

## Thermal stability study of NiAl2O4 binders for Chemical Looping Combustion application

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### Abstract

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The influence of the preparation method of  $NiAl_2O_4$  binders on their thermal stability was studied. For this purpose, the reactivity of two different  $NiAl_2O_4$  binders with CO as fuel was studied in a fixed bed reactor device. Successive oxidation-reduction cycles were performed

on the two binders to study their reactivity with the fuel and their structural modifications as cycles proceed. Results reveal that binders are not inert in reducing atmosphere; they both react with the fuel to produce  $CO_2$ . The total reduction capacity (TRC) of the first binder (B1, synthetized by pyrolytic pulverization) increases during the first cycles and levels off after 20

- 5 cycles. However, the TRC of the second binder (B2, synthetized by calcination of a mixture of Ni(OH) and γ-Al<sub>2</sub>O<sub>3</sub>), increases progressively and reaches a maximum after 80 cycles. The growing amount of available oxygen in the binders leads both binders to structural modifications. X-Ray Diffraction studies performed on fresh and aged binders presented a shift of the peaks related to NiAl<sub>2</sub>O<sub>4</sub>. Moreover, quantitative X-Ray Diffraction studies and 10 Temperature Programmed Reduction measurements were performed in order to quantify the
- NiO present in each binder before and after oxidation-reduction cycles. These experiments revealed the presence of NiO in fresh binders due to the preparation method, and an increase of this amount after oxidation-reduction cycles. Therefore, NiAl<sub>2</sub>O<sub>4</sub> in the binder is progressively decomposed producing NiO and Al<sub>2</sub>O<sub>3</sub>. Finally, the decomposition of the binder
  15 NiAl<sub>2</sub>O<sub>4</sub> as cycles proceed was also observed in studies performed on the oxygen carrier NiO/NiAl<sub>2</sub>O<sub>4</sub>. This work showed that the binder reacts with the fuel and therefore it can

contribute to the modification of the oxygen carrier reactivity.

**Keywords:** Oxygen Carrier, NiAl<sub>2</sub>O<sub>4</sub> binder, X-Ray Diffraction, Standard Addition Method, Temperature Programmed Reduction

#### 1. Introduction

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To limit the increase of greenhouse gas emissions and stabilize climate at safe levels,  $CO_2$  capture and sequestration technologies are nowadays being studied and developed [1]. Among these, Chemical Looping Combustion (CLC) has been suggested as an interesting alternative to conventional combustion to produce energy with inherent  $CO_2$  capture [2-3]. CLC consists

of an indirect combustion, where the oxygen needed for fuel oxidation is provided by a solid oxygen carrier. During this process, the fuel is first oxidized by the oxygen carrier and the latter is afterwards regenerated (re-oxidized) by air [4]. The most common CLC device consists of two interconnected fluidized beds ("combustion" and "regeneration" reactors) with

5 a circulation of the solid oxygen carrier. However Noorman *et al.* [5-6] also proposed the possibility of working in a packed bed reactor where the oxygen carrier remains static and the different oxidation/reduction gas mixtures are alternatively injected. Gases produced in the combustion reactor are primarily CO<sub>2</sub> and H<sub>2</sub>O. Thus, after water condensation, pure CO<sub>2</sub> is obtained and it can be directly stored or used. Outlet gases from the regeneration step 10 (depleted air) can be directly emitted to the atmosphere. In conclusion, power generation by CLC technology does not require an energy intensive gas separation of CO<sub>2</sub> from exhaust gases, which is the most expensive step of CO<sub>2</sub> capture and sequestration.

