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Reduction and Oxidation Kinetics of a $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ Oxygen Carrier for Chemical Looping Combustion

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ABSTRACT.

The objective of this study was to establish the reaction kinetics involved in redox cycles of the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material to be used as an oxygen carrier in the Chemical Looping Combustion process. The oxygen transport capacity and reactivity of this material during consecutive reduction and oxidation steps with gaseous compounds (CH_4 , H_2 , CO and O_2) were studied in a TGA apparatus. The oxygen uncoupling properties of this material were also analysed. It was found that material reactivity increased with the number of redox cycles, whereas oxygen transport capacity decreased with the cycle number until it was stabilized or “activated”. Conversion vs. time curves at different temperatures (973-1273 K), and reacting gas

concentrations (5-60 vol.%) were used for kinetics determination. The grain model with control by chemical reaction and diffusion through the product layer was used to obtain the kinetic parameters for fresh and “activated” particles.

1. INTRODUCTION

According to the Intergovernmental Panel on Climate Change (IPCC), warming of the climate system is unequivocal and induced by human activities, as a consequence of the so-called greenhouse gases (GHG) emitted to the atmosphere.¹ CO₂ emissions from burning fossil fuels in power generation is considered to be the largest source of GHGs contributing to global warming. Therefore, it is generally accepted that a reduction in CO₂ emissions is necessary as soon as possible. CO₂ Capture and Storage (CSS) appears as a necessary option if significant reductions in CO₂ emissions are to be achieved. In this regard, Chemical Looping Combustion (CLC) is suggested as one of the best alternatives for reducing the economic and energy costs associated with the obtention of a highly concentrated CO₂ stream from processes where a carbon based fuel is used in power generation.^{2,3}

The CLC process is based on the transfer of oxygen from air to the fuel by means of a solid oxygen carrier, thereby avoiding direct contact between fuel and air. The oxygen carrier consists of a metal oxide, Me_xO_y , which often is supported on an inert material in order to provide a porous structure and to provide particle stability throughout the cycles. Figure 1 shows a general scheme of this process. In a first step, the fuel is oxidized to CO₂ and H₂O by the oxygen carrier, which is reduced to a metal or a reduced form ($\text{Me}_x\text{O}_{y-1}$). The reduced oxygen carrier is further oxidized with air in a second step, and the regenerated material is ready to start a new cycle. To carry out the CLC process, most of the experimental CLC plants that exist worldwide use a

configuration composed of two interconnected fluidized bed reactors, similar to the Circulating Fluidized Bed (CFB) concept. Thus, conversion of the fuel happens in the so-called fuel reactor, while the oxygen carrier is regenerated in the so-called air reactor. The gas produced in the fuel reactor primarily contains CO_2 and H_2O . After water condensation and purification, a highly concentrated stream of CO_2 is achieved that is ready for transport and storage. CLC is therefore a combustion process with inherent CO_2 separation. Fuels such as gases, liquids and solids can be processed in a CLC system. A review of the development status of this technology can be found elsewhere.⁴

Figure 1. General scheme of a Chemical Looping Combustion system for gaseous fuels.

A key issue for the implantation of CLC technology in a thermal power plant for energy generation with CO_2 capture is the development of suitable oxygen carrier materials. Mainly, the oxygen carrier must allow high fuel conversion towards CO_2 and H_2O in order to be able to transfer a high enough oxygen mass fraction of material that is highly reactive during repeated reduction and oxidation cycles, and resistant to attrition, fragmentation and agglomeration phenomena. Moreover, additional issues as toxicity, environmental impact and cost are relevant during material selection.

Materials based on one metal oxide are frequently proposed for use as the oxygen carrier in CLC.⁴⁻⁵ Consequently, most of oxygen carrier materials to date are based on nickel, copper, iron or manganese oxides. Copper and manganese materials have received attention of late because they can generate gaseous oxygen at conditions existing in a fuel reactor. The Chemical Looping with Oxygen Uncoupling (CLOU) process takes advantage of this property in order to reach complete combustion of the fuel.⁶ A proof of concept for the CLOU process has been successfully demonstrated burning coal or biomass with a Cu-based oxygen carrier.⁷⁻⁹

Mn-based particles can be considered a promising material because they fulfil most of the basic requirements to be considered an oxygen carrier.¹⁰ Thus, manganese oxide supported on magnesia-stabilized zirconia was shown to operate successfully with syngas as fuel. However, this material suffered from lower reactivity with methane. Moreover, the oxidation state Mn_2O_3 could not be exploited for this kind of material because only oxidation from MnO to Mn_3O_4 was possible at the temperature of interest to the CLC process.¹¹ It would be very interesting to increase the oxidation state to Mn(III) or even Mn(IV), because the oxygen uncoupling property of manganese could be used; additionally, the oxygen transport capacity would be increased.⁶ $\text{ABO}_{3-\delta}$ perovskite type structures ($\text{B} = \text{Mn}$) have shown to improve the oxidation degree of Mn^{12,13} and oxygen uncoupling behaviour was observed.¹⁴ $\text{CaMnO}_{3-\delta}$ perovskite type materials showed high reactivity with methane.^{15,16} Nevertheless, $\text{CaMnO}_{3-\delta}$ doped with several cations - e.g. La, Mg, Ti, Fe or Cu- is believed to increase the stability of perovskite structure under CLC conditions.¹⁶

A perovskite type material with composition $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ was seen to have the desired thermodynamic properties during continuous operation in a CLC unit.¹⁷ Oxygen uncoupling behaviour was evidenced, which was not previously found for $\text{Mn}_3\text{O}_4/\text{Mg-ZrO}_2$ particles.¹⁰

Similar conversion of methane with $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ and $\text{Mn}_3\text{O}_4/\text{Mg-ZrO}_2$ particles was found in the same CLC unit at a similar fuel reactor temperature and for a similar amount of solids per thermal fuel energy produced. Thus, a combustion efficiency of 99% was achieved in both cases at 1223 K and with an inventory corresponding to 600 kg/MW_{th}. However, changes in the perovskite structure were found which could result in a loss of the oxygen uncoupling property of this material.¹⁷

Results recently obtained at lab scale with a perovskite type material doped with Mg showed that this material is suitable for an oxygen carrier.^{18,19} Tests with a $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material in continuously operating units showed near complete methane conversion.^{19,20} A combustion efficiency of 98% at 1173 K and with a solids inventory of 600 kg/MW_{th} was achieved. Moreover, the oxygen carrier showed excellent stability of the perovskite structure and good fluidization behaviour under a non-sulphurous environment. For these reasons, $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material can be considered a promising oxygen carrier material.

Further development is needed in order to estimate the relevant design parameters for the use of the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material in CLC, e.g. solids circulation flow rate or solids inventory in the fuel and air reactors. These parameters depend on the oxygen transport capacity and reactivity of the oxygen carrier. The use of proper kinetics data for oxygen carrier reduction with reacting gases resulted in the successful validation of reactor models for chemical looping combustion or reforming (CLC or CLR) systems with Cu-, Ni-, Fe-, Mn- and CaSO_4 -based oxygen carriers both for methane and coal combustion.²¹⁻³⁴ It must be considered that the oxygen carrier will react in different environments during its stage in the fluidized bed fuel reactor. Therefore, to determine the kinetic parameters from experimental data obtained under different

operating conditions of temperature and gas concentration, it is necessary to make proper use of the reaction kinetics in a reactor model.³⁵

The objective of this study was to determine the kinetics of both reduction and oxidation reactions taking place in the CLC process using $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ oxygen carrier particles. The selected material was studied in a thermogravimetric analyser (TGA) apparatus, analysing its reactivity with CH_4 , H_2 and CO as reducing gases and O_2 for oxidation reaction. The effect of temperature and gas concentration over the reaction rate was examined. In addition, the oxygen uncoupling kinetics was determined. In the future, kinetics data obtained in this work will be implemented in a reactor model for the prediction, design and optimization purposes of a CLC system with $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ as the oxygen carrier.

