

Effect of support on reactivity and selectivity of Ni-based oxygen carriers for Chemical-Looping Combustion

Pilar Gayán*, Luis F. de Diego, Francisco García-Labiano, Juan Adánez, Alberto Abad, and Cristina Dueso

Department of Energy and Environment, Instituto de Carboquímica (C.S.I.C.)

Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Phone number: +34 976 733 977

Fax number: +34 976 733 318

E-mail: pgayan@icb.csic.es

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Corresponding Author. Tel.: +34-976-733977; fax: +34-976-733318; *E-mail address:* pgayan@icbc.csic.es (P. Gayan)

Abstract

Different Ni-based oxygen carriers were prepared by dry impregnation using γ -Al₂O₃ as support. The reactivity, selectivity during methane combustion, attrition rate and agglomeration behaviour of the oxygen carriers were measured and analyzed in a termogravimetric analyzer and in a batch fluidized bed during multicycle reduction-oxidation tests.

Ni-based oxygen carriers prepared on γ - Al_2O_3 showed low reactivity and low methane combustion selectivity to CO_2 and H_2O , because most of the impregnated NiO reacted to NiAl_2O_4 . To avoid or to minimize the interaction of NiO with alumina some modifications of the support via thermal treatment or chemical deactivation with Mg or Ca oxides were analyzed. Thermal treatment of γ - Al_2O_3 at 1150°C produced the phase transformation to α - Al_2O_3 . Ni-based oxygen carriers prepared on α - Al_2O_3 , MgAl_2O_4 , or CaAl_2O_4 as support showed very high reactivity and high methane combustion selectivity to CO_2 and H_2O because the interaction between the NiO and the support was decreased. In addition, these oxygen carriers had very low attrition rates and did not show any agglomeration problems during operation in fluidized beds, and so, they seem to be suitable for the chemical-looping combustion process.

Keywords: chemical-looping combustion, oxygen carrier, nickel, CO_2 capture.

1. Introduction

It is well known that CO_2 emissions affect the climate of Earth. Therefore, there is a need to decrease CO_2 emissions or to even stop production of CO_2 in combustion processes. A novel combustion process using chemical-looping combustion (CLC) has been proposed to separate CO_2 efficiently during combustion and some countries have searched actively for such technologies [1]. The key to the success of implementing a CLC system (see Figure 1) is the development of a suitable oxygen carrier, consisting of an active metal oxide component and a support material. The active metal oxide oxidizes the fuel in the absence of a flame in the reduction reactor (fuel reactor) and the reduced metal is oxidized by the

oxygen of the air in the oxidation reactor (air reactor). The flue gas leaving the air reactor contains N_2 and un-reacted O_2 . The exit gas from the fuel reactor contains CO_2 and H_2O , which are kept apart from the rest of the flue gas. After water condensation, almost pure CO_2 can be obtained with little energy loss for component separation. CLC has the advantages of saving energy, reducing NO_x , and increasing by 10-20% the overall efficiency when compared to traditional combustion processes with CO_2 capture [2, 3]. The oxygen carrier should provide the following properties: high oxygen transport capacity that depends on the metal oxide used and its content in the oxygen carrier; high reactivity through cycles to reduce the solids inventory; high resistance to attrition to minimize losses of elutriated solid; complete fuel conversion to CO_2 and H_2O ; negligible carbon deposition what would release CO_2 in the air reactor; and good properties for fluidization (no presence of agglomeration). In addition, other characteristics such as easy preparation to reduce costs are interesting. Iron, nickel, copper, and manganese have been selected as the most promising active metals to be used in a CLC process [4-6]. Also the selection of a suitable support material is very important.

Ni-based oxygen carriers allow working at high temperatures (900-1100°C) in a CLC process with full CH_4 conversion, although thermodynamic restrictions result in a small presence of CO and H_2 in the gas outlet of the fuel reactor [7]. There are in the literature many works studying Ni-based oxygen carriers [5-20], and in some of these works alumina was used as support [5-7, 11-20]. Mattisson et al. [7] found that the Ni spinel ($NiAl_2O_4$) was present when using high calcination temperatures ($T > 800^\circ C$) due to the solid-solid reaction of NiO with Al_2O_3 . This aluminate can react with methane in the reduction reaction of the oxygen carrier, but the thermodynamics of this reaction show a low methane

conversion to $\text{CO}_2+\text{H}_2\text{O}$ at temperatures typical for the CLC process (gas conversion < 95%, $T > 800^\circ\text{C}$). However, thermodynamics also shows that the conversion of methane to $\text{CO}_2+\text{H}_2\text{O}$ for NiO is higher than 98% at temperatures lower than 1150°C . Low selectivity to $\text{CO}_2+\text{H}_2\text{O}$ during methane combustion implies that high amounts of $\text{CO}+\text{H}_2$ will be produced in the CLC process, and this is an undesirable situation. It is possible to increase the quantity of the free active metal oxide in the oxygen carrier by using an adequate support that minimizes the interaction of metal oxide and support. Therefore, it seems that an optimized Ni-Al oxygen carrier for the CLC process should have the biggest fraction of the Ni introduced as free NiO phase instead of as the spinel form.

In the Grangemouth Capture Project (GRACE) [6], three different methods of preparation of oxygen carriers were used: freeze-granulation, mechanical mixing and extrusion, and impregnation. It was found that most of the oxygen carriers prepared by mechanical mixing had an unacceptable reactivity and/or mechanical properties [5]. On the other hand, oxygen carriers prepared by impregnation or freeze granulation exhibited high reactivities and good chemical and mechanical properties [4, 14, and 21].

In this paper, Ni-based oxygen carriers were prepared by dry impregnation using alumina as support. Different routes to minimize the NiO interaction with the alumina were studied using γ -alumina and introducing some modifications via thermal treatment or chemical deactivation with Mg or Ca oxides. The study focuses on the analysis of the parameters of the oxygen carriers which are important for their use in the CLC process, such as reactivity in redox cycles, selectivity to complete methane combustion, mechanical strength of particles, and attrition and agglomeration behaviour in fluidized beds.

