Novel perovskite ceramics for chemical looping combustion application

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Abstract

New modified calcium manganese (CM) perovskite structures applicable in chemical looping combustion were synthesized in this study. These modifications were applied by doping the A-site with Lanthanum and strontium and B-site by iron and zirconium (CLMF, CLMZ, CSMF, and CSMZ). TGA, XRD, SEM and BET techniques have been used to characterize the prepared structures. According to the results obtained from TGA analysis, the oxygen capacity of the samples ranged between 1.2 for CLMZ and 1.75 for CSMF. All prepared samples showed to possess a porous surface and the perovskites phase formation was confirmed by XRD results. Iodometric titration experiments were also conducted for evaluating the manganese ion charge and its variability in association with different doping elements. Reactivity and oxygen uncoupling behaviors of the prepared samples were also evaluated using a fluidized bed chemical looping reactor using methane as the fuel at four different temperatures (800, 850, 900, 950 °C).

All of the oxygen carriers showed oxygen uncoupling behavior and they were able to capture and release oxygen. Mass-based conversion of the perovskites was calculated and temperature increase proved to increase the mass-based conversion rate in all of the samples under study. Gas yield was calculated at 950°C as well, and results showed that CLMZ, CM and CSMF showed 100% gas yields and CLMF and CSMZ showed approximately 85% yield in fluidized bed reactor, which is a high and acceptable quantity.

Keywords: Porous perovskite, chemical looping combustion and calcium manganese

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1. Introduction

Chemical looping combustion (CLC) is a novel method of pure CO₂ production during carbonaceous fuel combustion with the least energy penalty among currently introduced methods. This system is commonly composed of two interconnected fluidized bed reactors, called air and fuel reactors. In order for the combustion to occur, the oxygen in the air reactor, should be transferred to the fuel reactor (containing carbonaceous fuel, C_nH_{2m}) using metal oxides (Me_xO_y) called oxygen carriers. These materials are oxidized in the presence of air in the air reactor and are then transferred to the fuel reactor. In the fuel reactor, the fuel reacts with the oxygen carriers, utilizing their captured oxygen and consequently fuel oxidation and oxygen carrier reduction occur simultaneously. Afterwards, the oxygen carriers are transferred to the air reactor for reoxidation and a new cycle begins [1-3].

There are several factors that make CLC superior to a conventional combustion process. As mentioned earlier, in CLC oxygen is transferred between reactors and hence the combustion occurs in the presence of pure oxygen. This way, the only products of the combustion reaction are CO₂ and water vapor which can be separated by using a simple condensation unit, as opposed to a combustion that takes place in air which can have several byproducts and CO₂ separation requires energy intensive utilities. It is also of great interest in CLC processes that the sum of the heat released during the oxidation and reduction reactions is the same as the heat released during a normal combustion process [2].

The two main reactions during oxidation and reduction are shown below:

The Chemical Looping Combustion with Oxygen Uncoupling (CLOU) process is also a CLC technology with a different mechanism for burning the fuel. In CLOU, the fuel reacts with the oxygen released by the oxygen carriers via the following oxidation and reduction reactions [4, 5]:

As mentioned earlier, oxygen carriers are responsible for oxygen transport between reactors. As a result, an effective oxygen carrier is one of the main determinants of a successful CLC process and hence there have been numerous studies investigating various oxygen carriers applicable in CLC. For an efficient CLC process, these oxygen carriers should have specific qualifications such as: high reactivity with the fuel to result in complete combustion, stability, resistance to agglomeration, durability throughout multiple oxidation and reduction cycles and mechanical strength. They should also be non-toxic, environmentally friendly and cost effective [2]. Oxides of transition metals (Ni, Fe, Co, Mn, Cu) [6, 7] and their combinations; natural ores such as ilmenite [8]; and mixed metal oxides called perovskites [9-11] have been investigated by many research groups and have proven to be viable options as oxygen carriers for chemical looping purposes. In recent years, special attention has been devoted to perovskite ceramics because of their special characteristics [2, 12-14]. These structures are important because they are composed of a combination of metal oxides with different features. It is also of great importance to know that around 90% of elements in the periodic table can be successfully incorporated into a perovskite structure [15]. This provides us with a wide range of elements to choose from and tune the properties of the perovskites as desired for their intended applications. Perovskite materials have a general formula of ABO_3 , in which A and B are both cations, with A as a larger cation than B. Transition metals will usually locate on the B-site, whereas larger cations (such as Na^+ ,

K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+}) will be located on the A-site [14, 16]. In recent years, several studies have been conducted in order to synthesize more efficient perovskites applicable to CLC as oxygen carriers [10]. The most promising material that has been used extensively during the past decade is $CaMnO_3$ [17, 18]. In this structure, the release and capture of oxygen is due to the transformation of Mn^{4+} to Mn^{3+} , thereby facilitating the oxygen release within the fuel reactor. However, this structure is subject to change into Ca_2MnO_4 and $CaMn_2O_4$, which might cause a decrease in the perovskite efficiency during oxidation-reduction cycles at high temperatures. According to the literature, to resolve this problem, transition metals such as Ti, Fe, Zr and Cu can be doped with the B-site cation (Mn), leading to a more stable structure during the process [2].

Although, the ideal perovskite structure is cubic, the small ionic radius of the doped ions, compared with the voids between the octahedral, will result in a cooperative tilting of the corner shared octahedral, such that structure distorts into the orthorhombic space group $Pnma$ [19].

In ternary oxides, the BO_6 octahedral tilting is possible when employing smaller A-site cations in the ABO_3 structure. If tilting occurs, the BO_6 octahedral distort such that the B-O-B bonds are no longer equal to 180° [19, 20]. Distortion in ABO_3 type perovskites can occur by changes in B–O bond lengths. This will result in deviation from the ideal cubic structure. These types of distortions are prompted by orbital degeneracies, polar distortions, bond-valence requirements, and/or valence fluctuations. Changes in B–O bond lengths in the systems with d^4 or d^7 electronic configurations on their B atoms are possible and expected. These changes can lead to Jahn–Teller-type anti-symmetric breathing of the BO_6 octahedral[21].