2. EXPERIMENTAL

2.1. Material

The oxygen carrier particles were manufactured by VITO (Flemish Institute for Technological Research, Belgium) using the spray drying method. Raw materials were 46.8 wt.% Mn_3O_4 , 50.5 wt.% $\text{Ca}(\text{OH})_2$ and 2.7 wt.% MgO . After preparation, particles were calcined at 1573 K for 4 h. The general formula of the calcined particles was $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$. The 125-200 μm size fraction was used for kinetic determination. Particles did not show any gain in mass during additional thermal treatment in air at temperatures in the interval 973-1273 K; therefore the calcined material was in the oxidized state.

2.2. Experimental setup

The reactivity and the oxygen transport capacity of the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material was determined in a TGA CI Electronics Ltd. Reduction with CH_4 , H_2 and CO , and oxygen carrier oxidation with O_2 was performed by exposing the sample to CH_4 , H_2 , CO and O_2 , respectively, diluted in nitrogen. To avoid carbon formation in the reactor, 20 vol.% H_2O was used in the reacting gas mixture when CH_4 was the reducing gas, whereas 20 vol.% CO_2 was present together with CO . Also, the oxygen release rate of fully oxidized material was studied in an inert environment using high purity N_2 . Every experimental condition was evaluated starting with a new fresh sample. About 50 mg of oxygen carrier particles were loaded on a platinum basket, and a gas flow of 25 $\text{L}_\text{N}/\text{h}$ was fed. External and interparticle diffusion were of low relevance under these conditions. Moreover, previous calculations showed a high enough rate of mass and heat transfer inside and outside of similar particles, so the particles could be considered isothermally and homogeneously converted.³⁶

Temperature programmed reductions (TPR) were carried out to determine the maximum oxygen transport capacity of the oxygen carrier material. Later, ten redox cycles at fixed temperature (1173 K) were carried out to evaluate the evolution of the redox properties with the cycle number. These experiments were focused on the analysis of the oxygen transport capacity and reactivity both for oxygen uncoupling and reaction with a gas (CH_4 , H_2 , O_2 or N_2). Experiments with CH_4 , H_2 , O_2 or N_2 in the reacting atmosphere were subsequently performed at several reacting temperatures and gas concentrations to determine the kinetics of reduction and oxidation of the oxygen carrier. More information about the experimental setup is found in the Supporting Information.

2.2.1. Determination of oxygen transport capacity (TPR)

TPR were carried out in three different environments: high purity N_2 , 15 vol.% H_2 and 15 vol.% CH_4 . The oxygen carrier sample was heated to 473 K in air atmosphere. No reaction occurred during this pre-heating step. After reaching this temperature the desired gas composition was introduced into the reactor and the weight loss was recorded while the temperature was increased up to 1273 K at a constant rate of 20 K/min.

2.2.2. Evolution of the redox properties with the cycle number

The oxygen carrier sample was heated to the desired temperature in air atmosphere. After reaching the set temperature, the experiment started by exposing the oxygen carrier to alternating reducing and oxidizing conditions. In order to prevent the fuel and air mixing, a nitrogen flow was passed after the oxidizing and reducing processes. In general, the inert period was 10 s in order to minimize the decomposition of the oxygen carrier before the reaction with the fuel gas.

To evaluate the stability of the $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ material with the redox cycle number, two series of ten redox cycles each were carried in N_2 or CH_4 . The reduction period was 350 s long, whereas oxidation was continued until no change in mass was observed, which was usually confirmed in 300 s. A temperature of 1173 K and 15 vol.% CH_4 was chosen for these experiments because these conditions are often used during the evaluation of a material as an oxygen carrier. Thus, results obtained can be compared to results available in the literature for other materials.

Three additional series of 10 cycles were carried out at 1173 K and with 15 vol.% CH_4 in order to evaluate the stability of the oxygen uncoupling property through redox cycles. In this case, the reducing period was different in each series (40, 90 and 600 s), thus achieving a different conversion of solids.

2.2.3. Redox cycles for kinetics determination

Different gas concentration and temperature values were used to obtain the conversion vs. time curves necessary for the kinetic determination. To analyse the effect of the fuel gas concentration (CH_4 , CO or H_2) on the reduction reaction rate, four different concentrations were used: 5, 15, 30 and 60 vol.%. To determine the oxidation kinetics, oxygen concentrations of 5, 10, 15 and 21 vol.% were used. These oxidation experiments were performed using 15 vol.% H_2 during the reduction step. All these experiments were carried out at 1073 K. To observe the effect of the temperature on the reaction rate, the reduction and oxidation reactions were carried out at the following temperatures: 973, 1023, 1073, 1123, 1173, 1223 and 1273 K. The fuel gas concentration during these experiments was 15 vol.%, while the oxygen concentration was 10 vol.%. Moreover, the oxygen release in nitrogen atmosphere was analysed at temperatures in the same temperature interval.

For kinetic determination, five redox cycles were carried out under every condition in TGA. Variation in reactivity with redox cycles was observed. Thus, the data corresponding to the first cycle were used to determine the kinetics of fresh particles, whereas data corresponding to the fifth cycle were considered for the kinetics determination of "activated" particles.

3. RESULTS

The oxygen transport capacity and reactivity with several reacting gases (CH_4 , H_2 , CO and O_2) as well as the oxygen uncoupling properties of the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material were analysed in a

TGA apparatus. In addition, the evolution of these properties with the cycle number was determined. The kinetics of reduction and oxidation reactions of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles was obtained from the evolution of solids conversion with time, under different operating conditions, i.e. temperature and gas concentration.

3.1. Determination of oxygen transport capacity

A perovskite structure is characterized by a unit cell $\text{ABO}_{3-\delta}$, with A being a large cation and B a small cation. The oxygen vacancies in the solid are given by the parameter δ , which is related to the oxygen transport capacity. However, in $\text{ABO}_{3-\delta}$ perovskite materials, such as $\text{CaMnO}_{3-\delta}$, the stoichiometric amount of oxygen depends on temperature and oxygen concentration.³⁷ Thus, the mass of fully oxidized oxygen carrier will depend on these parameters. Discussion regarding the equilibrium composition in the Ca-Mn-O system and its application to $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material is given in the Supporting Information. It should be pointed out here that the degree of oxidation depends on temperature. Thus, for $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ oxidation in air, the value of $3-\delta$ decreases from 2.9 to 2.83 when temperature increases from 1073 K to 1273 K. The lower limit for the fraction of oxygen in perovskite, i.e. $(3-\delta)$, is taken as the boundary between the cubic structure of perovskite and Ca_2MnO_4 or CaMn_2O_4 formation.³⁷ In this case, $\delta < 0.25$ for $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ would be required in order to maintain the perovskite structure. A further loss of oxygen would produce a change in the solid structure and the appearance of other compounds.

Mass losses corresponding to the oxygen uncoupling property of this material, i.e. the generation of gaseous oxygen, according to the reaction:

Nevertheless, the material is able to transfer oxygen to a fuel, e.g. CH₄, H₂ or CO until CaMn_{0.9}Mg_{0.1}O₂ formation, i.e. the maximum value allowed for γ is 1. When CH₄, H₂ or CO is used as reducing gas, the chemical process corresponds to the general reactions:

with the condition that $\gamma > \delta$. For these cases, a descriptive formula is also shown in Table 1 as the Ca-Mg-Mn-O material is being reduced. The fully oxidized perovskite corresponds corresponded to the formula CaMn_{0.9}Mg_{0.1}O_{2.9}, whereas the limit in oxygen transference is found for a value of $\gamma = 0.9$, corresponding to the reduced compound CaMn_{0.9}Mg_{0.1}O₂.

