.158</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.353</td>
<td>-</td>
<td>6.489</td>
</tr>
<tr>
<td>SFM91</td>
<td>-</td>
<td>0.347</td>
<td>3.1603</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.493</td>
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<tr>
<td>SFM82</td>
<td>-</td>
<td>0.671</td>
<td>3.054</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.275</td>
</tr>
<tr>
<td>SFM83</td>
<td>-</td>
<td>0.974</td>
<td>2.955</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.071</td>
</tr>
<tr>
<td>CS91MF91</td>
<td>4.155</td>
<td>4.427</td>
<td>-</td>
<td>0.498</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.919</td>
</tr>
<tr>
<td>CB91MF91</td>
<td>4.141</td>
<td>4.411</td>
<td>-</td>
<td>0.496</td>
<td>-</td>
<td>0.952</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Each mixed batch was transferred to a 250 mL plastic drum with 33 g of water, which was placed in a rotary tumbler for one and a half hours. In accordance with the literature, 30 vol. % solid loading with 1 wt. % of the dispersant (ammonium polyacrylate, NH₄PAA, dispersant) was used. The aqueous slurry was thoroughly mixed and homogenized in a rotary tumbler unit. The slurry was poured into a shallow pan (Pyrex) and dried at 150 °C in an air oven overnight. The dried soft mass was then crushed and ground to a homogeneous powder for each batch. Furthermore, the dried cake was pulverized and homogenized. This procedure is followed by extruding into rods.
In our case, the following components were used for preparing the extrusion paste: water both as binder/solvent, PVA as a binder (20 wt% solution), water soluble starch as a pore former and binder, and ammonium hydroxide as peptizing agent. After obtaining a suitable viscosity of the blended materials, they were extruded using a simple manual extruder. Extrudates were dried on a stainless steel plate at 75°C overnight. The extrudates were transferred to high-density alumina crucibles and calcined in air for 6 hours at 1200°C in a programmable muffle furnace using the temperature–time profile shown in figure 2.1. The particles should have a specific size range for use as oxygen carriers. To achieve this objective, the calcined extrudates were sieved through stainless-steel screens to yield particles in the range of 125–250 μm. The resulting powders were washed and put through an ultrasound for 5 min, each time for five times to remove the fine particles that may come from crushing stage.

![Figure 2-1 Temperature-time Schedules for the processing of carriers](image)

*Figure 2-1 Temperature-time Schedules for the processing of carriers*
2.2. Characterization of the oxygen carriers

In every case, the Brunauer–Emmett–Teller (BET) specific surface area was measured by N$_2$ adsorption (Micromeritics, TriStar 3000). The crushing strength (force needed to fracture a single particle) was measured using a digital force gauge (Shimpo, FGN-5) for particles in the size range of 125–250 μm. An average of 30 measurements was taken as the representative of the crushing strength.

Powder X-ray diffraction (XRD, PANalytical X’Pert Pro) with Cu Kα$_1$ radiation was used for crystalline phase determination of the prepared oxygen carriers. Scanning electron microscope (SEM) (Hitachi, S4800) was used for examining the morphology of the synthesized particles.

Oxygen capacity (Ro) of the prepared materials was measured using a thermogravimetric analyzer (TA Instrument, TGA Q50). An approximate amount of a sample (~12 mg) was placed inside a crucible, and the experiment was conducted by initiating the heating in an oxidizing ambient environment (20.8% O$_2$) with an inlet flow rate of 50 mL/min. The heating rate was a linear ramp of 45 °C/min, and after reaching 950 °C, the temperature was maintained constant for 35 min. While the temperature was kept constant, the sample was then in direct exposure to a stream of high-purity N$_2$ for 35 min with an inlet flow rate of 50 mL/min. These reduction–oxidation cycles were repeated 3 times. The thermo balance was calibrated with an empty platinum crucible under identical experimental conditions before each experiment.

Experiments for examining oxygen uncoupling and reactivity characteristics were performed in a quartz fluidized-bed reactor (designed in Chalmers University and
fabricated in The University of Toledo), 870 mm high and 22 mm in inner diameter. A porous quartz plate is located at a height of 370 mm from the bottom, and the reactor temperature is measured with chromel-alumel (type K) thermocouples enclosed in inconel-600 in quartz shells located about 25 mm above and 5 mm below the plate. The experiments were performed at 800, 850, 900 and 950°C, as measured by the upper thermocouple.

To determine if the particles are fluidized or not, the pressure drop over the bed of particles and the quartz plate was recorded by using pressure transducers. In order to be able to preserve the temperature at the desired level over the progress of the experiment, the fluidized bed quartz reactor was placed inside an electric cylindrical furnace (Applied test system. INC).

The oven was insulated, and the openings through which the gases enter and exit the reactor were also insulated with a silica blanket type SB-2000 from Zicar refractory composites. In order to remove water and small solid particles generated during oxidation of the fuel, the exhaust gas stream from the reactor was led to a condenser (IMR 500 P). The composition of the dry gas was measured by IMR 2800 P analyzer, which measures the concentrations (sensitivity of 0.001%) of O₂ through a paramagnetic channel and CO₂, CO, and CH₄ through infrared channels. The tubing and fittings were made from stainless steel and were made by Swagelok. In order to connect the tubing to the quartz reactor, graphite ferrules (GRACE, USA) were used. There are two advantages for using these ferrules; one is the high temperature resistivity (near 450 °C), and the other is the suitability for the glass fitting.

The CLOU properties of the particles were investigated by examining the oxygen release from the oxidized particles in nitrogen while fuel reactivity is examined by reaction
with methane. The experiments were conducted in cyclic approach, in which a period of oxidation followed by a period of reduction constitute one cycle. Reduction was performed either with inert gas, in order to examine O\textsubscript{2} release, or with fuel in order to examine fuel reduction.

The oxidation is conducted with a flow of 900 mL\text{N} \text{min}^{-1} (normalized to 1 bar and 25°C) of N\textsubscript{2} with 8 \% O\textsubscript{2}. The fuel reduction is examined with a flow of 200 mL\text{N} \text{min}^{-1} of CH\textsubscript{4}. In order to control the flow rates, mass flow controls (Smart-Trak® 100 Series) were used. In addition a computer program was written using Visual C++.net to program the flow meters in the desired cyclic approach.

Batches of 30 g of oxygen carrier are used with a particle size of 125–250 μm. The composition of the reducing gas was 18 vol \% CH\textsubscript{4} in N\textsubscript{2}, and it was selected to avoid exceeding the terminal velocity of the particles due to the increase in gas velocity produced during the CH\textsubscript{4} conversion. A mixture of O\textsubscript{2} with N\textsubscript{2} was used during the oxidation with a low O\textsubscript{2} concentration (8 vol \%). Since the reactor had no cooling system, to avoid a large temperature increase during the combustion reaction, 8\% O\textsubscript{2} concentration was used instead of air. The reduction/combustion period was 20 s. The oxidation period necessary for the complete oxidation varies between 600 and 900 s. To avoid mixing of CH\textsubscript{4} and O\textsubscript{2}, N\textsubscript{2} was introduced for 45 s after each reducing and oxidizing period. The tests were carried out at 800, 850, 900 and 950 °C.
Chapter 3

3. Results and Discussion

3.1. Iron-based perovskites as oxygen carriers

As previously mentioned due to shortcomings of CaMnO₃, different approaches have been followed to improve the redox properties of this material and lower its production costs.