2. Experimental

2.1. Preparation of oxygen carriers

Different Ni-based oxygen carriers were prepared by dry impregnation using different supports: γ -alumina, α -alumina, magnesium aluminate, and calcium aluminate.

Supports

Commercial γ -Al₂O₃ (Puralox NWA-155, Sasol Germany GmbH) particles of +100-300 μ m, with a density of 1.3 g/cm³ and a porosity of 55.4%, and α -Al₂O₃ particles of +100-300 μ m, obtained by calcination of the γ -Al₂O₃ particles at 1150°C during 2 hours, with a density of 2 g/cm³ and a porosity of 47.3%, were used as support to prepare different Ni-based oxygen carriers.

Commercial MgAl₂O₄ spinel (Baikowski S30CR, Baikowski Chimie, France), with $d_p < 10$ μ m, and 10 wt% of graphite (as a high-temperature pore forming additive) was converted by water addition into a paste of suitable viscosity to be extruded in a syringe, obtaining cylindrical extrudates of about 2 mm diameter. These extrudates were softly dried at 80 °C overnight, cut at the desired length (about 4 mm), and sintered at 1200 °C for 6 h in a muffle oven. The pellets were milled and sieved to obtain particles of 100-500 μ m, with a density of 1.4 g/cm³ and a porosity of 59.2 %, to be impregnated.

In a similar way, CaAl₂O₄ support was obtained by mixing the correct amounts of commercial γ -Al₂O₃ (Panreac, $d_p < 10\mu$ m) with CaCO₃ (Panreac, $d_p < 10\mu$ m) and graphite. The mixture was converted by water addition into a paste of suitable viscosity to be extruded into cylinders. The sample was dried (80 °C overnight), and calcined at 1400°C for 18 h to complete the solid reaction between the two oxides and to increase the crushing

strength of the final product. Finally, the pellets were milled and sieved to obtain particles of 100-500 μm , with a density of 1.3 g/cm^3 and a porosity of 30.1 %.

Dry impregnation

Ni-based oxygen carriers were prepared by addition of a volume of a saturated solution (20°C, 4.2 M) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.5 % Panreac) corresponding to the total pore volume of the support particles. The aqueous solution was slowly added to the support particles, with thorough stirring at room temperature. The desired active phase loading was achieved by applying successive impregnations 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 the desired calcination temperature. Oxygen carriers impregnated on $\gamma\text{-Al}_2\text{O}_3$ with a NiO weight content of 21% and oxygen carriers impregnated on $\alpha\text{-Al}_2\text{O}_3$ with NiO weight contents ranging from 11 to 38 % were prepared.

Other oxygen carriers were prepared by dry impregnation on alumina modified by thermal or chemical pretreatment. The thermal treatment was carried out by sintering the $\gamma\text{-Al}_2\text{O}_3$ in a furnace at different temperatures between 800 and 1100°C during two hours. The support was then impregnated with nickel nitrate solution and calcined as indicated above.

The chemical pretreatment consisted in precoating the support with MgO or CaO. The precoating was carried out by dry impregnation on $\gamma\text{-Al}_2\text{O}_3$ with (20°C, 3.5 M) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.5 % Panreac) or (20°C, 4.8 M) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (>99.5 % Panreac) solutions and forming the corresponding aluminates by sintering at high temperature (800°C for Mg and 1100°C for Ca) during 1 hour in air atmosphere. The modified alumina support was later impregnated with the nickel nitrate solution and calcined at 950°C as commented before. Table 1 shows all the different oxygen carriers prepared. The samples

were designated with the chemical symbols referred to the metal oxides followed by the weight content, and the inert used as support. In brackets is shown the calcination temperature of the support before the impregnation with the nickel solution. The last number is the sintering temperature of the oxygen carrier after introducing the nickel. As examples, “Ni21- γ Al 1000” indicates an oxygen carrier with 21 wt. % of NiO prepared by dry impregnation on γ -Al₂O₃ and sintered at 1000°C, and “Ni20-Mg5 γ Al (800) 950” indicates an oxygen carrier with 20 wt. % of NiO prepared by dry impregnation on γ -Al₂O₃ (which was previously precoated with 5wt% of MgO and calcined at 800°C) and finally it was sintered at 950°C.

2.2 Oxygen carrier characterization

The oxygen carriers were physically and chemically characterized by several techniques. The bulk density of the oxygen carrier particles was calculated weighting a known volume of solid and assuming that the void was 0.45 corresponding to loosely packed bed. The force needed to fracture a particle was determined using a Shimpo FGN-5X crushing strength apparatus. The mechanical strength was taken as the average value of at least 20 measurements. Support porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by powder X-ray diffraction (XRD) patterns acquired in an X-ray diffractometer Bruker AXS D8ADVANCE using Ni-filtered Cu K α radiation equipped with a graphite monochromator.

2.3. Reactivity tests in TGA

Reactivity tests of the oxygen carriers were carried out in a thermogravimetric analyzer (TGA), CI Electronics type, described elsewhere [5]. For the experiments, the oxygen

carrier was loaded in a platinum basket and heated to the set operating temperature in air atmosphere. After weight stabilization, the experiment was started by exposing the oxygen carrier to alternating reducing and oxidizing conditions.

The reducing gas was saturated in water by bubbling it through a water containing saturator at the selected temperature to reach the desired water concentration. The gas selected for the reducing experiments was composed by 15 vol. % CH₄, and 20 vol. % H₂O (N₂ balance) and the gas used for oxidation was 100 vol. % air. To avoid mixing of combustible gas and air, nitrogen was introduced for two minutes after each reducing and oxidizing period. The experiments were usually carried out at 950 °C.