The mass difference between the oxidized and the reduced forms defines the oxygen transport capacity of the oxygen carrier, R_{OC} , which is calculated as:

$$R_{OC} = \frac{m_o - m_r}{m_o} \quad (5)$$

where m_o and m_r are the masses of the oxidized and reduced forms of the material, respectively. In this work, two different definitions of oxygen transport capacity, $R_{OC,t}$ and $R_{OC,ou}$, are used depending on the fraction of oxygen involved in the chemical process. Thus, $R_{OC,t}$ is used to describe the solids conversion for the total fraction of oxygen which can be transferred to a fuel, e.g. CH₄, H₂ or CO. $R_{OC,ou}$ is used to describe the conversion during the oxygen uncoupling reaction, which can occur without the presence of a reducing gas. A detailed description of the calculations of $R_{OC,t}$ and $R_{OC,ou}$ can be found in the Supporting Information.

Table 1 shows the variations in the oxidation state of Mn and the oxygen transport capacity as the material is reduced from CaMn_{0.9}Mg_{0.1}O_{3- δ} to CaMn_{0.9}Mg_{0.1}O₂. Results showed in this

section are based on thermodynamic properties of the $\text{CaMnO}_{3-\delta}$ material³⁷, see Supporting Information. Because of the special thermodynamic properties of the perovskite material, the value of δ in the oxidized state depends on the oxygen concentration and temperature at which the oxidation is carried out. The fully oxidized state, i.e. $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$, can be reached during oxidation in air at a temperature lower than 1100 K. When oxygen is evolved in nitrogen, the perovskite structure is stable up to a minimum value of $(3-\delta)$. For example, the boundary of $(3-\delta)$ is 2.73 at 1273 K, but has a low dependence on temperature. Thus, the oxygen transport capacity for oxygen uncoupling is $R_{OC,ou} = 2.0$ wt.% at 1273 K, with the perovskite considered to be completely oxidized, see Table 1. Nevertheless, if a complete oxidation-reduction cycle (oxidation in air and reduction in nitrogen) is considered at isothermal conditions, the oxygen transport capacity for oxygen uncoupling depends on temperature. Thus, $R_{OC,ou} = 1.7$ wt.% at 1073 K but decreases to 1.2 wt.% at 1273 K.

Table 1. Oxygen transport capacity for different redox systems with $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$.

Stoichiometric formula	Descriptive formula	Mn oxidation state	Accumulated R_{OC} (wt.%) ^(a)	Accumulated R_{OC} (wt.%) ^(b)
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$	$\text{CaO} \cdot (\text{MgO})_{0.1} \cdot (\text{MnO}_2)_{0.9}$	Mn(IV)	0.0	--
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.83}$	--	--	--	0.0
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.73}$	--	--	2.0	1.2
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.45}$	$\text{CaO} \cdot (\text{MgO})_{0.1} \cdot (\text{Mn}_2\text{O}_3)_{0.45}$	Mn(III)	5.2	4.4
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.3}$	$\text{CaO} \cdot (\text{MgO})_{0.1} \cdot (\text{Mn}_3\text{O}_4)_{0.3}$	Mn(II)+Mn(III)	6.9	6.2
$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_2$	$\text{CaO} \cdot (\text{MgO})_{0.1} \cdot (\text{MnO})_{0.9}$	Mn(II)	10.4	9.7

^(a) Expected oxygen transport capacity considering reduction from $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$ at 1273 K

^(b) Expected oxygen transport capacity considering reduction from $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.83}$ at 1273 K

The total oxygen transport capacity at 1273 K is $R_{OC,t} = 10.4$ wt.% in the case of reduction of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$ to $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_2$. Nevertheless, the oxygen transport capacity also depends on oxidation temperature as the nonstoichiometry of perovskite decreases with temperature. Thus, if the temperature in a complete oxidation-reduction cycle is 1273 K, then $R_{OC,t} = 9.7$ wt.% for reduction from $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.83}$ to $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_2$.

TPR experiments were conducted in the TGA to determine the mass in the reducing state. The oxidized state was considered to be fresh particles as received after calcination in air. Thus, the mass loaded in the sample holder of the TGA was considered to be m_o as $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$, i.e. the fully oxidation degree for the perovskite material. This assumption is supported by thermodynamic equilibrium at initial conditions.³⁷

Figure 2 shows the normalized mass-loss variation, ω , during TPR experiments in N_2 , H_2 or CH_4 . The parameter ω represents the fraction of mass lost during reduction of the fully oxidized oxygen carrier, and was calculated as

$$\omega = \frac{m}{m_o} \quad (6)$$

According to eqs (5) and (6), the oxygen transport capacity can be calculated as

$$R_{OC} = 1 - \omega_r \quad (7)$$

where ω_r is the normalized mass-loss when the sample was fully reduced. Here, the oxidized compound is $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$.

When only N_2 was fed to the reactor, oxygen generation started at a temperature of 930 K and slowly continued at the maximum temperature of 1273 K. In addition, the maximum normalized mass-loss variation corresponded to an oxygen transport capacity for the oxygen uncoupling

property of $R_{OC,ou} = 1.92$ wt.%. In this case, a value of $\gamma-\delta = 0.166$ was deduced, indicating that only a fraction of the oxygen atoms participated in the oxygen uncoupling behaviour. The oxygen released was slightly lower than that required to induce a change in the perovskite structure, see Table 1. After that, the reaction rate was slow due to the low driving force under this condition: the oxygen concentration at equilibrium conditions for the composition $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.734}$ is 0.03 vol.% at 1273 K (see Supporting Information).

Figure 2. Normalized mass-loss profiles for TPR (20 K/min) in TGA in (—) 100 vol.% high purity N_2 , (---) 15 vol.% CH_4 + 20 vol.% H_2O and (-·-·-) 15 vol.% H_2 , as well as temperature evolution (·····).

TPR tests were also carried out with 15 vol.% CH_4 or H_2 , see Figure 2. This reduction is representative of what would happen in the fuel reactor of a CLC system. Thus, the oxygen transport capacity in a reducing environment was determined. In these cases, the reaction started

at 610 and 580 K with CH₄ or H₂, respectively. The reaction rate with CH₄ or H₂ was faster than the oxygen generation. Moreover, the reduction with H₂ was faster than with CH₄; in fact, reduction with H₂ finished when the reaction temperature was 1100 K, whereas reduction with CH₄ proceeded until the maximum temperature, i.e. 1273 K, was reached. Nevertheless, the normalized mass-loss of the fully reduced sample was the same in both cases ($\omega_r = 0.895$). This indicates that the total oxygen transport capacity was the same regardless of the reducing gas used. The oxygen transport capacity of the CaMn_{0.9}Mg_{0.1}O_{3- δ} material to oxidize a fuel gas was $R_{OC,t} = 10.5$ wt.%, which corresponds to a value of $\gamma - \delta = 0.92$. So, approximately one atom of oxygen can be transferred to the fuel per mol of CaMn_{0.9}Mg_{0.1}O_{3- δ} . This value correlates well with the theoretical reduction from CaMn_{0.9}Mg_{0.1}O_{2.9} to CaMn_{0.9}Mg_{0.1}O₂, see Table 1.

3.2. Evolution of the redox properties with the cycle number

3.2.1. Oxygen transport capacity and reactivity related to oxygen uncoupling property

The CaMn_{0.9}Mg_{0.1}O_{2.9} material has a maximum capacity to release gaseous oxygen in an inert environment of about 2 wt.%, see Table 1 and Figure 2. The stability of this capability with the cycle number was analysed by performing two different test series of 10 redox cycles at 1173 K. At this temperature, the fully oxidized state is CaMn_{0.9}Mg_{0.1}O_{2.87}, and the theoretical capacity to release oxygen is 1.5 wt.%. In the first series, the reduction stage consisted of pure N₂ for 350 s, and therefore the mass loss during reduction was solely due to gaseous oxygen evolution from the oxygen carrier following reaction (1). Figure 3 shows the variation of the normalized mass with nitrogen and oxygen alternated during the stages of reduction and oxidation, respectively. The oxygen carrier showed good stability regarding regeneration capability during the oxidation step. The mass loss during the reduction step was about 1.1 wt.% and was constant throughout

the cycles. The reduction reaction rate was slow at the end of every cycle because of the low driving force under these conditions: oxygen concentration at equilibrium was 0.01 vol.%,³⁷ and the total mass loss expected, i.e. 1.5 wt.% was not reached.

