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## Promising impregnated Mn-based oxygen carriers for Chemical Looping Combustion of gaseous fuels

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### Abstract

Promising impregnated oxygen carriers, based on copper and iron, have been previously developed for CLC with gaseous fuels (CH<sub>4</sub>, syngas, LHC). Recently, because of its low cost and environmental compatibility, Mn-based oxygen carriers are now being considered as an attractive option for chemical-looping combustion (CLC) applications. In this work, a screening of different commercial supports in fluidizable particle size for impregnated Mn-based materials has been carried out. Different oxygen carriers have been prepared by incipient impregnation on ZrO<sub>2</sub>, and CaAl<sub>2</sub>O<sub>4</sub>, and evaluated with respect to their mechanical resistance, fuel gas reactivity and fluidization properties such as agglomeration and attrition rate. In a first step, particles showing high enough crushing strength values were selected for the reactivity investigation. The redox reactivity was evaluated through TGA experiments at suitable temperatures for the CLC process (i.e. 850-950 °C) using H<sub>2</sub>, CO and CH<sub>4</sub>. Multi cycle redox analysis and full physical and chemical characterization was also performed. In a second step, materials with high enough reactivity were prepared for fluidized bed evaluation. A batch fluidized bed installation with continuous gaseous fuel feed was used to analyze the product gas distribution during reduction and oxidation reactions at different operation temperatures, and agglomeration and attrition behavior of the selected materials. Results showed that an oxygen carrier impregnated using ZrO<sub>2</sub> as support, had high enough reactivity and low attrition rate. Therefore, this material can be selected as a candidate for the development of CLC with syngas with promising results.

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**Keywords:** Chemical Looping Combustion; oxygen carrier; Mn-based; impregnation

## 1. Introduction

Carbon dioxide is the main anthropogenic gas responsible for intensifying the greenhouse effect. Because of this, scientists and politicians around the world have suggested a number of strategies and technologies to reduce CO<sub>2</sub> emissions to the atmosphere for the next decades. Studies conducted by the International Energy Agency (IEA) and the Intergovernmental Panel on Climate Change (IPCC) suggest various scenarios of economic growing and energy demand, indicating that in most cases the CO<sub>2</sub> Capture and Storage technologies will contribute between 10-55% of the global effort to reduce CO<sub>2</sub> concentrations in the atmosphere by 2100 [1, 2]. In this context, the Chemical Looping Combustion (CLC) is considered one of the better alternatives to reduce the cost of CO<sub>2</sub> capture, especially when compared to conventional capture processes, since it does not require the separation of CO<sub>2</sub> from N<sub>2</sub>, once fuel is not mixed directly with air or oxygen. Besides, during the process it does not occur NO<sub>x</sub> formation and the energy required is the same as in conventional combustion.

The process CLC is a form of unmixed combustion where air and fuel never come in direct contact, the transfer of oxygen from air to the fuel is made by means a metal oxide which acts as an oxygen carrier [3, 4]. Fig. 1 shows a CLC system schematic design. The system is composed of two reactors, named they air and a fuel reactor. In the fuel reactor (FR), the oxygen carrier is reduced the Me<sub>x</sub>O<sub>y-1</sub> and oxidizes the fuel to H<sub>2</sub>O and CO<sub>2</sub>, which can be easily separated by condensation obtaining a high concentrated CO<sub>2</sub> stream ready be transported and stored [5].

Major reactions in the fuel and air reactor are the following [5-7]:

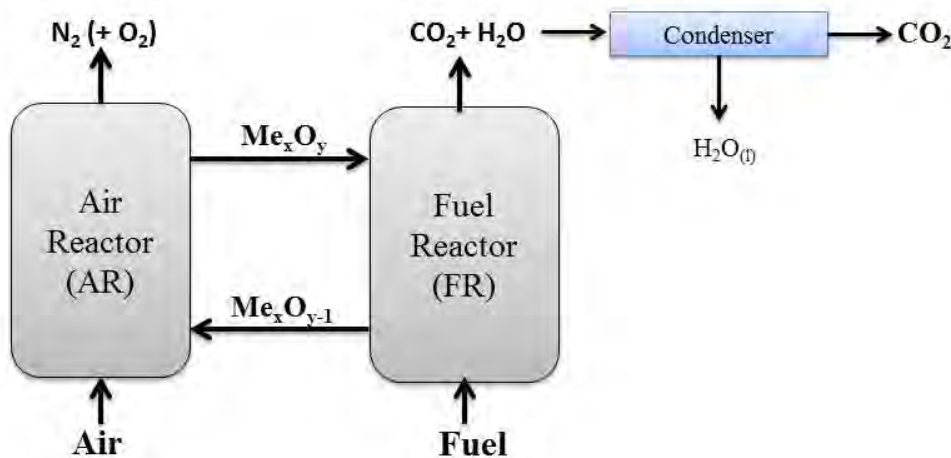
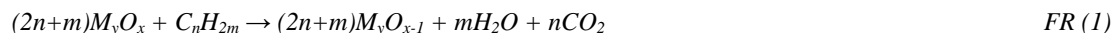


Fig. 1. CLC system schematic design.

Depending upon the metal oxide which is used, the reaction 1 can be endothermic or exothermic, while reaction 2 is always exothermic. The total amount of heat evolved over the two reactors in the CLC process is the same as in a conventional combustion reactor [8]. The selection of suitable oxygen-carriers is a key factor for the chemical looping technology development. Oxides of Cu, Ni, Co, Fe and Mn have favourable thermodynamics for CH<sub>4</sub>, H<sub>2</sub> and CO conversion [4, 9]. However, there are also other aspects different from chemical and physical properties, such as the cost of the oxygen-carrier, and environmental and health aspects. Ni and Co present environmental and health problems, and Cu is a relatively expensive metal. By contrast, Mn-based materials are three times cheaper than copper materials, non-toxic and environmentally friendly. Besides, it has higher melting point and oxygen transport capacity when it is compared to iron oxides.

A disadvantage of the manganese oxides as oxygen carrier is its interaction with several materials, commonly used as supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> or sepiolite), reducing the number of possible supports for the metal [3, 8]. The use of ZrO<sub>2</sub> or ZrO<sub>2</sub>-stabilized as support for manganese oxides revealed promising results for the Mn-based oxygen carriers [3,8,10-13].

In this work, the development of suitable manganese-based oxygen carriers by impregnation is carried out. A screening of different commercial supports in fluidizable particle size has been analyzed. Different oxygen carriers have been prepared by incipient impregnation on ZrO<sub>2</sub>, or CaAl<sub>2</sub>O<sub>4</sub>, and evaluated with respect to their mechanical resistance, fuel gas reactivity and fluidization properties such as agglomeration and attrition rate, in order to select promising materials to be evaluated in a fluidized bed reactor. After being used, the oxygen carrier particles were subjected to several characterization techniques to evaluate possible changes in their properties.

## 2. Experimental

### 2.1. Preparation and material properties

The oxygen carriers were composed of Mn<sub>3</sub>O<sub>4</sub> as an oxygen source for the combustion process, and an inert support as a binder for increasing the mechanical strength and to improve fluidization properties. Five several OC were prepared by impregnation with different Mn contents and using different inert supports. The supports used were CaAl<sub>2</sub>O<sub>4</sub> prepared following the methodology of Cabello et al. [15] and three zirconia-based commercial: MELChemicals, YanYu Industrial and Saint Gobain. The MELChemicals support is a highly porous Zr doped hydrocalcite material.

*Incipient wetness impregnation:* Mn-based oxygen carriers were prepared by addition of a volume of an aqueous solution of manganese nitrate corresponding to the total pore volume of the support particles ( $d_p = 100\text{-}300\ \mu\text{m}$ ). The hot impregnation method was used using a saturated solution of Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O to reach high metal content in few impregnation steps. An oxygen carrier with MelChemicals support was also prepared with lower Mn content using a diluted solution (5 M) at ambient temperature. The desired active phase loading was achieved by applying one or two stages of impregnation followed by calcination at 550 °C, in air atmosphere for 30 min, to decompose the impregnated metal nitrates into insoluble metal oxide. Finally, the carriers were sintered for 1 h at 950 °C.