One proposed approach is using iron as the B-site cation (instead of manganese) to evaluate the redox properties compared to CaMnO₃. Hence, CaFeO₃ was synthesized as the base material. The XRD results as shown in figure 3.1 reveal that Ca₂Fe₂O₅, a brownmillerite structure, instead of CaFeO₃ has been formed. Brownmillerite structures have the general formula of A₂B₂O₅. They usually are known to have two dimensional layers of BO₄ corner-shared tetrahedral and BO₆ corner-shared octahedral. A general schematic of brownmillerite structure is shown in figure 3.2. It is known that at high defect concentrations, it is energetically desired for the structure to add two vacancies in one octahedron resulting in a brownmillerite structure [77]. The observation in XRD patterns is due to high defect concentration in the structure which shows that calcium has a low ionic radii (1.34 Å) to fit the A-site in the structure. It is of great importance to know that
the preparation method plays an important role in surface physicochemical properties, surface area, porosity, purity, stability, and crystal size. The synthesis method can be another reason for calcium not being incorporated into the structure.

Figure 3-1 XRD results obtained for Cr₂Fe₂O₅
It is obvious that calcium needs to be replaced with a cation with a larger ionic radii. Hence, other substitutions for calcium are going to be proposed. Substitutions are chosen in different sizes to assess how this parameter affects the structure and performance of the oxygen carriers.

3.1.1. Size effect investigations on A-site cations

A-site cations in perovskites are usually chosen from group IA and IIA in the periodic table because of their relatively large ionic radius. Since metals in the first group possess low melting temperatures (which makes them undesirable for CLC purposes), the A-site choices are going to be from group IIA.
Figure 3-3 XRD results for (a) SrFeO$_3$ and (b) BaFeO$_3$ perovskites, the blue color represents perovskite BaFeO$_3$ and the red color shows BaFeO$_3$-Delta phase.
In this group, Strontium and Barium are the only choices of higher ionic radii than calcium. \( \text{SrFeO}_3 \) (SF) and \( \text{BaFeO}_3 \) (BF) were synthesized to evaluate the size effects of A-site cations. The XRD results are shown in figure 3.3.

As is shown in figure 3.3.a, \( \text{SrFeO}_{3.6} \) is proven to be a perovskite structure with no additional phase present with the formula of \( \text{SrFeO}_{2.75} \). Figure 3.3.b, on the other hand, represents impurities present along with \( \text{BaFeO}_3 \). As mentioned before, the synthesis method can have a huge effect on the perovskite materials by affecting the crystal size, surface area, porosity, purity, and stability. Hence, Barium not being incorporated to the structure can be a result of the chosen synthesis method. This phenomenon can also be explained by the large ionic radius of \( \text{Ba}^{2+} \) (1.61 Å). It has been proven that \( \text{BaFeO}_3 \) has a high oxygen permeability due to its relatively large lattice free volume. However, as shown by current XRD results, using a great amount of this cation in perovskite structure results in structure deterioration and a decrease in structural stability [78]. For this reason, the lattice enlargement abilities may be employed by using it as a dopant on the A-site in low quantities.

So far, \( \text{SrFeO}_{3.6} \) has proven to be a potential basis candidate for further modifications of the iron-based perovskites. The thermogravimetric analysis (TGA) of this material in comparison with \( \text{CaMnO}_3 \) is shown in figure 3.4. It can be concluded from the TGA results that both structures need improvement in terms of stability since their oxygen capacity differs from cycle to cycle.
However, it is evident that SrFeO$_3$-δ needs further modifications to reach the oxygen capacity of CaMnO$_3$-$\delta$.

As expressed in earlier chapters, one strategy to increase the oxygen release of a perovskite is adding dopants to the A and B-site cations. The following sections present the results obtained by doping the A and B-site cations with different cations of various charges and sizes.

### 3.1.2. B-site dopants

As mentioned earlier in chapter 1, B-site cations are influential in oxygen transport properties of the perovskite structure on the account of their multivalent nature. If used properly and in right amount (depending on other materials incorporated in the structure
and ambient atmosphere characteristics) their role in performance enhancement of oxygen carriers will be substantial. As a result the choice of B-site dopant can be as important as the choice of B-site cations. B-site cations are usually selected by following criteria: size, charge, electron configurations and redox properties. The choice of B-site dopants in this study was based on the proximity of ionic size of the B-site and the dopant to ensure the crystal structure stability of the compounds.

Titanium is chosen as one of the B-site dopants. This material as shown by Hallberg et al. [58] can be incorporated as a B-site dopant on CaMn_{1-x}M_xO_{3-δ} (M = Ti, Fe, Mg) structure. Doping Ti on the B-site has also been proven to be beneficial for the reactivity improvements by arjmand et al. as well [62]. Consequently choosing it as a B-site dopant on Fe-based perovskites may also be beneficial. Manganese has also been chosen for B-site substitution. This material has been employed as the B-site cation in many studies and is one of the best candidates. Hence using it as a B-site dopant can also be of importance. Aluminum is not a transition metal with a multivalent nature. However, this material is chosen to be doped on the B-site. Using Al on the B-site can be effective on the performance of the perovskite structure mainly because it has one valence state (3+). Incorporating Al^{3+} can carry a shortage of positive charge into the lattice and this should be compensated. Compensation can be affected by formation of oxygen vacancies. This can allow for more oxygen release during reduction (Fe^{4+} → Fe^{3+} + O_2).

Due to its toxic nature and high cost, Cobalt is not usually considered as a viable option for perovskite synthesis for CLC purposes especially at an industrial scale. However, if Cobalt doped perovskites are effective enough and cobalt effects on the oxygen carrier performance are significant, its advantages can overweight its disadvantages
since this material have proven to be influential in oxygen carrier performance in many studies [21, 67, 69].

Several formulations were synthesized with partial substitution of the B-site with Ti, Al, Co and Mn by 10 mol%. The XRD results are shown in figure 3.5. It can be observed from the XRD results demonstrated in figure 3.5.a, that all synthesized materials have the same crystal structure as the base perovskite, SrFeO$_3$. The main peak shifts are also shown in figure 3.5.b.

*Figure 3-5 (a) Comparative XRD results for B-site doped oxygen carriers (b) zooming on the main peaks*
Comprehensive information on the elements used in the above mentioned structures is presented in table 3.1.

The information provided in table 3.1 facilitates the way towards better understanding of the elemental behavior in the synthesized structures. As shown in XRD results (figure 3.5.a), all Materials have shown the similar XRD pattern as SrFeO_{2.75}. However, according to figure 3.5.b, a peak shift to the left is observed for all the prepared samples. According to Bragg’s law, since $\theta$ has been reduced, the d-spacing in the structures should have been increased. One main reason for changes in d-spacing can be lattice contractions and expansions caused by adding dopants and modifying the structure.