Finding suitable oxygen carriers with sufficient reactivity, good mechanical properties and stability is strategic to increase the efficiency of CLC processes. Oxygen carriers are generally

15 composed of an active phase (generally a metal oxide based on Ni, Fe, Cu, Mn or Co) and a porous binder (Al<sub>2</sub>O<sub>3</sub>, NiAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, yttrium-stabilized zirconia...), which provides higher surface area for reaction, mechanical strength and attrition resistance [7-8]. The final properties of the oxygen carrier (reactivity, mechanical strength, thermal and chemical stability...) depend mainly on the metal oxide used, but also on the binder, as well as the 20 preparation method. Several methods have been studied in the literature and can be classified

in three groups:

- Mixing of metal oxide and binder powders (mechanical mixing [9-10], freeze granulation [11-12], spray drying [13-14], spin flash [15-16]...).
- Preparation by precipitation (co-precipitation [17-18], sol-gel [19-20]...).
- 25
- Preparation by impregnation (wet and incipient wetness impregnation...) [21-22].

The Freeze granulation is the most common preparation method at laboratory scale. However, only spray drying, spin flash and impregnation methods can be used at large scale for industrial production.

- Numerous materials based on Ni, Fe, Cu, Mn and Co oxides have been studied and tested as oxygen carriers for CLC, at different working scales (laboratory and pilot scale) [7-10]; [17]; [21-35]. Among all these candidates, NiO/NiAl<sub>2</sub>O<sub>4</sub> oxygen carrier is considered as a model oxygen carrier, due to its high reactivity and its good thermal stability. Indeed, it can work at high temperatures (900-1100°C) owing to the high melting points of NiO and metallic Ni [7], [9], [17], [23]. For these reasons Ni-based oxygen carriers are widely studied at laboratory
- 10 scale, however their use should be minimized at industrial scale due to the high toxicity of this metal and health/safety issues.

Among all the possible metal oxide/binder combinations, some authors studied the use of γ-Al<sub>2</sub>O<sub>3</sub> as a binder for NiO, but they observed that at high operating temperatures (> 800°C) the binder reacts with NiO to form NiAl<sub>2</sub>O<sub>4</sub> [17], [36], [37]. NiAl<sub>2</sub>O<sub>4</sub> is less reactive with fuel
for CLC operations, although it can be partially reduced by the fuel[38]. Thus, the formation of NiAl<sub>2</sub>O<sub>4</sub> reduces the amount of NiO able to deliver oxygen for combustion and so, the global performance of the oxygen carrier. To avoid the decrease of reactivity due to NiAl<sub>2</sub>O<sub>4</sub> formation, Cho *et al.* [39] studied adding nickel in excess to get enough free NiO inside the particle and compensate for the loss of "reactive" nickel species. They showed that the initial
NiO content must be very high (around 80 wt. %) to obtain a NiO free content of 60 wt. %. Gayán *et al.* [7] demonstrated that the formation of the spinel NiAl<sub>2</sub>O<sub>4</sub> depends on the crystalline nature of the binder. They proposed to use a thermal treatment (at 1150°C) to perform the phase transformation of γ-Al<sub>2</sub>O<sub>3</sub> to α-Al<sub>2</sub>O<sub>3</sub> partially reduced the formation of NiAl<sub>2</sub>O<sub>4</sub>.

