Influence of the Oxidation Step on the Behaviour and the Performances of an Oxygen Carrier in Fixed Bed Reactor

Lucia Blas[a], Sophie Dorge[a]*, Nabila Zouaoui[a], Arnold Lambert[b], Patrick Dutournié[c]

[a]*Laboratoire de Gestion des Risques et Environnement – GRE, Université de Haute Alsace – UHA, 3bis, rue Alfred Werner, 68093 Mulhouse, France*
[b]*IFP Energies Nouvelles, BP 3, 69360 Solaize, France*
[c]*Institut de Science des Matériaux de Mulhouse – IS2M, CNRS LRC 7228, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse, France*

Chemical Looping Combustion is a promising technology for clean power generation with integrated CO_2 capture. In this process the oxygen required for combustion is provided by a metal oxide. This work deals with the development of an experimental procedure to study performances of an oxygen carrier during oxidation/reduction cycles and the influence of the oxidation step on its behaviour. Tests were performed in a laboratory fixed bed reactor, with $NiO/NiAl_2O_4$ a promising oxygen carrier, and CO as fuel. Two different protocols of oxidation were studied. Results reveal that the oxidation step conditions can change the performances of the oxygen carrier. A significant decrease in total reduction capacity was observed using the regeneration step at high temperature due to structural changes in particles. SEM analysis reveals that particle surface contains different crystallites according to this procedure. With the second procedure (oxidation in temperature ramp), nickel is partially agglomerated.

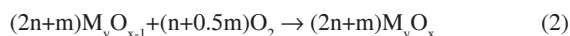**Keywords:** *CLC, oxygen carrier, CO oxidation, SEM, nickel agglomeration*

1. Introduction

It is well known that the combustion of fossil fuels for power generation emits large amounts of carbon dioxide, which is one of the most important greenhouse gases contributing to global warming. The CO_2 concentration in the atmosphere has increased considerably in recent decades (from 318 ppm in 1958 to 400 ppm in may 2013[1]), and although the effects of increased levels of greenhouse gases are difficult to quantify, it is generally accepted that a reduction in emissions of these gases is necessary[2]. Fossil fuels will continue to be used as principal sources of energy during the next decades. Therefore it is important to minimize CO_2 emissions. It can be achieved by energy savings and development of renewable energy sources, but also by developing new efficient processes for CO_2 capture and sequestration (CCS). Current CO_2 capture technologies consist in the CO_2 separation from industrial flue gas streams. This last one can be stored or mineralised[3]. These processes have the major disadvantage of high costs and energy penalties, because of the significant quantities of gas which must be treated. These processes lead to a relative reduction of 15-20% of the overall efficiency of a power plant[4].

Chemical Looping Combustion (CLC) is an innovative technology that can be used for clean power generation or as an alternative process for oxidizing organic wastes, because the CO_2 capture process can be easily integrated with lower energy penalties[5]. The main advantage of this technology compared to conventional combustion is that combustion occurs without air, the oxygen required for this reaction is directly provided by a metal oxide as an oxygen carrier. During CLC process, the oxygen carrier is continuously circulated between two interconnected fluidized bed reactors where it is alternatively oxidized and reduced[6,7]. In the fuel reactor, the oxygen carrier is reduced by the combustible according to reaction (1), and in the air reactor it is regenerated according to reaction (2).

The flue gases released from the air reactor contain mainly N_2 and unreacted O_2. They can be emitted to the atmosphere without any treatment. Exhaust fumes from the fuel reactor contain mostly CO_2 and H_2O. After water condensation, almost pure CO_2 can be obtained, therefore CO_2 capture occurs at low energy consumption. This process also ensures that no thermal NOx will be produced by Zeldovitch mechanism in the flue gas, due to the absence of extremely high temperatures as it is seen in classical combustion for both premixed and diffusion flames[8,9].

$$(2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m)M_yO_{x-1} + mH_2O + nCO_2 \quad x \geq 1 \quad (1)$$

$$(2n+m)M_yO_{x-1} + (n+0.5m)O_2 \rightarrow (2n+m)M_yO_x \quad (2)$$

Reaction (2) is strongly exothermic, while reaction (1) can be either endothermic or exothermic depending on the fuel and the oxygen carrier used. The total amount of heat released from both reactions is the same as the heat released during conventional combustion, and no additional energy is needed in the CO_2 separation process, except the energy required for the fluidized bed reactor operation.

*e-mail: sophie.dorge@uha.fr

The selection of suitable oxygen carrier is a key issue for the large-scale application of CLC, and the performance of oxygen carrier particles will determine the feasibility of the process. Many efforts have been made to develop efficient oxygen carriers for the CLC process. More than 700 different products have been developed and tested[10], and several oxides of transition metals such as Ni, Cu[11], Mn[12] and Fe[13] have been proposed as the most suitable materials for oxygen carriers in CLC[14,15]. The metallic oxides are generally supported on a porous material (Al_2O_3, SiO_2, TiO_2, ZrO_2 and Yttria-Stabilized Zirconia), which is inert and stable at high temperature and increases the particles' mechanical strength and attrition resistance. The binder also provides a higher surface area needed for the reaction[16].

Ni-based oxygen carriers which show high reactivity and good performances, in large range of temperature, are the most analysed materials in the literature. Nevertheless, thermodynamic restrictions prevent complete conversion of methane into CO_2 and H_2O with this oxygen carrier, and this generates small amounts of CO and H_2 in the exhaust gas of the fuel reactor[17,18]. For Ni-based oxygen carriers, $NiAl_2O_4$ is considered one of the best binders[19].

