CaMn_{1-x}B_xO_{3-δ} (B=Al, V, Fe, Co, and Ni) Perovskite Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU)

Nathan Galinsky¹, Marwan Sendi¹, Lindsay Bowers¹, and Fanxing Li^{1,*}

1. North Carolina State University, Campus Box 7905 Raleigh, NC 27695-7905 Raleigh, NC, USA

**Corresponding Author, fli5@ncsu.edu 919-515-7328*

Abstract

Operated under a cyclic redox mode in the presence of an oxygen carrier, the chemical looping with oxygen uncoupling (CLOU) process has the potential to effectively combust solid carbonaceous fuels while capturing CO₂. The overall process is enabled by an oxygen carrier that is capable of reversibly exchanging its lattice oxygen (O²⁻) with gaseous oxygen (O₂) under varying external oxygen partial pressures (P_{O₂}). As such, further improvements of the CLOU process relies largely on the identification of oxygen carriers with higher activity, better recyclability, and improved resistance towards physical degradation. This article investigates dopant effects on CLOU properties of oxygen carriers with a CaMnO₃ parent structure. Various B-site compatible metal cations including Fe, Ni, Co, V, and Al are incorporated into the perovskite. While CaMnO₃ suffers from stability issues resulting from irreversible transitions to spinel (CaMn₂O₄) and Ruddlesden-Popper (Ca₂MnO₄) structures under typical CLOU redox conditions, a number of B-site doped perovskites exhibited promising phase stability and redox activity. Of the oxygen carriers investigated, Fe-doped CaMnO₃ exhibits the most promising CLOU properties while showing high compatibility with the CaMnO₃ parent structure. In terms of redox performance, CaMn_{1-x}Fe_xO_{3-δ} exhibit notable redox activity at temperatures as low as 600°C. No deactivation was observed over 100 redox cycles. The doped perovskite structure was also significantly more stable than undoped CaMnO₃, showing no signs of decomposition at 1,200°C. When operated under identical conditions, the Fe-doped oxygen carrier is observed to achieve significantly higher conversion of Pittsburgh #8 coal char compared to undoped CaMnO₃ oxygen carrier, when operated at 850°C.

Introduction

Concerns over global climate change resulting from anthropogenic CO₂ emissions necessitate development of new power generation technologies with lower carbon footprints. Of the various carbon capture technologies, chemical looping combustion (CLC) has emerged as a promising option. [1,2] The CLC processes aims at lowering the energy penalty for CO₂ separation in combustion processes. This is achieved through cyclic redox reactions using interconnected fluidized bed or moving bed reactors. [3–8] Solid oxygen carrier particles are used to carry oxygen and heat from air to the fuel without mixing these two components. As a result, a concentrated CO₂ stream can be generated in the fuel reactor. The oxygen depleted carrier is then

1 transported to a second reactor referred to as the air reactor. Here, air is used to regenerate the
2 oxygen carrier while producing heat for power generation.

3 Development of low cost oxygen carriers with high activity for carbonaceous fuel conversions is
4 highly desirable for chemical looping processes. While many oxygen carriers are effective for
5 gaseous fuel combustion, they tend to be less active in converting solid fuels such as biomass or
6 coal due to mass transfer and kinetic limitations. Enhancement of oxygen carrier activity towards
7 solid carbon-based fuels is typically achieved through two methods. First, *in-situ* gasification
8 uses CO₂ or steam to gasify the solid fuel into syngas for oxygen carrier conversion. [6–11]
9 However, gasification of solid fuels with steam or CO₂ is often slow and becomes a rate limiting
10 step. A variety of oxygen carriers including oxides of Fe [8,10,12–14], Mn [13,15], and Ni
11 [16,17] have been used in the conversion of solid fuels through the *in-situ* gasification approach.
12 The second method is known as chemical looping with oxygen uncoupling (CLOU). [3,18,19] In
13 CLOU, the oxygen carrier is selected from metal oxides with significant equilibrium partial
14 pressure of oxygen (P_{O₂}) at high temperature. As a result, the oxygen carrier is able to release a
15 portion of its lattice oxygen into the gas phase. The gaseous oxygen then reacts with the solid
16 fuel, leading to improved combustion kinetics. Typical oxygen carriers that exhibit CLOU
17 properties include oxides and mixed oxides containing Cu, Mn, and/or Co. [18–30] However,
18 each oxide exhibits challenges, such as high cost and agglomeration of Cu oxides [19,26–28],
19 low decomposition temperature and toxicity of Co oxides [18,23], and difficulty of regeneration
20 of Mn oxides [15,19,21–25,31–36].

21 Recently, perovskite structured oxides have received increasing attention as oxygen carriers for
22 redox applications. [23,31,33–56] Typically, perovskites take the form of ABO_{3-δ}, where A is a
23 large cation of either the alkali or rare earth metal, and B is a smaller cation of the transition
24 metal group. [57] Perovskite structured oxides have been used both as supports and primary
25 oxygen carriers. As a support, mixed ionic and electronic conductive (MIEC) perovskites such as
26 La_{1-x}Sr_xFeO₃ (LSF) have shown to enhance the redox activity of iron oxides by nearly two orders
27 of magnitude. [51–54] Perovskite and perovskite supported iron oxides have also been explored
28 as redox catalysts for syngas generation and water-splitting. [42,56,57] La containing perovskite
29 supports have been shown to enhance the oxygen donation properties of Mn-Fe and Co-Fe
30 oxides. [23] Up to 8.8% decrease in the initial decomposition temperature was reported for
31 perovskite supported mixed metal oxides.