2.4 Batch fluidized bed tests

The reduction-oxidation multi-cycle tests carried out in a fluidized bed reactor allow determining the gas product distribution during the reaction of an oxygen carrier in similar operating conditions to those existing in a CLC process. The fluidization behavior of the different materials with respect to the attrition and agglomeration phenomena can also be analyzed.

The experimental set-up used for testing the oxygen carriers was shown elsewhere [22]. It consists of a system for gas feeding, a fluidized bed reactor (FB), a two way system to recover the solids elutriated from the FB, and a gas analysis system. The gas feeding system had different mass flow controllers connected to an automatic three-way valve. The FB reactor of 54 mm D.I. and 500 mm height, with a preheating zone just under the distributor, was fed with ~400 g of oxygen carrier. The entire system was inside an electrically heated furnace. The reactor had two connected pressure taps in order to measure the differential pressure drop in the bed. Two hot filters located downstream from the FB

recovered the solids elutriated from the bed during the successive reduction-oxidation cycles, which allowed obtaining elutriation data at different times or number of cycles. Different gas analyzers continuously measured the gas composition. CO, CO₂, and CH₄ were determined in an infrared analyzer (in dry basis, after water condensation), the O₂ in a paramagnetic analyzer, and the H₂ by gas conductivity. A FTIR analyzer measured the H₂O concentration. For better data analysis, the gas concentrations versus time profiles measured were corrected for gas flow dispersion through the sampling line and analyzers.

The tests were normally carried out at 950°C with an inlet superficial gas velocity into the reactor of 0.1 m/s. The composition of the gas was 25 vol. % CH₄ in N₂ during reduction and 10-15 % O₂ in N₂ during oxidation. The reduction periods were varied between 120 and 300 s. The oxidation periods necessary for complete oxygen carrier oxidation varied between 600 and 1800 s. To avoid mixing of CH₄ and O₂, nitrogen was introduced for two minutes after each reducing and oxidizing period. Each oxygen carrier was exposed to more than 50 reduction/oxidation cycles.

3. Results and discussion

Table 1 shows the density, the mechanical strength, and the crystalline phases of the fresh oxygen carriers. The oxygen carriers prepared using γ -alumina as support had a lower density than the oxygen carriers prepared using α -alumina. The XRD patterns obtained showed the formation of nickel-aluminum mixed oxides in the majority of the oxygen carriers.

3.1 Reactivity results

The TGA tests allowed us to analyze the reactivity of the oxygen carriers under well-defined conditions, and in the absence of complex fluidizing factors such as those derived from particle attrition and interphase mass transfer processes. Five cycles of reduction and oxidation were carried out to determine the reactivity of the carriers. The carriers usually stabilized after the first cycle, for which the reduction reaction rate was slower. The oxygen carrier reactivity corresponding to the cycle 5 was used for comparison purposes. Reactivity data were obtained in TGA tests from the weight variations during the reduction and oxidation cycles as a function of time. To convert weight data into oxygen carrier conversions the involved chemical reactions were considered.

The effect of the calcination temperature of oxygen carriers impregnated on γ -Al₂O₃ was first investigated. Figure 2 shows the reduction and oxidation reactivities of these carriers calcined at different temperatures. The Ni-based oxygen carriers impregnated on γ -Al₂O₃ and calcined at temperatures higher than 950°C showed very similar reactivities, but these reactivities were low during all the reduction reaction. Only the sample calcined at 800°C showed a high reactivity in the reduction reaction. It should be pointed out that the TGA test of this sample was carried out at 800°C. In another test run at 950°C, not shown here, the reactivity of the sample calcined at 800°C was decreasing with cycles until reaching the same low reactivity of the sample calcined at 950°C. The low reactivity of the carriers of NiO on γ -Al₂O₃ was due to the solid state reaction between the NiO and the γ -Al₂O₃ to form NiAl₂O₄. Cheng et al. [23] commented that when a γ -Al₂O₃ support is impregnated with Ni(II) ions and heated to a temperature of about 600°C, two reactions occur concurrently on the alumina surface; one produces a surface spinel somewhat like NiAl₂O₄

and the other gives segregation of free nickel oxide. The nickel oxide supported on alumina surface is in weak interaction with alumina surface and easily reducible at temperatures between 350 and 700°C (by H₂), while the nickel surface compound like NiAl₂O₄ is in strong interaction with alumina and difficult to be reduced below 700°C in H₂. The proportion of nickel surface compound to free nickel oxide increases with increasing calcination temperature.

From the results shown in Figure 2, it seems that in the samples calcined at temperatures higher than 950°C all the impregnated NiO is combined with the alumina to form the aluminate, as it is shown in the XRD patterns (see Table 1). The reaction rate of methane with nickel aluminate is slow compared to free nickel oxide. As a consequence, the carrier conversion reached in the first minutes of the reduction reaction was far from being completed (below 80%). On the other hand, as can be also observed in Figure 2, all oxygen carriers exhibited very high reactivity during oxidation, and this reactivity was not affected by the calcination temperature.

The effect of the thermal pretreatment of the support was also investigated. Figure 3 shows the reactivity of several carriers where the γ -Al₂O₃ was previously sintered at a high temperature in order to produce the deactivation of the γ -Al₂O₃, and in this way to decrease the interaction between the NiO and the support to form the aluminate. It was observed that the sintering of the support before impregnation improved the oxygen carrier reduction reactivity. Moreover, it was found that the oxygen carrier with the support sintered at 1150°C (γ Al (1150), named as α Al) had the highest reduction and oxidation rates (carrier conversion > 95% in less than 1 minute). This result can be explained by the sintering of γ -Al₂O₃ at temperatures higher than 1150°C produced the phase transformation to α -Al₂O₃,

and the interaction between the metal oxide and the support is reduced using the α - Al_2O_3 . Therefore samples prepared with α - Al_2O_3 had free NiO (see Table 1). The presence of an important fraction of active NiO was also visually confirmed because the oxygen carriers prepared with α - Al_2O_3 were green colored compared to blue samples containing high fractions of NiAl_2O_4 [24], as it was the case of the carriers prepared with γ - Al_2O_3 .