Intensive works have been performed in the past about the reactivity and kinetic determination of the reduction and oxidation steps of oxygen carriers. These results are strategic for the development of industrial reactors. Different studies dealing with the performances of oxygen carriers can be found in the literature; they have been carried out at laboratory scale: usually Thermogravimetric Analyses TGA[20] or at pilot scale[21,22]. With TGA studies, the degree of conversion of the materials can be obtained, but this analysis is not carried out in the same operating conditions as it is observed in CLC reactors. Indeed, residence and diffusion times (fuel vs. oxygen carrier) are very different in the two operating configurations.

Another way to study an oxygen carriers' performance at laboratory scale is the fixed bed reactor. In this case, the gas flow goes through the bed and the mass transfer is mainly governed by forced convection. Therefore, this technique allows working at laboratory scale in conditions that are closer to the ones used in a CLC process. However, there are few studies operated in fixed bed reactors. For example, Mattisson et al.[23] investigated the feasibility of using Fe_2O_3 as an oxygen carrier in a fixed bed reactor (in quartz) at 950 °C. They observed that the rates of reduction and oxidation are sufficient to use it in a CLC process. Q. Song et al.[24] studied in a fixed bed reactor, the reactivity and stability of $CaSO_4$. They showed that 950 °C is the optimal reduction temperature to minimize secondary products and agglomeration, and they concluded that $CaSO_4$ is a potential oxygen carrier for CLC. Ryu et al.[25] studied in a fixed bed reactor the reactivity and the carbon deposition during reduction, with NiO as oxygen carrier supported on bentonite.

There are several works devoted to the behaviour of oxygen carriers with CH_4 as a fuel; however, few studies concerning the reactivity of CO or syngas have been performed[26].

The present study deals with laboratory scale experiments on $NiO/NiAl_2O_4$ oxygen carrier (one of the most powerful material) in a fixed bed reactor with CO as fuel. The objective of this work is to develop an experimental procedure to study the behaviour of an oxygen carrier during reduction-oxidation cycles, in terms of fuel oxidation performances and regenerability to optimize its life time. To find the best procedure of oxygen carrier regeneration, we have studied the influence of the oxidation step on the reduction capacity. Two different oxidation protocols were studied and compared.

2. Experimental

2.1. *Materials*

The oxygen carrier used in this study is NiO supported on $NiAl_2O_4$. It was supplied by *IFP Energies Nouvelles*, its composition is of 60 wt. % NiO and 40 wt. % $NiAl_2O_4$ and the particle size is in the range of 100-300 μm. The particles were prepared by granulation (in a Guedu granulator) and then, they were calcined at 1200 °C for 2 hours.

2.2. *Experimental device*

Laboratory scale experiments were performed in a vertical quartz reactor of 6 mm of internal diameter, with a fused silica frit (Figure 1). This small reactor allows us working with a minimal mass of oxygen carrier and a significant bed height. The reactor is in a vertical tubular Pekly/ Herrmann-Moritz furnace (the sample is placed in the isothermal area of the oven). Two K-type thermocouples are placed below the silica frit and just above the sample, to control the temperature in the reactor and in the material.

The fuel used in this study is a mixture of CO and nitrogen (concentration 0.2 vol.%), it was chosen because it simplifies the analysis of the results and also it avoids the implementation of considerable resources. It is also an intermediate of reaction when hydrocarbons are used as fuel.

The injected gas flow rate (oxidising and reducing mixtures) is controlled by four BROOKS 5850 mass flow controllers and fixed at 50 NL.h^{-1} for all the tests. Mole fractions of CO and CO_2 of exhaust gases are measured online by an infrared analyser (Rosemont NG2000, range 0-1%). In addition, the oxygen concentration is measured by a paramagnetic analyser (Rosemount X-stream with two ranges 0-20% and 0-100%). The data acquisition (time, temperature and concentrations) is carried out using a module NUDAM and all the data are recorded in real time throughout the tests.

2.3. *Procedure*

Two different procedures to oxidize and reduce the sample have been studied and compared.

Procedure 1 consists of an oxidation of the oxygen carrier under air from ambient temperature to operating temperature (750 °C, at 10 °C.min^{-1}). When the operating temperature is reached, the inerting step under nitrogen starts and it is finished when the oxygen analyser shows that the concentration of oxygen in the device is zero (about 30 minutes). At this time, a mixture of CO (concentration 0.2 vol. %) and nitrogen is introduced in the reactor to reduce the sample. This step is finished when the concentration of
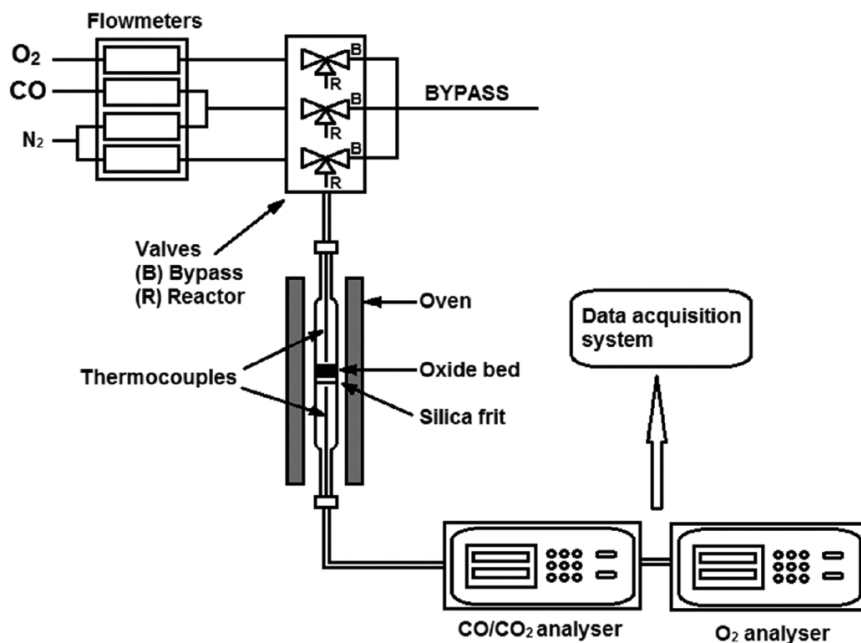
Figure 1. Experimental set-up.