Figure 3. Normalized mass variations during reduction-oxidation cycles in TGA starting from fresh particles. Reduction environment: (—) 100 vol.% N₂ during 350 s; (---) 100 vol.% N₂ during 350 s followed by 600 s in 15 vol.% CH₄ + 20 vol.% H₂O. Oxidation by air. T = 1173 K.

Nevertheless, the oxygen carrier should react with a fuel gas in a real case. A second test series of 10 redox cycles was carried out with the reduction step consisting of 350 s in N₂ followed by 600 s with 15 vol.% CH₄ to analyse the behaviour of its oxygen uncoupling property when the oxygen carrier reacted with a fuel gas, see Figure 3. In this case, the capability of the oxygen carrier to transport oxygen decreased through the cycles. But most remarkable was the loss of the oxygen uncoupling capacity with the cycle number.

To evaluate the variation in reactivity with the cycle number, the normalized conversion of solids was calculated for every reaction, i.e. reduction ($X_{N,r}$) or oxidation ($X_{N,o}$) as:

$$X_{N,r} = \frac{m_o - m}{R_{OC}m_o} \quad (8)$$

$$X_{N,o} = \frac{m - m_r}{R_{OC}m_o} \quad (9)$$

In this case, the oxygen transport capacity to calculate the normalized conversion was $R_{OC,ou} = 1.5$ wt.%. Figures 4(a) and 4(b) show the evolution of $X_{N,r}$ vs. time curves obtained in the 10 consecutives cycles for the cases that the reduction in N_2 and reduction in N_2 followed by reduction with CH_4 . In the case of reduction with N_2 only, the reactivity was maintained throughout the redox cycles. On the contrary, the reactivity and the oxygen uncoupling capacity were seriously reduced when the reduction in N_2 was followed by reaction with CH_4 , see Figure 4(b).

Figure 4. Evolution of normalized conversion vs. time through 10 redox cycles of $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ material during the reduction period. Environment during reduction step: (a)

100 vol.% N₂ during 350 s; (b) 100 vol.% N₂ during 350 s followed by 600 s in 15 vol.% CH₄ + 20 vol.% H₂O. Oxidation by air. T = 1173 K.

The maintenance of the oxygen uncoupling property may be connected to the stability of the perovskite structure, which in turn is related to the reduction degree reached during reaction with CH₄. A deep reduction will produce a change in the solid structure and the appearance of other compounds, e.g. CaMn₂O₄,³⁷ with a lower capacity for oxygen uncoupling and likely a different reactivity.

3.2.2. Oxygen transport capacity and reactivity with reacting gases

Three series of ten reduction-oxidation cycles each were carried out in the TGA to analyse the variation in oxygen transport capacity and reactivity of the oxygen carrier with the cycle number. Each cycle consisted of a reduction step with 15 vol.% CH₄ at 1173 K followed by an oxidation period in air. The reduction period was different for each series. Times of 40 s, 90 s, and 600 s were used. The oxidation period lasted 220 s in all cases, assuring the maximum oxidation degree possible in every cycle, corresponding to the formula CaMn_{0.9}Mg_{0.1}O_{2.87}. The corresponding total oxygen transport capacity was $R_{OC,t} = 10.1$ wt.% at 1173 K.

Figure 5(a-c) shows the normalized mass variation during each series of 10 cycles. Different behaviour was observed depending on the length of the reduction period. Obviously, the oxygen carrier became more reduced as the reduction period increased. When the reduction period was as short as 40 s, see Figure 5(a), the reduction degree of the oxygen carrier was low and stayed constant through the 10 redox cycles. Also, the oxygen carrier was completely oxidized in air during the oxidation step, indicating good oxygen carrier particle stability under these conditions.

Reduction proceeded up to the stoichiometry $3-\delta = 2.7$. The results agree with the good recyclability found for $\text{CaMnO}_{3-\delta}$ reduction to $\text{CaMnO}_{2.5}$,³⁸ which corresponds to $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.45}$, see Table 1.

Figure 5. Normalized mass variations during reduction-oxidation cycles in TGA starting from fresh particles. Reducing gas: 15 vol.% CH₄ + 20 vol.% H₂O. Oxidation by air. T = 1173 K.

After the 10 redox cycles under these conditions, a reduction step was carried out until complete reduction was achieved. It was confirmed that the oxygen transport capacity was maintained constant at 10 wt.%, which agrees with the reduction to CaMn_{0.9}Mg_{0.1}O₂. Figure 6(a) shows the normalized conversion for the reduction reaction over time for consecutive cycles when the reduction period lasted 40 s. CaMn_{0.9}Mg_{0.1}O_{3-δ} material presented a rather low reactivity, which was maintained constant under these conditions.

The behaviour of the CaMn_{0.9}Mg_{0.1}O_{3-δ} material was different when the reduction period was longer. Figure 5(b) shows the normalized mass variation during 10 redox cycles with the reduction period lasting 90 s. Again, the oxygen carrier was not completely reduced, but the reduction degree increased with the cycle number. The value of 3-δ was 2.5 for the first reduction, but decreased to 3-δ = 2.3 for the 10th reduction. At the same time, the oxygen carrier was not oxidized up to the same initial level. In fact, the degree of oxidation decreased with the cycle number. This indicates that the effective oxygen transport capacity decreases with the cycle number under these conditions. The final oxygen transport capacity was evaluated by the complete reduction of the sample after the 10th redox cycle, where $R_{OC,t} = 8.5$ wt.%. With regard to the reactivity evolution, see Figure 6(b), the oxygen carrier had a gradual gain in its reduction reaction rate for reduction periods of 90 s.

The changes in reactivity and oxygen transport capacity were more intense when the reduction was complete in every cycle, see Figure 5(c). The oxidation degree after every complete redox cycle clearly decreased through the cycles. This decrease was of lower relevance as of the 5th

cycle. The oxygen transport capacity after 10 redox cycles was $R_{OC,t} = 7.5$ wt.%. The oxygen transport capacity may have been affected by the formation of a compound with a lower oxidation state for manganese, i.e. CaMn_2O_4 , which has been confirmed in cycled particles.¹⁸ In this case, the oxygen uncoupling property of this material decreased with the cycle number, but reactivity increased up to the 4th-5th cycle and then stabilized, see Figure 6(c). From the 5th cycle, the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material could be considered to have achieved a maximum conversion rate in reduction reaction. Therefore, an activation process was observed which made the reduction reactivity increase about 4 times during the first redox cycles.

Figure 6. Evolution of normalized conversion vs. time through 10 redox cycles of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material during the reduction period. Reducing gas: 15 vol.% CH_4 + 20% H_2O . $T = 1173$ K.

Figure 7(a) shows the normalized conversion during the oxidation reaction for 10 consecutive cycles in the series where the oxygen carrier was completely reduced in the reduction step. From these data it was concluded that the oxidation rate remained constant through consecutive redox cycles. Nevertheless, the oxidation degree decreased with the cycle number, and therefore the

oxygen transport capacity decreased. The final values of the normalized conversion for reduction and oxidation reactions decreased as far as a value of 0.75, which corresponds to an oxygen transport capacity of $R_{OC,t} = 7.5$ wt.%. This value was lower than the initial $R_{OC,t}$ of fresh particles because the oxygen carrier was not able to recover the initial oxidation state. Figure 7(b) shows the evolution of the oxygen transport capacity, $R_{OC,t}$, with the cycle number. It is observed that $R_{OC,t}$ mainly decreased during the first five cycles, but the decrease in the $R_{OC,t}$ value was slower during the subsequent cycles. The formula for the oxidized state corresponding to the $R_{OC,t}$ value obtained from the 5th cycle is $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{2.63}$, which is a value between oxidation of manganese to Mn(III) and Mn(IV), see Table 1. This means that 60 wt.% of Mn remains as Mn(III), whereas 40 wt.% is regenerated to the upper oxidation state Mn(IV).