Furthermore, Jin et al. [40] suggested to use NiAl<sub>2</sub>O<sub>4</sub> directly as a binder instead of Al<sub>2</sub>O<sub>3</sub>. Afterwards, several authors studied the performances of the oxygen carrier NiO/NiAl<sub>2</sub>O<sub>4</sub> and they generally observed high reactivity towards oxidation of different fuels (CH<sub>4</sub>, syngas...) and high stability. The reactivity of Al<sub>2</sub>O<sub>3</sub> (used as binder) with NiO to form NiAl<sub>2</sub>O<sub>4</sub> was 5 studied by Adánez et al. [41] and Dueso et al. [36], [42]. Adánez et al. [41] studied methane combustion (30 vol. % in N<sub>2</sub>) in a CLC plant of 500 Wth during 100 hours. The oxygen carrier used for this study was composed of 18 wt. % of NiO and 82 wt. % of α-Al<sub>2</sub>O<sub>3</sub>. They observed that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reacted partially with NiO at high temperature to produce NiAl<sub>2</sub>O<sub>4</sub>. Moreover, their results revealed that both phases (NiO and produced NiAl<sub>2</sub>O<sub>4</sub>) could react 10 with the fuel. Therefore, NiAl<sub>2</sub>O<sub>4</sub> (used as binder or produced by reaction between NiO and the binder Al<sub>2</sub>O<sub>3</sub>) cannot be considered as an inert material in CLC processes: it is an additional source of oxygen for combustion [43]. The experiments also showed that the relative amount of free NiO in the oxygen carrier (after metal oxide NiO and binder Al<sub>2</sub>O<sub>3</sub> reaction) depends on the oxygen carrier/fuel ratio ( $\phi$ ). Therefore, the production of NiAl<sub>2</sub>O<sub>4</sub> 15 decreased when  $\phi$  decreased. Dueso *et al.* [36] performed thermogravimetric analyses simulating oxidation/reduction cycles with the same oxygen carrier (NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and CH<sub>4</sub> as fuel. They observed that the produced NiAl<sub>2</sub>O<sub>4</sub> was less reactive than NiO. Furthermore, there was a direct relation between oxygen carrier conversion during the reduction step and the proportion of free NiO and NiAl<sub>2</sub>O<sub>4</sub> present in the oxygen carrier after re-oxidation. 80% 20 of nickel reduced in the previous cycle was reoxidized into free NiO while the rest was reoxidised into NiAl<sub>2</sub>O<sub>4</sub> (fresh oxygen carrier composition: 18 wt. NiO, 82 wt. % Al<sub>2</sub>O<sub>3</sub>; final composition: 14.4 wt. % NiO, 77 wt. % Al<sub>2</sub>O<sub>3</sub> and 8.6 wt. % NiAl<sub>2</sub>O<sub>4</sub>). However, these authors have not studied the reactivity of the binder NiAl<sub>2</sub>O<sub>4</sub> alone.

The stability of the nickel aluminate binder used in CLC is a very important parameter to ensure good mechanical strength of the oxygen carrier, and so, limit particles agglomeration

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and fragmentation which could damage the CLC process. In previous work [43], we studied the reactivity of the NiAl<sub>2</sub>O<sub>4</sub> binder by performing oxidation/reduction cycles in a fixed bed reactor with CO as fuel. The major observation was that the binder underwent a structural modification, which modified its reactivity. X-Ray Diffraction analyses showed that peaks

5 related to NiAl<sub>2</sub>O<sub>4</sub> were enlarged and shifted to wide diffraction angles. These results were explained by the gradual decomposition of NiAl<sub>2</sub>O<sub>4</sub> to produce NiO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The purpose of the present work is to study the influence of the preparation method on the

reactivity and stability of the binder  $NiAl_2O_4$  and to quantify the amount of NiO produced by decomposition of the  $NiAl_2O_4$  spinel phase during successive reduction/oxidation experiments.

The reactivity of two different binders was studied in a fixed bed reactor with CO as fuel. The evolution of both binders, in terms of reactivity and structural changes, was also investigated by the measurement of the amount of produced CO<sub>2</sub> during successive cycles.-The materials were analyzed by X-Ray Diffraction and Temperature Programmed Reduction to quantify the amount of NiO present in both materials before and after oxidation/reduction cycles. Additional tests were performed to compare the evolution of nickel aluminate in the binders and in the oxygen carrier (NiO/NiAl<sub>2</sub>O<sub>4</sub>).

#### 2. Experimental section

#### 20 2.1 Materials

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Two NiAl<sub>2</sub>O<sub>4</sub> binders were studied in this work. Cabot Corp. synthetized the first one (noted as B1) by spray pyrolysis of a mixture of nickel nitrate Ni(NO<sub>3</sub>)<sub>2</sub> and gamma alumina  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (spectral 100). Afterwards the mixture was calcined at 800°C and 1000°C (during 24 hours at each temperature). The material was pelletized by *IFP Energies Nouvelles* (Solaize, France),

25 these pellets were ground and sieved to obtain particle sizes between 125 and 300  $\mu$ m.