CO in the exhaust gas is equal to the concentration of CO injected (complete reduction). After the reduction step the inert gas is injected again to avoid mixing of oxidant and reducing gases. Then a new oxidation-reduction cycle is started and performed at operating temperature (750 °C).

Procedure 2 is similar to the first one, the first cycle is carried out exactly in the same conditions, but for the following ones, the sample is cooled down to ambient temperature under nitrogen before starting a new oxidation cycle.

Therefore the main difference between both procedures is that the oxidation in the first one is carried out at the operating temperature (750 °C) while in the second one the sample is always cooled after the reduction, and during the oxidation step it is heated from room to operating temperature.

2.4. *Sample characterization*

Specific surface area measurements are performed by nitrogen adsorption (BET methodology) at 77K (MICROMERITICS ASAP 2010) after sample degassing at 250 °C overnight.

Oxygen carrier surface observations are carried out at various magnifications using a Philips XL30 FEG Scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometers (EDX).

3. Results

3.1. *Experimental results using procedure 1.*

The initial test is performed according to the first procedure (oxidation step at operating temperature), with 0.28 g of $NiO/NiAl_2O_4$ and the concentration of CO injected during the reduction step is fixed at 2000 ppm (total gas

flow of 50 NL.h^{-1}). Figure 2 shows the temperature and the outlet gas concentration as a function of time for the first three oxidation-reduction cycles. It can be observed that at the beginning of the first reduction cycle there is a high conversion (almost complete) of CO to CO_2. However, at the beginning of the second and the third reduction cycles, the conversion of CO is not complete. The curves are integrated to obtain the amount of CO_2 produced and CO oxidised during each cycle. The maximum experimental error observed for the CO/CO_2 analyser is about 3 ppm. We have integrated the curves with this error in each point (±3 ppm) and from these two additional integrations, we obtained a systematic error for the total capacity around 0.01 mmol. Results are shown in Table 1.

A decrease of the reduction capacity of the oxygen carrier (around 10%) is observed from cycle 2. This decrease is probably due to a local important exothermicity (100-120 °C) during the oxidation step as observed on Figure 2. This high temperature during regeneration step probably modifies the Ni-based particles.

3.2. *Cycles performed using procedure 2*

To avoid the local rising in temperature during the oxidation step observed with the first procedure, the following tests are performed according to the second one (the sample is preliminary cooled to room temperature before the regeneration step). The obtained results for the first oxidation- reduction (after an activation cycle) test are shown in Figure 3.

In these conditions no exothermicity is observed during the regeneration of the oxygen carrier.

3.3. *Reproducibility of cycles*

Using the first procedure it is observed that the successive cycles are not reproducible, and there is a

Table 1. Amount of CO_2 produced and CO oxidised during reduction cycles (procedure 1 and 2).

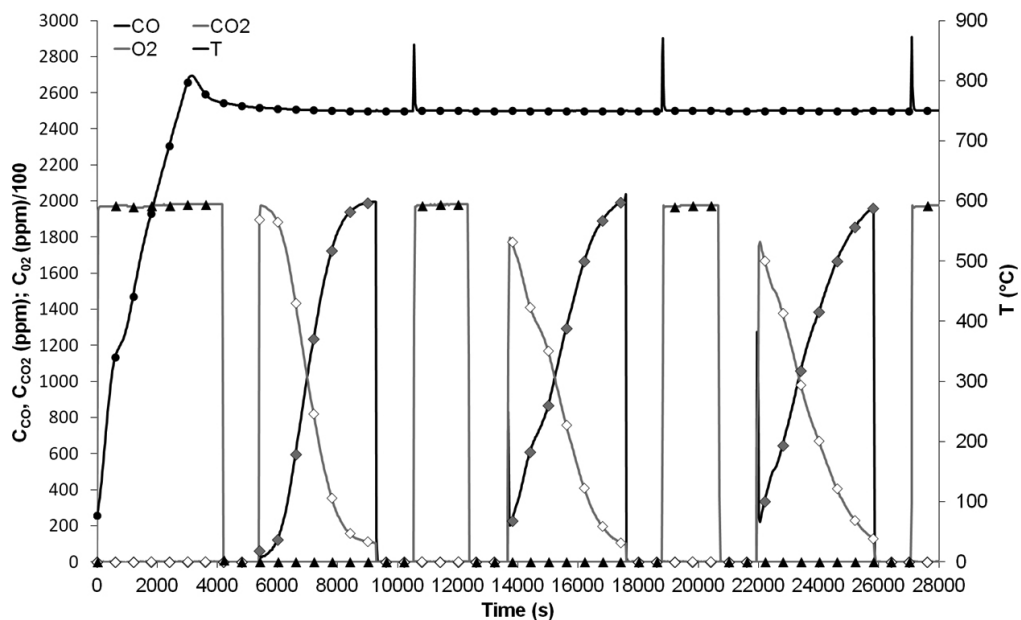|	Procedure 1		Procedure 2	
	Moles of CO_2 produced	**Moles of CO oxidised**	**Moles of CO_2 produced**	**Moles of CO oxidised**
Cycle 1	$2.15\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.21\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.32\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.35\ 10^{-3} \pm 0.01\ 10^{-3}$
Cycle 2	$1.96\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.04\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.33\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.36\ 10^{-3} \pm 0.01\ 10^{-3}$
Cycle 3	$1.94\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.01\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.31\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.35\ 10^{-3} \pm 0.01\ 10^{-3}$
Cycle 4			$2.30\ 10^{-3} \pm 0.01\ 10^{-3}$	$2.33\ 10^{-3} \pm 0.01\ 10^{-3}$
			Total capacity= $2.33\ 10^{-3} \pm 0.02\ 10^{-3}$ CO/CO_2 moles	