Table 3.1. Information on the most common oxidation states and electron configurations of elements incorporated in the perovskite structure

<table>
<thead>
<tr>
<th>Element name</th>
<th>Atomic Number</th>
<th>Common oxidation states</th>
<th>Electronic configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>13</td>
<td>3+</td>
<td>$1s^22s^22p^63s^23p^1 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>27</td>
<td>2+,3+</td>
<td>$[\text{Ar}]4s^23d^7 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>25</td>
<td>2+,3+,4+,6+,7+</td>
<td>$[\text{Ar}]4s^23d^8 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>22</td>
<td>4+</td>
<td>$[\text{Ar}]4s^23d^2 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>26</td>
<td>2+,3+</td>
<td>$[\text{Ar}]4s^23d^6 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$</td>
</tr>
</tbody>
</table>
Information on the Ionic radii of the cations can be useful information in this matter. The ionic radius of cations with coordination number of 6 are reported by Dronskowski and Hoffmann [79] and are shown in table 3.2.

Table 3.2. Possible Ionic radius of cations incorporated in B-site

<table>
<thead>
<tr>
<th>Element name and symbol</th>
<th>Oxidation state</th>
<th>Ionic Radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>3+</td>
<td>0.535</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>4+ 3+ 2+</td>
<td>0.530 0.61 0.745</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>4+ 3+ 2+</td>
<td>0.53 0.645 0.83</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>4+ 3+ 2+</td>
<td>0.605 0.670 0.860</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>4+ 3+ 2+</td>
<td>0.585 0.645 0.780</td>
</tr>
</tbody>
</table>

By considering the ionic radius of Al$^{3+}$, it can be expected that since this cation has a less ionic radii than iron, there should have been lattice contraction and a peak shift to the right. However, it is observed otherwise. This incident can be because of the change in valence of iron when associated with aluminum. Since iron has larger ionic radii in smaller oxidation states, the lattice expansion can be justified.
In case of Cobalt as the B-site dopant, since oxidation states of 3+ and 2+ are more common and easily transferrable to one another, the increase in d-spacing can be explained. Titanium with the oxidation state of 4+ being the most common is expected to expand the lattice and consequently increase d-spacing.

Doping manganese has also been a reason for lattice expansion. Since Mn$^{4+}$ can be produced from Mn$^{3+}$ more easily than Fe$^{4+}$ from Fe$^{3+}$, it seems like manganese has changed iron’s oxidation states to a lower quantity. As a result the d-spacing has increased and the observation is reasonable.

TGA is the next step to evaluate the performance of the synthesized materials. The TGA results are shown in figure 3.6. As is shown in figure 3.6, the TGA results comply with the XRD results. Since aluminum has decreased iron’s oxidation state, the oxygen release capacity of the structure has decreased substantially. The Cobalt doped structure on the other hand, shows noticeable oxygen release increase compared to SrFeO$_{2.75}$. This is because of the reason that cobalt can change states between 2 and 3 easily and it has caused iron to be at its higher oxidation states which is a result of such high oxygen transport properties. In case of manganese doped structure, manganese is acting as the multivalent cation since its oxidation states are easily transferable. Hence, iron is acting as a fixed valence cation facilitating oxidation and reduction of manganese and resulting in the highest oxygen capacity. However, the titanium doped structures do not show significant oxygen release in an inert atmosphere. The main reason can be explained by XRD results. Since this material does not change states easily and it has lowered the oxidation state of iron, the oxygen capacity of the structure has decreased substantially (in the same order of magnitude as the aluminum doped structure).
Figure 3-6 TGA results for B-site doped samples

Manganese doped structure possessed the highest oxygen capacity. As a result, adding more manganese has been proposed. Manganese has been doped on the original structure in amounts of 20 and 30%. The XRD results and TGA results are shown in figure 3.7 and 3.8 respectively.
Figure 3.7 demonstrates the perovskites with 10, 20 and 30 mol % manganese doped in their structures. As is shown, all of the XRD patterns are similar to the parent compound SrFeO$_{2.75}$. The XRD patterns shown in figure 3.7.b indicate different amounts of lattice contraction and expansion with different amounts of doped Mn. As testified by the previous XRD results, manganese forces iron to its lower oxidation states and this results in lattice enlargement. However, as the amount of manganese in the structure increases the amount of Mn$^{4+}$ (which has a lower ionic radii) in the perovskite oxide
increases. This can result in a lattice contraction and consequently a shift to the right for the amount of 30 mol%.

It can be observed from the TGA results (Figure 3.8) that as the amount of manganese in the structure increases, the amount of oxygen capacity increases as well. As mentioned before, manganese has a more effortless change of valence in comparison with iron. Hence, in manganese doped structures, iron will act as a single valence cation facilitating the way for manganese to change its valence upon oxidation and reduction and towards a more stable structure. This will lead to a structure with more oxygen capacity and enhanced oxygen transfer properties. The stability of the SrFe$_{0.7}$Mn$_{0.3}$O$_{3-\delta}$ is clearly shown in TGA results as this material did not change its oxygen release amount during 3 oxidation and reduction cycles. As it is obvious, the amount of doped manganese directly correlates with the oxygen capacity of the structure. This means that adding more manganese to the structure definitely has a positive effect on the oxygen transport properties. However, by using more Mn in the structure, the perovskite will be a Mn-based perovskite and this is not the aim of current approach. The comparison with the parent compound SrFeO$_{3-\delta}$, the base compound CaMnO$_{3-\delta}$ and the SrFe$_{0.7}$Mn$_{0.3}$O$_{3-\delta}$ in terms of oxygen capacity is shown in figure 3.9.
Figure 3-8 TGA results for manganese doped perovskites with 10, 20 and 30 mol% manganese compared to the parent compound.
As is demonstrated above, the synthesized oxygen carrier SFM73, has clearly achieved enhanced oxygen transport properties compared to the parent compound. This structure shows more mass change in an inert atmosphere and has shown to be more stable during 3 oxidation and reduction cycles. However, there is still a relatively large gap between the oxygen capacity of SFM73 and CaMnO$_{3-\delta}$.

Another proposed approach for modification of the parent compound, as mentioned at the beginning of this chapter is doping the A-site cation with cations of various sizes and charges which will be explained in the following section.
3.1.3. A-site dopants

Doping the A-site of the parent compound with a 3+ ion increases the ease and amount of Fe$^{4+}$ reduction to Fe$^{3+}$ which results in conductivity enhancement [80]. There are numerous examples of lanthanum as an A-site cation being doped by Strontium and vice versa [26, 52, 72, 81, 82]. By doping lanthanum on the A-site, due to the charge unbalancing effect it brings to the structure, iron at the B-site will be forced to be at its higher oxidation state (4+) which allows more oxygen capture during oxidation and consequently more oxygen release during reduction. So adding lanthanum can enhance the redox properties of the oxygen carrier. On the other hand, as previously mentioned, Barium has been proposed to be effective as an A-site dopant in small amounts because of its large ionic radii and lattice enlargement abilities.