32 Besides its role as a support, perovskite oxygen carriers have been shown to be effective as
33 standalone oxygen carriers in CLOU and CLC applications. CaMnO₃ perovskites are of interest
34 due to its low cost, availability, and CLOU properties. [20,29–39,49,58–62] CaMnO₃ based
35 oxygen carriers have lower oxygen uncoupling capacities than copper oxides but can be
36 synthesized from cheap manganese ores and Ca precursors [29,61], while obtaining high solid
37 fuel conversions. [29,31,34,36] CaMnO₃ faces the challenge of long term stability. CaMnO₃
38 oxygen carriers undergo an irreversible phase change to spinel (CaMn₂O₄) and Ruddlesden-
39 Popper (Ca₂MnO₄) phases. [19,20,32,59,60] In addition, CaMnO₃ has also been shown to be

1 susceptible to sulfur poisoning, forming CaSO_4 . [32,36,60] Stabilization of the perovskite
2 structure has been investigated through addition of secondary metal atoms into the A- and B-sites
3 of the parent CaMnO_3 . [29,31–38,60,61,63–65]

4 Arjmand et. al. investigated $\text{Ca}_{1-x}\text{La}_x\text{Mn}_{1-y}\text{M}_y\text{O}_3$ (where $x=0$ or 0.1 and $M= \text{Mg, Ti, Fe, or Cu}$)
5 oxygen carriers for CLOU properties between $900\text{--}1,000^\circ\text{C}$ in a laboratory scale fluidized bed
6 reactor. [31] It was determined that undoped CaMnO_3 had the highest oxygen release capability
7 ($\sim 0.7\%$ after 360s). Doping of the A- and B-site was shown to decrease the oxygen release
8 capability except when Cu was used. However, Cu-doped samples were prone to defluidization.
9 Rydén et. al. studied a Ti-doped CaMnO_3 oxygen carrier for CLOU. [35] The oxygen carrier
10 exhibited oxygen uncoupling properties above 720°C in a fluidized bed reactor. The maximum
11 rate for oxygen uncoupling was observed to be $0.03\text{L}_\text{N}/\text{min}$ at 950°C with a maximum
12 concentration at 4 volume% when a mass of 200 g of the oxygen carrier is used. The oxygen
13 carrier was also tested in a redox mode using methane as a fuel. Slight deactivation was
14 observed. The deactivation was attributed to CaMn_2O_4 formation. Kallén et. al. used CaMn_{1-}
15 $x\text{Mg}_x\text{O}_3$ oxygen carrier in a 10kW_th gas-fired CLC unit. [37] The oxygen carrier was observed to
16 release oxygen above 700°C . No agglomeration was observed for 120 hr of high temperature
17 operations. The total attrition of fines ($<45\ \mu\text{m}$) was determined to be less than 0.01%. Hallberg
18 et. al. investigated Mg, Ti, and Fe doped CaMnO_3 oxygen carriers prepared by spray drying for
19 CLOU properties and redox activity with methane. [33] The oxygen carriers had oxygen release
20 of 0.3–0.5% by weight at 900°C with a maximum release of nearly 1% by weight at $1,000^\circ\text{C}$.
21 After 3 cycles of oxygen uncoupling and one methane cycle, the authors reported the formation
22 of CaMn_2O_4 spinel phase in all tested oxygen carriers. CaMnO_3 oxygen carriers have also been
23 synthesized from combinations of manganese ores and $\text{Ca}(\text{OH})_2$. [29] In reaction with methane,
24 ores containing high concentrations of Al showed poor performance due to spinel formation
25 between Al and Mn. The best performing oxygen carrier had an oxygen uncoupling capacity of
26 0.68 w.t.%. Although a number of doped CaMnO_3 oxygen carriers have shown promise for the
27 CLOU process, detailed characterization of dopant effects on B-site doped CaMnO_3 oxygen
28 carriers and their long term performance has not been extensively studied.

29 In this study, we investigate the effect of B-site doping for CaMnO_3 based oxygen carriers. Fe,
30 Co, V, Ni, and Al are chosen as potential dopants. It was determined that oxygen release
31 properties of the oxygen carriers vary with dopant type and concentrations. Of the various
32 dopants chosen, Fe doped oxygen carrier exhibits long term stability and has low temperature
33 CLOU properties around 650°C . Fe dopants also induced noticeable α -oxygen release between
34 $350\text{--}500^\circ\text{C}$. The Fe-doped samples exhibit long term stability (100 cycles) of its uncoupling
35 properties. As a result, Fe-doped samples observe more facile oxygen release for solid fuel
36 conversions relative to undoped CaMnO_3 oxygen carriers.

37 **Experimental:**

38 **Oxygen Carrier Synthesis:**

Mixed oxides with a general formula of $\text{CaMn}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{V}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Al}$ and $x \leq 0.5$) are prepared using a citric acid sol-gel method. General procedure for the sol-gel samples includes dispersion of cation precursors $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98+%, Sigma Aldrich), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ACS Reagent, Noah), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), VCl_3 (97%, Sigma Aldrich), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACS Reagent, Sigma Aldrich) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich) in distilled water followed by addition of citric acid. In the synthesis procedure used, citric acid (Sigma Aldrich) is added to the solution in a molar ratio of 2.5:1 (citric acid: total cations) as a chelating agent. The mixture is heated to 80°C , and ethylene glycol (Sigma Aldrich) is added as a gel promoter in a molar ratio of 1.5:1 (ethylene glycol: citric acid). After most of the water is boiled out, the sol-gel sample is dried in a vacuum oven for 12 hours to remove any extra moisture. The dried sample is then annealed in air at $1,200^\circ\text{C}$ for 12 hours. The resulting powder is crushed and sieved to under 90 micron particle size.

A solid state reaction (SSR) method is used to scale up the synthesis process. The SSR method procedure requires powder preparation, followed by pelletization, and annealing/solid state reaction. Preparation of CaMnO_3 and $\text{CaMn}_{0.75}\text{Fe}_{0.25}\text{O}_3$ oxygen carriers are conducted by mixing calculated amounts of CaCO_3 ($\geq 99.0\%$, Sigma-Aldrich), Fe_2O_3 (99.9%, Noah), and Mn_3O_4 (99.0%, Noah) precursors for 12 hours in a planetary ball mill (XBM4X, Columbia International) at a rotation speed of 250 rpm. The mixture is then pressed into $\frac{3}{4}$ " pellets by a hydraulic press (YLJ-15T, MTI Corporation) at a pressure of 20MPa and sintered in a high temperature furnace (GSL-1500-X50, MTI Corporation) at $1,200^\circ\text{C}$ for 24 hours. After annealing, the particles are fractured and sieved into a range of 150-300 microns.