Figure 2. Oxidation-reduction cycles of 0.28 g of $NiO/NiAl_2O_4$ (0.2% CO, 750 °C, 50 NL.h^{-1}) according to first procedure.
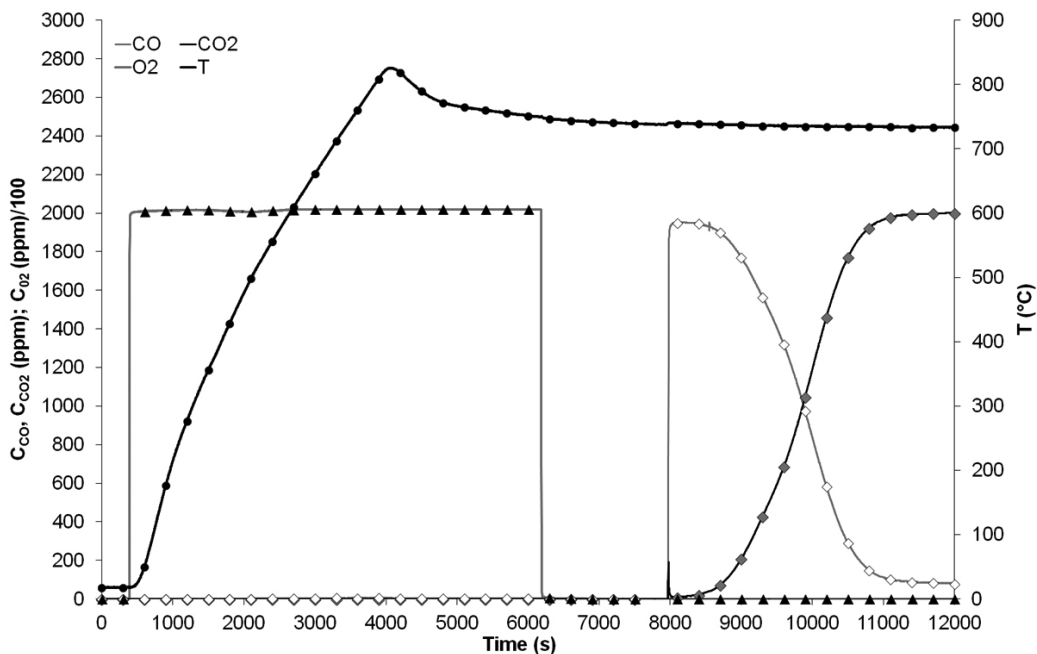

Figure 3. First oxidation-reduction cycle (after activation cycle) of 0.28 g of $NiO/NiAl_2O_4$ (0.2% CO, 750 °C, 50 NL.h^{-1}) according procedure 2.

decrease in potential reduction capacity. Using the second procedure the evolution of the oxygen carrier activity has been studied during successive oxidation-reduction cycles. The aim is to verify that no loss of reduction capacity is observed on the $NiO/NiAl_2O_4$ with these experimental conditions over several successive cycles.

The evolution of CO and CO_2 concentrations in the gas at the reactor outlet, during the reduction step, for 4 successive oxidation – reduction cycles is shown in Figure 4. All the reduction steps have been carried out at 750 °C, with a total flow rate of 50 $NL.h^{-1}$, with a composition of 0.2 vol.% of CO in nitrogen.

Figure 4 shows the concentration profiles of CO and CO_2 versus time for cycles 1 to 4. Results show a relatively good reproducibility of the reduction cycles. The total oxygen transfer capacity of the $NiO/NiAl_2O_4$ particles is practically constant for the different successive cycles (Table 1). The systematic errors for each integration is calculated as described before. Starting from these eight values we have calculated the average total capacity of the oxygen carrier (in terms of moles of oxygen reacting with the fuel) and its standard deviation.

In addition, the intersection point of CO and CO_2 concentration curves for all the cycles, is approximately the same. Therefore, the behaviour of the oxygen carrier is similar for all the tests.

It can be also observed in these results a small peak of CO at the beginning of the reaction. This peak was already observed by Mattisson et al. during methane oxidation[18,27]. They found that this small peak appeared when the particles are fully oxidized, but disappeared when the O/Ni ratio decreases. They suggested that the reduction proceeds via CO and H_2, which may be catalyzed by metallic Ni.