Barium and lanthanum are used as substituents for strontium at the A-site for 10 mol%. Their crystal structures as shown in XRD results in figure 3.10 are the same as the parent compound. However, there are some traces of impurities (BaO) in the Barium doped structure. It seems like, Barium cannot be incorporated in the structure completely because of its large size. An easily distinguishable peak shift to the left is observed in figures 3.10.a and 3.10.b that is the large ionic radii of barium that is presenting itself.
A slight peak shift is also observed for the lanthanum doped sample. La$^{3+}$ (1.36 Å) has a smaller ionic radii than Sr$^{2+}$ (1.44 Å). Hence this peak shift cannot be due to ionic radii of lanthanum. Since lanthanum carries extra positive charge to the structure, iron changes to Fe$^{4+}$ for compensation. However, knowing this still does not justify the peak shift to the left since Fe$^{4+}$ has a smaller ionic radius than other oxidation states of this cation. This phenomena can be explained by first order Jahn-Teller distortion effect. Jahn-Teller effect can be observed in transition metals that have odd number of d-electrons in eg orbitals e.g. d$^4$ (high spin) Mn$^{3+}$, Cr$^{2+}$ and Fe$^{4+}$. This effect operates to remove the degeneracy of eg orbitals of B-site cation in an anion crystal field. This effect results in a regular distortion
of octahedral along axial position either by formation of two long bonds (elongation) or formation of short bonds on opposite sized of the axial position. Since Fe$^{4+}$ is categorized as a Jahn-Teller active ion, the peak shift to the left on the XRD results can be due to elongation along the Z-axis of the octahedral and resulting in an increase in the d-spacing.

TGA results are shown in figure 3.11 for A-site doped perovskite in comparison with SF. It is shown that the lanthanum doped perovskite has achieved enhanced oxygen release properties in terms of mass change and stability during 3 redox cycles as expected (due to the existence of more Fe$^{4+}$). However, Barium has proven to have less mass change and poor performance during TGA experiments in terms of oxygen release and stability.

Figure 3-11 TGA results for A-site doped perovskites
A comparison between the lanthanum-doped sample on the A-site and the manganese doped sample on the B-site is also shown in figure 3.12.

![TGA results demonstrating a comparison between lanthanum-doped samples on A-site and manganese doped samples on B-site](image)

**Figure 3.12** TGA results demonstrating a comparison between lanthanum-doped samples on A-site and manganese doped samples on B-site

### 3.1.4. Doubly doped perovskites

As the results demonstrate, doping lanthanum at the A-site and manganese at the B-site have so far resulted in achieving the best prepared perovskites among A and B-site dopants respectively. By comparing the mass changes of these two samples (shown in figure 3.12) it can be seen that the manganese doped sample (30 mol %) has the highest oxygen release.
It is commonly believed that the doubly doped perovskites (doped on A and B-sites) are less prone to phase separation as opposed to undoped and single doped perovskites [62]. Hence, doping the parent compound with lanthanum and manganese at the A and B-site respectively is proposed next.

\[
\text{Figure 3-13 (a) XRD results for doubly doped perovskite (b) main peaks}
\]

The XRD patterns (shown in figure 3.13) are the same as SrFeO$_{3.5}$ which means the desired structure is formed. The TGA results are also presented in figure 3.14.
Adding lanthanum and manganese to the structure, as proven before, has a positive effect on the oxygen capacity of the structure. However, simultaneous doping of these elements tends to decrease the amount of oxygen release in an inert atmosphere even lower than the parent compound. In absence of lanthanum, manganese is at its higher oxidation state (4+), and iron is acting as a fixed valence cation facilitating the oxygen release process. When lanthanum is added to the structure, iron as well as manganese can change its oxidation state to compensate the charge imbalance introduced to the structure. Due to the charge balance effect it causes, iron tends to go to its higher state (4+) to compensate the charge unbalance of the structure. As this happens, manganese finds less freedom to
change states during oxidation and reduction, and this explains the oxygen capacity reduction and less stability of the perovskite oxide (SL91MF91).

3.2. Size investigations of A-site dopants in CLMF

As previously proved by Arjmand et al., CLMF can be a promising candidate as an oxygen carrier in CLC applications, especially with methane used as the fuel. The charge effect was evaluated by doping the A-site (Ca$^{2+}$) with La$^{3+}$. The outcome was a more stable structure than CaMnO$_{3-δ}$ with a large difference in oxygen capacity. In this study, the effect of the size of the A-site dopant is being assessed. Accordingly, Sr$^{2+}$ and Ba$^{2+}$ are used for this specific purpose. These cations are categorized as A-site cations as shown in figure 1.3, and they have larger ionic radii compared to Ca$^{2+}$.

Ca$^{2+}$: 1.34 Å

Sr$^{2+}$: 1.44 Å

Ba$^{2+}$: 1.61 Å

The XRD results followed by TGA results are represented in figures 3.15 and 3.16 respectively. As shown in figure 3.15, CS91MF91 has the same XRD pattern as the CM, which proves that they have the same structures. Although the XRD results for CB91MF91 have the same peaks as the pattern observed for CM, a lot of impurities and separate phases can be distinguished by having a glance at the figure 3.15. Barium tends to be bigger than it is supposed to be to fit the A-site of the structure in this case as well as SB91F.
Figure 3-15 A comparison between XRD patterns of CM and A-site doped perovskites
As is shown, the strontium doped sample is proved to have the best oxygen transport properties in terms of oxygen capacity and stability even compared to CaMnO$_3$-$\delta$. Since Barium cannot completely be incorporated into the structure, with the current choice of synthesis method, and due to several phases associated with the desired perovskite structure, it isn’t able to capture and release oxygen as is expected. On the contrary, since strontium is of the suitable ionic radius to be doped into the structure, it has a strong effect in lattice enlargement and oxygen vacancy concentration. Consequently, it has more oxygen capacity than CaMnO$_{3-\delta}$ and is proven to be more stable during three oxidation and reduction cycles.

*Figure 3-16 TGA results represented for CM and CM doped at A-site with La, Ba and Sr*

As is shown, the strontium doped sample is proved to have the best oxygen transport properties in terms of oxygen capacity and stability even compared to CaMnO$_3$-$\delta$. Since Barium cannot completely be incorporated into the structure, with the current choice of synthesis method, and due to several phases associated with the desired perovskite structure, it isn’t able to capture and release oxygen as is expected. On the contrary, since strontium is of the suitable ionic radius to be doped into the structure, it has a strong effect in lattice enlargement and oxygen vacancy concentration. Consequently, it has more oxygen capacity than CaMnO$_{3-\delta}$ and is proven to be more stable during three oxidation and reduction cycles.
3.3. SFM73 and CS91MF91

Two approaches have been proposed and evaluated to improve the redox properties of CaMnO$_{3-\delta}$ which have been widely studied and proved to have a high oxygen capacity with low stability during multiple redox cycles. In the first strategy, the highest mass change was observed for SFM73 which was 0.72 wt. %, and in the second one this was observed for CS91MF91 which was 1.78 wt. %. The synthesized compounds were characterized and analyzed. The TGA results for CS91MF91, SFM73, SF and CM are shown below in figure 3.17.

![TGA results for B-site doped iron-based perovskites and doubly doped manganese-based perovskite in comparison with their parent compounds](image)

*Figure 3-17 TGA results for B-site doped iron-based perovskites and doubly doped manganese-based perovskite in comparison with their parent compounds*
3.3.1 Scanning Electron Microscope Analysis (SEM)

The SEM images of the synthesized perovskites are shown in figure 3.18. As shown in the images, starch used in the extrusion formula acts as a pore-forming agent. It is obvious in the SEM images that all the samples have a porous structure.
Figure 3-18 SEM images of synthesized perovskites (a) CS91MF91 (b) SFM73 (c) CM

EDS (Energy Dispersive Spectroscopy) analysis of the prepared samples was performed after calibration of the detector with a pure copper sample. The results are shown
in table 3.3. The results shown in table 3.3 are in complete agreement with the computational data and calculations based on which the precursors (metal oxides) of the perovskites were mixed and produced the perovskite structures.