The preparation of the second binder (noted as B2) was performed by IFP Energies Nouvelles (Solaize, France). A mixture of nickel hydroxide Ni(OH) and gamma alumina  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was calcined at 1200°C during 24 hours. The material was pelletized, ground and sieved to 100 and 300 µm. While calcining binder B1 at 1000°C was enough to obtain nearly pure NiAl<sub>2</sub>O<sub>4</sub>,

5 the second preparation method required an increase of the calcination temperature up to 1200°C for most of the nickel oxide to react with alumina and produce NiAl<sub>2</sub>O<sub>4</sub>. Despite this very high calcination temperature, some NiO was still unreacted (vide infra).

Both binders were characterized by X-Ray Diffraction, analyses were performed in Lindemann tubes with the same quantity of material for each sample. Peak identification was carried out by means of the PDF (Powder Diffraction File) database.

An oxygen carrier NiO/NiAl<sub>2</sub>O<sub>4</sub> was also studied in this work. The composition of the oxygen carrier was 60 wt. % metallic oxide (NiO) and 40 wt. % of binder (NiAl<sub>2</sub>O<sub>4</sub>) and it was supplied by IFP Energies nouvelles (Solaize, France). The particles were first produced by granulation in a Guedu granulator and then calcined at 1200°C for 2 hours under air flow. Only particles in the range between 100 and 300  $\mu$ m were used in this study.

#### 2.2 Experimental set-up

Several oxidation-reduction cycles were performed on all materials in a fixed bed reactor device described in previous work [44], [45]. The binder was placed in a quartz reactor with

20 an inner diameter of 6 mm. The mass introduced (around 0.2 g) was estimated to have a bed height of around 5 mm. The reactor was heated by a tubular furnace (Pekly/Herrmann-Moritz), and the operating temperature was measured by two thermocouples placed above and below the material bed. The fuel used in this study was carbon monoxide ([CO] = 0.55 vol. % in N<sub>2</sub>), and the regeneration step was carried out under air. All gas flow rates were controlled and maintained constant at 50 NL h<sup>-1</sup> by four mass flow controllers (BROOKS 5850). The

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gases concentrations (CO and CO<sub>2</sub>) at the outlet of the reactor were continuously measured by an infrared analyzer NG2000 (CO and CO<sub>2</sub> concentration in the range 0-1 vol. %).

#### 2.3 Experimental methodology

- 5 Oxidation / reduction cycling experiments started with an oxidation step, carried out under air from ambient temperature to the operating temperature (heating rate of  $10^{\circ}$ C min<sup>-1</sup>). When operating temperature was reached, an inerting step was performed under pure N<sub>2</sub> to avoid contact between fuel and air. Afterwards, a mixture of CO/N<sub>2</sub> was injected in the reactor (reduction step) at the operating temperature. The reaction was finished when the CO
- 10 concentration at the reactor's outlet was the same as the inlet concentration. The material was finally cooled down to ambient temperature under inert atmosphere and a new oxidation step could be started (new cycle).

#### 2.4 Sample characterization

15 X-Ray Diffraction (XRD) analyses were performed using a PAN analytical, X'Pert Pro diffractometer operating with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) equipped with a X'Celerator detector. Measurements were achieved for 2 $\theta$  angles in the 10–90° range, by step of 0.02° (220 s per step).

Temperature Programmed Reduction (TPR) experiments were performed in a SDT Q-600

20 thermobalance of TA Instruments. Operating conditions for TPR experiments were: 6 NL  $h^{-1}$  of H<sub>2</sub>/N<sub>2</sub> (5 vol. %) gas flow rate and 2°C min<sup>-1</sup> of temperature heating ramp, from ambient temperature to 1200°C.

Surface area analysis by krypton adsorption were performed on aged samples (after several oxidation-reduction cycles) using a Micromeritics ASAP 2420 apparatus.