3.4. *Carbon and oxygen balance*

Table 1 shows the amount of CO_2 produced and CO oxidised obtained by integration of the experimental curves.

It can be assumed that the oxidation of the CO injected follows the next equation:

$$CO+NiO \rightarrow CO_2+Ni \qquad (3)$$

According to Equation 3, it has been considered that the oxygen available for the oxidation reaction only comes from the NiO supported on $NiAl_2O_4$ (which amounts to $2.28.10^{-3}$ moles of oxygen).

Results of moles of CO_2 produced and CO oxidised (for tests carried out according to procedure 2) are close to the theoretical number of oxygen moles available on the nickel oxide (calculated from the mass of oxygen carrier used for the tests).

In the nickel aluminate binder, there is some oxygen potentially available for the reduction of the fuel. Mattisson et al. have studied in detail the reaction of $NiO/NiAl_2O_4$ with alternating methane and oxygen. They have found experimentally that $NiAl_2O_4$ can release oxygen to the fuel, but this reaction is extremely slow compared to the reaction of CH_4 with NiO[20,27]. In our case, results obtained do not allow us to conclude that the aluminate is also partially reduced by CO.

3.5. *Characterisation of oxygen carriers*

According to the procedure used, the behaviour of the oxygen carrier seems to be different. Indeed, the total reduction capacity (moles of CO_2 produced) of the $NiO/NiAl_2O_4$ changes significantly depending on the conditions (procedure 1 versus procedure 2) used during the oxidation step.
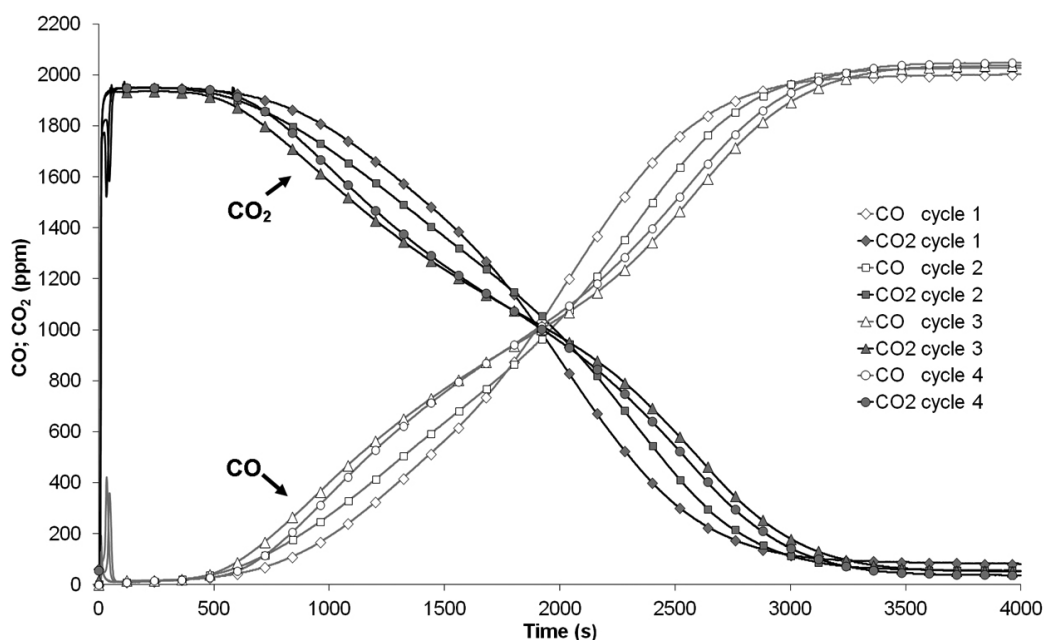

Figure 4. Reduction cycles of 0.28g of $NiO/NiAl_2O_4$ (0.2% CO, 750 °C, 50 $NL.h^{-1}$).

To explain the observed differences, a characterization of the metallic oxide samples before and after oxidation/reduction cycles was carried out. The first observed difference in the three samples is the colour, fresh NiO/NiAl$_2$O$_4$ and the sample used with the first procedure are green, by contrast the one used with the second procedure is dark grey/black. This difference in colours could be explained by the fact that the NiO is green when the Ni/O ratio is stoichiometric, and black when it is not[28].

The metallic oxide samples were collected after the tests. On one side, particle agglomeration is observed in the sample oxidised by procedure 1 and a portion of the sample is stuck to the silica frit. On the other side, no agglomeration is observed on the sample oxidised by procedure 2. In this case, the grain size distribution has not apparently changed. Specific surface measurements on the two samples indicate no difference between them in term of BET surface area (around 6 m².g^{-1}).

After these preliminary studies, SEM analyses were performed to study the differences between the surface of particles, depending on the oxidation procedure used. Some representative SEM micrographs are shown in Figure 5.

At a relatively low magnification, it is observed that the shape and the surface of the particles are the same before and after the tests (Figures 5A, C and E). The particles are almost spherical and for the three samples we can also see broken particles. This is probably a consequence of the preparation method because it is also observed in fresh samples.