Table 3.3 EDS analysis of the samples CS91MF91 and SFM73 investigated in this work

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ca</th>
<th>Sr</th>
<th>Mn</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS91MF91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated data</td>
<td>18</td>
<td>2</td>
<td>18</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>Experimental data</td>
<td>16.12</td>
<td>1.57</td>
<td>15.30</td>
<td>1.91</td>
<td>65.10</td>
</tr>
<tr>
<td>SFM73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated data</td>
<td>-</td>
<td>20</td>
<td>6</td>
<td>14</td>
<td>60</td>
</tr>
<tr>
<td>Experimental data</td>
<td>-</td>
<td>26.77</td>
<td>8.40</td>
<td>18.85</td>
<td>45.98</td>
</tr>
<tr>
<td>CM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated data</td>
<td>18</td>
<td>-</td>
<td>18</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>Experimental data</td>
<td>18.63</td>
<td>-</td>
<td>18.75</td>
<td>-</td>
<td>62.62</td>
</tr>
</tbody>
</table>

3.3.2. Oxygen uncoupling behavior of the oxygen carriers

Fig. 3.19 shows the oxygen release profiles during inert gas purge at four different temperatures for the samples. As it can be seen, both perovskite formulations showed oxygen uncoupling behavior. A steady decay in the amount of released oxygen as a function of time was seen for the samples that heated at 950 °C temperatures, and this is quite similar for the other three temperatures.

This phenomena is typical for the perovskite-type materials and was reported in several papers, where two mechanisms are assumed to be involved: (a) the oxygen non-
stoichiometry is an object of defect chemistry, and (b) the release or uptake of oxygen as a function of the oxygen partial pressure in the ambient [42, 83].

The temperature did not show a significant effect on oxygen release profile of the samples. It only decreased the rate of oxygen uptake and release in both systems. The CLOU experiments were repeated several times to establish the reproducibility of the observed behavior; there was slight difference from cycle to cycle, specifying that these oxygen carriers were stable and were not deactivated during several cycles.
Figure 3-19 Oxygen release profiles for perovskites during cycling between air (20.8% O2) and high-purity inert gas (N2) inert gas at 800, CM-Black, SFM73-Green, CS91MF91- Dark cyan, Inert-Blue

3.3.3. Reactivity of the oxygen carriers

The reactivity experiments were done in four different temperatures 800, 850, 900 and 950°C using methane as fuel and 30 g of particles in the bed. The concentration profile during the combustion period for oxygen carriers investigated in this work is shown in Figure 3.20. Initially, the carriers were oxidized in 8% O2. In the next step, when the oxidizing stream is switched with pure nitrogen (inert), the oxygen concentration decreases gradually corresponding to the way that it was shown in the Figure 3.19.
When methane was purged to the reactor, CO$_2$ was produced as a result of methane conversion; no traces CH$_4$ or CO were identified. The oxygen concentration decreased to almost zero (zero in some cases) at the same time. Some uncombusted methane was detected in the reactor outlet in some cases, after complete conversion of methane in the initial part of reduction. Therefore, it seems that the reduction of perovskite carrier by methane involves a mixture of two reactions: (1) direct reaction of solid particles with the methane (via CLC) and (2) indirect reaction of methane with the gaseous oxygen released from the carrier (via CLOU) [84, 85]. The oxygen concentration profiles during oxidation (in 8% O$_2$) at four different temperatures are shown in Fig3.20. Initially, all of the oxygen in the inlet stream was consumed by the particles that have been reduced severely. This is due to the combustion process. At the end of the oxidation period, the oxygen concentration rapidly increased until 8 vol %. The temperature of the bed increased only 10-20 °C in the whole oxidation period due to the diluted oxygen concentration used for the experiments. After about 2 min, oxygen increases steadily, approaching the inlet concentration (8%). High degree of reduction seems to be the reason that no oxygen is detected during the initial stages of oxidation. Accordingly, the oxygen partial pressure is relatively low at that time, as the oxygen-depleted carrier taking most of the oxygen in the early part of the oxidation period. The amount of uncombusted CH$_4$ was increasing by decreasing the temperature of the bed. All samples that have been tested at temperatures lower than 950 °C have more than 10% uncombusted CH$_4$ in the outlet.

The experiments carried out in the fluidized bed reactor allows us to know the behavior of the carriers during successive reduction-oxidation cycles. Moreover, the
chemical and structural changes due to the chemical reaction and the attrition phenomena existing in the fluidized beds can be investigated.
Figure 3-20 Concentration of various gaseous species (CO₂, CH₄ and O₂) during conversion of CH₄ at 800, 850, 900 and 950 °C for 20 s using 30 g of sample followed by oxidation in 8% O₂, CM-Black, SFM73-Green, CS91MF91- Dark cyan, Inert-Blue
Table 3.4 shows the bulk density of the fresh and used samples. The bulk density did not change considerably; small changes could be due to measurement uncertainties. BET measurements were performed before and after the test for CM and as the results indicate, there is not a significant difference between the surface area of the samples before and after the reactor test. As a result the surface area analysis was performed for the rest of the samples before the reactor test.

All samples have crushing strength more than 1 N, which is suggested for the CLC application.

There is no huge weight loss among the samples which can indicates they have enough strength for withstanding erosion and high temperature reactions during the tests.

The BET results represent the fact that although CS91MF91 has a lower surface area than other synthesized perovskites, due to large ionic radii of strontium in the structure, there are several formed vacancies that result in better ionic conduction across the lattice an the best observed performance as an oxygen carrier.

Table 3.4. Bulk density (g/cm³), sample weight before and after the reactor test, BET and crushing strength of the Oxygen Carriers before and after the Reactivity Test (±0.001 error)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Bulk density before reactor test (gr/cm³)</th>
<th>Bulk density after reactor test (gr/cm³)</th>
<th>Sample weight before reactor test (gr)</th>
<th>Sample weight after reactor test (gr)</th>
<th>BET(m²/g) before/after test</th>
<th>Crushing Strength N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>4.49</td>
<td>4.56</td>
<td>30</td>
<td>29.47</td>
<td>0.95/0.92</td>
<td>2.19±0.7</td>
</tr>
<tr>
<td>CS91MF91</td>
<td>4.66</td>
<td>4.59</td>
<td>30.027</td>
<td>29.66</td>
<td>0.42/-</td>
<td>2.3±0.7</td>
</tr>
<tr>
<td>SFM73</td>
<td>5.49</td>
<td>5.44</td>
<td>30</td>
<td>28.99</td>
<td>0.62/-</td>
<td>1.39±0.6</td>
</tr>
<tr>
<td>Inert</td>
<td>2.22</td>
<td>2.21</td>
<td>30</td>
<td>29.99</td>
<td>0.09/-</td>
<td>-</td>
</tr>
</tbody>
</table>
A cost comparison has also been made between SFM73, CM and CS91MF91. The results are shown in table 3.5.