Oxygen Uncoupling Experiments

Initial oxygen uncoupling properties of the oxygen carriers are characterized in a TGA (Q600 TA Instruments). Two primary experiments are conducted in the TGA: (1) temperature programmed desorption TPD experiments using inert helium (5.0, Airgas) and argon (5.0, Airgas) up to $1,000^\circ\text{C}$ at a ramp of $10^\circ\text{C}/\text{min}$ and (2) isothermal experiments between 650 - 950°C . During the TPD experiments, the oxygen carriers are pre-treated in 25% O_2 (Extra Dry, Airgas) balanced with Ar at 850°C for one hour and cooled down at a rate of $10^\circ\text{C}/\text{min}$ to 100°C where the system is purged with a mixture of helium and argon to remove any excess oxygen gas. A TPD experiment is then performed on the oxygen carriers using a $10^\circ\text{C}/\text{min}$ ramp to 1000°C in a helium and argon mixture. Isothermal experiments are conducted at various temperatures to determine the oxygen uncoupling capabilities at different temperatures. At each temperature, 5 cycles of switching between pure inert and 10% O_2 balanced with a mixture of argon and helium are conducted for short term recyclability of the oxygen carrier. Best performing oxygen carriers are also tested for 100 cycles at 850°C to demonstrate the oxygen uncoupling performance of the perovskite oxygen carriers over the long term.

Fluidized Bed Experiments

A laboratory-scale fluidized-bed reactor is used for solid fuel conversion experiment (see Figure S1). The quartz fluidized-bed reactor has an outer diameter of 25.4mm. The reactor is heated through external heating from a tube furnace (MTI OTF-1200X-S-VT). Temperature is measured inside the reactor with an Inconel (Type K) thermocouple to set the temperature of the reactor to 850°C. A 3.75mm ID stainless steel tube is used for solid fuel injection into the reactor. A gas mixing panel is used to send the desired ratio of gases from both the bottom of the reactor for fluidization and through the smaller stainless steel tube for solid fuel injection. For maintaining fluidization, flow rates of 1,080 and 1,200mL/min (at S.T.P) are used for solid fuel conversion and oxygen carrier regeneration (in 10% O₂), respectively. The flow rates correspond to 6-7 times of the calculated minimum fluidization velocity (U_{mf}) for the synthesized oxygen carriers. Prior to experiments, the reactor is loaded with 16 mesh silicon carbide (Kramer Industries) at the bottom of the reactor. The SiC particles act as a gas preheater and distributor. Approximately 15 grams of the oxygen carrier is placed into the reactor for the experiments.

For redox reactions of solid fuel, Pittsburgh #8 coal (-60 mesh) is converted into coal char through heating in the reactor at 950°C in a N₂ environment. The resulting char is sieved into a range of 150-250 microns. Injection of the coal is conducted in a pulse mode by loading from the top of the reactor through the small stainless steel tube and is pulsed into the bottom of the oxygen carrier layer of the reactor bed using N₂. 20 redox cycles are tested using the fluidized bed reactor conducting two experiments in those 20 cycles. The conditions for each cycle are given in Table 1. Exhaust gas concentrations are measured using a quadrupole mass spectrometer (MKS Cirrus 2) and a near-IR based gas analyzer (Emerson X-Stream).

Table 1- Gas conditions for redox cycles used during fluidized bed experiments.

Cycle Number	Gas conditions
1-3	10% O ₂ with coal injection for reference (balance grade 5.0 N ₂)
4-8	100% N ₂ with char injection (reduction step)/10% O ₂ balance N ₂ (oxidation step)
9-18	100% N ₂ without coal injection (reduction step)/10% O ₂ balanced with N ₂ for oxidation (oxidation step)
19-20	100% N ₂ with char injection (reduction step)/10% O ₂ balanced with N ₂ for oxidation (oxidation step)

Sample Characterizations

Phase identification of the oxygen carriers is conducted using X-ray powder diffraction. Powdered samples are prepared and tested using a Rigaku SmartLab X-ray diffractometer with Cu-K α ($\lambda=0.1542\text{nm}$) radiation operating at 40kV and 44mA. A scanning range of 20-80° (2 θ)

with a step size of 0.1° holding for 3.5 seconds at each step is used to generate the XRD patterns. To examine phase properties during TPD experiments, *in-situ* X-ray diffraction was conducted using an Empyrean PANalytical XRD using a similar Cu-K α radiation operating at 45kV and 40mA. A 2θ range of 20-80 is used at a ramp rate of 0.1° holding each step for 0.1s. A TPD experiment is conducted in the *in-situ* XRD by heating the sample at $5^\circ\text{C}/\text{min}$ in pure argon (Grade 5.0). XRD scans are conducted the entire length of the ramp to $1,200^\circ\text{C}$.

Results and Discussion

Effect of dopant into the B-site

Effectiveness of dopant addition largely relies on the compatibility of the dopant and its parent structure. Ideally, dopants should be fully incorporated into the host structure to form a homogeneous solid solution. Figure 1 illustrates the XRD spectra of the various B-site doped CaMnO_3 oxygen carriers.

Figure 1- XRD spectra of the $\text{CaMn}_{0.8}\text{B}_{0.2}\text{O}_3$ oxygen carriers. (★) CaMnO_3 , (○) $\text{Ca}_3\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_6$, (Δ) V_2O_5 and (▲) NiO phases

Of the dopants, Fe is effectively incorporated into the structure without any secondary phases. Ni, V, and Co doped CaMnO_3 oxygen carriers are present with separate identified phases of NiO , V_2O_5 , and mixed oxide phases respectively. Al has an insignificant amount of unidentified phase or phases, this resulted from the low intensity of these peaks and limited database of the HighScore Plus© software.

Lattice parameter refinement of the base orthorhombic CaMnO_3 crystal structure with and without dopants from Figure 1 can be seen in Table 2. The change of the lattice parameters and volume of the unit cell stems from the ionic radii and oxygen vacancies formed during preparation. From table 2, it is observed that the volume of the unit cell decreases with all dopants. The decrease in volume is likely to stem from the stabilization of the crystal structure. As a result, less oxygen vacancy formation at higher temperature is observed despite a change in ionic radii when these dopants replace the Mn^{4+} ion in the CaMnO_3 structure. This is confirmed through isothermal oxygen uncoupling studies of the undoped and Fe-doped oxygen carriers (see

Figure 6) which we will discuss later. Additionally, shifts in peak locations can indicate substitution into the A- or B-site of the perovskite. For example, the diffraction peak for the (110) plane of CaMnO_3 shifts from 33.95° to 33.8° corresponding to shift in the lattice from Fe incorporation.