At high magnification, the first thing noticed is that each particle is composed of secondary particles. In these pictures it can be clearly seen that the secondary particles are different for each sample (Figures 5B, D and F). We can appreciate that the secondary particles of the two aged oxygen carriers are larger than those of the fresh material. For the first procedure it can be observed (picture 5D) that the secondary particles are partially crystallised. However, for the second one, the secondary particles are bigger and
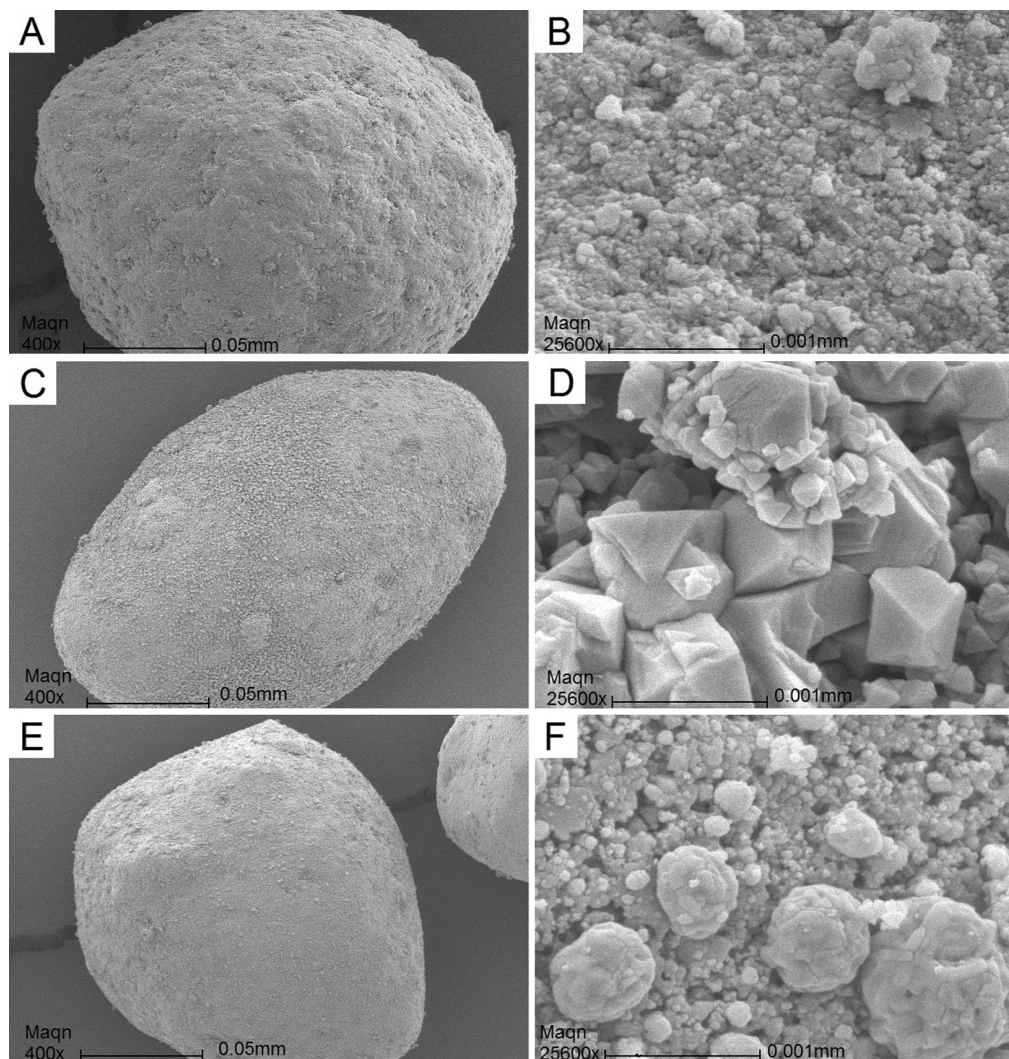

Figure 5. SEM micrographs of oxidised NiO/NiAl$_2$O$_4$. In the left micrographs at low magnification (400x), in the right the same particles at high magnification (25600x). A and B (Before reactivity test), C and D (after reactivity tests with procedure 1), E and F (after reactivity tests with procedure 2).
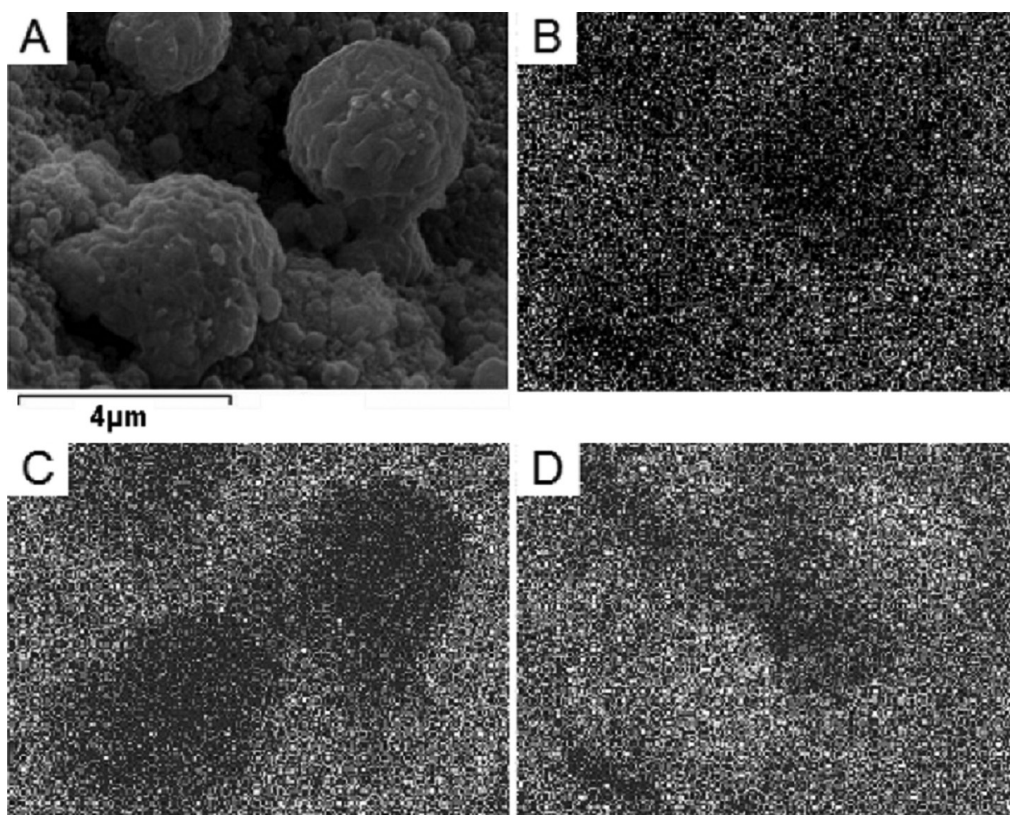
Figure 6. SEM micrograph of agglomerates (A) on $NiO/NiAl_2O_4$ after reactivity tests performed with the second procedure and corresponding EDX analyses. Oxygen (B), aluminium (C), nickel (D).