In a previous work, the effect of the NiO content on the reactivity of the oxygen carriers was studied using γ - Al_2O_3 (12-30 wt. % NiO) and α - Al_2O_3 (6-16 wt. % NiO) as supports [11]. It was found that the NiO contents hardly affected the reduction and oxidation reactivities. In this work, the amount of NiO impregnated on α - Al_2O_3 was increased up to 38% using several impregnation steps, and the reactivities of the samples were subsequently measured. Figure 4 shows the reactivity results of the carriers with the different NiO contents. The oxygen carriers had very high reactivities both during the reduction and the oxidation reactions and the carrier conversions were nearly complete in less than 1 minute; which is indicative of almost all the NiO content in these carriers was as free NiO (as commented before, the free NiO reacts faster than the NiAl_2O_4). It can be also observed that the NiO content did not affect to the reduction and oxidation reactivities of the carriers. However, an increase in the NiO content means an increase in the amount of methane converted for the same sample weight.

In order to minimize the interaction of the nickel with the support, other routes of deactivation of the support can be used. It is well known [25, 26] that the proportion of nickel surface compound to free NiO might be lowered through an addition of other metal ions prior to Ni(II) on the alumina surface. A cation of alkaline earth oxides (Mg or Ca) could also interact with the alumina surface during thermal treatment of the sample

containing such metal nitrates, and could serve as a competitor to interact with the alumina when they coexist with Ni (II) ions [23].

Villa et al. [12] found that the presence of Mg in Ni-Al-O mixed oxides limits the sintering of the NiO and stabilizes the Ni²⁺ in the oxide phase. Also, Zafar et al. [13] found that using a NiO/MgAl₂O₄ oxygen carrier there was not or a limited interaction between the support and the active phase during cycling experiments.

In this work, chemical modification of the support was studied using γ -Al₂O₃ precoated with different amounts of MgO or CaO to form the alkaline earth aluminates. In order to compare the effect of the fraction of these oxides, the pure aluminates (MgAl₂O₄ and CaAl₂O₄) were also used as supports.

When the support is precoated with MgO at high calcination temperature, there is a solid-solid reaction between the MgO and the alumina in the support pore surface, forming a stable protective layer of spinel at the MgO-support interface. This protective layer is responsible for eliminating the chemical interaction between the active components of the support and the NiO, after its deposition on the MgO precoated support [27]. The fraction of free NiO is increased with increasing the MgO loading. This shows that enough MgO on the support is essential for having a perfect NiO-MgO solid solution and for stabilizing nickel in the carrier.

Figure 5 shows the reactivity of the carriers precoated with MgO, the reactivity of the carrier using pure MgAl₂O₄ as support, and for comparison purposes the reactivities of the carriers prepared using γ - and α - alumina as support. The carrier prepared using the spinel MgAl₂O₄ as support showed a high reaction rate although the carrier conversion reached only a value of 75%. After that point the reaction rate was very slow. The XRD analysis of

the fresh sample showed only free NiO and MgAl₂O₄, although the phase MgAl₂O₄ is undistinguished of the NiAl₂O₄ by XRD analysis. The samples prepared using precoated γ -alumina with MgO showed an improvement of the reduction reaction reactivity compared with the carrier prepared without MgO. However, the reduction reactivity was lower than the reactivity of the carriers prepared on MgAl₂O₄ and α -Al₂O₃ maybe because the amount of MgO was not enough to avoid the interaction of the NiO with the support to form the NiAl₂O₄ compound (see Table 1). The results using 5 or 9 wt. % of MgO were similar for this reason. Moreover, the improvements in the reduction reactivities were similar to those obtained with the thermal pre-treatment of the support at 800°C (see Figure 3). It must be pointed out that in the preparation of these carriers, after the impregnation with magnesium nitrate, a calcination step at 800°C was carried out to form the aluminate compound. Therefore, it can be concluded that precoating with weight fractions of MgO lower than 9% has little effect on the carrier reactivity. On the contrary, when the amount of MgO is high enough to transform all the γ -Al₂O₃ into the spinel MgAl₂O₄ the initial reactivity is increased ($t < 1$ min).

Figure 6 shows the reactivity of the carriers precoated with CaO, the reactivity of the carrier using CaAl₂O₄ as support, and for comparison purposes the reactivities of the carriers prepared with γ - and α - alumina as supports. The carrier prepared by precoating the γ -Al₂O₃ with 9 wt% of CaO showed an important enhancement of the reduction reactivity. This improvement cannot be explained only by the effect of the thermal treatment of the γ -alumina at 1100°C (see Figure 4, sample Ni16 γ Al (1100)), but also by the interaction of calcium with alumina. However, higher reduction reactivity was obtained with the carrier prepared using pure CaAl₂O₄ as support. The XRD analysis of this carrier showed that most

of the NiO impregnated was as free NiO. The reduction reactivity of this sample was similar to that obtained with the oxygen carrier prepared using α -Al₂O₃ as support.

Figures 5 and 6 also show that the oxygen carriers prepared by chemical deactivation of the γ -Al₂O₃ exhibited very high reactivities during oxidation reaction. As the oxidation reactivities were in all carriers very high, the effect of the different supports and treatments on the oxidation reactivity of the oxygen carriers cannot be well analyzed. However, it seems that the oxidation reaction was not affected by the precoating of the support with MgO or CaO.