Table 3.5. Raw material cost estimation for perovskites

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Price ($)/ton</th>
<th>Perovskite</th>
<th>Price ($)/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>119</td>
<td>CaMnO₃</td>
<td>753.9498</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>1350</td>
<td>Ca₀.₉Sr₀.₁Mn₀.₉Fe₀.₁O₃</td>
<td>765.4295</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>900</td>
<td>SrFe₀.₇Mn₀.₃O₃</td>
<td>883.12</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>800</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By taking a look at the estimated priced for production of each perovskite, it is obvious that CM has a lower production cost in comparison with SFM73. However, the production cost of CS91MF91 and CM are in the approximate range of one another. Owing to its high stability and oxygen capacity, CS91MF91 can be a more favorable choice when considering performing CLC in industrial scales.
Chapter 4

Conclusions

Iron and manganese-based perovskites were investigated for their use in Chemical Looping Combustion processes. The materials were synthesized using solid state reaction followed by mechanical extrusion. The main objective of using such synthesis method was the mass production ability of it. The perovskite oxides were generally evaluated for their oxygen release, reactivity and performance. Detailed characterizations and analysis for synthesized oxygen carriers were implemented. The best performing oxygen carriers were examined for their oxygen uncoupling behavior during a CLC process using a Lab-scale fluidized bed reactor at various temperatures. The Lab-scale CLC experiment was conducted by using methane as fuel.

CaMnO$_{3-\delta}$ is a perovskite material that due to its high oxygen capacity and low stability has been the subject of numerous studies. In this study, manganese has been replaced by iron which is of lower cost and the structure was doped on A and B-sites for performance enhancement.

XRD investigations on the iron-based oxygen carriers revealed that among Ca$^{2+}$,Sr$^{2+}$ and Ba$^{2+}$ with the current synthesis method, Sr$^{2+}$ acts as a better A-site cation forming a pure perovskite structure (SrFeO$_{3-\delta}$). Regardless of its stability, this structure showed less oxygen capacity than CaMnO$_{3-\delta}$. This shortcoming was partially compensated
by doping the structure at A-site with La$^{3+}$ and Ba$^{2+}$ and at B-site with Al, Ti, Mn, and Co for 10 mol %. Among all fabricated structures the manganese doped structure proved to have the highest oxygen capacity and stability of all. Adding more Mn to the structure (20 mol% and 30 mol %) tended to increase the oxygen capacity of the structure even further. Introducing additional manganese led the structure to a manganese based structure and since the structure is intended to be iron-based, no more manganese addition is allowed. This structure showed 0.28% mass change during TGA analysis that compared to CaMnO$_3$-$\delta$ (1.64%) is substantially low.

XRD patterns of the Ba$^{2+}$ and Sr$^{2+}$ doped (10 mol %) CaMn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$, reveal that Ba$^{2+}$ cannot be completely incorporated into the structure. Furthermore, Sr$^{2+}$ doped samples showed high purity in XRD patterns. TGA results of Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ presented excellent oxygen transport properties for the material in terms of oxygen capacity and stability. Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ had higher mass change in an inert atmosphere (1.78%). This amount of oxygen release exceeds the amount of oxygen release observed by CaMnO$_{3-\delta}$. It was concluded from TGA experiments that the synthesized compound had high stability during three oxidation and reduction cycles.

The best synthesized perovskites, SrFe$_{0.7}$Mn$_{0.3}$O$_{3-\delta}$ and Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$, were analyzed by BET and SEM as well as XRD and TGA. SEM images and BET analyses proved that the structures possess a porous surface area which is a key factor to good oxygen uptake and release.

The iron-based and manganese-based perovskite were synthesized by the extrusion technique and examined with respect to their oxygen uncoupling properties (CLOU) and reactivity with methane as a fuel. Almost complete methane combustion was obtained at
950 °C for SFM73 and full conversion was observed for CS91MF91. Neither particle fragmentation nor agglomeration was noticed during the experiments. Whereas the bed temperature did not show significant effect on CLOU behavior, it has a tremendous effect on reaction of methane.

In the current study, CaMnO$_3$-$\delta$ has been successfully modified to a structure possessing improved oxygen transport properties. The modified structure, Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_3$-$\delta$, resulted in complete conversion of methane and suitable stability at high temperatures and oxygen capacity of this compound exceeds the oxygen capacity of CaMnO$_3$-$\delta$.

The iron-based perovskites (SrFeO$_3$-$\delta$) were modified (SrFe$_{0.7}$Mn$_{0.3}$O$_3$-$\delta$) and presented improved oxygen transport properties in comparison with SrFeO$_3$-$\delta$. However, they did not prove to be promising candidates in comparison with Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_3$-$\delta$ because of their lower stability and oxygen capacity.
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Appendix A

Zeta Potential

Introduction

In synthesizing slurries it is always important to keep the particles deflocculated in the mixture in order for the slurry to become an optimum mixture for further calcination and reaction. There are several parameters that have an important role in particle dispersion in a mixture.

Zeta potential is a measure of stability of a mixture. In most colloidal dispersions, particles will have surface charge. This surface charge and its quantity strongly depends on the nature of the particle and the surrounding aqueous media. But there are a few general factors that may have an effect on the amount of this surface charge. These factors are preferential loss of ions from a crystal lattice, ionization of groups present on a particle surface and adsorption of ions or ionic molecules onto the particle surface. Around each particle in an aqueous media, there is an electrical double layer. This double layer consists of two regions. One inner region called stern layer, in which ions are bound strongly together. The other one is the outer region or diffuse layer in which the ions are bound less firmly together. Within this region there is a notional boundary (see figure A.1). In this
boundary when ions move due to outer forces, other ions around them, move with them. The potential in this region is called zeta potential. In fact, this potential is a measure of attractive and repulsive forces between the particles which exist within the region. If the particles have more repulsive forces than attraction forces, this means that they will have a better chance of dispersion and no flocculating will occur. This potential shows the long term stability of a mixture. When zeta potential is more positive than +30 or more negative than -30, is when a colloidal mixture will be stable [86, 87].

![Figure A-1 A schematic view of stern layer, diffuse layer and zeta potential](image)

**Experimental procedure**

Among all factors that can affect the zeta potential of a mixture, pH is the most important factor involved. Also using a dispersant can help the particle dispersion. To understand the effect of mixing duration, dispersant and pH on zeta potential, some experiments were conducted using a zeta meter. First, perovskites were synthesized as follows. Ca(OH)2 (Alfa-Aesar, 95 wt %) and Mn2CO3 (Alfa-Aesar, 99 wt %) powders
with an average particle size of ~46 μm (325 mesh) were mixed in an appropriate weight ratio with La2O3 (Alfa-Aesar, 99.9 wt %), Fe2O3 (Alfa-Aesar, 99 wt %), to make 15 g batches of the final product in each case. Table A.1 shows the compounds and their required amount for synthesizing the perovskites.

Table A.1. the components and the used amount for conducting the experiments

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>gr</th>
<th>% wt of solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>5.144951</td>
<td>52.21</td>
</tr>
<tr>
<td>Mn₂CO₃</td>
<td>7.98207</td>
<td>80.99</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>1.256926</td>
<td>12.75</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.616054</td>
<td>6.25</td>
</tr>
<tr>
<td>50 gr water, 43.4 % total weight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 gr ball, 43.4% total weight</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each mixed batch was transferred to a plastic drum with 50 g of water, which was placed in a rotary tumbler for 3 hours. The aqueous slurry was thoroughly mixed and homogenized in a rotary tumbler unit. During these 3 hours, samples were taken from the slurry in different time intervals to evaluate the effect of time on dispersion of the particles in the mixture. These samples were diluted with the same pH and NH₄PAA, in order for the zeta meter to be able to calculate zeta potential. The results are shown in figure A.2.
At first, particles in the slurry have started the wetting stage. In this stage forces between particles start to break down. The next step is the separation of the particles and the last stage is stabilization. The aim here is to make the particles as disperse as possible in the mixture.