It is also important to note that the degree of distortion and the properties of the perovskites are highly dependent on the synthesis conditions. As a result, several methods of synthesis have been

introduced for perovskite production to date, which strongly influence its surface physicochemical properties, surface area, porosity, purity, stability and crystal size [22, 23]. 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 [24]. 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 and impregnation [3]. Extrusion is an important forming technique in the ceramics industry owing to its ability to provide complex shapes and forms with dimensional accuracy, and to its flexibility for mass production [25]. One of the main goals of the proposed method is to use the mass production capability of extrusion technique. Therefore, the extrusion technique is selected for production of oxygen carriers in the present study.

There is a relationship between composition, structure and properties, which have been well studied in recent years [2, 26, 27]. However, many questions remain in this relationship that need to be explored in the future.

As discussed earlier, several studies have tried to improve the stability and oxygen capacity of CaMnO_3 [2]. Although, some of them have been successful in addressing the stability of calcium manganese by doping the A- or B- sites, the oxygen capacity has decreased as a result of doping [17, 28-30]. Here, we have tried to find doping elements that can increase both the oxygen capacity and stability of CaMnO_3 by investigating the effect of ion size on A- and B- site positions of this perovskite structure i.e. replacing the Mn and Ca sites with larger cations, such as Zr and Sr respectively. Undoped calcium manganese is also prepared for comparison (CM) purposes, while a lanthanum and iron doped sample (CLMF) is chosen to identify the effects of

starch optimization and preparation method on physical properties of the samples. CLMF has been reported by Arjmand et. al. [28], using rotary evaporation as the mixing method with the starch amount not being optimized.

2. Experimental procedure

The perovskite-based oxygen carrier particles, which are investigated in this study, are synthesized as follows. $\text{Ca}(\text{OH})_2$ (Alfa-Aesar, 95 wt %) and MnCO_3 (Alfa-Aesar, 99 wt %) powders with an average particle size of $\sim 46 \mu\text{m}$ (325 mesh) are mixed in an appropriate weight ratio with or without La_2O_3 (Alfa-Aesar, 99.9 wt %), Fe_2O_3 (Alfa-Aesar, 99 wt %), ZrO_2 (Acros Organics, 99 wt %), and SrCO_3 (Alfa-Aesar, 99 wt %), to make 500 g batches of the final product in each case. A simple coding label C (S or L) M (F or Z) is used for each sample, where C=Ca, S=Sr, L=La, M=Mn, F=Fe and Z=Zr. Hence the synthesized samples are CLMF, CLMZ, CSMF, CSMZ and CM. The list of prepared samples can be found in Table 1. In this study the mixed batch of raw materials is transferred to a 3000 mL plastic drum with 1500 g of water, which is placed in a rotary tumbler for 6 hours. In accordance with the literature [31-33], 30 vol. % solid loading with 0.1 wt. % of the dispersant (ammonium polyacrylate, NH_4PAA , dispersant) is used. The aqueous slurry is thoroughly mixed and homogenized in a rotary tumbler unit. The slurry is poured into a shallow pan (Pyrex) and dried at 150°C in an air oven overnight. The dried soft mass is then crushed and ground to a homogeneous powder for each batch. Furthermore, the dried cake is pulverized and homogenized, and this process is followed by extrusion into rods.

The composition of the extrusion paste is selected based on Imanieh et. al conference paper [34]. They have optimized the starch amount for calcium manganese structure doped with iron and lanthanum at the B and A sites respectively, and they have further proved that their suggested

composition is suitable for other systems using solid state reaction as the preparation method. In our case, the following components are 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 a peptizing agent. After obtaining a suitable viscosity of blended materials, they are extruded using a simple manual extruder. Extrudates are dried on a stainless steel plate at 75°C overnight. The extrudes are then transferred to high-density alumina crucibles and calcined in air for 6 hours at 1300°C (the temperature is chosen to be either 1200 °C for compositions without lanthanum or 1300 °C for lanthanum containing compositions) in a programmable furnace. To yield particles in the range of 125–250 µm, the calcined extrudates are sieved through stainless-steel screens. The resulting powders are washed and ultra-sounded five times each for 5 minutes, to remove the fine particles that may have been formed during the crushing stage.

To measure the oxygen capacity (R_O) of the investigated formulations for CLOU, reduction–oxidation cycles are carried out in a thermogravimetric analyzer (TA Instrument, TGA Q50), cycling between air (20.8% O_2) and high-purity N_2 , using the detailed procedure mentioned in Arjmand et. al. [28].

In every case, the Brunauer–Emmett–Teller (BET) specific surface area is measured by N_2 adsorption (Micromeritics, TriStar 3000). Digital force gauge (Shimpo, FGN-5) is used to measure the crushing strength (the force needed to fracture a single particle). To determine the crushing strength, an average of 30 measurements is taken from the particles in the range of 125–250 µm.

163 The microstructure of the samples is studied using a Hitachi S-4800 Scanning Electron
164 Microscope (SEM). EDS (Energy Dispersive Spectroscopy) analyses of the samples is also
165 performed after calibrating the detector with a pure copper sample.

166 Crystalline phase determination of the oxygen carriers is carried out using powder X-ray
167 diffraction (XRD, PANalytical X'Pert Pro) with Cu $K\alpha_1$ radiation. The morphology of the
168 particles is studied with a scanning electron microscope (Hitachi, S4800).