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#### 3. Results

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3.1 Evolution of the Total Reduction Capacity (TRC) of binders B1 and B2 as cycles proceed

Two binders stability and reactivity were studied under the same operating conditions: 0.2 g of material (B1 or B2), 900°C, 0.55 vol. % of CO as fuel in  $N_2$ , gas flow rate fixed at 50 NL

h<sup>-1</sup>. The Total Reduction Capacity (TRC) was the parameter chosen to study the evolution of the materials reactivity. TRC corresponds to the number of CO<sub>2</sub> moles produced per gram of material, and it is calculated by the integration of the CO<sub>2</sub> breakthrough curves obtained during the reduction step. Oxidation-reduction cycles were performed with both binders (B1 and B2) until the TRC stabilisation. The results obtained with each binder are represented in figure 1 for the CO<sub>2</sub> concentration curves and in table 1 for the TRC values.

The  $CO_2$  curves obtained on both binders clearly indicate a notable activity of the materials in the oxidation of CO. This activity could partially be explained by the presence of residual NiO in the materials due to the preparation method. However, the amount of  $CO_2$  produced clearly increases as cycles proceed for binders B1 and B2, indicating an evolution of the oxidizing ability of the two binders. Indeed, this TRC increase (table 1) cannot solely be explained by the presence of residual NiO.

As it is observed in table 1, TRC of B1 increases during the first cycles and tends to level off (after 20 cycles), whereas for B2, TRC increases progressively and converges slowly to the maximal TRC (after 80 cycles). If we consider that only  $\frac{1}{4}$  of the oxygen in NiAl<sub>2</sub>O<sub>4</sub> is

- 20 available to oxidize CO (we consider that the oxygen of alumina is not available at all), 75% of this oxygen reacts in B1 during the 20<sup>th</sup> cycle, and 43% for B2 during the 80<sup>th</sup> cycle. During the first reduction cycle, the amount of available oxygen which reacts is equal to 56% and 10% for B1 and B2 respectively. In conclusion, at 900°C, a non-negligible amount of oxygen is available in both binders, which does not only come from residual NiO in the fresh
- 25 materials. The growing amount of available oxygen in the binders as cycles proceed shows

structural modifications of the two binders that depend on the preparation method. Indeed, reactivity and stability of B1 and B2 during oxidation-reduction cycles are not the same. B1 reacts more rapidly than B2 and generates more available oxygen.

#### 5 3.2 Binder characterization by X-Ray Diffraction investigation

Both binders were characterized by X-Ray Diffraction (XRD) to understand the evolution of their structures. XRD analyses were performed on the fresh and the aged binders (after successive cycles). On the fresh binders, two different crystalline phases with cubic structure were identified: NiO (ICDD PDF 00-047-1049) and NiAl<sub>2</sub>O<sub>4</sub> (ICDD PDF 01-081-0715). The 10 principal peaks of NiO and NiAl<sub>2</sub>O<sub>4</sub> are represented in figure 2. The nickel and aluminum were introduced in stoechiometric proportions ( $\frac{Ni}{AI} = 1$ ). XRD patterns show the presence of NiO traces, which leads us to suppose that there are traces of alumina in the mixture. For binder B1, as the diffraction peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are at 2 $\theta$  angles close to the NiAl<sub>2</sub>O<sub>4</sub> ones, it is impossible to distinguish traces of alumina in the fresh material. However, low intensity peaks of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are detected in fresh B2 (ICDD PDF 00-046-1212) (2 $\theta$  = 57.4 and 68.1). The 15 presence of NiO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> traces in this material is due to the preparation method (the

reactants did not fully react to produce NiAl<sub>2</sub>O<sub>4</sub>). The alumina present in B2 is in its alpha polymorph because of the high calcination temperature used for its preparation (1200°C). Indeed, at temperatures higher than 1100°C, there is a phase transformation from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