more agglomerated (picture 5F) than in the fresh sample (SEM micrograph 5B). Therefore, we can conclude that each sample has undergone different structural changes according to the operating conditions used in the cycles. Fresh and aged oxygen carrier particles were also characterized by EDX (Energy dispersive X-ray) analysis, for all samples. EDX analyses of samples from procedure 1 were not carried out owing to the instability of the particles under the electron beam. Ni, Al and O were observed. The EDX analysis on the fresh material reveals that dispersion of Ni, Al and O is uniform over all the surface of the particles. However, the secondary particles partially agglomerated during tests with the second procedure, are enriched in nickel and depleted in aluminium and oxygen as can be seen in Figures 6A-D. Similar accumulations of Ni have been observed by E. Jerndal et al.[29], and they have found that these accumulations can facilitate agglomeration, causing defluidization.

4. Conclusion

In this work, the influence of the oxidation step on the performances of an oxygen carrier often used in CLC ($NiO/NiAl_2O_4$) has been studied. With this objective, several oxidation and reduction cycles have been carried out in a fixed bed reactor.

Two different procedures were studied. On one hand, with the first one (oxidation at high temperature) an

important exothermicity and a decrease in total reduction capacity is observed. On the other hand, using the second procedure (oxidation with air under a temperature ramp from ambient to the operation temperature) no exothermicity is observed and the cycles are apparently reproducible. The total capacity of the oxygen carrier remains constant after several cycles (no loss of activity) and the intersection point of CO and CO_2 concentration curves is almost the same for all cycles. Furthermore, carbon balance sheets correspond very well to the oxygen balance sheet available on the metallic oxide.

Some characterization studies of the $NiO/NiAl_2O_4$ were performed to explain the different behaviours depending on the procedure used. In a first observation, at low magnification, particles have apparently the same size and shape for the three samples. At higher magnification, significant differences between samples are observed. The secondary particles in the sample obtained from procedure 1 are partially crystallised. Instead, the ones from procedure 2, are partially agglomerated and enriched in nickel. Therefore we can observe that the particles have undergone different structural changes according to the oxidation conditions used in the cycles. Consequently, the chosen experimental protocol used to regenerate the oxygen carrier can significantly decrease the reduction capacity and so, can modify the process performances.

References

1. CO₂Now.org. Available from: <http://co2now.org/>.

2. International Energy Agency - IEA. *CO₂ emissions from fuel combustion*. IEA; 2012. Available from: <http://www.iea.org/co2highlights/co2highlights.pdf>.

3. Hossain MM and De Lasa HI. Chemical-looping combustion (CLC) for inherent separations—a review. *Chemical Engineering Science*. 2008; 63(18):4433-4451. http://dx.doi.org/10.1016/j.ces.2008.05.028

4. Herzog HJ. *The economics of CO₂ capture*. London: Pergamon Press; 1999. p. 101-106.

5. Ishida M, Zheng D and Akehata T. Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis. *Energy*. 1987; 12(2):147-154. http://dx.doi.org/10.1016/0360-5442(87)90119-8

6. Richter HJ and Knoche KF. Reversibility of combustion process. *ACS Symposium Series*. 1983; 235(3):71-85.

7. Lyngfelt A, Leckner B and Mattisson T. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chemical Engineering Science.* 2001; 56(10):3101-3113. http://dx.doi.org/10.1016/S0009-2509(01)00007-0

8. Ishida M and Jin H. A Novel Chemical-Looping Combustor without NOx Formation. *Industrial & Engineering Chemistry Research*. 1996; 35(7):2469-2472. http://dx.doi.org/10.1021/ie950680s

9. Son SR and Kim SD. Chemical-Looping Combustion with NiO and Fe₂O₃ in a Thermobalance and Circulating Fluidized Bed Reactor with Double Loops. *Industrial & Engineering Chemistry Research.* 2006; 45(8):2689-2696. http://dx.doi.org/10.1021/ie050919x

10. Adanez J, Abad A, Garcia-Labiano F, Gayan P and De Diego LF. Progress in Chemical-Looping Combustion and Reforming technologies. *Progress in Energy and Combustion Science*. 2012; 38(2):215-282. http://dx.doi.org/10.1016/j.pecs.2011.09.001