169 Iodometric titration experiments are also conducted to evaluate the manganese ion charge and
170 consequently the number of oxygen atoms in the prepared structures. The design of the
171 iodometric titration experiments in this study, is based on dissolving the samples in a
172 concentrated HCl solution. The detailed procedure is addressed in Tali et. al. [35]

173 Experiments for examining oxygen uncoupling behaviors (CLOU) and reactivity characteristics
174 (CLC) are performed in a quartz fluidized-bed reactor that is 870 mm high and 22 mm in inner
175 diameter (designed at Chalmers University and fabricated in University of Toledo)[28].
176 Information about the reactor design and set up of controllers can be found in Arjmand et.al.
177 [28]. The scheme of the experimental setup is shown in Fig.1. In order to be able to preserve the
178 temperature at the desired level throughout the course of the experiment, the quartz fluidized-bed
179 reactor is placed inside an electric cylindrical furnace (Applied test system. INC). The oven is
180 insulated and the openings through which the gases enter and exit the reactor are insulated with
181 silica blanket type SB-2000 from Zicar refractory composites. In order to remove water and
182 small solid particles, which are generated during oxidation of the fuel, the exhaust gas stream
183 from the reactor is led into a condenser (IMR 500 P). The composition of the dry gas is measured
184 by an IMR 2800 P analyzer. The tubing and fittings are made from stainless steel and are made
185 by Swagelok. In order to connect the tubing to the quartz reactor, graphite ferrules (GRACE,

USA) are used. There are two advantages for using these ferrules; one is their high temperature resistivity (near 450 °C) and the other is their suitability for the glass fitting.

The fuel reactivity is examined through a reaction with CH₄ gas (methane) and the CLOU properties of the particles are investigated by measuring the oxygen release from the oxidized particles in nitrogen. The experiments are performed in a cyclic fashion, in which a period of oxidation is followed by a period of reduction, which constitutes one cycle.

In order to control the flow rates mass flow controllers (Smart-Trak® 100 Series) are used. In addition a computer program is written by Visual C++.net to program the flow meters in the desired cyclic approach.

30 grams of oxygen carriers with size distribution of 125–250 µm are used. The tests are carried out at 800, 850, 900 and 950 °C. As the reactor has no cooling system and in order to avoid a large temperature increase during the combustion reaction, 8.5% O₂ concentration is utilized. The oxidation is conducted with stream containing 8.5 % O₂ and 91.5% N₂ with flow rate of 900 mL_N min⁻¹ (normalized to 1 bar and 25°C). The oxidation periods necessary for complete oxidation vary between 600 and 900 s. N₂ is introduced for 45 s after each oxidation-reduction period to avoid the mixing of CH₄ and O₂.

In order to avoid exceeding the terminal velocity of the particles due to the increase of the gas velocity produced during the CH₄ conversion, the fuel reduction is conducted with a stream containing 18.8 vol % CH₄ and 81.2 vol % N₂ with a flow rate of 1150 mL_N min⁻¹. The reduction period is 20 s.

3. Results and discussion

3.1 Thermogravimetric analysis (TGA)

The mass change of oxygen in the samples assigned to the oxygen carrying capacity (R_O) of the carriers and defined as follows:

$$R = \frac{(m_{ox} - m_{red})}{m_{ox}}$$

Where m_{red} and m_{ox} represent the mass of the oxygen carriers in oxidized and reduced states respectively.

If simply assumed that all of the Mn^{4+} inside the sample is converted to Mn^{2+} during the heating reaction in the presence of inert gas, the oxygen loss should be 20 mol% according to the following reaction. One mole of oxygen out of five mole atoms in $CaMnO_3$ is released which is 20 mol % and equals to approximately 11.2 wt. %.

Fig.2 shows the oxygen capacity of the materials performed by the thermogravimetric analyzer. As seen in figure 2, the weight loss is less than 2 % after 300 minutes, which is considerably lower than the calculated value. Due to thermodynamic and kinetic conditions, this is expected and is discussed further in this study. In Fig.2, R_O varies between 1.2 (CLMZ) and 1.75 (CSMF) for the prepared single perovskites. Comparing the oxygen capacity of all prepared perovskites represented in this figure (the experiments are performed in a cyclic fashion in order to achieve a more stabilized data, therefore the last cycle is more reliable and normalized in a way that all the spectra have the same starting point, which is 100), except for CSMF the oxygen capacity has been decreased by doping the A- and B- sites of calcium manganese perovskite.

In addition, by comparing the obtained data for CM and CLMF samples in our study and Arjmand et. al. [28] results for these samples (The R_O values are 0.37 ,for CLMF, and 0.76 ,for CM, in their study), it is clear that the oxygen capacity has been increased three times which can be due to starch optimization and preparation method. Moreover, as will be shown in the BET

analysis, the surface area of mentioned samples has been increased twice in comparison with Arjmand et. al. [28] reported data.

3.2 Scanning electron microscope analysis (SEM)

The SEM images of prepared perovskites are shown in Fig. 3. As it can be observed, starch acts successfully as a pore-forming agent and all samples prove to have a porous structure.

The EDS (Energy Dispersive Spectroscopy) results are listed at Table.1 and they are in agreement with the computed data, indicating that the stoichiometry of the precursors are correct for the production of the perovskite structures. According to the single perovskite formula ($\text{Ca}_{0.9}\text{A}_{0.1}\text{Mn}_{0.9}\text{B}_{0.1}\text{O}_3$ where A is Sr or La and B is Fe or Zr), there should be at least 2 % of the doping element in the samples. As it can be seen from table.1, the atomic percent of these doping elements is near the expected values.

3.3 X-ray diffraction analysis (XRD)

Initial identification phase is made using the PDF-4 Database and the results confirmed the presence of the $\text{CaMnO}_{3-\delta}$ perovskite phase. In some cases, also additional distorted $\text{CaMnO}_{3-\delta}$ phases have been observed to be present in the samples but in a very small percentage. Rietveld refinements are carried out using FULLPROF program.

According to XRD database (PDF-4 Release 2013), this phase is distorted calcium manganate ($\text{CaMnO}_{3\pm\delta}$) perovskite structure which is doped with lanthanum or strontium at the A site and iron or zirconium at the B site. Except for the zirconia doped sample, all other XRD patterns look very similar to each other. There is no evidence of another residual phase, indicating that the stoichiometry of the precursors is correct for the production of the perovskite structures. Although a very small amount of unreacted ZrO_2 is found in zirconia doped sample, . This is

expected as ZrO_2 has higher melting point compared to TiO_2 and Fe_2O_3 and probably lower diffusion rate in solid reactions.