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As it was observed in previous studies [43], XRD analyses reveal a shift and an enlargement of the peaks related to NiAl<sub>2</sub>O<sub>4</sub> for both aged binders, while NiO peaks remain at the same diffraction angles. These observed shifts reveal a structural modification of both binders as cycles proceed. It seems that the peaks of NiAl<sub>2</sub>O<sub>4</sub> shift towards  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> angles (cubic phase Fd-3m). This observation could be explained by the progressive decomposition of NiAl<sub>2</sub>O<sub>4</sub> to form NiO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Moreover, for the aged binder B2, a diffraction peak (2 $\theta$  = 66.6°) appears corresponding to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This hypothesis seems to be confirmed by the evolution of TRC during experiments, which increases for both binders. Indeed, NiO produced at high temperature is probably the compound which reacts with CO and which progressively increases TRC.

#### 3.3 Quantitative estimation of NiO content in the binders

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#### 3.3.1 Quantification by X-Ray Diffraction analyses: Standard Addition Method

To estimate the NiO content present in each binder, quantitative XRD analyses were performed by using the Standard Addition Method (SAM). This standard method is used in analytical chemistry and has the advantage of eliminating possible matrix effects due to the analyzed sample which can modify the values obtained by quantitative measurements. Particularly in XRD analyses, the shape of the diffraction patterns can be modified by the difference of X-ray adsorption coefficients according to the mass and the composition of the

- 15 sample. This method consists in measuring the response (in this case, the surface area of the integrated NiO diffraction peaks) for each successive addition (known masses) of the analyte NiO to the binder. 3 peaks of NiO were considered to perform the calculations. For example, figure 3 represents an enlargement of four XRD patterns corresponding to the fresh binder B2 and for three NiO additions. For each standard addition, the surface of the NiO peaks 20 increases while the surface of the peaks related to NiAl<sub>2</sub>O<sub>4</sub> remain almost constant.
  - The integration of the NiO peaks is systematically corrected by the integration of six peaks relative to NiAl<sub>2</sub>O<sub>4</sub> for each standard addition.

Finally, the initial mass fraction of NiO of the binders (before addition, noted %NiO(0)) is obtained by representing the ratio between mass fraction of NiO (addition k) calculated from

weighted masses versus exactly the same function calculated by peak integration (equation I). The initial content of NiO (%NiO(0)) is estimated by adjusting the latter to have a straight line with a slope equal to 1 and passing through the origin (first bisector). This mathematical analysis reduces classical calculation errors carried out by estimation of the slope and the interception of a linear curve. A minimum of four points (initial content + 3 additions) were used in calculations for a good precision.

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$$y = \frac{\%NiO(k)}{\%NiO(0)} = f\left(\frac{\%NiAl_2O_4(0)}{\%NiAl_2O_4(k)} \times \frac{\frac{1}{n}\sum_{i=1}^{n}\frac{S_{NiO}^{i}(k)}{S_{NiO}^{i}(0)}}{\frac{1}{m}\sum_{j=1}^{m}\frac{S_{NiAl_2O_4}^{j}(k)}{S_{NiAl_2O_4}^{j}(0)}}\right)$$

Eq. I

S corresponds to the surface of the peak of test k, i the number of peak related to NiO (i=1 to n=3), j the number of peak related to NiAl<sub>2</sub>O<sub>4</sub> (j=1 to m=6). The initial experiment (without addition) is named 0.

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This procedure was used for the four studied samples (fresh B1 and B2 and after oxidationreduction cycles). The best fit lines obtained have in all cases a correlation coefficient  $(R^2)$ higher than 0.999 (figure 4).

Table 2 shows the NiO mass fraction of the four samples (fresh and aged B1 and B2) estimated by using the Standard Addition Method

The results presented in table 2 confirm the observations obtained from TRC measurements. The initial NiO contents in the fresh binders are not equal: B1 contains more residual NiO than B2, which can explain the higher value of TRC obtained during the first cycle (3.17 moles CO<sub>2</sub>/mg for B1 against 0.59 moles CO<sub>2</sub>/mg for B2). The NiO content of the two

20 binders increases as cycles proceed and can be explained by a decomposition of nickel aluminate to form NiO and probably alumina. These results show that nickel aluminate is reacting with the fuel from the first cycle (0.75 and 0.23 moles of NiO per milligram of B1 and B2 respectively).