Second set of experiments were conducted to evaluate the effect of pH on dispersion of the particles. The slurry was mixed for 3 hours and then sample was taken out for pH measurement. The primary pH of the mixture was basic (pH=12) since we have Ca(OH)$_2$ in the mixture, OH$^-$ will be released and as a result the environment will be basic. So citric acid was added to the slurry for understanding the effect of pH on dispersion of
particles and zeta potential of the slurry. Each time that a specific amount of citric acid was added to the mixture, 20 minute intervals was given to the slurry to be mixed on the jar mill. The results are shown in figure A.3.

![Zeta potential vs pH](image)

*Figure A-3 Effect of pH on zeta potential on a mixed slurry*

In a basic environment, because the zeta potential is negative, adding an acid to the mixture will neutralize the negative charges to a point where surface charges are neutralized and then adding additional acid will make surface charge positive and zeta potential will become positive [88].

Electrostatic stabilization exists between particles which have sufficient surface charge and repel one another. For achieving a better dispersion a polymer often will be introduced to the system as a dispersant. In the next step, steric stabilization occurs as a result of adsorption of the polymer to the particles surface. When both surface charge and
adsorbed polymer coexist, the mechanism is referred to as electrosteric which is a better stabilization mechanism. As a result by adding a dispersant one must achieve a better dispersion of particles in the slurry [89].

Another set of conducted experiments, were done to evaluate the effect of dispersant on dispersion of particles. In the next step, ammonium polycarbonate (NH4PAA) was added to the slurry in different intervals (every half an hour). In intervals 0.05g, 0.3g, 2g of dispersant was added to the slurry respectively. The pH of the mixture was set to 7 after adding specific amount of dispersant. The results are shown in figure A.4.

Figure A-4 Changes of zeta potential with change in the amount of dispersant. Dispersant was added in amounts of 0.05gr, 0.3gr and 2 g to the slurry.
A visual inspection also was done considering pH and dispersant as changing factors. Samples were taken in basic and acidic environment with varying amount of dispersant. Some pictures were taken from the samples which are shown in figures A.5 and A.6.

Figure A-5 Samples taken from the slurry in basic environment, amount of NH4PAA is increasing from left to right 0 g, 0.05 g, 0.35 g, and 2.35g respectively (a) shortly after measuring zeta potential, (b) after 2 days.
Figure A-6 samples taken from slurry in acidic environment, the amount of dispersant is increasing from left to right 0 g, 0.05 g, 0.35 g, and 2.35 g respectively, (a) shortly after measuring zeta potential, (b) after 2 days

As it can be seen from the figures above, the basic environment is a better environment for particles to be dispersed in. It can clearly be seen that the acidic environment can’t be a stable environment since almost all particles in the slurry were settled down after two days, while samples in the basic environment, and especially the ones with higher amount of dispersant (2.35 g) have been settled down in small amounts.

Conclusions

From the conducted experiments and the results shown in previous sections, one can conclude that there are some major factors that have effects on the amount of zeta potential and the dispersion of particles in a slurry depending on the nature of the mixture and particles in it. These factors are pH, Amount of dispersant and time of mixing. In our case (with specific oxides that are used in the slurry) it can be seen that better dispersion of the particles takes place in a basic environment in a higher amount (2.35g) of proper dispersant (NH4PAA) and in the right amount of time (3 hours).
Appendix B

Photocatalytic activity of perovskites

Introduction

Majority of chemicals, papers, industrial, medicinal and cosmetic wastes are responsible for a tremendous release of pollutants, such as detergents, dyes, pesticides and volatile organic compounds in aquatic environments [90, 91]. These impurities and pollutants in most cases are dangerous and cannot easily decompose. Photo degradation of these pollutants with the solar radiation can be an attractive solution to this problem. Regardless of the ambient conditions, the photocatalyst and the pollutant, the basic photocatalytic reaction occurs in the following steps (as shown in figure B.1). The first step is the exposure of the photocatalyst to the light energy. The light energy absorbed by the photocatalyst needs to be equivalent or equal to the band gap of the semi-conductor for the reaction to occur. The light photons excite the electrons on the valence band by providing energy. The excited electrons will then transfer to the conduction band leaving free holes on the valence band. The generated electron-holes can be recombined either on the surface of the semi-conductor on in the bulk in a very small period of time. The recombination results in energy release in forms of heat of photons. If not recombined, the electrons can afterwards take part in reduction reactions with electron acceptors that have been absorbed
on the surface of the photocatalyst. The absorbed molecules can also be oxidized by free holes. The surface hydroxyl groups, can react with the electron holes producing free radicals (free radicals are strong oxidizing agents). These redox reactions followed by some secondary reactions are the basic mechanism for photocatalysis reaction [92].

![Diagram of Photocatalytic Reaction](image)

*Figure B-1 Photocatalytic reaction taking place on a photocatalyst surface by electron excitement caused by light irradiation*

\(\text{TiO}_2, \text{ZnO and Fe}_2\text{O}_3\) are some of many highly active catalysts that can be used for photocatalysis. However, these semi-conductor oxides have large band gaps and cannot be considered as promising candidates when dealing with the solar radiation. Many of these photocatalysts can perform under UV-light which is about 4-5% of the solar radiation. With that been said, utilizing such catalysts can reduce the efficiency of the whole process substantially [90]. \(\text{TiO}_2\) specifically is known for its photocatalytic activity due to high stability and low cost. However, because of its high band gap energy (\(~3\text{eV}\)), \(\text{TiO}_2\) cannot be an efficient option while utilizing solar spectrum. The high recombination of photogenerated electrons and holes and difficulty in separating it from effluent after
degradation are other reasons for extensive research on finding better substituents for this material [93, 94]. Perovskite oxides have been studied for their special properties for use as photocatalysts in pollution degradations [95]. Perovskite with the general formula of ABO$_3$ have shown to be promising photocatalysts owing to their crystal structures and have been studied extensively due to possibility of promising photocatalytic activity during exposure to visible light. These compounds are preferable to their corresponding metal oxides for three main reasons[96].

- Perovskites have favorable band edge potential that facilitates several reactions caused by light photons.

- As almost 90% of the periodic table can be incorporated into the perovskite crystal structure, a broad choice of A and B-cations can facilitate the design and alteration of band structures and photo physical characteristics, e.g. different degrees of tilting in these materials can affect the electron and hole transport, photoluminescence and band structure.

- The effects of piezoelectricity or ferroelectricity can be combined with the photocatalytic activity effect to improve the photocatalytic reactions.

Several perovskites for the CLC applications were synthesized in our laboratory that in some cases did not show promising oxygen transport behavior and proven not to be viable in CLC applications. Hence to find other applications for these perovskites, they were the subjects of pollution degradation experiments acting as photocatalysts.

