

Submitted, accepted and published by

Industrial & Engineering Chemistry Research 2006, 45, 2617-2625

Ni-Cu OXYGEN CARRIERS TO REACH ZERO CO AND H₂ EMISSIONS IN CHEMICAL-LOOPING COMBUSTION

Juan Adánez, Francisco García-Labiano, Luis F. de Diego,*

Pilar Gayán, Javier Celaya, Alberto Abad

Instituto de Carboquímica (CSIC). Dept. Energy & Environment

Miguel Luesma Castán, 4, 50015, Zaragoza, Spain

*Corresponding author. Tel.: 34-976733977. Fax: 34-976733318. E-mail: jadanez@icb.csic.es

ABSTRACT

Ni-based oxygen carriers allow to work at high temperatures (900-1100°C) in a Chemical-Looping Combustion (CLC) process with full CH₄ conversion, although thermodynamic restrictions result in the presence of CO and H₂ in the gas outlet of the fuel reactor. On the other hand, Cu-based oxygen carriers allow complete fuel combustion to CO₂ and H₂O, but the operating temperature is limited due to the low melting point of the metallic Cu. The objective of this research was to analyze the behavior of several Ni-Cu oxygen carriers to reduce or avoid CO and H₂ emissions during a CLC process working at high temperatures. Commercial γ -Al₂O₃ and α -Al₂O₃ were used as support to prepare by dry impregnation different oxygen carriers based on nickel and copper. The reactivity of these oxygen carriers was determined in a thermogravimetric analyzer (TGA). The effect of the mixture of NiO and CuO on the CO and H₂ generation was analyzed in a fixed bed reactor, and the gas product distribution during reduction/oxidation reactions was studied in a batch fluidized bed reactor working with CH₄ as fuel and diluted air for oxidation. The fluidization behavior of the oxygen carriers with respect to the attrition and agglomeration processes was also analyzed during the multi-cycle batch fluidized bed tests.

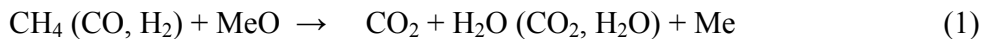
The presence of CuO in the Ni-Cu oxygen carriers allows the full conversion of CH₄ to CO₂ and H₂O in the batch fluidized bed reactor during the initial part of the reduction time, and this time depended on the CuO content of the oxygen carrier. TGA and X-ray diffraction studies indicated that CuO is used for the reduction reaction before NiO. In addition, it was observed that the presence of NiO stabilized the CuO and allowed to work at 950 °C with Ni-Cu oxygen carriers with a high metal oxide utilization.

Keywords: Chemical Looping Combustion, Oxygen Carriers, CO₂ Capture

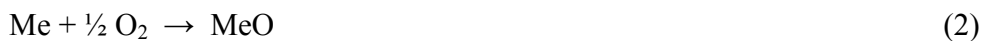
1. Introduction

Carbon dioxide coming from fossil fuel combustion is one of the most important greenhouse gases contributing to global warming. One of the options to overcome greenhouse effect is the development of CO₂ capture and separation technologies from flue gases. Ritcher and Knoche¹ proposed a reversible combustion method, named as Chemical Looping Combustion (CLC), which utilizes oxidation and reduction of metals. This technology offers a tremendous potential to reduce the cost associated with CO₂ separation because the only by-product of combustion with air is wet carbon dioxide that can be easily collected for subsequent use.

In a CLC process, fuel gas (natural gas, syngas, etc.) is burnt in two reactors designated as fuel and air reactors. In the fuel reactor, the fuel gas is oxidized to CO₂ and H₂O by a metal oxide through the chemical reaction:



The metal or reduced oxide is further transferred into the air reactor in which it is oxidized with air:



and the material regenerated is ready to start a new cycle.

The flue gas leaving the air reactor contains N₂ and unreacted O₂. The exit gas from the fuel reactor contains CO₂ and H₂O, which are kept apart from the rest of the flue gas. After water condensation, almost pure CO₂ can be obtained with little energy lost for component separation.

The development of the CLC process relies on the availability of redox materials to match the following requirements: high redox reactivity, high selectivity towards complete oxidation products, high oxygen

exchange capability, high regenerability at high temperatures, high mechanical resistance to the friction stresses associated with the recirculation of solid particles, and low cost.

On the basis of thermodynamic consideration oxides based on Ni, Cu, Fe, Co or Mn were identified as potential candidates for the CLC process². In general, these metal oxides are combined with an inert which acts as a porous support providing a higher surface area for reaction, as a binder for increasing the mechanical strength and attrition resistance, and, additionally, as an ion conductor enhancing the ion permeability in the solid^{3,4}.