#### 3.3.2 NiO content estimation by Temperature Programmed Reduction measurements

5 To confirm the X-Ray Diffraction data, Temperature Programmed Reduction (TPR) experiments were performed with the same samples (fresh and aged B1 and B2). These experiments consist in the reduction of the different crystalline phases contained in the two binders (NiO and NiAl<sub>2</sub>O<sub>4</sub>) which occurs at different temperatures under a H<sub>2</sub> gas flow. Alumina is probably present in the sample, but does not react with H<sub>2</sub>. TPR investigations were conducted in a thermobalance, where mass variations were measured as a function of temperature with a slow ramp of temperature to ensure separation of the two reductions of NiO and NiAl<sub>2</sub>O<sub>4</sub>. The operating conditions were: 8 mg of sample, gas flow rate 6 NL h<sup>-1</sup>, 5 vol. % H<sub>2</sub> in nitrogen, 2°C min<sup>-1</sup> heating rate, from ambient temperature to 1200°C. Results obtained for the fresh and the aged B1 and B2 are presented in figure 5.

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Figures 5 shows the mass variation and its first derivative as a function of temperature for each studied material. In all cases we observe a first mass loss between 350° and 600°C corresponding to the reduction of NiO and a second one at temperatures higher than 600°C corresponding to the reduction of NiAl<sub>2</sub>O<sub>4</sub>. The NiO content of each material have been estimated from this data and are given in table 2.

#### 3.3.3 Discussion

Both quantitative X-Ray Diffraction analyses and TPR experiments confirm that the NiO content present in both binders increases as oxidation-reduction experiments are performed.

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From these results, the partial decomposition of the spinel phase  $NiAl_2O_4$  to form NiO and  $Al_2O_3$  is demonstrated and quantified. This decomposition and its kinetics depend on the binder's preparation method. Indeed, binder B2 obtained with a higher calcination temperature (1200°C) generates lower quantities of available oxygen than binder B1. The

5 binder B2 is also less reactive. These observations can be explained by the fact that the surface available for reaction is higher for B1 (31.5 m<sup>2</sup> g<sup>-1</sup>) than for B2 (2.9 m<sup>2</sup> g<sup>-1</sup>) (measured by krypton adsorption after several oxidation-reduction cycles).

The TPR analyses indicate the same trend. The reduction reaction of NiO present in the two binders started approximately at the same temperature (around  $350^{\circ}$ C), whereas NiAl<sub>2</sub>O<sub>4</sub> starts to reduce around 600°C for B1 and around 700°C for B2. In both cases (binders B1 and B2), the peaks related to NiAl<sub>2</sub>O<sub>4</sub> reduction shift to higher temperatures after numerous cycles. These results could be the consequence of accessibility decrease of reaction sites (NiAl<sub>2</sub>O<sub>4</sub>) due to the presence of alumina and nickel. Some authors [46] observed an influence of the calcination temperature on the final reactivity of the material. They postulate

- 15 that a higher calcination temperature leads to a less reactive binder. Moreover, these shifts could not be explained by a diffusion limitation in the particles. Han et al. [47] did a comprehensive analysis of the diffusion limitations of a very similar system and demonstrated that the internal diffusion resistance was significant only for particles with mean diameter greater than 1.0 mm.
- Gayán *et al.* [10] performed comparative reactivity studies of different NiO-based oxygen carriers prepared by dry impregnation and supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (21 wt. % of NiO) or on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (11-38 wt. % of NiO). They observed that using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a binder, most of the impregnated NiO reacted to form NiAl<sub>2</sub>O<sub>4</sub>, therefore the reactivity of the oxygen carrier decreased. On the other side, if  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as binder, the reactivity between the

alumina and NiO was decreased, less  $NiAl_2O_4$  was produced, and the reactivity of the oxygen carrier was higher.