Table 2-Lattice parameters for the $\text{CaMn}_{0.8}\text{B}_{0.2}\text{O}_3$ oxygen carriers

Dopant	a (Å)	b (Å)	c (Å)	Volume (Å ³)
No Dopant	5.29	7.47	5.27	208.15
Fe	5.32	7.41	5.02	197.93
Co	5.31	7.45	5.20	205.59
V	5.30	7.24	5.18	198.88
Ni	5.30	7.45	5.13	202.80
Al	5.28	7.45	5.22	204.88

Through addition of secondary metals into the A- or B-site of the perovskite, it is possible to improve the stability of the parent CaMnO_3 structure while obtaining more favorable oxygen uncoupling properties. [63] Figure 2 examines the addition of the dopants on the oxygen uncoupling properties of the oxygen carriers using temperature programmed desorption (TPD) and differential thermal gravimetry (DTG) curves.

Figure 2- DTG/TPD curves of $\text{CaMn}_{0.8}\text{B}_{0.2}\text{O}_3$ oxygen carriers (B=Fe, V, Co, Ni, and Al) to $1,000^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$. in a pure inert atmosphere after treatment in 25% O_2 at 850°C . Sample weight: 30-35mg Gas flow rate: 20mL/min He (grade 5.0) and 100mL/min Ar (grade 5.0).

From Figure 2, it can be observed that dopants have a noticeable impact on the oxygen uncoupling properties. Undoped CaMnO_3 sees most of its oxygen released between 800-

1,000°C. Cobalt and vanadium doped perovskites observe a very sharp peak at 775 and 800°C respectively. The peaks correspond to approximately 0.08 and 0.12mg of oxygen released for the Co-doped and V-doped oxygen carriers. The sharp peaks observed can be explained by the oxidation state change of Co and V cations. The Al-doped oxygen carrier exhibits a small peak around 700°C and at higher temperatures follows a trend similar to pure CaMnO_3 . The Ni-doped oxygen carrier is observed to follow the pure CaMnO_3 behavior at a slightly lower oxygen uncoupling capacity. As the XRD profile (see Figure 1) shows, NiO is observed to have formed, which does not exhibit CLOU properties under the conditions tested and is likely to contribute to the slightly lower oxygen uncoupling capacity compared to pure CaMnO_3 . The Fe-doped oxygen carrier is the only sample that observes a noticeable amount of oxygen at temperatures lower than 700°C. The Fe-doped oxygen carrier peak around 400°C is most likely α -oxygen which is attributed to chemisorbed oxygen in oxygen vacancies of the perovskite structure. [66–68] A previous study by Fino et. al showed that perovskites with high α -oxygen content correlated to high activity in catalytic combustion of soot. [67] As a result, it is considered advantageous of oxygen carriers for CLOU to have properties that include having suitable amounts of α -oxygen to achieve high activity with solid fuels. Coupling of the low temperature α -oxygen, incorporation of the metal into the perovskite, and the comparable high temperature CLOU properties, the Fe-doping effect on the CaMnO_3 parent structure is further investigated for CLOU applications.

Effects of Iron Dopant Concentrations

It is expected that the amount of dopant could have significant impact on the oxygen uncoupling properties. Figure 3 shows the XRD patterns for various dopant amounts of Fe into the CaMnO_3 structure. Fe dopant concentrations at or below 20% observe only the CaMnO_3 phase with no secondary phase present. However, a high dopant concentration (50%) induces a Ruddlesden-Popper structured $\text{Ca}_2(\text{Mn,Fe})\text{O}_4$ phase.

Figure 3- XRD spectra of the $\text{CaMn}_{1-x}\text{Fe}_x\text{O}_3$ spectra.

1

2 Figure 4 examines the effect of Fe dopant amount into the parent CaMnO_3 oxygen carrier for the
 3 CLOU capabilities of the oxygen carriers.

Figure 4- DTG/TPD curves of $\text{CaMn}_{1-x}\text{Fe}_x\text{O}_3$ oxygen carriers ($x=0, 0.05, 0.2$, and 0.5) to $1,000^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$. in a pure argon atmosphere after treatment in 25% O_2 at 850°C . Sample weight: 30-35mg Gas flow rate: 20mL/min He (grade 5.0) and 100mL/min Ar (grade 5.0).

4

5 Doping of iron in the structure noticeably lowers the oxygen uncoupling properties compared to
 6 the undoped CaMnO_3 . Addition of dopants creates an increase in the amount of α -oxygen that is
 7 observed. At 5% dopant, a peak around 500°C is observed, while increasing the dopant to 20%
 8 shows the peak shift to a lower temperature around 400°C . The amount of α -oxygen released by
 9 the 5% and 20% Fe doped oxygen carriers is 0.04 and 0.08 mg respectively. While the 50% Fe-
 10 doped CaMnO_3 loses noticeable α -oxygen around 500°C , the higher temperature properties of
 11 the oxygen carrier is minimal. The undesirable CLOU properties of the 50% dopant oxygen
 12 carrier can be explained through the formation of the Ruddlesden-Popper phase which is known
 13 to be very stable. [59]

14 The motivation behind B-site doping is to stabilize the perovskite oxygen carrier's stability.
 15 Undoped CaMnO_3 is observed to decompose from the CaMnO_3 structure into the Ruddlesden-
 16 Popper and spinel structures above 1050°C in an inert atmosphere (See Figure 5 (c) and (d))
 17 Reduction to these phases have been observed at lower temperatures (900 - 950°C) in highly
 18 reductive environments that are typically observed in chemical looping schemes. [33,35] These
 19 phases are undesirable due to their difficulty to regenerate back to the CaMnO_3 structure in air
 20 under temperatures typical of chemical looping systems. Figure 5 (a) and (b) shows the *in-situ*
 21 XRD spectra of the 5% Fe doped CaMnO_3 .

Figure 5- (a) and (c) *In-situ* XRD spectra of the $\text{CaMn}_{0.95}\text{Mn}_{0.05}\text{O}_3$ and CaMnO_3 perovskite oxygen carrier and (b) and (d) a better resolution of the (110) plane for both oxygen carriers.

1
2 As can be seen, the perovskite consists of a single $\text{CaMn}_{1-x}\text{Fe}_x\text{O}_3$ phase at room temperature.
3 During the ramping, no phase transformation is seen as the 5 peaks observed at 2θ 's of 24, 34,
4 48, 60, and 71° are present at all temperatures tested (up to 1200°C). The observation of a sharp
5 peak shift around 650°C agrees with the oxygen release temperature in TPD experiments. In
6 contrast, undoped CaMnO_3 sample undergoes decomposition to CaMn_2O_4 and Ca_2MnO_4 phases
7 at around 1050°C . Therefore, Fe doping is shown to be effective to enhance the phase stability
8 of CaMnO_3 .