Recently Wolf et al.⁵ carried out a comparative study regarding system's electrical and exergy efficiencies with Fe- and Ni-based oxygen carriers, and found that CLC seems easier to be technically realized with a Ni-based oxygen carrier. Ishida, Jin, and co-workers^{3,6-10} investigated the redox properties of NiO with different binders in a thermogravimetric analyzer (TGA). The NiO/NiAl₂O₄ carrier was reported as the best material in terms of regenerability using H₂ and CH₄ as fuel. Ryu et al.¹¹ prepared oxygen carrier with NiO and bentonite as support, and carried out TGA cyclic tests using CH₄ as fuel. They found an optimum temperature of 900°C to avoid carbon deposition with high reaction rate. Villa et al.¹² investigated the redox properties of Ni-Al-O and Ni-Mg-Al-O mixed oxides for CH₄ combustion, indicating the poor selectivity towards CO₂ and H₂O, being CO and H₂ the most abundant products. Mattisson and co-workers¹³⁻¹⁵ prepared Ni-, Cu-, Co-, and Mn-based oxygen carriers on alumina support by dry impregnation and their reactivity was studied in a TGA. Moreover, these authors compared the behavior of Fe-, Ni-, Cu- and Mn-based oxygen carriers prepared by freeze granulation in a fluidized bed reactor and observed that the oxygen carriers based on Ni- or Cu- showed the highest reactivity. They found agglomeration problems working with some Fe-based oxygen carriers and specially working with Cu-based oxygen carriers. Copeland et al.¹⁶ developed oxygen carriers, containing Cu, Fe, and Ni with a variety of binder materials and active metal oxide contents. They eliminated Cu as a potential oxygen carrier due to agglomeration problems in the fluidized bed facility, and obtained successfully results with Fe- and Ni- based carriers. On the other hand, de Diego et al.¹⁷

prepared by impregnation CuO/Al₂O₃ oxygen carriers, which did not present agglomeration problems. These oxygen carriers had high oxygen transport capacity and achieved complete CH₄ conversion without emission of CO and H₂. However, the temperature of utilisation of these carriers is limited to avoid the sinterization due to the low melting point of Cu (1063°C).

It should be noticed that the operating temperature of the oxygen carrier is an important variable because a higher reactor temperature leads to higher gas turbine inlet temperatures and efficiencies. Ni-based oxygen carriers allow working at high temperatures (900-1100°C) although thermodynamic restrictions make that CO and H₂ are always present in the gas outlet of the fuel reactor. These limitations could make it necessary to include some process modifications to reduce the amount of non-condensable gases in the CO₂ compression and condensation stages.

Considering the different properties of the individual Ni- and Cu-based oxygen carriers, the objective of the this work was to join the advantages of both metal oxides to reduce the CO and H₂ emissions at the outlet of the fuel reactor working with at high temperature with new mixed Ni-Cu oxygen carriers.

2. Experimental Section

2.1 Materials

Commercial γ -Al₂O₃ (Puralox NWA-155, Sasol Germany GmbH) and α - Al₂O₃ (obtained by calcination of γ - Al₂O₃ at 1100 °C during 2 hours) particles of 0.1-0.32 mm, with densities of 1.3 and 1.7 g/cm³ and porosities of 56.5 % and 54.9 % respectively, were used as support to prepare oxygen carriers by dry impregnation. Ni-based oxygen carriers were prepared by addition of a volume of an aqueous solution of Ni(NO₃)₂·6H₂O (>99.5 % Panreac) corresponding to the total pore volume of the support particles. The aqueous solution was slowly added to the alumina 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 950 °C. Oxygen carriers

with NiO weight contents ranging from 12 to 30 % for the impregnated on γ -Al₂O₃, and from 6 to 16 % for the impregnated on α -Al₂O₃ were prepared.

Other oxygen carriers were prepared by impregnation with mixed nitrate solutions of Ni and Cu (Cu(NO₃)₂·3H₂O > 99.5 % Panreac) in the necessary concentration to produce carriers with NiO/CuO weight ratios from 0.06 to 4. To test the effect of the preparation method, some Ni-Cu oxygen carriers were prepared in two steps. Fresh α -Al₂O₃ was impregnated with nickel nitrate and calcined (550°C), then the sample was impregnated with a copper nitrate solution, calcined at 550 °C and finally calcined for 1 h at 950 °C. In other sample the order of the impregnation was changed. Finally, oxygen carriers were prepared adding several additives (K, or La nitrate) in the solution used for impregnation in the amount necessary to obtain the desired oxide weight contents in each case. For comparison purposes, a Cu-based oxygen carrier with 15 % of CuO, Cu15- γ Al, was prepared by dry impregnation on γ -Al₂O₃ as described in a previous work¹⁷.