Our present results show that nickel aluminate partially decomposes to form nickel oxide and alumina (NiAl<sub>2</sub>O<sub>4</sub> = NiO+Al<sub>2</sub>O<sub>3</sub>) under reducing conditions. This chemical decomposition

- 5 seems to reach a thermodynamic equilibrium after several cycles. At the beginning (in the fresh binder) the reaction quotient is almost zero (no products) and NiO and Al<sub>2</sub>O<sub>3</sub> are preferably generated (until the reaction quotient is inferior to the equilibrium constant). Moreover, during the reduction step, the reduction of nickel oxide (to produce metallic Ni) leads to a decrease of the reaction quotient and so, to the decomposition of nickel aluminate.
- 10 In these operating conditions, the reaction is slow (in terms of kinetics), because 20 and 80 successive cycles are necessary to reach the equilibrium for binder B1 and B2 respectively.

#### 3.4 Binder evolution in the oxygen carrier NiO/NiAl<sub>2</sub>O<sub>4</sub>

To check if results obtained with the binder  $(NiAl_2O_4)$  could be extrapolated to the oxygen

- 15 carrier (NiO/NiAl<sub>2</sub>O<sub>4</sub>), a long reduction cycle (8 hours) at 900°C was performed with the oxygen carrier. The aim is to sufficiently reduce the oxygen carrier to observe NiAl<sub>2</sub>O<sub>4</sub> reduction, despite the high content of NiO present in the material (60 wt. % of NiO). After reduction, the obtained material was oxidized and analyzed by XRD. Figure 6 shows the XRD pattern (enlargement between 57 and 69°) of the fresh and the reduced NiO/NiAl<sub>2</sub>O<sub>4</sub>.
- 20 The figure reveals (as with the binder alone) that peaks relative to NiO are at the same diffraction angles before and after oxidation reduction cycles, whereas peaks related to NiAl<sub>2</sub>O<sub>4</sub> are enlarged and shifted to wider diffraction angles. As it was previously deduced for the binder, this shift shows a decomposition of NiAl<sub>2</sub>O<sub>4</sub> to form NiO and Al<sub>2</sub>O<sub>3</sub>. These results demonstrate that the binder in the oxygen carrier NiO/NiAl<sub>2</sub>O<sub>4</sub> can also react with the fuel

during the reduction phase, producing additional NiO. The major role of the binder is to ensure the stability of the oxygen carrier and good mechanical properties. However the binder reactivity with the fuel modifies the oxygen carrier performance.

#### 5 4. Conclusion

Oxidation-reduction cycles performed on both binders showed that they cannot be considered as inert materials, because they react with the fuel. The evolution of the Total Reduction Capacity revealed that the reactivity of the two binders is different, and it depends on their synthesis method. The first binder (B1) has a higher initial content of NiO (5.6 wt. % by XRD

- 10 and 6.2 wt. % by TPR) and its Total Reduction Capacity increases during the first cycles and reaches a maximum after 20 oxidation-reduction cycles. The aged binder has a final amount of 17.3 wt. % calculated by XRD, 24% by TPR. An increase of the NiO content is also observed on the second binder, from 1.7% (XRD and TPR) to 11.8 % (XRD); 15.8% (TPR). The Total Reduction Capacity levels off after 80 cycles. Two different methods have been
- 15 used in this work to calculate the NIO content present in these materials. Results obtained by both methods are in good agreement for lower contents of NiO and their deviations increase moderately for higher contents. These results are in good agreement with experimental measurements of Total Reduction Capacity.

The increase of NiO present in binder is explained by the progressive decomposition of NiAl<sub>2</sub>O<sub>4</sub> to produce NiO and Al<sub>2</sub>O<sub>3</sub>. Moreover, the decomposition of the binder as cycles proceed, was also observed on the oxygen carrier (NiO/NiAl<sub>2</sub>O<sub>4</sub>). This study revealed the influence of the preparation method on the binder final reactivity.

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