In the insets of Fig. 4 the main peak shifts of the XRD patterns are shown. Replacing ions with different sizes results in lattice expansion or contraction. The order of ionic size of ions used in this study is as follows: For the B site $\text{Mn}^{4+} < \text{Fe}^{3+} < \text{Mn}^{3+} < \text{Zr}^{4+}$ and for the A site $\text{La}^{3+} < \text{Ca}^{2+} < \text{Sr}^{2+}$. As it is represented, zirconium in the B site and strontium ions in the A site are bigger than the others, which may have resulted in higher lattice distortion with respect to the others and hence lead to Bragg shift to the left as it can be seen in Fig. 4. In other words, as the ionic radius of all stated ions is larger than that of the Mn^{4+} ion, the increase in the lattice constant is expected. All the lattice constants have been increased in the same order, showing the expansion of the structure.

3-5 Iodometric titrations Since the analysis of the mixed oxides containing Mn is very difficult because of the transformation of samples into the solution state and due to multiple oxidation states of manganese, iodometric titration experiments are performed. In order to investigate the effect of manganese charge variations in nitrogen and oxygen atmospheres, iodometric titration experiments are conducted on the samples after air and nitrogen treatment at 950°C for 3 hr. The results are summarized in Table. 2. The number of oxygen atoms that exist in the compound, is calculated based on the amount of Mn^{3+} and Mn^{4+} present in the structure. The final calculations represent the probability of existence of a mixed valence for Mn, i.e. $\text{Mn}^{3+}/\text{Mn}^{4+}$, in the system [35].

The iodometric titration analysis also reveals that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio can be changed and modified in the samples by nitrogen treatment. This conclusion is made based on the Mn^{3+} formed inside the structure as a result of nitrogen treatment in all cases. In other words,

275 manganese ions change their electron valance to a lower state while exposed to a nitrogen
 276 atmosphere. Thus, oxygen ions should be released from the lattice to compensate for the charge
 277 unbalancing effect. In the case of undoped CaMnO_3 , more than 70 % of Mn^{4+} ions are converted
 278 to Mn^{3+} , while in the doped samples this conversion is between 20 to 50 %. This observation can
 279 explain the consistency between the doped samples. As fewer Mn^{4+} ions are converted to Mn^{3+} in
 280 the doped samples, their structure does not go through extreme contractions or expansions and
 281 remains steady. On the other hand, the undoped samples go through severe contractions and
 282 expansions due to the formation of oxygen vacancies and variations on the size of manganese
 283 ions 53 (Mn^{4+}) to 58(Mn^{3+}) pm. Hence, the structure has higher potential for segregation [36].
 284 According to the literature [37], Mn^{4+} ions in CaMnO_3 can be substituted with Zr^{4+} ions. Similar
 285 behavior is observed in the analyzed samples. More than 60 % of Mn^{4+} is reduced to Mn^{3+} in
 286 zirconium doped samples. Since only 20 % Mn^{4+} remains inside the samples, the oxygen
 287 capacity of the material decreases as it can be seen from the TGA analysis.
 288 In the iron doped samples, the amount of Mn^{4+} does not decrease remarkably and more than 45
 289 % of Mn ions remain in their 4^+ coordination state. As iodometric titration results show, in iron
 290 doped samples, more than 30% and 50 % conversion for Mn^{4+} to Mn^{3+} is detected. This is
 291 expected as the TGA analysis represents higher oxygen capacity for these samples compared to
 292 zirconia doped perovskites.
 293 Surprisingly, in the strontium doped sample (CSMF), the amount of Mn^{4+} does not decrease
 294 considerably and is even 20% higher than the lanthanum doped sample (CLMF). This inspection
 295 consequently explains the main reason for high oxygen capacity of strontium doped samples.
 296 When some of the Ca^{2+} ions are replaced by La^{3+} ions, it becomes a necessity for a
 297 corresponding number of Mn^{4+} ions to be replaced by Mn^{3+} ions. Accordingly, in all lanthanum

298 doped samples (CLMF and CLMZ), a decrease in oxygen capacity can be expected. On the
299 contrary, in the case of the strontium doped samples, no charge difference is observed between
300 calcium and strontium and as a result the majority of manganese ions remain at their higher
301 oxidation state and the oxygen capacity of these groups (CSMF and CSMZ) is higher than the
302 lanthanum doped samples.

303 Occurrence of octahedral deformation phenomenon in CaMnO_3 structures, indicates the
304 existence of Mn^{3+} to some extent in the structure as well as oxygen vacancies. Therefore, it is
305 more desirable to observe CaMnO_3 as the nonstoichiometric phase $\text{CaMnO}_{3-\delta}$.

306 The Mn atoms can have two valences, i.e. Mn^{3+} and Mn^{4+} and different structures of the MnO_6
307 octahedron are expected as the ionic sizes of Mn^{3+} and Mn^{4+} are different and the Mn^{3+} ion is a
308 Jahn-Teller active ion (character of Mn^{3+} , $t_{2g}^3 e_g^1$, with a single e_g electron with orbital
309 degeneracy).

310 Substitution of A- or B- site ions with different ions with different charges or sizes, provokes the
311 reduction of equivalent amount of Mn^{4+} into Mn^{3+} [6]. As the reactivity of these structures is
312 likely associated with the capacity of manganese to form various oxidation states, e.g., redox
313 reaction of $\text{Mn}^{2+}/\text{Mn}^{3+}$ or $\text{Mn}^{3+}/\text{Mn}^{4+}$, and “oxygen mobility” in the oxide lattice [38],
314 decreasing the manganese valance from four to three decreases the oxygen capacity of the
315 perovskite structure.

The oxygen capacity of the perovskite is also directly related to ionic motion mechanism. To find the effect of atom sizes at A- or B-sites (in perovskite system) on oxygen capacity of the perovskite the ion motion mechanism should be discussed. The ionic motion in perovskite type systems is controlled by the vacancy mechanism. In this mechanism, one vacancy changes its position with a neighboring oxygen ion in a normal lattice position. In the case of perovskites, the most obvious pathway for oxygen ion hopping is through a triangle formed by two large A-cations and one small B-cation (Fig.5). The circle defined by this triangle is identified as the bottleneck for ionic transport. To optimize the size of the above mentioned bottleneck (r_C), simple relations between cation sizes and lattice parameters can be assumed [39, 40]. Having bigger atoms at A- or B-sites, makes the oxygen path larger, leading to a higher ion transition rate and oxygen capacity.