The main physical and chemical properties of the materials were determined by several techniques. The porosity of the support was measured by Hg intrusion in a Quantachrome PoreMaster 33. The force needed to fracture of the oxygen carrier was taken as an average value of at least 20 measurements, by a Shimpo FGN-5x crushing strength apparatus. The identification of crystalline phases was carried out by powder X-ray Diffraction (XRD) in a Bruker AXS D8 Advance, with Bragg-Brentano geometry configuration, Cu K $\alpha$  radiation and equipped with secondary graphite monochromator. The oxygen transport capacity ( $R_{oc}$ ) was experimentally determined by thermogravimetric analysis in a CI Electronics, using H<sub>2</sub> as reducing agent, considering the mass loss from Mn<sub>3</sub>O<sub>4</sub> to MnO phase. Table 1 shows all the supports used, the oxygen carriers prepared, methods used, number of impregnation steps, nomenclature used and main properties obtained during this work.

Table 1: Support, porosity of the support, impregnation steps, methodology, nomenclature and main properties of the oxygen carriers prepared.

Support	Porosity (%)	Stages	Method	Nomenclature of OC's	Crushing strength (N)	Active phase	R <sub>oc</sub>
CaAl <sub>2</sub> O <sub>4</sub>	28.6	2	IHI	Mn-CaAl	0.8	Mn <sub>3</sub> O <sub>4</sub>	1.1
ZrO <sub>2</sub> (Yanyu)	56.0	2	IHI	Mn-ZrY	7.3	Mn <sub>3</sub> O <sub>4</sub>	1.3
ZrO <sub>2</sub> (Saint Gobain)	50.1	2	IHI	Mn-ZrSG	2.5	Mn <sub>3</sub> O <sub>4</sub>	1.1
ZrO <sub>2</sub> (MELChemicals)	57.2	1	IHI	Mn-ZrMA	4.6	Mn <sub>3</sub> O <sub>4</sub> , Mg <sub>6</sub> MnO <sub>8</sub>	2.7
ZrO <sub>2</sub> (MELChemicals)	57.2	1	IAI	Mn-ZrMF	3.4	Mn <sub>3</sub> O <sub>4</sub> , Mg <sub>6</sub> MnO <sub>8</sub>	2.0

Example of nomenclature of the oxygen-carriers: Mn-ZrSG: The Mn matches the active phase (manganese oxides); the Zr is an inert binder (ZrO<sub>2</sub>), SG the commercial source (Saint Gobain). In case of the support MELChemical “A” is the incipient hot impregnation and “F” is incipient impregnation at ambient temperature.

## 2.2. Experimental set-up

### 2.2.1. Thermogravimetric analyzer

Firstly, it was analyzed the reactivity of the oxygen carriers during three reduction-oxidation cycles in a TGA, CI Electronics type. For the experiments, the oxygen carrier particles were loaded in a platinum basket and heated to the set operating temperature in air atmosphere. After stabilization, the experiment started by exposing the oxygen carrier to alternating reductive and oxidative conditions. The reduction gas was 15% methane and 20% steam in N<sub>2</sub> and the gas used for oxidation was 100 % air. The experiments were carried out at 950 °C for the reduction and oxidation reactions. Best materials were further subjected to 100 redox cycles at the same operating conditions to analyze the effect of the number of cycles in the reactivity properties.

### 2.2.2. Fluidized bed facility

The oxygen carriers selected in the TGA reactivity tests were evaluated in a discontinuous fluidized bed reactor where the behaviour is similar to the operating conditions existing in a CLC process. The tests were carried out at 850, 900 and 950°C with an inlet superficial gas velocity into the reactor of 0.15 m/s, using 25 % CH<sub>4</sub>+10% H<sub>2</sub>O in N<sub>2</sub>; 50%H<sub>2</sub>+20% H<sub>2</sub>O in N<sub>2</sub> and 50%CO+20%CO<sub>2</sub> in N<sub>2</sub> as reacting gases for reduction, and 5% O<sub>2</sub> for oxidation. To avoid the mixture of combustible gas with air, 100% N<sub>2</sub> was introduced during 120 s after each reducing and oxidizing period. The fluidization behaviour with respect to the agglomeration phenomena and the attrition rate can be also determined.