9 Redox Testing

10 CLOU performance can be characterized by testing oxygen carriers under redox cycles. For
11 CLOU, cycles of inert (mixture of helium and argon) and air are used to typically test for oxygen
12 carriers recyclability and stability. Our tests use both undoped CaMnO_3 and the Fe doped sample
13 under a small number of redox cycles at various temperatures to investigate the ability of these
14 oxygen carriers to perform under numerous conditions. Figure 6 shows the oxygen uncoupling
15 capacity under isothermal conditions between 650 - 950°C

Figure 6- Isothermal weight loss at temperatures between 650-950°C. Sample weight: 30mg. Flow Rates: Reduction step: 30mL/min He (5.0 grade) and 60mL/min Ar (5.0 grade). Oxidation step: additional 10mL/min O₂ (Extra Dry grade) added to aforementioned gas stream.

1
2 Consistent with TPD results, CaMnO₃ has no noticeable oxygen release at 650°C, while the
3 incorporation of iron allows for noticeable amounts of oxygen to be released. Once the
4 temperature reaches a temperature high enough to drive oxygen release in undoped CaMnO₃
5 (>850 °C), CaMnO₃ releases approximately 20% more oxygen than the Fe doped samples.
6 This result confirms that the Fe doped sample can accommodate less oxygen vacancy than
7 undoped CaMnO₃ under high temperature, low P_{O2} environments. This is consistent with the
8 observed phase stability of the doped sample under *in-situ* XRD. It also explains the smaller
9 unit cell sizes for the doped samples (see Table 2). The spontaneous oxygen release at low
10 temperature coupled with the improved phase stability make the Fe doped oxygen carriers
11 promising for CLOU. The oxygen carriers were cycled 5 times at each temperature with no
12 noticeable change in performance.

Figure 7- 100 cycle tests at 850°C for $\text{CaMn}_{0.95}\text{Fe}_{0.05}\text{O}_3$ oxygen carrier. Sample weight: 50mg. Gas flow rates: Reduction step: 30mL/min He (5.0 grade) and 60mL/min Ar (5.0 grade). Oxidation step: additional 10mL/min O_2 (Extra Dry grade) added to aforementioned inert gas. The XRD pattern of the fresh and post 100 CLOU cycles XRD of the oxygen carrier is embedded.

1
2 In chemical looping schemes, long term cycling is important due to the need to replenish the
3 solid oxygen carriers over time. Figure 7 investigates a 100 redox cycles of Fe-doped CaMnO_3 at
4 850°C. From the long term cycling, the Fe-doped oxygen carrier exhibits little to no deactivation.
5 After the 100 cycles, the oxygen carrier was tested for redox reactions at lower temperatures, and
6 comparable results of the oxygen uncoupling properties shown in Figure 6 were observed.
7 Previous studies on B-site doped perovskites have shown the formation of undesired CaMn_2O_4
8 and Ca_2MnO_4 phases after as few as 3 cycles. [31,33,35] After 100 cycles, the 5% Fe doped
9 oxygen carrier was not observed to undergo any undesired phase transitions.

10 Oxygen carriers for CLOU are highly effective in converting solid fuels due to their ability to
11 release gaseous O_2 . Solid fuel conversion is then of utmost importance of these oxygen carriers.
12 Fluidized bed experiments are conducted to test the undoped CaMnO_3 and Fe-doped oxygen
13 carriers' ability to convert char prepared from Pittsburgh # 8 coal. The results are shown in
14 Figure 8.

Figure 8- Char conversion and CO₂ selectivity of the CaMn_{0.95}Fe_{0.05}O₃ oxygen carrier in a fluidized bed reactor. Sample weight: 15 gms. Oxygen carrier and 10mg of char Temperature: 850°C Gas Flow Rates: nitrogen: 800mL/min (Grade 5.0) and helium (Grade 5.0): 280mL/min (Char Reduction) and oxygen (Extra dry grade): 120mL/min (during oxidation only).

The Fe-doped oxygen carrier was able to convert, on average, 90% char during each cycle with close to 99% selectivity to CO₂ conversion at 850°C. During the first 3 cycles, coal char is injected while 10% O₂ is present resulting in complete combustion of the char. The less than 100% conversion of coal char is likely to be due to the limitation of solids inventory in the tubular reactor, which results in relatively low oxygen generation rate (and concentration) when compared to the flow rate of the inert fluidization gas. The Fe-doped oxygen carrier shows an attrition rate of 0.003w.t.% per hour. For comparison purpose, undoped CaMnO₃ oxygen carrier was also tested for coal char conversion under identical conditions. The char conversion of the undoped CaMnO₃ oxygen carrier was approximately 50%. This is a significant drop in performance compared to when Fe was doped into the B-site. A higher temperature experiment at 950°C was also tested for the undoped CaMnO₃ oxygen carrier. At this temperature, a conversion of 90 – 97 % is obtained within 5 redox cycles (see Figure S3). This correlates with the superior low temperature CLOU activity for Fe doped CaMnO₃. Therefore, the Fe-doped oxygen carrier is observed to have facile oxygen release for effective conversion of solid fuels. It is also capable of maintaining long term stability compared to undoped CaMnO₃.

Conclusion

The present study investigates the effect of B-site doping on oxygen carriers with a general composition of CaMn_xM_{1-x}O₃ (M = Fe, V, CO, Ni, Al). The phase compatibility with CaMnO₃ parent structure, oxygen carrying capacity, oxygen release temperature, phase stability, and CLOU performance of these B-site doped oxygen carriers are investigated. Secondary phases are formed for all dopants except for Fe. For V and Ni doped oxygen carriers, pure oxides of the dopant metals are formed along with a doped CaMnO₃ structure. Fe dopants are found to be fully

compatible with the CaMnO_3 parent structure for up to 20% B-site doping. These Fe doped oxygen carriers also exhibit excellent CLOU property, especially at lower temperatures ($\sim 600^\circ\text{C}$) when compared to the undoped CaMnO_3 oxygen carrier. Fe dopant is also found to significantly improve the phase stability of CaMnO_3 based oxygen carriers. No phase transformation was observed in both high temperature operation (up to 1200°C) and 100 oxygen uncoupling cycles (at 850°C). The Fe doped oxygen carrier also demonstrated significantly higher activity for coal char conversion when compared to the undoped CaMnO_3 oxygen carrier at 850°C .