3-6 Oxygen Uncoupling of the Carriers (CLOU)

Fig.6 shows the oxygen release profiles for the samples during inert gas purge at four different temperatures. As it can be seen, all prepared perovskites show oxygen uncoupling behavior. A steady decay in the amount of released oxygen as a function of time is observed for all of the samples at the four different temperatures.

This phenomena is typical for the perovskite-type materials and is reported in several papers, where two mechanisms are assumed to be involved: (a) the oxygen non-stoichiometry is the object of defect chemistry, and (b) the release or uptake of oxygen as a function of the oxygen partial pressure in the ambient conditions [28, 29].

The temperature does not show a significant effect on oxygen release profiles of the samples and it only decreases the rate of oxygen uptake and release. The CLOU experiments are repeated several times to establish the reproducibility of the observed behavior; only a slight difference

from cycle to cycle is observed, specifying that these oxygen carriers are stable and are not deactivated during several cycles.

3-7 Reactivity of the Oxygen Carriers (CLC)

The reactivity experiments are conducted at four different temperatures: 800, 850, 900 and 950 °C, using methane as the fuel and 30 grams of the prepared particles in the reactor bed.

For a more thorough understanding of the obtained CLC results, a new variable, mass-based conversion of the oxygen carrier (ω), should be introduced. ω is calculated via the following formula in which m is the actual mass of the prepared carriers.

$$\omega = \frac{m}{m_{ox}}$$

During the CLC process, the mass-based conversion of the oxygen carriers throughout the reduction reaction can be calculated using the following equation in which y_i represents the concentration (vol %) of the respective gas:

$$\omega_i = \omega_{i-1} - \int_{t_0}^{t_1} \frac{\dot{n}_{out} M_O}{m_{ox}} (4y_{CO_2} + 3y_{CO} + 2y_{O_2} - y_{H_2})$$

ω_i = Instantaneous mass-based conversion at time i

ω_{i-1} = Mass-based conversion in the preceding instant

t_0 = Initial time of measurement

t_1 = Final time of measurement

$\dot{n}_{out}$ = Molar flow rate of the dry gas at the reactor outlet

M_O = Molar mass of oxygen

Figure 7 shows the variation of mass-based conversion, ω , with time for reduction with methane at four different temperatures. The ω profiles are a combination of the direct reaction of methane

with the solid carrier either via CLC or gaseous oxygen via CLOU. As it can be seen, ω starts to decrease faster by increasing the temperature.

Gas yield is another defining parameter in evaluating the performance of the oxygen carriers in CLC processes. This parameter is usually evaluated in fluidized bed reactors and can be measured using the following equation:

$$\gamma_{CH_4} = \frac{y_{CO_2}}{y_{CO_2} + y_{CH_4} + y_{CO}}$$

Figure 8 shows the gas yield, γ_{CH_4} , over the mass-based conversion, ω , for methane exposure period for all of the investigated carriers. As it can be seen from Fig 8, CM, CSMF and CLMZ show gas yield of 100%, while the other two compositions show lower gas yields but still high enough (more than 85%) during the entire reduction period. Comparing the results with other similar works [28], indicates that the fabricated oxygen carriers in this study can be promising candidates for CLC applications since they have shown the highest gas yields and have resulted in complete combustion of methane over the entire reduction period.

Doping the A and B sites seems to be an important controlling factor in governing the combustion mechanism of perovskite oxides in CLC and CLOU reactions. It has two major roles in determining the oxygen capacity of the perovskites. First, it can change the $Mn^{4+}/Mn^{3+}/Mn^{2+}$ ratio in the system and change the oxygen capacity of the carriers consequently. Moreover, as discussed earlier, the oxygen migration path through the perovskite crystal is controlled by the size of A- and B- atoms. B- atoms specifically play a more crucial role in this case as the critical radius of bottleneck, r_c , is defined by two B- and one A- atom.

Thermodynamic and kinetic parameters also affect the CLC and CLOU reactions. The thermodynamic factor is defined by partial pressure of oxygen, which is set by the temperature of

the reaction, whereas the kinetic factor is controlled by diffusion parameters (temperature and time) and crystallographic limitations of the oxygen carriers. One important feature of CLC which distinguishes it from CLOU is the necessity of combustion reaction or oxygen concentration gradient on the surface of oxygen carriers in CLC process. In other words, if there is no combustion or fuel on the surface of the particles, CLC does not occur. However, the CLOU process can continue its progress until the reaction reaches the equilibrium partial pressure of oxygen on the surface of the oxygen carriers. Both mechanisms are controlled by diffusion of oxygen atoms. Therefore, temperature and time play an important role in them. In the case of CLOU, the partial pressure of oxygen on the surface which is set by the temperature is also involved in the reaction. If the partial pressure of oxygen in a specific temperature is low, the CLOU process will stop due to thermodynamic limitations. Whereas, CLC can occur if sufficient fuel exists on the surface.

The oxygen capacities of the materials evaluated by the thermogravimetric analyzer and oxygen release profiles during inert gas purge are good indications of CLOU process taking place at different temperatures and with different samples, whereas the mass-based conversion shows the contribution of both.