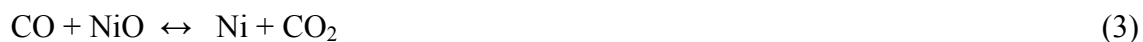
The TGA results showed that carriers prepared by dry impregnation on α -Al₂O₃, MgAl₂O₄ and CaAl₂O₄ have a very high reactivity for the CLC process.

3.2 Selectivity results

Reduction-oxidation multicycles with the prepared Ni-based oxygen carriers were carried out in a batch fluidized bed to determine the gas product distribution in similar conditions to those found in a CLC process and to analyze the fluidization behavior of the oxygen carriers with respect to attrition and agglomeration phenomena.

The main reactions happening with different contribution in a batch fluidized bed during the oxygen carrier reduction period are:

Oxidation



Partial oxidation



Catalytic reforming



Catalytic decomposition



Methanation



Carbon gasification



Water gas shift



And during the oxygen carrier oxidation period:



Taking into account these reactions, methane conversion is defined as:

$$X_{\text{CH}_4} = 1 - \frac{\text{mol}_{\text{CH}_4, \text{out}}}{\text{mol}_{\text{CH}_4, \text{in}}} \quad (15)$$

Being $\text{mol}_{\text{CH}_4, \text{in}}$, the moles of methane fed to the reactor and $\text{mol}_{\text{CH}_4, \text{out}}$, the moles of methane leaving the reactor. Similarly, the selectivity to gas i , is defined as the ratio between the moles of gas i leaving the reactor and the moles of methane fed to the reactor.

Figure 7 shows the gas product distribution during the reduction and oxidation reactions with the carrier prepared on γ -Al₂O₃ without any modifications (Ni21- γ Al 950). CO₂, H₂O, CO, and H₂ were formed immediately after introduction of CH₄ into the reactor. The CH₄ conversion was complete, since no detectable CH₄ concentration was measured during reduction, although high H₂ and CO concentrations were present in the gas outlet together with CO₂ and H₂O during all the reduction period. This behavior indicated that the reduction process had an important selectivity towards the formation of H₂ and CO. During the oxidation period, CO and CO₂ were formed by the combustion of C generated during the reduction period.

With the carrier prepared on α -Al₂O₃ (Ni11- α Al 950), see Figure 8, CO₂ and H₂O were formed immediately after the CH₄ feeding, and no CH₄ was detected during the whole carrier reduction time. During the first period, CO and H₂ concentrations were corresponding to the equilibrium at the reaction temperature. After that, CO₂ and H₂O concentrations decreased, whereas the concentrations of CO and H₂ increased, indicating that the reduction process was mainly selective towards the formation of H₂ and CO. It seems that the CO and H₂ generation rates were higher than the oxidation rates in the last part of the reduction reaction period, where most of the Ni content in the oxygen carrier was as metallic Ni. In the initial stages of the oxygen carrier reduction, which will correspond to high solid circulation rates between the air and fuel reactor, CH₄ was almost completely converted to CO₂ and H₂O.

Figure 9 shows the gas product distribution during the reduction reaction working with the oxygen carrier Ni16- γ Al (1100) 950. With this carrier, the gas product distribution was

similar to the one measured with the carrier Ni11- α Al 950, but the reduction time with almost complete CH₄ conversion to CO₂ and H₂O was smaller.

The effect of the chemical deactivation of the support on the gas product distribution during the reduction and oxidation reactions was studied with the oxygen carrier prepared precoating the support with CaO and using CaAl₂O₄ and the spinel MgAl₂O₄ as supports. Figure 10 shows the outlet concentrations of CH₄, CO₂, CO, and H₂ in dry basis, during the reduction period for a typical cycle working with the carrier prepared by dry impregnation using the spinel MgAl₂O₄ as support. CO₂ and H₂O were formed just immediately after the introduction of CH₄ to the reactor, and no CH₄ were observed during most of the reduction period, thus indicating that CH₄ conversion was almost complete and mainly selective towards CO₂ and H₂O, (CO and H₂ concentrations were those corresponding to the thermodynamic equilibrium of NiO-CH₄ at the reaction temperature). Only when most of the oxygen carrier was reduced, the CO₂ and H₂O concentrations decreased and the formation of CO and H₂ increased. In the oxidation period, it was observed that the CO and CO₂ concentrations were zero since the reduction period was stopped before starting the CH₄ decomposition.

Figure 11 shows the results obtained with the oxygen carrier Ni14-Ca9 γ Al (1100) 950. As can be observed a poor selectivity to CO₂ and H₂O was found with this carrier. In addition, it can be seen comparing these results with those obtained with the carrier Ni16- γ Al (1100) 950, Fig. 9, that the addition of CaO increased the C formation during the reduction reaction, as it is inferred by the high CO₂ and CO concentrations measured during the oxidation period.

The gas product distribution, not showed here, working with the carrier prepared over the CaAl_2O_4 support (Ni11-CaAl₂O₄ 950) was similar to the one found with MgAl_2O_4 spinel.

These results show that oxygen carriers with high contents of free NiO have high reactivity and high methane combustion selectivity to CO_2 and H_2O . The NiO interaction with the alumina forms NiAl_2O_4 that affects negatively to the methane combustion selectivity to CO_2 and H_2O during the reduction reaction, since the kinetics of oxygen release by NiAl_2O_4 is slower than the one of NiO. As a consequence less oxygen is available for full oxidation of H_2 and CO (reactions 2 and 3).

The minimization of this Ni-Al interaction can be achieved by thermal or chemical treatment of the support. Oxygen carriers prepared by dry impregnation over α -alumina, MgAl_2O_4 or CaAl_2O_4 have high content of free NiO, see Table 1, and so these carriers have high selectivity to CO_2 and H_2O during the combustion of CH_4 . For that reason, it seems that they are the most suitable materials for the CLC process.