Acknowledgements

Funding supports from the U.S. Department of Energy (Award Number FE001247) and Kenan Institute are greatly appreciated. We acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

References

- [1] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO_2 capture technology—The U.S. Department of Energy’s Carbon Sequestration Program. *Int J Greenh Gas Con*. 2008;2:9–20. doi:10.1016/S1750-5836(07)00094-1.
- [2] Hansen J, Sato M. Greenhouse gas growth rates. *Proc. Natl. Acad. Sci. USA* 2004;101:16109–14.
- [3] Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in chemical-looping combustion and reforming technologies. *Prog Energy Combust* 2012;38:215–82. doi:10.1016/j.pecs.2011.09.001.
- [4] Fan L-S, Li F. Chemical looping technology and its fossil energy conversion applications. *Ind Eng Chem Res* 2010;49:10200–11. doi:10.1021/ie1005542.
- [5] Fan L-S. Chemical Looping Systems for Fossil Energy Conversions. 2010.
- [6] Lyngfelt A. Chemical-looping combustion of solid fuels – status of development. *Appl Energ* 2014;113:1869–73. doi:10.1016/j.apenergy.2013.05.043.
- [7] Sorgenfrei M, Tsatsaronis G. Design and evaluation of an IGCC power plant using iron-based syngas chemical-looping (SCL) combustion. *Appl Energ* 2014;113:1958–64. doi:10.1016/j.apenergy.2013.03.089.
- [8] Tong A, Bayham S, Kathe MV, Zeng L, Luo S, Fan L-S. Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University. *Appl Energ* 2014;113:1836–45. doi:10.1016/j.apenergy.2013.05.024.
- [9] Scott SA, Dennis JS, Hayhurst AN, Brown T. *In situ* gasification of a solid fuel and CO_2 separation using chemical looping. *AIChE J* 2006;52:3325–8. doi:10.1002/aic.10942.
- [10] Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* 2007;86:1947–58. doi:10.1016/j.fuel.2006.11.037.
- [11] Luo S, Bayham S, Zeng L, McGiveron O, Chung E, Majumder A, et al. Conversion of metallurgical coke and coal using a Coal Direct Chemical Looping (CDCL) moving bed reactor. *Appl Energ* 2014;118:300–8. doi:10.1016/j.apenergy.2013.11.068.
- [12] Cuadrat A, Linderholm C, Abad A, Lyngfelt A, Adánez J. Influence of limestone addition in a 10 kW_{th} chemical-looping combustion unit operated with petcoke. *Energ Fuel* 2011;25:4818–28. doi:10.1021/ef200806q.

- [13] Linderholm C, Lyngfelt A, Cuadrat A, Jerndal E. Chemical-looping combustion of solid fuels – operation in a 10kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. *Fuel* 2012;102:808–22. doi:10.1016/j.fuel.2012.05.010.
- [14] Leion H, Mattisson T, Lyngfelt A. Solid fuels in chemical-looping combustion. *Int J Greenh Gas Con* 2008;2:180–93. doi:10.1016/S1750-5836(07)00117-X.
- [15] Arjmand M, Leion H, Mattisson T, Lyngfelt A. Investigation of different manganese ores as oxygen carriers in chemical-looping combustion (CLC) for solid fuels. *Appl Energy* 2014;113:1883–94. doi:10.1016/j.apenergy.2013.06.015.
- [16] Shen L, Wu J, Xiao J. Experiments on chemical looping combustion of coal with a NiO based oxygen carrier. *Combust Flame* 2009;156:721–8. doi:10.1016/j.combustflame.2008.08.004.
- [17] Shen L, Wu J, Xiao J, Song Q, Xiao R. Chemical-Looping Combustion of biomass in a 10 kW_{th} reactor with iron oxide as an oxygen carrier. *Energ Fuel* 2009;23:2498–505. doi:10.1021/ef900033n.
- [18] Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int J Greenh Gas Con* 2009;3:11–9. doi:10.1016/j.ijggc.2008.06.002.
- [19] Mattisson T. Materials for chemical-looping with oxygen uncoupling. *ISRN Chem Eng* 2013;2013:1–19. doi:10.1155/2013/526375.
- [20] Imtiaz Q, Hosseini D, Müller CR. Review of oxygen carriers for chemical looping with oxygen uncoupling (CLOU): thermodynamics, material development, and synthesis. *Energy Technol* 2013;1:633–47. doi:10.1002/ente.201300099.
- [21] Azimi G, Leion H, Mattisson T, Lyngfelt A. Chemical-looping with oxygen uncoupling using combined Mn-Fe oxides, testing in batch fluidized bed. *Energy Procedia* 2011;4:370–7. doi:10.1016/j.egypro.2011.01.064.
- [22] Azimi G, Leion H, Rydén M, Mattisson T, Lyngfelt A. Investigation of different Mn–Fe Oxides as oxygen carrier for chemical-looping with oxygen uncoupling (CLOU). *Energ Fuel* 2013;27:367–77. doi:10.1021/ef301120r.
- [23] Shafiefarhood A, Stewart A, Li F. Iron-containing mixed-oxide composites as oxygen carriers for chemical looping with oxygen uncoupling (CLOU). *Fuel* 2015;139:1–10. doi:10.1016/j.fuel.2014.08.014.
- [24] Shulman A, Cleverstam E, Mattisson T, Lyngfelt A. Manganese/iron, manganese/nickel, and manganese/silicon oxides used in chemical-looping with oxygen uncoupling (CLOU) for combustion of methane. *Energ Fuel* 2009;23:5269–75. doi:10.1021/ef9005466.
- [25] Shulman A, Cleverstam E, Mattisson T, Lyngfelt A. Chemical-looping with oxygen uncoupling using Mn/Mg-based oxygen carriers – oxygen release and reactivity with methane. *Fuel* 2011;90:941–50. doi:10.1016/j.fuel.2010.11.044.
- [26] Arjmand M, Azad A-M, Leion H, Lyngfelt A, Mattisson T. Prospects of Al₂O₃ and MgAl₂O₄-supported CuO oxygen carriers in chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU). *Energ Fuel* 2011;25:5493–502. doi:10.1021/ef201329x.
- [27] Arjmand M, Keller M, Leion H, Mattisson T, Lyngfelt A. Oxygen release and oxidation rates of MgAl₂O₄-supported CuO oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU). *Energ Fuel* 2012;26:6528–39. doi:10.1021/ef3010064.