Figure 7. (a) Evolution of normalized conversion vs. time through 10 redox cycles of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material during the oxidation period in air; and (b) evolution of the oxygen transport capacity with the redox cycle. $T = 1173$ K. Reduction period in the cycles with 15 vol.% CH_4 for 600 s.

3.3. Redox cycles for kinetics determination

As shown above, the reactivity and oxygen transport capacity of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles differs depending on the operational conditions and the number of redox cycles. Thus, the reaction rate of fresh and activated $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material is obtained under different temperatures (973-1273 K) and gas concentrations (5-60 vol.%). These results are presented as conversion vs. time curves and are used to determine the kinetic parameters of the reduction and oxidation reactions. Results obtained for the first reduction or oxidation are considered for kinetic determination of fresh particles. The fifth redox cycle was selected for kinetic determination of activated particles, as it was previously shown that the reactivity barely changed after this cycle; see Figures 6(c) and 7(a).

The conversion values are obtained from eqs (8) and (9) by using the oxygen transport capacity corresponding to the reaction considered and reacting temperature, see Supporting Information. Thus the conversion values ranged from 0 to 1 in all cases. When reduction by a fuel gas is considered, $R_{OC,t}$ varies from 10.4 wt.% at 973 K to 9.7 wt.% at 1273 K for fresh particles. For activated particles the $R_{OC,t}$ value is 7.5 wt.%. For the oxygen uncoupling reaction, the $R_{OC,ou}$ value also depends on temperature because $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ is more oxidized as temperature decreases, i.e. the δ parameter is higher with temperature. Thus, values for $R_{OC,ou}$ of 1.74 and 1.05 wt.% corresponds to 1073 and 1273 K, respectively. Kinetics of the oxygen uncoupling reaction with activated particles are not calculated because of its low relevance.

3.3.1. Effect of fuel type

Common reducing gases during fuel combustion in a CLC system are CH_4 , H_2 and CO . So, reactivity with these gases was evaluated. To compare the oxygen carrier reactivity with these

gases, Figure 8(a) shows the conversion vs. time curves for the different reducing gases. The reactivity of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material followed the order $\text{H}_2 > \text{CO} > \text{CH}_4$ for fresh particles, while it was $\text{H}_2 > \text{CH}_4 > \text{CO}$ for activated particles. Oxidation was relatively fast, reaching a conversion value of 80% in 60 s for fresh particles, and in 45 s for activated particles. Moreover, the oxidation rate was not dependent on the fuel gas used in the previous reduction stage. The rate index, calculated by eq (10), is often used for reactivity comparison purposes.

$$\text{Rate index (\%/min)} = 100 * 60 * R_{oc} \frac{dX}{dt} \quad (10)$$

Figure 8. Conversion vs. time curves during reduction period with CH_4 , H_2 or CO and oxidation period by O_2 for (a) fresh particles and (b) activated particles. $T = 1173 \text{ K}$; fuel: 15 vol.%; O_2 : 10 vol.%.

The rate index at 1173 K and 15 vol.% of fuel gas or 10 vol.% O_2 is shown in Table 2. For reduction reaction, higher rate index values were found for activated particles. It should be noted that the rate index depended on both reactivity and oxygen transport capacity. Therefore, the increase in reactivity could have been compensated to some degree by the decrease in oxygen

transport capacity, as was the case for CO. Mention should be made of the increase in the rate index shown by CH₄ after activation. Thus, it was necessary to activate the particles in order to achieve high reactivity with methane, although in this case the oxygen uncoupling property was significantly reduced. Furthermore, the rate index for oxidation was lower for activated particles, as a consequence of unchanged reactivity with the redox cycles, but of a decrease in the oxygen transport capacity. In general, values for activated particles were in the medium-upper range of values of rate index for oxygen carrier materials.³⁹⁻⁴¹

Table 2. Oxygen transport capacity and rate index for the CaMn_{0.9}Mg_{0.1}O_{3-δ} material with different reacting gases at 1173 K.

	Fresh particles		Activated particles	
	R_{OC} (wt.%)	Rate index	R_{OC} (wt.%)	Rate index
CH ₄	10.1	1.9	7.5	11.2
H ₂	10.1	13.7	7.5	16.7
CO	10.1	6.3	7.5	6.6
O ₂	10.1	8.2	7.5	7.8
N ₂	1.5	0.8	0.6	n.a.

3.3.2. Effect of gas concentration

To determine the effect of the gas concentration on the kinetics of the reduction reaction, several experiments were carried out at 1073 K and with different gas concentrations. At this temperature, the material was able to be fully oxidized to CaMn_{0.9}Mg_{0.1}O_{2.9}, with the oxygen transport capacity $R_{OC,t} = 10.4$ wt.%. The conversion vs. time curves obtained with CH₄, H₂, CO

or O_2 as reacting gases are shown in Figures 9 and 10 for fresh and activated particles, respectively.

There was a direct relationship between fuel concentration and reaction rate. As expected, an increase in fuel gas concentration produced an increase in reaction rate. In addition, a decrease in the reaction rate was observed with the conversion of solids, particularly for CO. This may indicate a change in the controlling mechanism of the reaction, most likely from chemical reaction control to control by the diffusion in the product layer of the grains at high conversion values. This had to be taken into account when the kinetic model was formulated.

3.3.3. Effect of reacting temperature

The effect of temperature on the reaction rate of $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ material was investigated in the interval 973-1273 K. Figures 11(a-d) show the conversion vs. time curves for reduction of fresh material with CH_4 , H_2 and CO, as well as oxidation with O_2 . Similarly, Figures 12(a-d) show conversion vs. time curves for activated particles. In all cases, the reaction rate was affected by the temperature. An increase in temperature produced an increase in the reduction rate, although this effect was rather low for oxidation.

A decrease was observed in the reaction rate as solids conversion increased, particularly for reduction with CO. As mentioned previously, this may have been due to a change in the controlling mechanism from chemical reaction to diffusion in the product layer. Nevertheless, the decrease in the reaction rate was less relevant at high temperatures (≥ 1173 K), suggesting that the diffusion in the product layer had less importance at these temperatures.

Figure 9. Effect of gas concentration on the reaction rate of fresh $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles with (a) CH_4 ; (b) H_2 ; (c) CO ; and (d) O_2 . $T = 1073 \text{ K}$. Continuous line: model predictions. Gas concentration for reduction reactions: 5 vol.%: $\blacksquare$ —; 15 vol.%: $\blacklozenge$ —; 30 vol.%: $\blacktriangle$ —; 60 vol.%: $\bullet$ —. Oxygen concentration: 5 vol.%: $\blacksquare$ —; 10 vol.%: $\blacklozenge$ —; 15 vol.%: $\blacktriangle$ —; 21 vol.%: $\bullet$ —.

Figure 10. Effect of gas concentration on the reaction rate of activated $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles with (a) CH_4 ; (b) H_2 ; (c) CO ; and (d) O_2 . $T = 1073$ K. Continuous line: model predictions. Gas concentration for reduction reactions: 5 vol.%: $\blacksquare$ —; 15 vol.%: $\blacklozenge$ —; 30 vol.%: $\blacktriangle$ —; 60 vol.%: $\bullet$ —. Oxygen concentration: 5 vol.%: $\blacksquare$ —; 10 vol.%: $\blacklozenge$ —; 15 vol.%: $\blacktriangle$ —; 21 vol.%: $\bullet$ —.