3.3 Attrition and agglomeration

It is important that oxygen carriers maintain high reactivity and particle integrity for many red-ox cycles. The multi-cycle tests carried out in the batch fluidized bed were useful to determine the fluidization behavior of the oxygen carriers with respect to the attrition and agglomeration phenomena.

In this work, the oxygen carriers prepared were evaluated in the fluidized bed reactor with respect to the agglomeration process. Agglomeration can be detected by a sharp decrease in the bed pressure drop of the fluidized bed reactor, due to the sticking of the particles causing defluidization [22]. It was found that none of the samples agglomerated or defluidized in the fluidized bed reactor during operation.

The attrition rate of the carriers is another important parameter to be accounted as a criterion for using a specific oxygen carrier in a fluidized bed reactor. High attrition rates will decrease the lifetime of the particles increasing the cost of the CLC process.

Figure 12 shows the attrition rates measured with several different oxygen carriers. The attrition rates were usually high in the first cycles due to the rounding effects on the irregularities of the particles and because of the fines stuck to the particles during their preparation. Later, the attrition rate due to the internal changes produced in the particles by the successive reduction and oxidation cycles decreased, and in general, the oxygen carriers showed low attrition rates that did not change from cycles 20-40 to cycles 100-120. This good behavior with respect to attrition was not strange considering that the alumina is used as support in the catalyst manufacture industry for use in fluidized beds at similar conditions to those existing in a CLC process.

It can be also seen in Figure 12, that the carriers prepared using a support with a thermal treatment (α - Al_2O_3 and γ - Al_2O_3 (1100)) and the carrier prepared using MgAl_2O_4 as support had the lowest attrition rates since these supports had the highest mechanical strengths (see Table 1). On the contrary, the oxygen carriers prepared using γ - Al_2O_3 and CaAl_2O_4 as supports had the highest attrition rates due to their low mechanical strengths.

4. Conclusions

Different Ni-based oxygen carriers were prepared using different supports to study their reactivity and selectivity during methane combustion in a CLC process.

Ni-based oxygen carriers prepared on γ - Al_2O_3 showed low reactivity and low methane combustion selectivity to CO_2 and H_2O , because most of the impregnated NiO reacted to NiAl_2O_4 . Thermal and chemical deactivation of the support improved the reactivity of the

carriers and the methane combustion selectivity to CO₂ and H₂O because the interaction between the NiO and the support to form the aluminate was minimized.

Ni-based oxygen carriers prepared by impregnation on α -Al₂O₃, CaAl₂O₄ and MgAl₂O₄ showed very high reactivity and high methane combustion selectivity to CO₂ and H₂O. In addition, these oxygen carriers had low attrition rates and did not show agglomeration problems during operation in fluidized beds. They seem the most suitable for the CLC process

5. Acknowledgments

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Table 1. Physical properties and solid composition of the different oxygen carriers.

Sample	Bulk	Crushing	XRD
	Density	Strength	
	g /cm ³	N	
Ni21- γ Al 500	1.7	2.2	γ -Al ₂ O ₃ , NiO
Ni21- γ Al 800	1.7	2.0	γ -Al ₂ O ₃ , NiO
Ni21- γ Al 950	1.7	2.6	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni21- γ Al 1000	1.8	2.5	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni21- γ Al 1100	1.9	3.2	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni20- γ Al (800) 950	1.7	3.6	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni19- γ Al (950) 950	1.7	3.0	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni16- γ Al (1100) 950	2.0	3.3	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni11- α Al 950	2.3	5.2	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni26- α Al 950	2.5	4.4	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni38- α Al 950	3.1	4.7	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni20-Mg5 γ Al (800) 950	1.9	3.4	MgAl ₂ O ₄ , NiAl ₂ O ₄
Ni20-Mg9 γ Al (800) 950	1.9	3.0	MgAl ₂ O ₄ , NiAl ₂ O ₄
Ni20-MgAl ₂ O ₄ 950	1.5	4.3	MgAl ₂ O ₄ , NiO
Ni14-Ca9 γ Al (1100) 950	2.0	3.2	CaAl ₄ O ₇ , NiAl ₂ O ₄
Ni11-CaAl ₂ O ₄ 950	1.4	2.4	CaAl ₄ O ₇ , CaAl ₂ O ₄ , NiO

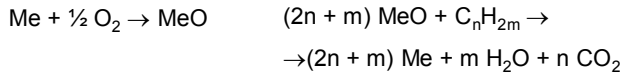
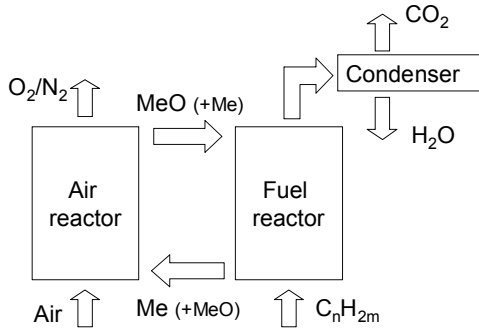


Figure 1. Schematic diagram of the chemical looping combustion (CLC) concept.

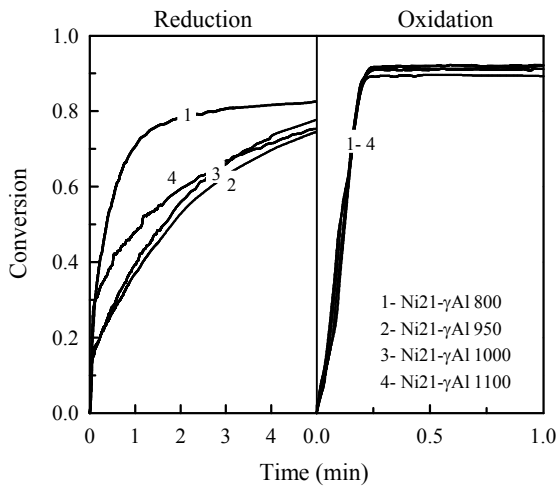


Figure 2. Effect of the oxygen carrier calcination temperature in the reactivity of Ni-based oxygen carriers. T= 950°C, except (1) T=800°C.