The discontinuous fluidized bed reactor system used for testing the oxygen carriers consisted of a system for gas feeding, a fluidized-bed (FB) reactor, two filters to recover the solids elutriated from the FB, and a continuous gas analysis system [14]. A batch of 250-300g of oxygen carrier was used to ensure a bed height of about 8-10 cm depending on the density of solids. Agglomeration problems, causing defluidization of the bed, could be detected by a sharp decrease in the pressure drop during operation. The attrition rate was determined from the solids elutriated and recovered in two hot filters located downstream from the FB, during the successive reduction-oxidation cycles.

### 3. Results

#### 3.1. Oxygen carrier reactivity in TGA

The reactivity of the five different oxygen carriers was determined in a TGA, the experiments allowed to analyze the reactivity of the oxygen-carriers under well-defined conditions. The oxygen carrier's reactivity corresponding to the 3<sup>rd</sup> cycle was used for comparison purposes.

Fig. 2 shows the OC conversion versus time of five different Mn-based oxygen carriers prepared by impregnation. The Mn-ZrY oxygen carriers showed the lowest reactivity during the reduction reaction and a slow reactivity during oxidation stage. The Mn-CaAl material has a fast reduction and oxidation rate, but this oxygen carrier had a low mechanical resistance. The Mn-ZrSG material presented the best reactivity both in reduction and oxidation reactions.

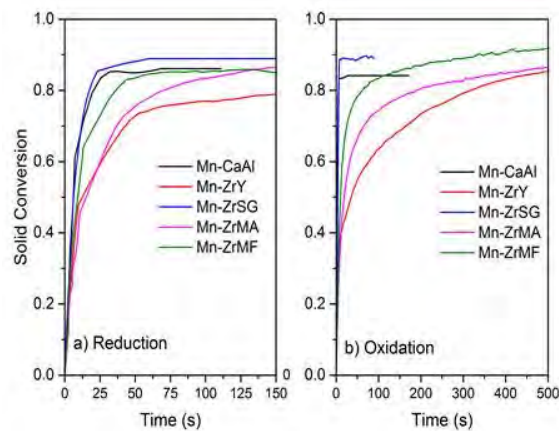


Fig. 2. Conversion versus time curves of different oxygen carriers prepared by incipient impregnation: (a) reduction using CH<sub>4</sub>, (b) oxidation using air. T = 950 °C.

To compare the reaction rate of the different materials, the rate index was calculated [10] according to:

$$\text{Rate Index} = 60 \times 100 \times \left( \frac{d w}{d t} \right)_{\text{norm}} \quad (3)$$

Table 2 shows the rate index of the OC obtained from the reactivity data of Fig. 2. As it can be seen, the Mn-CaAl and Mn-ZrSG presented the highest values both for oxidation and reduction. However, the Mn-ZrMA and Mn-ZrMF oxygen carriers had lower oxidation index than its reduction ones indicating that these materials, in spite of its high oxygen transport capacities, had low oxidation rates.

Table 2: Rate index of the oxygen carriers using methane reduction gas and air as oxidation at 950°C.

Rate index / OC	Mn-CaAl	Mn-ZrY	Mn-ZrSG	Mn-ZrMF	Mn-ZrMA
Reduction (%/min)	4.1	3.0	13.1	6.8	5.9
Oxidation (%/min)	9.5	2.1	8.5	4.1	5.7

To further evaluation of the suitability of Mn-based impregnated materials for the CLC process, other properties such as the mechanical strength were considered together with the reactivity with fuel gases (CH<sub>4</sub>, H<sub>2</sub> and CO). In this

way the Mn-ZrSG and the Mn-ZrMF materials were selected for multicyle redox tests. The Mn-ZrSG oxygen carrier had a high mechanical strength (2.5N) and the highest rate index with CH<sub>4</sub> both for reduction and oxidation reactions. The Mn-ZrMF had also very high crushing streng and a high reactivity with CH<sub>4</sub> and H<sub>2</sub>. Other materials had a low crushing streng (Mn-CaAl) or a low rate index (Mn-ZrY). By these reasons these materials were rejected for selection.

### 3.2. Evaluation of the oxygen carrier selected

#### 3.2.1. Redox multicycles by TGA

The selected materials were subjected to 100 reduction/oxidation cycles in the TGA using methane and air at 950°C to evaluate the effect of the number of cycles and time on the reactivity. The reduction and oxidation reactions last 60 s each with a 30 s purge between them. Fig. 3 shows the solid conversion versus time of the different cycles for each material. As it can be seen, the Mn-ZrMF oxygen carrier had a high solid conversion during the first cycles, although it decreases to 20% after 50 cycles, both in the reduction and oxidation reactions, indicating that this material suffer from a deactivation of its reactivity and also a decrease in the oxygen transport capacity, mainly due to the non complete reoxidation of its Mn oxides (mainly Mg<sub>6</sub>MnO<sub>8</sub>) during the time of the cycle.