**Photocatalytic Properties experiments**
The perovskites were prepared by solid state reaction followed by mechanical extrusion. The photocatalytic degradation experiments were conducted in a 50 cc Pyrex crystallizing dish in full exposure with 100 W high intensity Ultraviolet Inspection Lamp. During the experiments, a cooling fan was used to cool down the solution to avoid evaporation as much as possible. Firstly, we prepared 10 ppm Rhodamine B (RhB) solution. Afterwards, we weighed up 0.1 g samples accurately and added the samples to a 25cc RhB solution. After adequate dispersion of the samples in the solution, they were exposed to the UV light. Absorbencies were measured by UV-2450 UV-VIS spectrometer at 459 nm. The absorbency of the original RhB solution was also measured and the value is named \( I_0 \).

Results and discussions

UV-VIS spectroscopy

The UV-Vis spectroscopy results (shown in table B.1) revealed that in most cases, the final concentration of RhB in the solution (I) is higher than its initial concentration (\( I_0 \)). This reveals the fact that the perovskites have not shown any photocatalytic activity and that evaporation has occurred. Since the powders are of black color, they can act as black objects that have high heat absorption. When the absorbed heat is released in the solution, it warms up the solution which results in evaporation. The higher concentration of pollutants than the initial concentration is because some water have been evaporated and there have been no photocatalytic behavior.

Table B.1. The photocatalytic degradation activity of perovskites after 2 hours of exposure to UV radiation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material /Perovskite</th>
<th>( I/I_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
RhB | Rhodamine B | 1.00
---|---|---
TiO$_2$ nano | TiO$_2$ with nano sized particles | 0.219
TiO$_2$ anatase | - | 0
SFT | SrFe$_{0.9}$Ti$_{0.1}$O$_{3.8}$ | 0.654
SFT-150 ml | SrFe$_{0.9}$Ti$_{0.1}$O$_{3.8}$- experiment was conducted in 150 cc of RhB solution/concentration effects | 0.845
SFT-under sieve 0.001 inches | SrFe$_{0.9}$Ti$_{0.1}$O$_{3.8}$- particles of smaller size / size effect | 0.990
SF-1000 | SrFeO$_{3.8}$- calcined at 1000°C | 0.764
SF-1300 | SrFeO$_{3.8}$- calcined at 3000°C/ Temperature effects | 1.152
CLMF9191 | Ca$_{0.8}$La$_{0.1}$Mn$_{0.9}$Fe$_{0.1}$O$_{3.8}$ | 1.413
CLMT9191-1200 | Ca$_{0.9}$La$_{0.1}$Mn$_{0.9}$Ti$_{0.1}$O$_{3.8}$- calcined at 1200 °C | 0.705
CLMT9191-1100 | Ca$_{0.9}$La$_{0.1}$Mn$_{0.9}$Ti$_{0.1}$O$_{3.8}$- calcined at 1100 °C | 0.993
CMT-1100 | CaMn$_{0.9}$Ti$_{0.1}$O$_{3.8}$- calcined at 1100°C | 1.351
CMT-1300 | CaMn$_{0.9}$Ti$_{0.1}$O$_{3.8}$- calcined at 1300°C | 3.310
CFM | CaFe$_{0.9}$Mn$_{0.1}$O$_{3.8}$ | 3.310
LMA-0.1 | LaMn$_{0.9}$Al$_{0.1}$O$_{3.8}$ | 1.467
LCMCo | La$_{0.9}$Ca$_{0.1}$Mn$_{0.9}$Co$_{0.1}$O$_{3.8}$ | 0.780
SMgMo-Dp-1100 | Sr$_2$Mg$_{0.9}$Mo$_{0.1}$O$_{5.8}$-double perovskite calcined at 1100 °C | 1.202
SMgMo-Dp-1000 | Sr$_2$Mg$_{0.9}$Mo$_{0.1}$O$_{5.8}$-double perovskite calcined at 1000 °C | 3.144
SMgMoF-1000 | SrMg$_{0.8}$Mo$_{0.1}$Fe$_{0.1}$O$_{3.8}$- calcined at 1000 °C | 0.735
SMgMoF-1100 | SrMg$_{0.8}$Mo$_{0.1}$Fe$_{0.1}$O$_{3.8}$- calcined at 1100 °C | 3.331
SMo-Dp-1000 | SrMoO$_{3.8}$- double perovskite-calcined at 1000 °C | 1.024
SMnF-Dp-1300 | SrMn$_{0.9}$Fe$_{0.1}$O$_{3.8}$- double perovskite-calcined at 1300 °C | 0.588

According to the literature the particle size and crystal size of the powders used in the photocatalytic reactions, play important roles in their photocatalytic activity. Among
most reported successful perovskite photocatalysts, the average particle sizes of the powders is in the order of nano meters [97-101]. Since particles synthesized by solid state reaction are in the order of micro meters, additional efforts to decrease the particle size of the powders is necessary.

Among perovskite oxides, SrFeO$_{3-\delta}$, has demonstrated successful oxidization of organic compounds. This perovskite oxide has redox behavior and catalytic activity for oxidation of organic compounds [100, 102]. Hence this perovskite is chosen for particle size evaluations. The particles were milled under the following conditions:

<table>
<thead>
<tr>
<th>Ball Mill: PM 100</th>
<th>Milling powder: SrFeO$_{3-\delta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder amount: 30 g</td>
<td>Milling jar volume (ml): 250</td>
</tr>
<tr>
<td>Ball to powder ratio: 10:1 (10 mm- ball)</td>
<td>Atmosphere: Air</td>
</tr>
<tr>
<td>RPM: 600</td>
<td>Milling time (h): 20h</td>
</tr>
<tr>
<td>(0.5h*40 times with 0.5h-interval break)</td>
<td></td>
</tr>
</tbody>
</table>

After completion of milling process, powders were collected. The chunk part was scrubbed, crushed and re-milled at 200 RPM for 2 minutes.

The crystal structure of the fresh samples and the ball milled samples are shown in XRD results demonstrated in figure B.2. As is shown in the XRD results, the ball milled samples have shown decomposition and structural changes due to agglomeration taking place because of numerous collision of the particles on one another. The SEM analysis obtained for fresh samples and the ball milled samples are shown in figure B.3. The reduced
particle size is evident in the SEM images. The agglomeration can also be observed in this images.

Figure B-2 The XRD results obtained for the fresh samples and the ball milled samples
Fresh samples

Ball milled samples
Although there was a substantial decrease in the particle sized of the SrFeO$_3$-$\delta$ powders, the photo catalytic experiments results were not as expected. As before, no photocatalytic activity was observed for the fresh and ball milled samples as shown in table B.2

Table B.2. UV-Vis degradation results investigating the size effects on the photocatalytic activity of SrFeO$_3$-$\delta$

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>$I/I_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ anatase</td>
<td>0</td>
</tr>
<tr>
<td>RhB (under UV-light with no photocatalyst)</td>
<td>1.239</td>
</tr>
<tr>
<td>SrFeO$_3$-$\delta$ fresh samples</td>
<td>1.152</td>
</tr>
<tr>
<td>SrFeO$_3$-$\delta$ ball milled for 20 hours</td>
<td>1.487</td>
</tr>
</tbody>
</table>

According to the obtained results, the micron sized powders synthesized by solid state reaction, cannot show photocatalytic activity even if their particle size is reduced to nano sized. It is better to use other methods of perovskite synthesis to ensure the particle size is in a nano range for the compound to be an effective photocatalyst as proven in numerous studies.