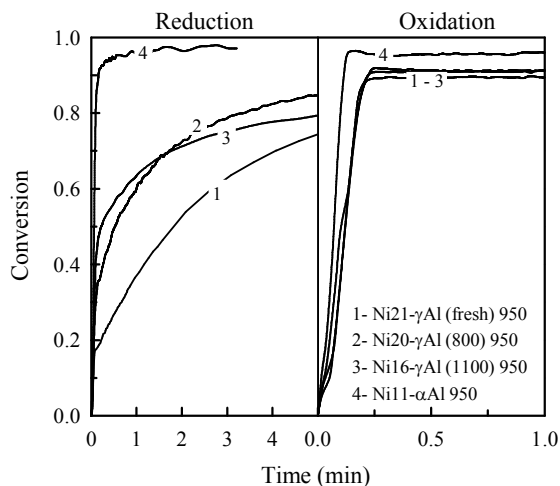


Figure 3. Effect of the thermal pretreatment of the support in the reactivity of Ni-based oxygen carriers. $T=950^{\circ}\text{C}$

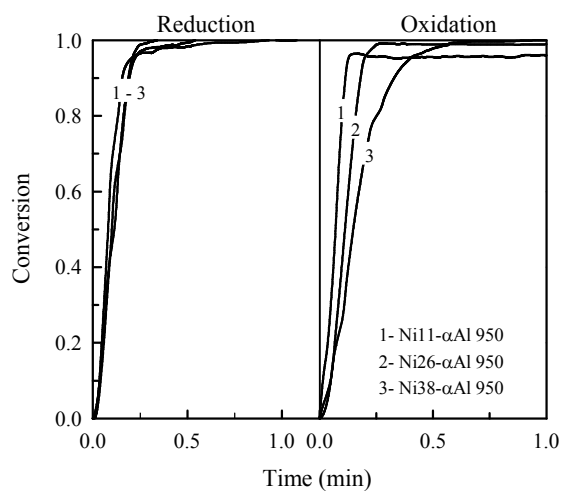


Figure 4. Effect of the NiO content in the reactivity of several Ni-based oxygen carriers. $T=950^{\circ}\text{C}$.

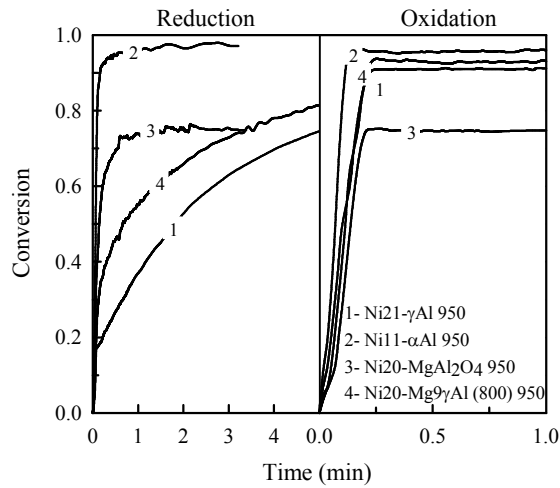


Figure 5. Effect of the chemical deactivation of the support with MgO in the reactivity of Ni-based oxygen carriers. T= 950°C.

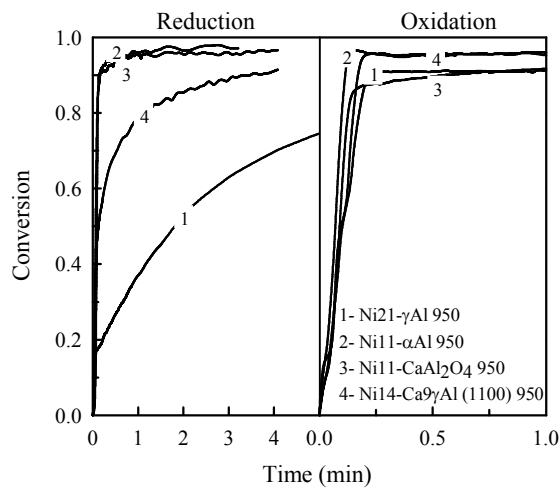


Figure 6. Effect of the chemical deactivation of the support with CaO in the reactivity of Ni-based oxygen carriers. T= 950°C.

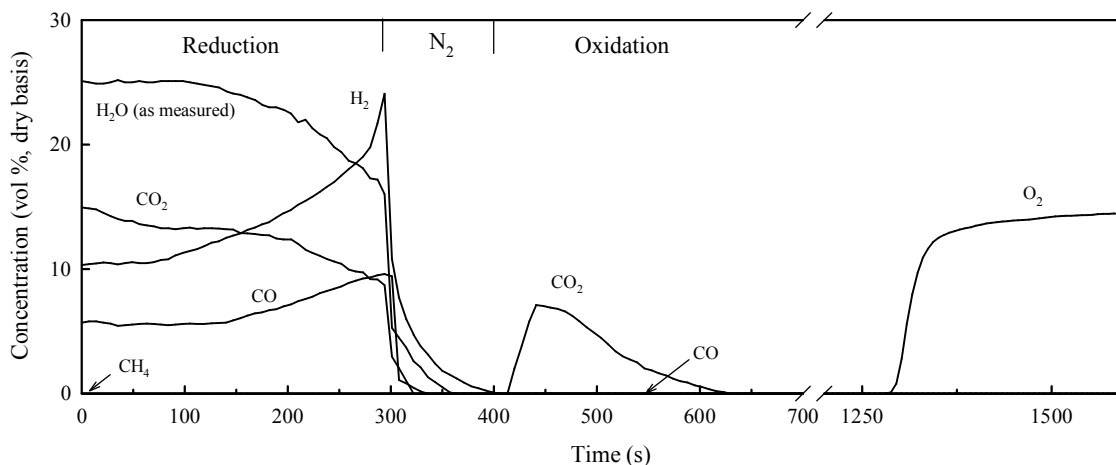


Figure 7. Gas product distribution (dry basis) during a cycle in the batch fluidized bed tests working with the Ni21- γ Al 950 oxygen carrier. H₂O concentration as measured in an FTIR analyzer.