11. De Diego LF, García-Labiano F, Adánez J, Gayán P, Abad A, Corbella BM et al. Development of Cu-based oxygen carriers for chemical-looping combustion. *Fuel*. 2004; 83(13):1749-1757. http://dx.doi.org/10.1016/j.fuel.2004.03.003

12. Leion H, Lyngfelt A, Johansson M, Jerndal E and Mattisson T. The use of ilmenite as an oxygen carrier in chemical-looping combustion. *Chemical Engineering Research and Design*. 2008; 86(9):1017-1026. http://dx.doi.org/10.1016/j.cherd.2008.03.019

13. Johansson M, Mattisson T and Lyngfelt A. Investigation of Mn₃O₄ With Stabilized ZrO₂ for Chemical-Looping Combustion. *Chemical Engineering Research and Design*. 2006; 84(9):807-818. http://dx.doi.org/10.1205/cherd.05206

14. Adánez J, De Diego LF, García-Labiano F, Gayán P, Abad A and Palacios JM. Selection of Oxygen Carriers for Chemical-Looping Combustion. *Energy & Fuels*. 2004; 18(2):371-377. http://dx.doi.org/10.1021/ef0301452

15. Cho P, Mattisson T and Lyngfelt A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel*. 2004; 83(9):1215-1225. http://dx.doi.org/10.1016/j.fuel.2003.11.013

16. Ishida M and Jin H. A Novel Combustor Based on Chemical-Looping Reactions and Its Reaction Kinetics. *Journal of Chemical Engineering of Japan*. 1994; 27(3):296-301.

17. Dueso C, Abad A, García-Labiano F, De Diego LF, Gayán P, Adánez J et al. Reactivity of a NiO/Al₂O₃ oxygen carrier prepared by impregnation for chemical-looping combustion. *Fuel*. 2010; 89(11):3399-3409. http://dx.doi.org/10.1016/j.fuel.2010.03.043

18. Mattisson T, Johansson M and Lyngfelt A. The use of NiO as an oxygen carrier in chemical-looping combustion. *Fuel*. 2006; 85(5-6):736-747. http://dx.doi.org/10.1016/j.fuel.2005.07.021

19. Jin H, Okamoto T and Ishida M. Development of a Novel Chemical-Looping Combustion: Synthesis of a Solid Looping Material of NiO/NiAl₂O₄. *Industrial & Engineering Chemistry Research*. 1999; 38(1):126-132. http://dx.doi.org/10.1021/ie9803265

20. Mattisson T, Johansson M, Jerndal E and Lyngfelt A. The reaction of NiO/NiAl₂O₄ particles with alternating methane and oxygen. *The Canadian Journal of Chemical Engineering*. 2008; 86(4):756-767. http://dx.doi.org/10.1002/cjce.20083

21. Linderholm C, Jerndal E, Mattisson T and Lyngfelt A. Investigation of NiO-based mixed oxides in a 300-W chemical-looping combustor. *Chemical Engineering Research and Design*. 2010; 88(5-6):661-672. http://dx.doi.org/10.1016/j.cherd.2009.11.004

22. Sedor KE, Hossain MM and De Lasa HI. Reducion Kinetics of a Fluidizable Nickel-Alumina Oxgen Carrier for Chemical-Loping Combustion. *Canadian journal of chemical engineering*. 2008; 86(3):323-334. http://dx.doi.org/10.1002/cjce.20072

23. Mattisson T, Lyngfelt A and Cho P. The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO₂. *Fuel*. 2001; 80(13):1953-1962. http://dx.doi.org/10.1016/S0016-2361(01)00051-5

24. Song Q, Xiao R, Deng Z, Zhang H, Shen L, Xiao J et al. Chemical-looping combustion of methane with CaSO₄ oxygen carrier in a fixed bed reactor. *Energy Conversion and Management*. 2008; 49(11):3178-3187. http://dx.doi.org/10.1016/j.enconman.2008.05.020

25. Ryu H-J, Bae D-H and Jin G-T. Effect of temperature on reduction reactivity of oxygen carrier particles in a fixed bed chemical-looping combustor. *Korean Journal of Chemical Engineering*. 2003; 20(5):960-966. http://dx.doi.org/10.1007/BF02697306

26. Abad A, García-Labiano F, De Diego LF, Gayán P and Adánez J. Reduction Kinetics of Cu-, Ni-, and Fe-Based Oxygen Carriers Using Syngas (CO + H₂) for Chemical-Looping Combustion. *Energy & Fuels*. 2007; 21(4):1843-1853. http://dx.doi.org/10.1021/ef070025k

27. Mattisson T, Jerndal E, Linderholm C and Lyngfelt A. Reactivity of a spray-dried NiO/NiAl₂O₄ oxygen carrier for chemical-looping combustion. *Chemical Engineering Science*. 2011; 66(20):4636-4644. http://dx.doi.org/10.1016/j.ces.2011.06.025

28. Earnshaw A and Greenwood N. *Chemistry of the Elements*. 2nd ed. Butterworth-Heinemann; 1997.

29. Jerndal E, Mattisson T, Thijs I, Snijkers F and Lyngfelt A. Investigation of NiO/NiAl₂O₄ oxygen carriers for chemical-looping combustion produced by spray-drying. *International Journal of Greenhouse Gas Control*. 2010; 4(1):23-35. http://dx.doi.org/10.1016/j.ijggc.2009.09.007