As it is observed in Fig.7, all of the prepared samples have similar oxygen release profiles at 800 °C, whereas increasing the temperature has noticeable increase on the oxygen release profile of CSMF at different temperatures. However, other samples do not show evident changes in oxygen release profiles by increasing the temperature. These results are also confirmed by thermogravimetric analyzer evaluating the oxygen capacity of the materials. Among the prepared samples, CSMF has shown the highest R_O capacity among the others at 950 °C. The main reason for this occurrence is the existence of kinetic barriers in different doping systems. The reaction

temperature is fixed for all of the samples and based on thermodynamic properties all sample are expected to release the same amount of oxygen or at least show the same trends for same temperatures based on their $\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ ratios. Since CSMF shows a completely different trend of oxygen release by increasing temperature, it seem this sample has a better crystallographic structure with respect to the others. Looking in more depth in the structural properties can reveal the reason behind this unexpected trend. This sample has strontium partially substituted at its A- site and as a result have been more distorted and spaced than Lanthanum doped or undoped samples. This can facilitate the oxidation and reduction reaction for the perovskite system undergoing extreme contractions and expansions. First, Mn ions have more freedom to change their valance as the radius of Mn changes almost 22% when it changes its valance from 4+ to 3+. Second, there will be more space for oxygen diffusion in the structure as discussed earlier. All these parameters can support the reason for high oxygen uncoupling behavior (CLOU) of CSMF.

The fluidized bed temperature increases during the oxidation period is in the range of 10-20 °C and this low increase in temperature is due to the diluted oxygen stream (low oxygen concentration) used for conducting the experiments. The amount of uncombusted CH_4 is increased by decreasing the temperature of the bed. All tested samples at temperatures lower than 950 °C have shown more than 10% uncombusted CH_4 in the reactor outlet stream.

The experiments carried out in the fluidized bed reactor allow us to understand the behavior of the carriers during reduction-oxidation cycles. Moreover, the chemical and structural changes can be investigated due to the existence of chemical reaction and the attrition phenomena in the fluidized beds. The data represented in table 3 demonstrates the bulk density of the fresh and

used samples. The bulk density as observed does not change considerably and the slight changes could be due to measurement uncertainties.

All of the samples have a crushing strength more than 1 N, which is suggested to be the suitable quantity for an oxygen carrier used in CLC applications.

No huge weight loss is detected for the samples, which indicates their apt strength for withstanding erosion and high temperature reactions during the tests.

By comparing the surface areas of the prepared samples with the inert sample (quartz frits, with no surface porosity) using BET analysis, it can be concluded that the starch plays an important role in increasing the surface area (between 5 to 10 times) of the samples.. This claim is also supported by comparing the surface area obtained for CLMF and CM perovskites in the literature and current work. The surface areas observed for CLMF and CM samples, are near 0.6 and 1 (m^2/g) respectively, which are three times higher than the reported quantities in the literature using the same preparation method (solid state reaction) and this is due to the optimization process [28, 41].

Although the surface area of the samples, synthesized by the solid state reaction, is much lower than the samples fabricated by reactive grinding or other expensive techniques (in the range of 25-50 m^2/g) [9, 11] there should always be a balance between the preparation cost and physical properties of the materials under investigation. Mostly in commercial applications, cost and simplicity are two major factors that play important roles for choosing the right preparation techniques.

4. Conclusions

Families of perovskites are prepared as oxygen carriers in chemical looping combustion using extrusion method followed by solid state reaction as the preparation technique presenting the

main advantage of mass production capability. SEM, BET, XRD and TGA analysis are used to analyze the prepared samples. The results show that doping strontium at the A- site and iron at the B- site increases the oxygen capacity as well as sustainability of the perovskites during the combustion reaction of methane. Based on the results obtained from the iodometric titration experiments, manganese ions alter their electron valance to lower a state while in exposure to nitrogen (inert) atmosphere. In CaMnO_3 , more than 70% of Mn^{4+} ions are converted to Mn^{3+} , while in the doped samples the conversion amount is between 10 to 50% to keep the structure stable.

Mass-based conversion and gas yield are calculated for the prepared samples to evaluate their oxygen uncoupling behavior as well as their reactivity during chemical looping combustion in a fluidized bed reactor. Mass-based conversion of the samples showed great dependence on temperature and a temperature increase showed a noticeable increase in the rate of mass-based conversion in all the prepared perovskites. Gas yields are also calculated for all of the oxygen carriers at 950°C. CLMZ, CM and CSMF showed 100% gas yield. CLMF and CSMZ on the other hand, showed gas yields around 85% which is higher than previous prepared perovskite oxides in comparison with previously prepared perovskites in other related studies. CSMF is the perovskite structure with the promising stability and high enough oxygen capacity to result in complete methane combustion during CLC and has proven to be a promising candidate as an oxygen carrier in CLC processes.