- [28] Gayán P, Adáñez-Rubio I, Abad A, de Diego LF, García-Labiano F, Adáñez J. Development of Cu-based oxygen carriers for chemical-looping with oxygen uncoupling (CLOU) process. *Fuel* 2012;96:226–38. doi:10.1016/j.fuel.2012.01.021.
- [29] Pour NM, Azimi G, Leion H, Rydén M, Lyngfelt A. Production and examination of oxygen-carrier materials based on manganese ores and $\text{Ca}(\text{OH})_2$ in chemical looping with oxygen uncoupling. *AIChE J* 2014;60:645–56. doi:10.1002/aic.14273.
- [30] Rydén M, Leion H, Mattisson T, Lyngfelt A. Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. *Appl Energ* 2014;113:1924–32. doi:10.1016/j.apenergy.2013.06.016.
- [31] Arjmand M, Hedayati A, Azad A-M, Leion H, Rydén M, Mattisson T. $\text{Ca}_x\text{La}_{1-x}\text{Mn}_{1-y}\text{M}_y\text{O}_{3-\delta}$ (M = Mg, Ti, Fe, or Cu) as oxygen carriers for chemical-looping with oxygen uncoupling (CLOU). *Energ Fuel* 2013. doi:10.1021/ef3020102.
- [32] Arjmand M, Kooiman RF, Rydén M, Leion H, Mattisson T, Lyngfelt A. Sulfur tolerance of $\text{Ca}_x\text{Mn}_{1-y}\text{M}_y\text{O}_{3-\delta}$ (M = Mg, Ti) perovskite-type oxygen carriers in chemical-looping with oxygen uncoupling (CLOU). *Energ Fuel* 2014;28:1312–24. doi:10.1021/ef402383v.
- [33] Hallberg P, Jing D, Rydén M, Mattisson T, Lyngfelt A. Chemical looping combustion and chemical looping with oxygen uncoupling experiments in a batch reactor using spray-dried $\text{CaMn}_{1-x}\text{M}_x\text{O}_{3-\delta}$ (M = Ti, Fe, Mg) particles as oxygen carriers. *Energ Fuel* 2013;27:1473–81. doi:10.1021/ef3013618.
- [34] Leion H, Larring Y, Bakken E, Bredesen R, Mattisson T, Lyngfelt A. Use of $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_3$ as oxygen carrier in chemical-looping with oxygen uncoupling. *Energ Fuel* 2009;23:5276–83. doi:10.1021/ef900444d.
- [35] Rydén M, Lyngfelt A, Mattisson T. $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_3$ as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU)—Experiments in a continuously operating fluidized-bed reactor system. *Int J Greenh Gas Con* 2011;5:356–66. doi:10.1016/j.ijggc.2010.08.004.
- [36] Sundqvist S, Leion H, Rydén M, Lyngfelt A, Mattisson T. $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ as an oxygen carrier for chemical-looping with oxygen uncoupling (CLOU)-solid-fuel testing and sulfur interaction. *Energy Technol* 2013;1:338–44. doi:10.1002/ente.201300007.
- [37] Källén M, Rydén M, Dueso C, Mattisson T, Lyngfelt A. $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ as oxygen carrier in a gas-fired 10 kW_{th} chemical-looping combustion unit. *Ind Eng Chem Res* 2013;52:6923–32. doi:10.1021/ie303070h.
- [38] Pishahang M, Larring Y, McCann M, Bredesen R. $\text{Ca}_{0.9}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$: A suitable oxygen carrier material for fixed-bed chemical looping combustion under syngas conditions. *Ind Eng Chem Res* 2014;53:10549–56. doi:10.1021/ie500928m.
- [39] Moldenhauer P, Rydén M, Mattisson T, Hoteit A, Jamal A, Lyngfelt A. Chemical-looping combustion with fuel oil in a 10 kW pilot plant. *Energ Fuel* 2014;28:5978–87. doi:10.1021/ef5014677.
- [40] Dai XP, Li J, Fan JT, Wei WS, Xu J. Synthesis gas generation by chemical-looping reforming in a circulating fluidized bed reactor using perovskite LaFeO_3 -based oxygen carriers. *Ind Eng Chem Res* 2012;51:11072–82. doi:10.1021/ie300033e.
- [41] He F, Li X, Zhao K, Huang Z, Wei G, Li H. The use of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskite-type oxides as oxygen carriers in chemical-looping reforming of methane. *Fuel* 2013;108:465–73. doi:10.1016/j.fuel.2012.11.035.