The samples were designated with the chemical symbols referred to the active metal oxides and additives followed in each case by the weight content, and finally the inert used for the impregnation. As an example, Ni10Cu2K0.7- α Al indicates an oxygen carrier composed by NiO (10 wt.%), and CuO (2 wt.%), with the addition of K₂O (0.7 wt.%), and impregnated on α -Al₂O₃.

Table 1 shows all the oxygen carriers prepared with the different metal oxides and additives, as well as the number of impregnations used in each case. The oxygen carriers were physically and chemically characterized by several techniques. Table 1 shows the density of the samples and the crystalline phases obtained from X-ray powder diffraction (XRD) of some selected carriers. The oxygen carriers prepared using γ -Al₂O₃ as support had lower density than the oxygen carriers prepared using α -Al₂O₃. XRD patterns obtained from a Bruker AXS D8ADVANCE showed the formation of aluminum spinel compounds in the majority of the oxygen carriers.

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

Sample	Number of impregnations	Particle density (g/cm ³)	Crystalline phases obtained from XRD
Ni12- γ Al	1	1.5	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni21- γ Al	2	1.5	
Ni30- γ Al	3	1.6	
Ni9Cu3 - γ Al	1	1.6	γ -Al ₂ O ₃ , NiAl ₂ O ₄ , Cu _{0.75} Ni _{0.25} Al ₂ O ₄
Ni10Cu2 - γ Al	1	1.6	γ -Al ₂ O ₃ , NiAl ₂ O ₄ , Cu _{0.75} Ni _{0.25} Al ₂ O ₄
Cu15 - γ Al	1	1.4	CuO, CuAl ₂ O ₄ , γ -Al ₂ O ₃
Ni6- α Al	1	2.0	
Ni10- α Al	2	2.1	
Ni16- α Al	2	2.0	α -Al ₂ O ₃ , NiAl ₂ O ₄ , NiO
Ni4Cu1- α Al	1	1.9	
Ni9Cu3- α Al	2	2.0	
Ni9Cu3- α Al ^a	2	2.0	
Ni9Cu3- α Al ^b	2	2.0	
Ni12Cu4- α Al	2	2.0	α -Al ₂ O ₃ , NiAl ₂ O ₄ , CuAl ₂ O ₄ , Cu _{0.75} Ni _{0.25} Al ₂ O ₄
Ni6Cu2K0.7- α Al	1	2.1	
Ni12Cu4K1.3- α Al	2	2.1	α -Al ₂ O ₃ , NiAl ₂ O ₄ , CuAl ₂ O ₄ , Cu _{0.75} Ni _{0.25} Al ₂ O ₄ , NiO(minor)
Ni12Cu4K2.5- α Al	2	2.1	
Ni6Cu2La0.7- α Al	1	2.0	
Ni8Cu8- α Al	2	2.0	α -Al ₂ O ₃ , NiAl ₂ O ₄ , CuAl ₂ O ₄
Ni8Cu8- α Al ^c	2	1.9	α -Al ₂ O ₃ , NiAl ₂ O ₄ , CuAl ₂ O ₄ , Cu
Ni4Cu12- α Al	2	2.0	α -Al ₂ O ₃ , NiAl ₂ O ₄ , CuAl ₂ O ₄ , CuO
Ni1Cu15- α Al	2	2.0	α -Al ₂ O ₃ , NiAl ₂ O ₄ (minor), CuAl ₂ O ₄ , CuO

a - 1st impregnation: Nickel nitrate / 2nd impregnation: Copper nitrate

b - 1st impregnation: Copper nitrate / 2nd impregnation: Nickel nitrate

c - partially reduced (X= 38%)

2.2 Thermogravimetric Analyzer

Multicycle tests to analyze the reactivity of the oxygen carriers during successive reduction-oxidation cycles were carried out in a TGA system, CI Electronics type, described elsewhere.¹⁸ For the experiments, the oxygen carrier was loaded in a platinum basket and heated to the set operating temperature in air atmosphere. After stabilization, the experiment started by exposing the oxygen carrier to alternating 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 composition of 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 carried out at temperatures up to 950 °C.

2.3 Fixed Bed Reactor

Tests in a fixed bed reactor were carried out to determine the equilibrium CO and H₂ gas concentrations obtained at the outlet during the reduction reaction of the different oxygen carriers. The experimental set up was composed by a gas feeding system, a fixed bed reactor of 27 mm I.D. and 600 mm length, and a gas analysis device. The gas was fed in at the top of the reactor to avoid the entrainment of the particles. The tests were carried out using batches of 300 g of oxygen carrier and gas flow rates of 60 to 120 l/h. Three different reducing gases, CH₄, H₂, and CO, were used. The composition of each reducing gas was varied between 20-100 vol.%. A gas with 4 vol.% of O₂ in N₂ was used during oxidation. This O₂ concentration was used instead of air to avoid a large temperature increase during the exothermic oxidation reaction. Also in this case, to avoid mixing of gases, nitrogen was introduced for 120 s after each reducing and oxidizing period.