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471 **References**

- 472 1. Ping-Chin Chiu, Y.K., *Chemical Looping Process - A Novel Technology for Inherent CO₂ Capture*.
 473 Aerosol and Air Quality Research, 2012. **12**(6): p. 1421-1432.
- 474 2. Rad Mina, H., H. Imanieh Mahammad, and A. Nadarajah, *Perovskite ceramics and recent*
 475 *experimental progress in reactor design for chemical looping combustion application*, in
 476 *Chemical Papers* 2015. p. 627.
- 477 3. Adanez, J., et al., *Progress in Chemical-Looping Combustion and Reforming technologies*.
 478 Progress in Energy and Combustion Science, 2012. **38**(2): p. 215-282.
- 479 4. Mattisson, T., *Materials for Chemical-Looping with Oxygen Uncoupling*. ISRN Chemical
 480 Engineering, 2013. **2013**: p. 19.
- 481 5. Leion, H., T. Mattisson, and A. Lyngfelt, *Using chemical-looping with oxygen uncoupling (CLOU)*
 482 *for combustion of six different solid fuels*. Energy Procedia, 2009. **1**(1): p. 447-453.
- 483 6. Arjmand, M., *Copper and Manganese-based Oxygen Carriers in Chemical-Looping Combustion*
 484 *(CLC) and Chemical-Looping with Oxygen Uncoupling (CLOU) in Department of Chemical and*
 485 *Biological Engineering* 2014, Chalmers University of Technology: Sweden p. 81.
- 486 7. Hossain, M.M. and H.I. de Lasa, *Chemical-looping combustion (CLC) for inherent separations—a*
 487 *review*. Chemical Engineering Science, 2008. **63**(18): p. 4433-4451.
- 488 8. Leion, H., et al., *The use of ilmenite as an oxygen carrier in chemical-looping combustion*.
 489 Chemical Engineering Research and Design, 2008. **86**(9): p. 1017-1026.
- 490 9. Sarshar, Z., et al., *Development of Sinter-Resistant Core–Shell LaMnxFe_{1-x}O₃@mSiO₂ Oxygen*
 491 *Carriers for Chemical Looping Combustion*. Energy & Fuels, 2012. **26**(5): p. 3091-3102.
- 492 10. Labhsetwar, N., et al., *Ceramics in Environmental Catalysis: Applications and Possibilities*.
 493 Chinese Journal of Catalysis, 2012. **33**(9–10): p. 1611-1621.
- 494 11. Sarshar, Z., F. Kleitz, and S. Kaliaguine, *Novel oxygen carriers for chemical looping combustion:*
 495 *La_{1-x}Ce_xBO₃ (B = Co, Mn) perovskites synthesized by reactive grinding and nanocasting*. Energy
 496 & Environmental Science, 2011. **4**(10): p. 4258-4269.
- 497 12. Richter, J., et al., *Materials design for perovskite SOFC cathodes*. Monatshefte für Chemie -
 498 Chemical Monthly, 2009. **140**(9): p. 985-999.
- 499 13. Oishi, M., et al., *Oxygen nonstoichiometry and defect structure analysis of B-site mixed*
 500 *perovskite-type oxide (La, Sr)(Cr, M)O_{3-δ} (M=Ti, Mn and Fe)*. Journal of Solid State Chemistry,
 501 2008. **181**(11): p. 3177-3184.
- 502 14. Feng, L.M., et al., *Formability of ABO₃ cubic perovskites*. Journal of Physics and Chemistry of
 503 Solids, 2008. **69**(4): p. 967-974.
- 504 15. Ishihara, T., *Perovskite Oxide for Solid Oxide Fuel Cells*, 2009, Springer US. p. 302.
- 505 16. Li, C., K.C.K. Soh, and P. Wu, *Formability of ABO₃ perovskites*. Journal of Alloys and Compounds,
 506 2004. **372**(1–2): p. 40-48.
- 507 17. Leion, H., et al., *Use of CaMn_{0.875}Ti_{0.125}O₃ as Oxygen Carrier in Chemical-Looping with Oxygen*
 508 *Uncoupling*. Energy & Fuels, 2009. **23**(10): p. 5276-5283.
- 509 18. Bakken, E., T. Norby, and S. Stølen, *Nonstoichiometry and reductive decomposition of*
 510 *CaMnO_{3-δ}*. Solid State Ionics, 2005. **176**(1–2): p. 217-223.
- 511 19. Virginia Lea Miller and S.C. Tidrow, *Investigation of Transition Metal Oxides with the Perovskite*
 512 *Structure as Potential Multiferroics*, 2008, U.S. Army Research Laboratory: Maryland, United
 513 States. p. 32.
- 514 20. Moser, W.R., J. Happel, and N.Y.A.o.S.S.o. Catalysis, *Catalytic Chemistry of Solid-state*
 515 *Inorganics* 1976: New York Academy of Sciences.

21. Mohammad A Islam, James M Rondinelli, and J.E. Spanier, *Normal mode determination of perovskite crystal structures with octahedral rotations: theory and applications*. Journal of Physics: Condensed MatterEmail alert RSS feed, 2013. **25**(17): p. 175902-1759015.
22. Zhu, L., et al., *Effects of Preparation Methods on the Catalytic Performance of LaMn_{0.8}Mg_{0.2}O₃ Perovskite for Methane Combustion*. Chinese Journal of Catalysis, 2010. **31**(8): p. 1006-1012.
23. Voorhoeve, R.J., et al., *Perovskite oxides: materials science in catalysis*. Science, 1977. **195**(4281): p. 827-33.
24. Andoulsi, R., K. Horchani-Naifer, and M. Férid, *Effect of the preparation route on the structure and microstructure of LaCoO₃*. Chemical Papers, 2014. **68**(5): p. 608-613.
25. Liu, F.J. and K.S. Chou, *Determining critical ceramic powder volume concentration from viscosity measurements*. Ceramics International, 2000. **26**(2): p. 159-164.
26. Gupta, S., M.K. Mahapatra, and P. Singh, *Lanthanum chromite based perovskites for oxygen transport membrane*. Materials Science and Engineering: R: Reports, 2015. **90**: p. 1-36.
27. Galasso, F.S., *Structure, Properties and Preparation of Perovskite-Type Compounds*, 2013, International Series of Monographs in Solid State Physics. p. 220.
28. Arjmand, M., et al., *CaxLa_{1-x}Mn_{1-y}MyO_{3-δ} (M = Mg, Ti, Fe, or Cu) as Oxygen Carriers for Chemical-Looping with Oxygen Uncoupling (CLOU)*. Energy & Fuels, 2013. **27**(8): p. 4097-4107.
29. Azimi, G., et al., *(MnzFe_{1-z})yOx combined oxides as oxygen carrier for chemical-looping with oxygen uncoupling*. AIChE Journal, 2013. **59**(2): p. 582-588.
30. Guo, H.Z., et al., *Influence of defects on structural and magnetic properties of multifunctional La₂NiMnO₆ thin films*. Physical Review B, 2008. **77**(17): p. 174423.
31. Isobe, T., et al., *Effect of dispersant on paste rheology in preparation of porous alumina with oriented pores by extrusion method*. Journal of Porous Materials, 2006. **13**(3-4): p. 269-273.
32. Azzolini, A., V. Sglavo, and J. Downs, *Novel method for the identification of the maximum solid loading suitable for optimal extrusion of ceramic pastes*. Journal of Advanced Ceramics, 2014. **3**(1): p. 7-16.
33. Leu, M.C., et al. *Freeze-form extrusion fabrication of composite structures*. in *Proceedings of the Solid Freeform Fabrication Symposium*. Austin, TX. 2011.
34. M.H.Imanieh, M.Hamed Rad, and A.Nadarajah, *Porous perovskite ceramics prepared with starch for chemical looping combustion application*, in *66th Southeastern Regional Meeting of the American Chemical Society-SERMACS2014*, American Achemical Society: Nashville. p. 119.
35. Tali, R., *Determination of average oxidation state of Mn in ScMnO₃ and CaMnO₃ by using iodometric titration*. Journal for BASIC SCIENCES, 2007. **23**(1): p. 9-19.
36. Priolkar, K.R. and R. Rawat, *Effect of heterovalent substitution at Mn site on the magnetic and transport properties of La_{0.67}Sr_{0.33}MnO₃*. Journal of Magnetism and Magnetic Materials, 2008. **320**(3-4): p. 325-330.
37. Taguchi, H., et al., *Effects of Mn³⁺ ions on the electrical and magnetic properties of Ca(Mn_{1-x}Zrx)O_{3-δ} (0 ≤ x ≤ 0.07)*. Physica B: Condensed Matter, 2005. **367**(1-4): p. 188-194.
38. Ramesh, K., et al., *Re-investigating the CO oxidation mechanism over unsupported MnO, Mn₂O₃ and MnO₂ catalysts*. Catalysis Today, 2008. **131**(1-4): p. 477-482.
39. L.S.M. TRAQUEIA, F.M.B. MARQUES, and V.V. KHARTON, *Oxygen Ion Conduction in Oxide Materials: Selected Examples and Basic Mechanisms*. Bol. Soc. Esp. Ceram., 2006. **45** (3): p. 115-121.
40. Bossche, M.v.d., *Oxygen vacancy ordering in iron-doped calcium titanate*, in *Science and Technology Inorganic Materials Science*2005, University of Twente: Enschede. p. 59.
41. Sundqvist, S., et al., *CaMn_{0.875}Ti_{0.125}O_{3-δ} as an Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling (CLOU)—Solid-Fuel Testing and Sulfur Interaction*. Energy Technology, 2013. **1**(5-6): p. 338-344.