However, the Mn-ZrSG material had a constant and high solid conversion and reactivity during all the number of cycles (95% in 10 s), indicating that this material maintains its oxygen transport capacity and reaction rates both in oxidation and reduction reactions.

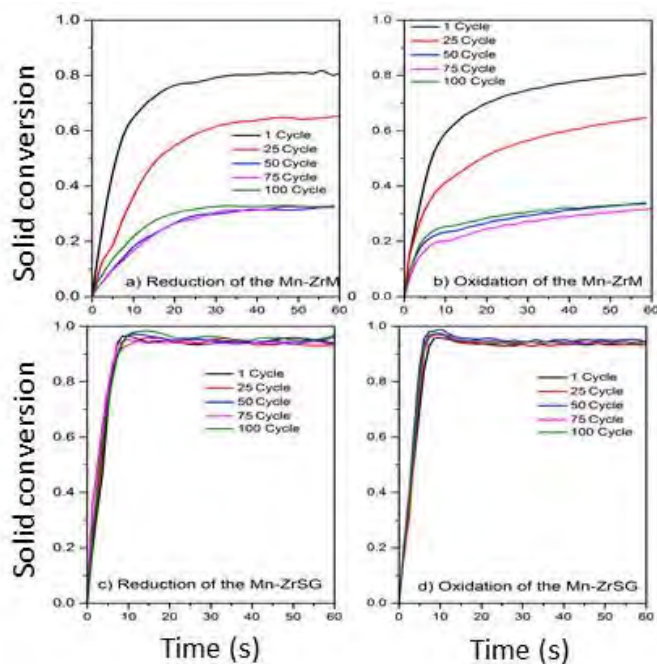


Fig. 3. TGA redox multicycles conversion of the oxygen carriers: (a) reduction of the Mn-ZrMF, (b) oxidation of the Mn-ZrMF, (c) reduction of the Mn-ZrSG and (d) oxidation of the Mn-ZrSG.

#### 3.2.2. Oxygen carrier behaviour in fluidized bed reactor

Several reduction-oxidation multicycles were carried out in a batch fluidized bed reactor to determine the gas product distribution, agglomeration behaviour and carbon formation of the selected oxygen carriers. Moreover, in this facility the attrition rate can be also determined during hot operation in redox cycles.

The tests were carried out at 850, 900 and 950°C with an inlet superficial gas velocity into the reactor of 15cm/s, using CH<sub>4</sub>, CO and H<sub>2</sub> reducing agents, and 5% O<sub>2</sub> in N<sub>2</sub> during oxidation. Pure nitrogen was introduced for two minutes after each reducing and oxidizing period to avoid mixing of the combustible gas and oxygen. The conversion of the oxygen carrier as a function of time during the reduction and oxidation periods were calculated from the oxygen outlet concentration by the equations:

Reduction:

$$X_r = \int_{t_0}^{t_r} \left\{ \frac{F_s}{n_0} (2y_{CO_2,s} + y_{CO,s} + y_{H_2O,s}) - \frac{F_e}{n_0} (2y_{CO_2,e} + y_{CO,e} - y_{H_2O,e}) \right\} dt \quad (4)$$

$$F_s = F_e \left( \frac{y_{N_2,e}}{y_{N_2,s}} \right) = F_e \left( \frac{y_{N_2,e}}{1 - y_{CH_4,s} - y_{CO_2,s} - y_{CO,s} - y_{H_2O,s}} \right)$$

Oxidation:

$$X_0 = \int_{t_0}^{t_o} \frac{2F_s}{n_0} \left( \frac{F_e}{F_s} y_{O_2,e} - y_{O_2,s} - \frac{1}{2} y_{CO,s} - y_{CO_2,s} \right) dt \quad (5)$$

$$F_s = \frac{F_e (1 - y_{O_2,e})}{(1 - y_{CO_2,s} - y_{CO,s} - y_{O_2,s})}$$

The Mn-ZrMF material presented important agglomeration problems during the test carried out and for that reason it was rejected for further characterization. However, the Mn-ZrSG material had a good behaviour during fluidization and was subjected to redox cycles at different operating conditions. In this way, it was found that the methane conversion increases as the temperature increases although some unburnt methane was always detected at the outlet of the reactor, as it was found in the works of Abad [11] e Rydén [16].