Figure 11. Effect of temperature on the reaction rate of fresh $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material with (a) CH_4 ; (b) H_2 ; (c) CO ; and (d) O_2 . 15 vol.% reducing agent or 10 vol.% O_2 . Continuous line: model predictions. Reacting temperature: 973 K: $\blacksquare$ —; 1023 K: $\blacklozenge$ —; 1073 K: $\blacktriangle$ —; 1123 K: $\bullet$ —; 1173 K: $\blacktriangledown$ —; 1223 K: $\bullet$ —; 1273 K: $\oplus$ —.

Figure 12. Effect of temperature on the reaction rate of activated $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material with (a) CH_4 ; (b) H_2 ; (c) CO ; and (d) O_2 . 15 vol.% reducing agent or 10 vol.% O_2 . Continuous line: model predictions. Reacting temperature: 973 K: $\blacksquare$ —; 1023 K: $\blacklozenge$ —; 1073 K: $\blacktriangle$ —; 1123 K: $\bullet$ —; 1173 K: $\blacktriangledown$ —; 1223 K: $\bullet$ —; 1273 K: $\oplus$ —.

The effect of temperature on the oxygen uncoupling rate of fresh $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles was also analysed. Figure 13 shows the conversion vs. time curves obtained during reaction in pure N_2 . The need for high temperatures in order to achieve high oxygen uncoupling reaction rates can be observed.

Figure 13. Effect of temperature on the oxygen uncoupling reaction rate of fresh $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material in pure N_2 . Continuous line: model predictions. Reacting temperature: 973 K: $\blacksquare$ —; 1023 K: $\blacklozenge$ —; 1073 K: $\blacktriangle$ —; 1123 K: $\bullet$ —; 1173 K: $\blacktriangledown$ —; 1223 K: $\bullet$ —; 1273 K: $\blacklozenge$ —.

4. KINETIC MODEL

The grain model was considered for reduction and oxidation reactions. The particle was assumed to be formed by a certain amount of spherical grains, each following the shrinking core model (SCM) during reduction or oxidation.⁴² Some information on the controlling mechanism can be extracted from the shape of the conversion vs. time curves. It was observed that reduction with a fuel gas or oxidation by oxygen showed linear dependence on the reacting time at low

conversion values, and that the reaction rate decreased over time at higher solids conversion values. In fact, there was a sharp decrease in the reaction rate in some cases. The linear dependence of conversion on time can be attributed to a reaction in the gas-solid interphase with chemical reaction control. Readman et al.⁴³ proposed that in this case the oxygen coverage on the surface of the grains was constant during the reduction period. The oxygen diffused from the bulk metal oxide onto the surface where the reaction took place, but this process did not limit the reaction rate under the applied conditions. Additionally, the decrease in the reaction rate at higher conversion values was attributed to a change in the controlling mechanism from chemical reaction to diffusion through the product layer around the grains.

With all the above considerations, and considering the resistance to gas film mass transfer and the diffusion inside the particle to be negligible, the equations that describe this model are the following:⁴⁴

$$t = \tau_{ch}X + \tau_{pl}\left(1 - 3(1 - X)^{2/3} + 2(1 - X)\right) \quad (11)$$

where

$$\tau_{ch} = \frac{1}{k_s \left(C_i^n - C_{i,eq}^n\right)} \quad (12)$$

$$k_s = k_{s,0} e^{-E_{ch}/R_g T} \quad (13)$$

and

$$\tau_{pl} = \frac{1}{D_{pl} \left(C_i^{n'} - C_{i,eq}^{n'}\right)} \quad (14)$$

$$D_{pl} = D_{pl,0} e^{-E_{pl}/R_g T} \quad (15)$$

where $C_{i,eq}$ is the equilibrium concentration of the reacting gas. The equilibrium concentration of each fuel gas, i.e. CH₄, H₂ or CO, was assumed to be zero; in other words, CaMn_{0.9}Mg_{0.1}O_{3-δ} material was able to fully convert the fuel gas to CO₂ and H₂O.

When a sharp decrease in the reaction rate with time was observed, an additional term that modified the effective diffusivity through the product layer became necessary, with D_{pl} calculated as

$$D_{pl} = D_{pl,0} e^{-E_{pl}/R_g T} e^{-k_X X} \quad (16)$$

where

$$k_X = k_{X,0} e^{-E_X/R_g T} \quad (17)$$

These two equations were only used for reduction of CaMn_{0.9}Mg_{0.1}O_{3-δ} material with CO.

In the case of the oxygen uncoupling reaction, see eq (1), the oxygen concentration at equilibrium concentration was considered. Only chemical reaction control was considered, and the evolution of conversion over time was defined by the following equation:

$$t = \frac{1}{k_s (C_{O_2,eq}^n - C_{O_2}^n)} X \quad (18)$$

The oxygen concentration at equilibrium conditions depends on temperature and sharply decreases with solids conversion. A detailed description of this dependence is given in the Supporting Information.

5. DETERMINATION OF KINETIC PARAMETERS

5.1. Reduction and oxidation reactions

The kinetic model described in Section 4 was used to determine the kinetic parameters for the reduction reaction with CH₄, H₂ and CO and oxidation with O₂. The kinetic parameters for the

chemical reaction for the reactions considered were obtained from an analysis of the τ_{ch} values obtained for different gas concentrations and temperatures, see Supporting Information for more details. Figures 14(a) and (b) show a plot of $\ln(1/\tau_{ch})$ vs. $\ln(C_i)$ for reaction with CH_4 , H_2 , CO or O_2 of fresh and activated particles, respectively. The reaction order, n , was obtained from the slope of the figure, with $\ln(k_s)$ being the intercept. The chemical reaction kinetic constant, k_s , as a function of the temperature was obtained from experiments carried out at different temperatures.

Figure 14. Plot to obtain the reaction order with respect to CH_4 ($\blacksquare$), H_2 ($\blacklozenge$), CO ($\blacktriangle$) and O_2 ($\bullet$) for (a) fresh and (b) activated particles. $T = 1073 \text{ K}$.

Figures 15(a) and (b) show the Arrhenius plots of the $\ln(k_s)$ values as a function of $1/T$ for fresh and activated particles. The slope of the curves is E_{ch}/R_g , whereas the intercept value is $\ln(k_{s,0})$. The calculated kinetic parameters for each reaction are shown in Tables 3 and 4. For the chemical reactions of fresh particles, values for activation energies ranged from 25 to 107 kJ/mol. The activation energies determined for H_2 and CO (85 and 40 kJ/mol, respectively) were lower than those for CH_4 (107 kJ/mol). In general, the activation energies were lower for

activated particles, except CO, which showed a similar value for both fresh and activated material. Also, the activation energy was the same for fresh and activated particles in the oxidation reaction, because reactivity was not affected by redox cycles. The calculated reaction order was $n = 1$ for all the reacting gases except CH₄, which was $n = 0.5$, both for fresh and activated particles.

Figure 15. Arrhenius plots for the kinetic constant k_s for the reaction of CH₄ (■), H₂ (◆), CO (▲) and O₂ (●) for (a) fresh and (b) activated particles. The kinetic constant values for oxygen uncoupling reaction in N₂ for fresh particles are also included (▼).

Once the kinetic parameters for chemical reaction were obtained, the kinetic parameters for diffusion through the product layer were obtained by fitting the conversion curves obtained at different gas concentrations and temperatures. It was found that the diffusion mechanism was not dependent on the reacting gas concentration in the reduction reactions with CH₄, H₂ or CO. However, it was dependent on the oxygen concentration during oxidation, with $n' = 1$. This

result suggests that the limiting process was the diffusion of oxygen anions towards the outer surface of the particle, which agrees with the formulation of the kinetic model.