Fig.1 Experimental setup. P= pressure transducer, F=flow meters, GA=gas analyzer, V=valves, G1= N₂, G2=N₂-5% O₂ and G3=CH₄

Fig.2 Oxygen capacity (RO) of the perovskites which were prepared in this study cycling between air (20.8% O₂) and high-purity inert gas (N₂) at 950 °C in a thermogravimetric analyzer.

Fig.3 SEM images of different perovskites which were studied CM (a), CLMF (b), CLMZ (c), CSMF (d) and CSMZ (e).

Fig.4 XRD patterns of fresh (after synthesis) for perovskite family prepared in this study.

Fig.5 Triangle formed by neighboring A- and B-site cations in a perovskite structure. The bottleneck has a critical radius r_c .

Fig.6 Oxygen release profiles for perovskites during cycling between air (8.5 % O₂) and high-purity inert gas (N₂) inert gas at 800 (a), 850 (b), 900 (c) and 950 °C (d) in a fluidized bed reactor.

Fig.7 Variation of the mass-based conversion, ω , of the oxygen carriers with time for reduction with methane (for 20 s) at 800 (a), 850 (b), 900 (c) and 950 °C (d).

Fig.8 Variation of gas yield, γ CH₄, with mass-based conversion, ω , for different oxygen carriers during conversion of CH₄ for 20 s at 950 °C.

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595 Table 1. EDS analysis of the samples (single perovskite) investigated in this work (at. %).

596 **Table. 2** Determination of Mn^{3+} , Mn^{4+} and oxygen non stoichiometry quantity in doped CaMnO_3
597 by Iodometric titration

598 **Table 3.** Bulk density (g/cm^3), sample weight before and after the reactor test, BET and crushing
599 strength of the Oxygen Carriers before and after the Reactivity Test (± 0.001 error)

Figure. 1

Figure. 2

Figure. 3

Figure. 4

Figure. 5

Figure. 6

Figure. 7

Figure. 8

Table .1

Table 1. EDS analysis of the samples (single perovskite) investigated in this work (at. %).

element	CM	CLMF	CLMZ	CSMF	CSMZ	computational data
Ca	18.63	16.63	16.94	16.12	17.67	18
Mn	18.75	15.74	17.03	15.30	17.57	18
O	62.62	63.84	62.20	65.10	61.43	60
La	-	1.91	1.95	-	-	2
Fe	-	1.88	-	1.91	-	2
Sr	-	-	-	1.57	1.64	2
Zr	-	-	1.87	-	1.68	2

Table. 2

Table. 2 Determination of Mn^{3+} , Mn^{4+} and oxygen non stoichiometry quantity in doped CaMnO_3 by Iodometric titration

Compound	O	δ	Mn^{3+}	Mn^{4+}	Oxygen difference
CM	2.91	0.09	0.19	0.81	0.36
CM- N_2	2.55	0.45	0.9	0.1	
CLMF	2.64	0.36	0.47	0.43	0.17
CLMF- N_2	2.47	0.53	0.77	0.13	
CLMZ	2.55	0.45	0.7	0.2	0.09
CLMZ- N_2	2.46	0.54	0.89	0.01	
CSMF	2.83	0.17	0.24	0.66	0.25
CSMF- N_2	2.58	0.42	0.74	0.16	

Table. 3

Table 3. 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)

Sample ID	Bulk density (gr/cm ³) before reactor test	Bulk density (gr/cm ³) after reactor test	Sample weight (gr) before reactor test	Sample weight (gr) after reactor test	BET(m ² /gr) before test	Crushing Strength N
CM	4.49	4.56	30	29.47	0.95	2.19 $\pm$ 0.7
CLMF	4.68	4.71	30.019	29.45	0.56	3.12 $\pm$ 0.9
CLMZ	4.76	4.83	30.005	29.47	0.82	1.67 $\pm$ 0.4
CSMF	4.66	4.59	30.027	29.66	0.42	2.3 $\pm$ 0.7
CSMZ	4.69	4.61	30	28.57	0.74	1.5 $\pm$ 0.5
Inert	2.22	2.21	30	29.99	0.09	-