Fig. 4 shows the gas concentration measured at the outlet of the reactor during reduction and oxidation periods using 25% CH<sub>4</sub>+10% H<sub>2</sub>O and 5% O<sub>2</sub> at 950 °C in the first cycle and in the 20<sup>th</sup>. As it can be seen, some CH<sub>4</sub>, H<sub>2</sub> and CO were detected during reduction reaction together with C deposition, which was released as CO<sub>2</sub> and CO during oxidation periods. Besides, the amount of unconverted methane increases as the number of cycles increases together with an increase in the H<sub>2</sub> concentration, changing the selectivity of the methane reaction from combustion to reforming. So, it can be concluded that this oxygen carrier is not suitable for methane combustion in a CLC process.

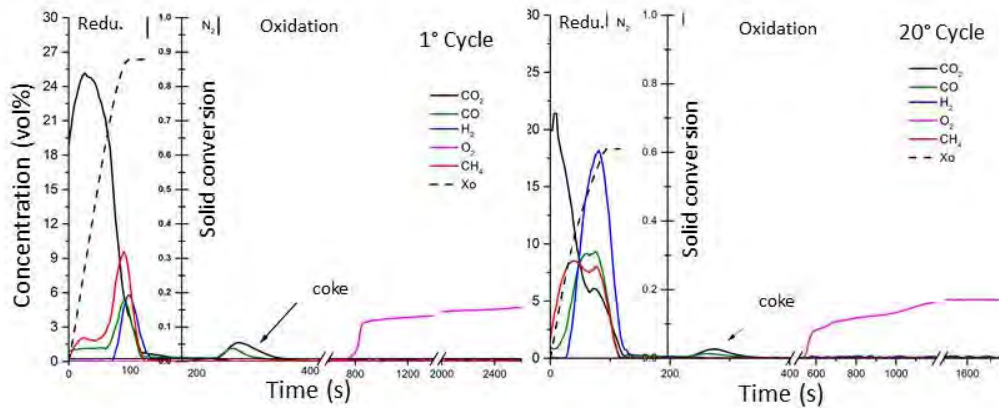


Fig. 4. BFB redox multicycles product distribution and solid conversion of the Mn-ZrSG oxygen carrier at 950° during CH<sub>4</sub> combustion for cycle number 1 and 20.

Regarding the redox cycles with CO and H<sub>2</sub>, Fig. 5 shows the first and 20<sup>th</sup> cycle for the reduction and oxidation periods using 50% CO + 20% CO<sub>2</sub> and 50 % H<sub>2</sub> + 20% H<sub>2</sub>O at 950 °C. It was found that complete fuel gas conversion was reached during the first seconds of reaction, and only when the oxygen carrier conversion was high, some CO was detected at the outlet due to the consumption of the oxygen in the particles. This fact is avoided in a CLC continuous process where oxidated particles are circulated between reactors. Similar results were found at all the temperatures tested (850 and 900°C) during all redox cycles, indicating the suitability of this material for syngas CLC combustion.