Values were obtained for the effective diffusivity in the product layer, D_{pl} , at each temperature. Furthermore, the decay constant for reduction with CO, k_X , was obtained at several temperatures. The values of the corresponding pre-exponential factor, and the activation energies were obtained assuming Arrhenius dependence for D_{pl} and k_X on temperature, see eqs (15) and (17). Figures 16(a) and (b) show the Arrhenius plots, and the kinetic parameters values are shown in Tables 3 and 4 for fresh and activated solids. A lower activation energy value can be observed for activated particles. Also, the activation energy was higher for CO, which could be a consequence of a variable diffusivity with the solids conversion. All the differences shown in the reduction with CO, which includes slight variation in activation energy for k_s after activation or the need for variable effective diffusivity in the product layer, suggest a different reaction mechanism during CO oxidation.

Figure 16. Arrhenius plots for effective diffusivity in the product layer D_{pl} for the reaction of CH_4 ($\blacksquare$), H_2 ($\blacklozenge$), CO ($\blacktriangle$) and O_2 ($\bullet$) for (a) fresh and (b) activated particles. k_X for CO also shown ($\bullet$).

Table 3. Kinetic parameters for reaction of fresh $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ particles with CH_4 , CO , H_2 and O_2 , and oxygen uncoupling in N_2 .

		units	CH_4	H_2	CO	O_2	N_2
n	Order of the reaction	-	0.5	1	1	1	0.5
$k_{s,0}$	Pre-exponential factor of k_s	$\text{m}^{3n} \text{mol}^{-n} \text{s}^{-1}$	$2.7 \cdot 10^2$	$7.2 \cdot 10^1$	$3.1 \cdot 10^{-1}$	$2.1 \cdot 10^{-1}$	4.4
E_{ch}	Activation energy for k_s	kJ/mol	107.3	84.7	39.7	25.1	55.6
n'	Order of diffusion	-	0	0	0	1	-
$D_{pl,0}$	Pre-exponential factor of D_{pl}	$\text{m}^{3m} \text{mol}^{-n} \text{s}^{-1}$	$4.1 \cdot 10^9$	$6.7 \cdot 10^8$	$4.9 \cdot 10^{18}$	$3.1 \cdot 10^{-2}$	-
E_{pl}	Activation energy for D_{pl}	kJ/mol	291.2	234.2	424.8	13.4	-
$k_{x,0}$	Pre-exponential factor of k_x	-	-	-	$5.4 \cdot 10^2$	-	-
E_X	Activation energy for k_x	kJ/mol	-	-	43.9	-	-

Table 4. Kinetic parameters for reaction of activated $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ with CH_4 , CO , H_2 and O_2 .

		units	CH_4	H_2	CO	O_2	N_2
n	Order of the reaction	-	0.5	1	1	1	-
$k_{s,0}$	Pre-exponential factor of k_s	$\text{m}^{3n} \text{mol}^{-n} \text{s}^{-1}$	$2.4 \cdot 10^1$	2.0	1.0	$2.8 \cdot 10^{-1}$	-
E_{ch}	Activation energy for k_s	kJ/mol	66.1	42.9	44.9	25.1	-
n'	Order of diffusion	-	0	0	0	1	-
$D_{pl,0}$	Pre-exponential factor of D_{pl}	$\text{m}^{3m} \text{mol}^{-n} \text{s}^{-1}$	$3.2 \cdot 10^5$	$3.5 \cdot 10^6$	$7.0 \cdot 10^9$	$4.2 \cdot 10^{-2}$	-
E_{pl}	Activation energy for D_{pl}	kJ/mol	187.8	170.4	242.2	13.4	-
$k_{x,0}$	Pre-exponential factor of k_x	-	-	-	$1.8 \cdot 10^1$	-	-
E_X	Activation energy for k_x	kJ/mol	-	-	16.2	-	-

5.2. Oxygen uncoupling reaction

In this case, a τ_{ch} value was not adequate to describe the reaction progress because the oxygen concentration at equilibrium conditions varied with solids conversion. So, a value of k_s was determined for every temperature by fitting experimental conversion vs. time curves by means of eq (18). The reaction order affected the curvature of the conversion vs. time lines. Reaction order was also determined by the fitting method, with $n = 0.5$. The dependence of k_s values on temperature for the oxygen uncoupling reaction is shown for fresh material in Figure 15(a), and the kinetic parameters are shown in Table 3.

5.3. Confidence in kinetic parameters

The conversion vs time curves predicted by the reaction model with the kinetic parameters obtained are shown in Figures 9-13. As can be seen, the conversion curves are well predicted in the entire range of operating conditions studied, i.e. gas concentration, temperature and reaction type. The kinetic data obtained in this work will be useful for inclusion in mathematical models for the design and optimization of CLC reactors. The choice of kinetic parameters must be suited to the characteristics of the particles used. For example, activation was not seen during 70 h of operation in a CLC unit operating at high oxygen carrier circulation rates,¹⁹ so the suitable kinetics for model validation should be those for fresh particles. Moreover, an oxygen uncoupling process may be relevant and this mechanism should be considered.

6. IMPLICATIONS OF REACTION KINETICS ON CLC PERFORMANCE

Optimum conditions are related to operating conditions in a CLC unit, and some indications can be drawn from the kinetics determination. In order to assure high oxygen transference rate,

high temperature would be advisable in all cases to improve methane conversion in a CLC unit. It can be asserted that the oxygen uncoupling mechanism should be dominant for fresh particles in order to achieve a high oxygen transfer rate. This is due to the low reactivity of fresh material with CH₄. The implication in a CLC unit is that a high solids circulation flow rate would be necessary. Considering that $R_{OC,ou}$ is about one tenth of $R_{OC,t}$, the required oxygen carrier to fuel ratio would be higher than 10. Here, the oxygen carrier to fuel ratio, ϕ , is defined as the flow of oxygen available in circulating solids divided by the oxygen required to fully convert the fuel to CO₂ and H₂O. Lower oxygen carrier to fuel ratio values will limit the relevance of the oxygen uncoupling, and poor methane conversion in a CLC unit can be expected. Taking 1 MW of fuel as a reference, and assuming full conversion of gas, the solids circulation flow rate can be calculated by:⁴⁰

$$\dot{m}_{OC} = \frac{2 d M_o}{R_{OC,t} \Delta H_c^0} \phi \quad (19)$$

Table 5 shows the solids circulation flow rate assuming $\phi = 1$ or $\phi = 10$ and for CH₄, H₂ and CO as fuel gas. A reacting temperature of 1223 K was assumed, thus $R_{OC,t} = 0.096$. If natural gas is used as fuel, the real value may be close to the value for CH₄. But if syngas is used as fuel, the real value could be between those for CO and H₂, depending on the syngas composition.⁴¹ A solids circulation flow rate as high as 16 kg/s per MW_{th} can be achieved with current CFB technology.⁴⁰ Thus, this oxygen carrier could be used inside the limits defined by the solids circulation flow rate required.⁴

However, with lower circulation rates, the oxygen carrier to fuel ratio is low enough to allow a high variation in the solids conversion. The activation process can then take place. Thus,

reactivity of the oxygen carrier with CH₄ is highly increased and lower oxygen carrier to fuel ratio could be allowed in order to achieve high conversion of methane in a CLC unit.