- [42] Mihai O, Chen D, Holmen A. Chemical looping methane partial oxidation: the effect of the crystal size and O content of LaFeO_3 . *J Catal* 2012;293:175–85. doi:10.1016/j.jcat.2012.06.022.
- [43] Murugan A, Thursfield A, Metcalfe IS. A chemical looping process for hydrogen production using iron-containing perovskites. *Energ Environ Sci* 2011;4:4639. doi:10.1039/c1ee02142g.
- [44] Readman JE, Olafsen A, Larring Y, Blom R. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ as a potential oxygen carrier in a chemical looping type reactor, an in-situ powder X-ray diffraction study. *J Mater Chem* 2005;15:1931. doi:10.1039/b416526h.
- [45] Rydén M, Lyngfelt A, Mattisson T, Chen D, Holmen A, Bjørgum E. Novel oxygen-carrier materials for chemical-looping combustion and chemical-looping reforming; $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$ perovskites and mixed-metal oxides of NiO , Fe_2O_3 and Mn_3O_4 . *Int J Greenh Gas Con* 2008;2:21–36. doi:10.1016/S1750-5836(07)00107-7.
- [46] Sarshar Z, Sun Z, Zhao D, Kaliaguine S. Development of sinter-resistant core-shell $\text{LaMn}_x\text{Fe}_{1-x}\text{O}_3@m\text{SiO}_2$ oxygen carriers for chemical looping combustion. *Energ Fuel* 2012;26:3091–102. doi:10.1021/ef3003137.
- [47] Zhao K, He F, Huang Z, Zheng A, Li H, Zhao Z. Three-dimensionally ordered macroporous LaFeO_3 perovskites for chemical-looping steam reforming of methane. *Int J Hydrog Energ* 2014;39:3243–52. doi:10.1016/j.ijhydene.2013.12.046.
- [48] Sarshar Z, Kleitz F, Kaliaguine S. Novel oxygen carriers for chemical looping combustion: $\text{La}_{1-x}\text{Ce}_x\text{BO}_3$ ($\text{B} = \text{Co}, \text{Mn}$) perovskites synthesized by reactive grinding and nanocasting. *Energ Environ Sci* 2011;4:4258–69. doi:10.1039/C1EE01716K.
- [49] Noorman S, Gallucci F, van Sint Annaland M, Kuipers JAM. Experimental Investigation of chemical-looping combustion in packed beds: a parametric study. *Ind Eng Chem Res* 2011;50:1968–80. doi:10.1021/ie1019112.
- [50] Chen Y, Galinsky N, Wang Z, Li F. Investigation of perovskite supported composite oxides for chemical looping conversion of syngas. *Fuel* 2014;134:521–30. doi:10.1016/j.fuel.2014.06.017.
- [51] Galinsky NL, Huang Y, Shafieifarhood A, Li F. Iron oxide with facilitated O^{2-} transport for facile fuel oxidation and CO_2 Capture in a Chemical Looping Scheme. *ACS Sustain Chem Eng* 2013;1:364–73. doi:10.1021/sc300177j.
- [52] Shafieifarhood A, Galinsky N, Huang Y, Chen Y, Li F. $\text{Fe}_2\text{O}_3@ \text{La}_x\text{Sr}_{1-x}\text{FeO}_3$ core-shell redox catalyst for methane partial oxidation. *ChemCatChem* 2014;6:790–9. doi:10.1002/cctc.201301104.
- [53] Neal LM, Shafieifarhood A, Li F. Dynamic methane partial oxidation using a $\text{Fe}_2\text{O}_3@ \text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ core-shell redox catalyst in the absence of gaseous oxygen. *ACS Catal* 2014;4:3560–9. doi:10.1021/cs5008415.
- [54] Galinsky NL, Shafieifarhood A, Chen Y, Neal L, Li F. Effect of support on redox stability of iron oxide for chemical looping conversion of methane. *Appl Catal B-Environ* 2015;164:371–9. doi:10.1016/j.apcatb.2014.09.023.
- [55] Peña MA, Fierro JLG. Chemical structures and performance of perovskite oxides. *Chem Rev* 2001;101:1981–2018. doi:10.1021/cr980129f.
- [56] He F, Trainham J, Parsons G, Newman JS, Li F. A hybrid solar-redox scheme for liquid fuel and hydrogen coproduction. *Energ Environ Sci* 2014;7:2033. doi:10.1039/c4ee00038b.
- [57] He F, Li F. Perovskite promoted iron oxide for hybrid water-splitting and syngas generation with exceptional conversion. *Energ Env Sci* 2015;8:535–9. doi:10.1039/C4EE03431G.

- [58] Jing D, Mattisson T, Leion H, Rydén M, Lyngfelt A. Examination of perovskite structure $\text{CaMnO}_{3-\delta}$ with MgO addition as oxygen carrier for chemical looping with oxygen uncoupling using methane and syngas. *Int J Chem Eng* 2013;2013:1–16. doi:10.1155/2013/679560.
- [59] Bakken E, Norby T, Stolen S. Nonstoichiometry and reductive decomposition of $\text{CaMnO}_{3-\delta}$. *Solid State Ionics* 2005;176:217–23. doi:10.1016/j.ssi.2004.07.001.
- [60] Cabello A, Abad A, Gayán P, de Diego LF, García-Labiano F, Adánez J. Effect of operating conditions and H_2S presence on the performance of $\text{CaMg}_{0.1}\text{Mn}_{0.9}\text{O}_{3-\delta}$ perovskite material in chemical looping combustion (CLC). *Energ Fuel* 2014;28:1262–74. doi:10.1021/ef4020718.
- [61] Fossdal A, Bakken E, Øye BA, Schøning C, Kaus I, Mokkelbost T, et al. Study of inexpensive oxygen carriers for chemical looping combustion. *Int J Greenh Gas Con* 2011;5:483–8. doi:10.1016/j.ijggc.2010.08.001.
- [62] Hallberg P, Källén M, Jing D, Snijkers F, van Noyen J, Rydén M, et al. Experimental investigation of based oxygen carriers used in continuous chemical-looping combustion. *Int J Chem Eng* 2014;2014:1–9. doi:10.1155/2014/412517.
- [63] Galinsky N, Mishra A, Zhang J, Li F. $\text{Ca}_{1-x}\text{A}_x\text{MnO}_3$ (A=Sr and Ba) perovskite based oxygen carriers for chemical looping with oxygen uncoupling (CLOU). *Appl Energ* 2015. doi:10.1016/j.apenergy.2015.04.020.
- [64] Hallberg P, Rydén M, Mattisson T, Lyngfelt A. $\text{CaMnO}_{3-\delta}$ made from low cost material examined as oxygen carrier in chemical-looping combustion. *Energy Procedia* 2014;63:80–6. doi:10.1016/j.egypro.2014.11.009.
- [65] Schmitz M, Linderholm C, Lyngfelt A. Chemical looping combustion of sulphurous solid fuels using spray-dried calcium manganate particles as oxygen carrier. *Energy Procedia* 2014;63:140–52. doi:10.1016/j.egypro.2014.11.014.
- [66] Ciambelli P, Cimino S, De Rossi S, Faticanti M, Lisi L, Minelli G, et al. AMnO_3 (A=La, Nd, Sm) and $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskites as combustion catalysts: structural, redox and catalytic properties. *Appl Catal B-Environ* 2000;24:243–53. doi:10.1016/S0926-3373(99)00110-1.
- [67] Fino D, Russo N, Saracco G, Specchia V. The role of suprafacial oxygen in some perovskites for the catalytic combustion of soot. *J Catal* 2003;217:367–75. doi:10.1016/S0021-9517(03)00143-X.
- [68] Zhu J, Li H, Zhong L, Xiao P, Xu X, Yang X, et al. Perovskite oxides: preparation, characterizations, and applications in heterogeneous catalysis. *ACS Catal* 2014;4:2917–40. doi:10.1021/cs500606g.