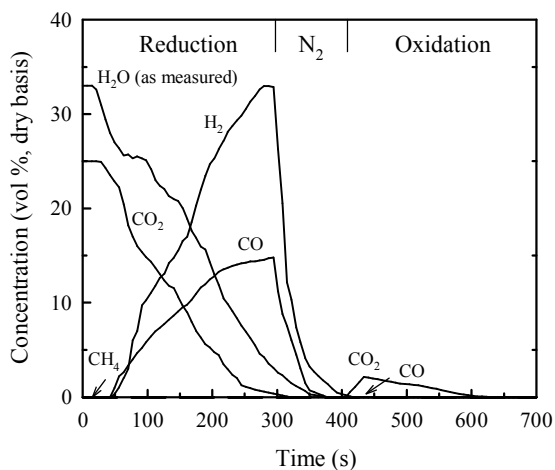


Figure 8. Gas product distribution (dry basis) during the reduction reaction in the batch fluidized bed tests working with the Ni11- α Al 950 oxygen carrier. H₂O concentration as measured in an FTIR analyzer.

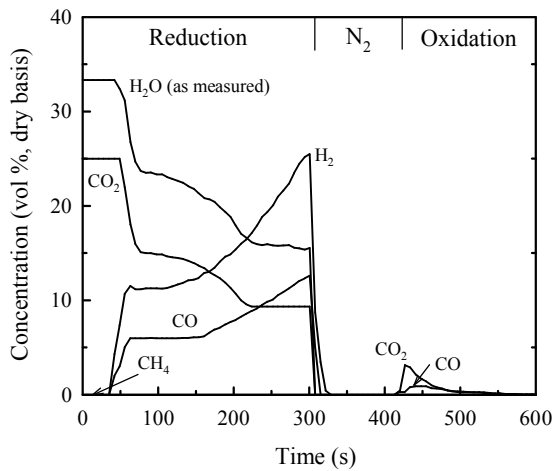


Figure 9. Gas product distribution (dry basis) during the reduction reaction in the batch fluidized bed tests working with the Ni16- γ Al (1100) 950 oxygen carrier. H₂O concentration as measured in an FTIR analyzer.

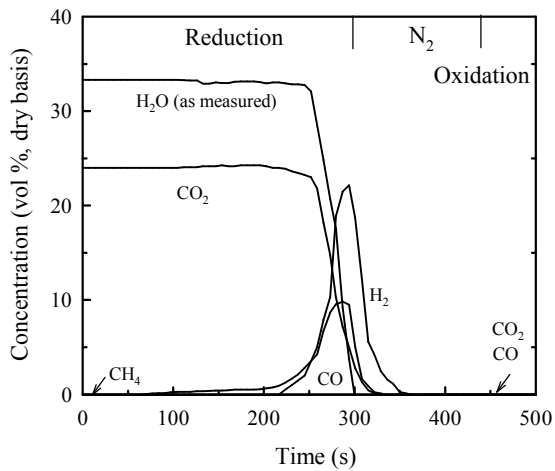


Figure 10. Gas product distribution (dry basis) during the reduction reaction in the batch fluidized bed tests working with the Ni20-MgAl₂O₄ 950 oxygen carrier. H₂O concentration as measured in an FTIR analyzer.

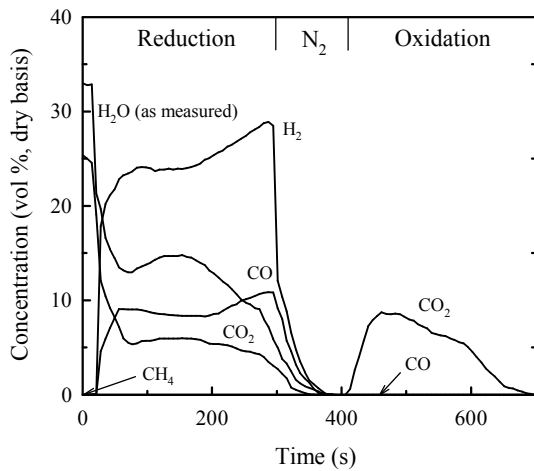


Figure 11. Gas product distribution (dry basis) during the reduction reaction in the batch fluidized bed tests working with the Ni14-Ca9 γ Al (1100) 950 oxygen carrier. H₂O concentration as measured in an FTIR analyzer.

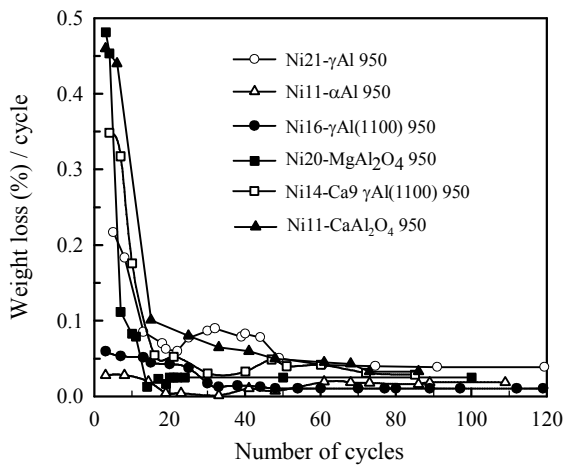


Figure 12. Attrition rates measured with the different Ni-based oxygen carriers in the multi-cycle tests carried out in the fluidized bed reactor.