Complementary to the rate index showed in Table 2, the minimum oxygen carrier inventory in the fuel and air reactor is a suitable parameter to compare the quality of a material as oxygen carrier. The minimum oxygen carrier inventory is determined following the methodology shown in a previous work.⁴⁰ Thus, the solids inventory in every reactor can be calculated by:

$$m_{FR} = \frac{2 d M_o}{R_{OC} \Delta H_c^0} \frac{1}{[dX_{red}/dt] \Phi_{FR}} \quad (20)$$

$$m_{AR} = \frac{2 d M_o}{R_{OC} \Delta H_c^0} \frac{1}{[dX_{ox}/dt] \Phi_{AR}} \quad (21)$$

where the parameters Φ_{FR} and Φ_{AR} are the characteristic reactivity in the fuel reactor and air reactor, respectively. For the kinetic model used in this work, the values for the characteristic reactivity were between 0 and 1.⁴⁰ The minimum solids inventory was calculated for the case of the upper limit of Φ_{FR} and Φ_{AR} , which meant that the variation in solids conversion was low.⁴ With this condition, the chemical reaction control was assumed to be the controlling mechanism to calculate the reduction rate, $[dX_{red}/dt]$, and the oxidation rate, $[dX_{ox}/dt]$.

Reduction with CH₄, H₂, or CO was considered in order to calculate the solids inventory in the fuel reactor. Reaction rates were calculated for an average gas concentration, which depended on the reaction order, the gas conversion and the possible gas expansion during fuel conversion.⁴⁰ The average gas concentration for a fuel conversion of 99.9% was used, which in this case were 12 vol.% CH₄ and 14 vol.% for H₂ and CO. For fresh particles, the oxygen uncoupling rate, $[dX_{ou}/dt]$, was also considered for fresh particles. In this case, R_{OC} was $R_{OC,ou}$ in Eq. (20), which corresponded to the oxygen transport capacity to calculate X_{ou} . An average oxygen concentration

of zero was assumed to calculate $[dX_{ou}/dt]$, whereas the oxygen concentration at equilibrium was given by the maximum oxidation state in the air reactor. Assuming the oxygen concentration at the air reactor exit was 4 vol.%, corresponding to an air excess of 20%, the perovskite material is oxidized to $\text{CaMg}_{0.1}\text{Mn}_{0.9}\text{O}_{2.824}$ at 1223 K. Thus, the oxygen concentration at equilibrium is 4 vol.% at 1223 K.

To calculate the solids inventory in the air reactor, the average concentration was 11 vol.%, corresponding to a concentration at the air reactor exit of 4 vol.% O_2 . Note that $R_{OC} = R_{OC,t}$ must be used to calculate the solids inventory in the air reactor; Eq. (21).

Table 5 shows the minimum solids inventory in the fuel and air reactor for fresh and activated particles. The solids inventory in the fuel reactor for fresh particles is higher than for activated particles owing to the lower reactivity of fresh particles. Also, the solids inventory follows the reactivity order with different gases. The minimum solids inventory values for this material can be used for comparison purposes. Thus, these values are lower than those reported for other Mn-based materials.^{4,11}

Note that the solids inventories corresponding only to the oxygen uncoupling mechanism are higher than those corresponding to reaction with gases. This is due to the low value of $R_{OC,ou}$ compared to $R_{OC,t}$. Nevertheless, the oxygen uncoupling mechanism can be relevant for fuel conversion where the fuel gas concentration seeing the particles is low. This fact can be relevant in the bottom bed, where fuel concentration in the emulsion phase can be low,^{21,22} or at the top of the reactor, where the fuel is highly converted. In these sections of the reactor the oxygen transference rate via oxygen uncoupling maybe faster than the direct gas-solid reaction between fuel and oxygen carrier.

Table 5. Minimum solids circulation flow rate and minimum solids inventory in the fuel and air reactors for fresh and activated $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ with CH_4 , H_2 and CO .

	Comments	units	CH_4	H_2	CO
$\dot{m}_{OC}$	$\phi = 1$	$\text{kg s}^{-1} \text{ MW}^{-1}$	0.8	0.7	0.6
$\dot{m}_{OC}$	$\phi = 10$	$\text{kg s}^{-1} \text{ MW}^{-1}$	8.3	6.9	5.9
Fresh particles					
m_{FR}	Reaction with gases	kg MW^{-1}	109	27	65
m_{FR}	Oxygen uncoupling	kg MW^{-1}	680	564	482
m_{AR}		kg MW^{-1}	42	35	30
Activated particles					
m_{FR}	Reaction with gases	kg MW^{-1}	27	21	43
m_{AR}		kg MW^{-1}	40	34	29

7. CONCLUSIONS

The oxygen transport capacity and reactivity of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material for the reduction and oxidation reactions were determined by TGA using CH_4 , H_2 , CO or O_2 as reacting gases. The oxygen uncoupling property of this material was also analysed.

Fresh particles showed an oxygen uncoupling property, with an oxygen loss of 1.1 wt.% at 1173 K in N_2 , but showed low reactivity against CH_4 . The oxygen uncoupling mechanism may have been dominant for fresh particles when a high solids circulation rate was used.

This material showed an activation process for reduction reaction when the variation of solids conversion in consecutive redox cycles was higher than 50%. During activation, the reactivity of oxygen carrier with CH_4 , H_2 or CO increased, but the oxidation reactivity was not affected by the cycle number. Also, the oxygen transport capacity decreased from an initial value of 10.5 wt.%

to a stable value of 7.5 wt.% after 10 redox cycles and the oxygen uncoupling property was strongly reduced. Kinetics of activated particles could be relevant if a low solids circulation rate were to be used in a CLC unit.

The grain model, assuming mixed control by the chemical reaction and the diffusion through the product layer, was able to predict the experimental results under different gas concentration, temperature or reaction type. Results suggested that the diffusion of oxygen anions in the product layer was the controlling mechanism during the diffusion stage. For comparison purposes, the minimum solids inventory in the fuel and air reactor was determined by using kinetics data. The total minimum solids inventory in a CLC unit is 151 kg/MW_{th} or 67 kg/MW_{th} for fresh or activated particles, respectively. These values are lower than values calculated for other Mn-based materials because of their higher reactivity.

In the future, the kinetic model can be included in reactor models to predict the performance of this perovskite material in a CLC unit.

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ASSOCIATED CONTENT

Supporting Information Available. Detailed description of TGA apparatus. Thermodynamics analysis of Ca-Mn-O system. Determination of kinetic parameters.

This material is available free of charge via the Internet at <http://pubs.acs.org>

NOMENCLATURE

C_i = reacting concentration of gas i (mol/m³)

D_{pl} = effective product layer diffusivity (m³ⁿ mol⁻ⁿ s⁻¹)

$D_{pl,0}$ = pre-exponential factor for effective product layer diffusivity (m³ⁿ mol⁻ⁿ s⁻¹)

E_i = activation energy of the process i (J/mol)

k_s = chemical kinetic constant (m³ⁿ mol⁻ⁿ s⁻¹)

$k_{s,0}$ = pre-exponential factor for chemical kinetic constant (m³ⁿ mol⁻ⁿ s⁻¹)

k_X = decay constant for the product layer diffusivity

$k_{X,0}$ = pre-exponential factor for decay constant for the product layer diffusivity

m = instantaneous mass of oxygen carrier (kg)

m_o = mass of the oxidized form of the oxygen carrier (kg)

m_r = mass of the reduced form of the oxygen carrier (kg)

n = reaction order for chemical reaction

n' = exponential constant for gas concentration in the product layer diffusion process

R_g = constant for ideal gases ($R_g = 8.314$ J mol⁻¹ K⁻¹)

R_{OC} = oxygen transport capacity

$R_{OC,ou}$ = oxygen transport capacity for oxygen uncoupling process

$R_{OC,t}$ = total oxygen transport capacity with a fuel gas

t = time (s)

T = temperature (K)

X = conversion of solids

X_N = normalized conversion of solids

Greek symbols

γ = parameter in subscript for oxygen in the reduced state, according the formula

δ = parameter in subscript for oxygen in the oxidized state, according the formula

ϕ = oxygen carrier to fuel ratio

τ_i = time for complete conversion when the reaction is controlled by the process i (s)

ω = normalized mass-loss variation

Subscripts

ch = chemical reaction

eq = equilibrium

o = oxidation

ou = oxygen uncoupling

pl = product layer

r = reduction

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