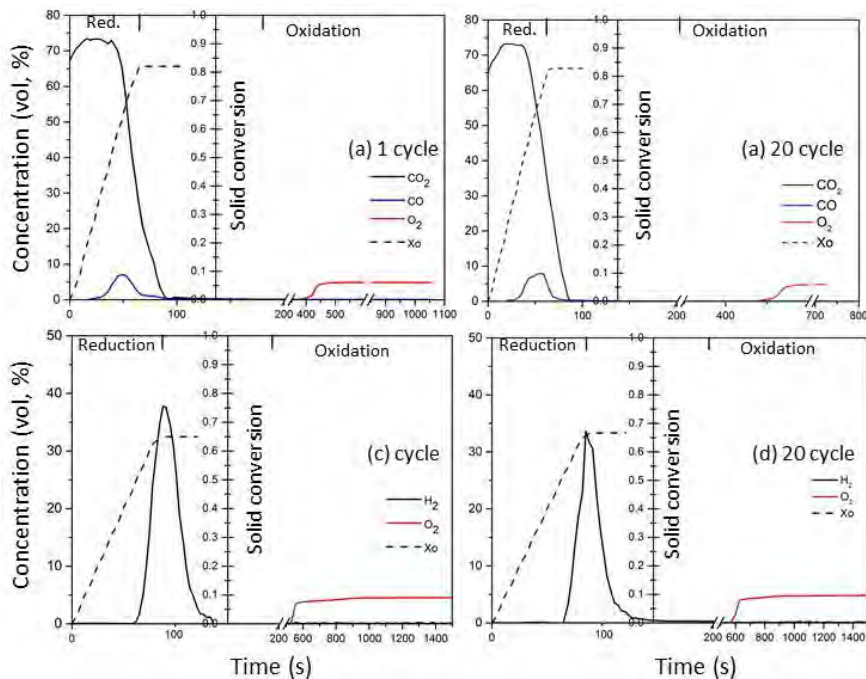


Fig. 5. BFB redox multicycles product distribution and solid conversion of the Mn-ZrSG oxygen carrier at 950° during (a) first cycle with CO; (b) 20th cycle with CO; (c) first cycle with H<sub>2</sub>; (d) 20th cycle with H<sub>2</sub>.



### 3.2.3. Attrition behaviour

An important parameter of the oxygen carrier in a CLC process is the attrition behaviour during fluidization. The attrition rate of the OC was evaluated as the weight of particles elutriated from the bed recovered in the filters with a  $d_p < 45 \mu\text{m}$  during a measured time. Fig. 6 shows the attrition rates for Mn-ZrSG as a function of time.

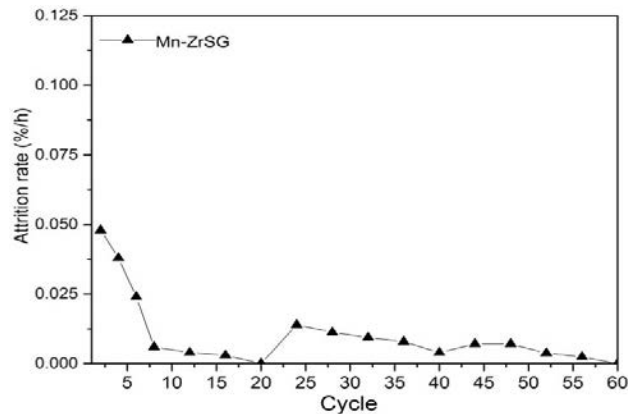


Fig. 6: Attrition rate of the Mn-ZrSG oxygen carrier during multi-cycle reaction in the fluidized bed using different bed temperatures (850, 900 and 950°C).

As it can be seen, at the beginning the attrition rate is high, probably due to rounding of oxygen carriers particles, but it quickly decreases and stabilizes at a low value 0.009 %wt./h after 39 h of hot fluidization in the batch reactor. This attrition rate corresponds to a particle lifetime of 11000 h, that it is a much higher than the one obtained by Abad [11] with a freeze granulation Mn-ZrO<sub>2</sub> material (~2600 h). Therefore, this oxygen carrier can be suitable for syngas combustion and coal CLC by an iG-CLC process, since it has a high reactivity with H<sub>2</sub> and CO, high particle lifetime and presents absence of agglomeration problems.

## 4. Conclusions

The different Mn-based oxygen carriers developed by impregnation over porous supports (CaAl<sub>2</sub>O<sub>4</sub>, ZrO<sub>2</sub> and ZrO<sub>2</sub> doped hydrotalcite) has been evaluated in a TGA and in a batch fluidized bed regarding its reactivity towards CH<sub>4</sub>, CO and H<sub>2</sub>, mechanical strength, agglomeration behavior, selectivity to combustion and attrition rate at different operation temperatures during multicycle tests.

A commercial support has been identified (ZrO<sub>2</sub> from Saint Gobain) as the best material for oxygen carrier preparation, since this oxygen carrier, Mn-ZrSG, presented high reactivity to H<sub>2</sub> and CO combustion, high particle lifetime and good properties for fluidization.

## 5. Acknowledgement

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