2.4 Fluidized Bed Reactor

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

The experimental set-up used for testing the oxygen carrier is described elsewhere.¹⁷ It consisted of a system for gas feeding, a fluidized bed (FB) reactor, a two ways 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 300 g of oxygen carrier with a particle size of 0.1-0.3 mm. 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. Agglomeration problems could be detected by a sharp decrease in the bed pressure drop during operation, causing defluidization of 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 to obtain elutriation data at different times or number of cycles. Different gas analyzers continuously measured the gas composition at each time. The 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.

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% 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 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. The oxygen carriers were exposed to a total number of 50 reduction/oxidation cycles.

3. Results

3.1 Oxygen carriers composed by one metal oxide

The behavior of oxygen carriers containing only NiO impregnated on Al₂O₃ was first analyzed. The reactivity of the oxygen carriers was initially determined in the TGA working with mixtures CH₄-N₂ at 950°C. Figure 1 shows the reduction and oxidation reactivities of the Ni-based oxygen carriers. The Ni-based oxygen carrier impregnated on α -Al₂O₃ showed initially a high reactivity, until 80 % of NiO conversion, and a second step of lower reactivity. However, the Ni-based oxygen carrier impregnated on γ -Al₂O₃ showed low reactivity during all the reaction. On the other hand, all oxygen carriers exhibited very high reactivity during oxidation.

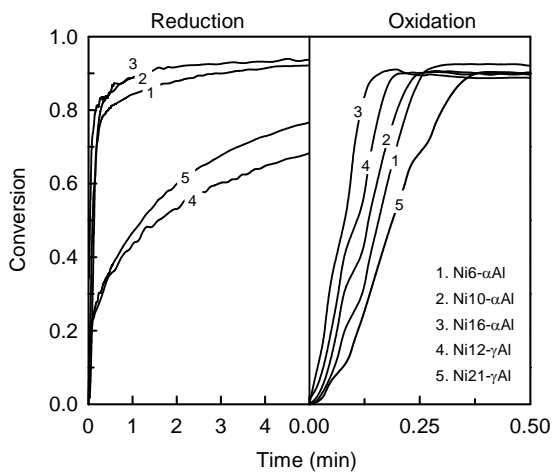


Figure 1. TGA reactivity data of several Ni-based oxygen carriers with 15 % CH₄ and air at 950°C.

The loss of reactivity of the carriers of NiO on γ -Al₂O₃ was due to solid state reaction between the NiO and the γ -Al₂O₃ to form NiAl₂O₄ during the sintering step in the carrier preparation, as it is shown in the XRD patterns (see Table 1). NiO was only detected in the oxygen carriers prepared with α -Al₂O₃, although it is necessary to consider that this technique does not detect crystalline phase contents lower than 5%. 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 against blue samples containing high fractions of NiAl_2O_4 ¹⁹, as it was the case of the carriers prepared with γ - Al_2O_3 .

The effect of the impregnated NiO content on the reactivity of the carriers was studied using different number of impregnations. TGA results showed that the NiO contents (Figure 1) hardly affected to the reduction and oxidation reactivities.

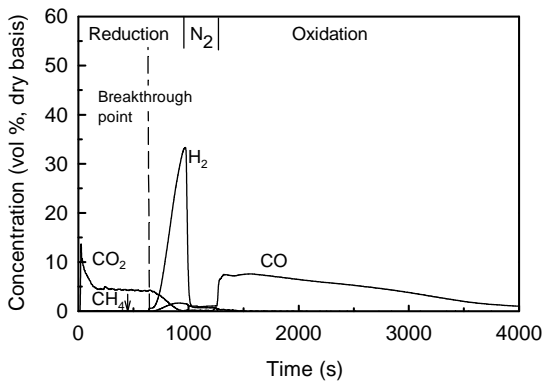


Figure 2. Gas product distribution obtained during the reduction with CH_4 (20%) and oxidation of Ni16- α Al in the fixed bed reactor at 950°C.

Experiments with CH_4 were also carried out at 950°C in the fixed bed reactor to determine the gas concentrations at the reactor outlet. Figure 2 shows the gas product distribution obtained during the reduction and oxidation steps of the oxygen carrier Ni16- α Al. The conversion of CH_4 was complete during all the reduction period. Small concentrations of H_2 and CO were found during the first part of the reduction reaction, with a further increase of CO and, especially, H_2 concentrations when the breakthrough point of the fixed bed was reached. A thermodynamic study on the reduction reaction of different metal oxides (NiO and CuO) with methane was carried out using the method of minimization of Gibbs free energy. For CuO it was found that CH_4 conversion to carbon dioxide was complete without any CO and H_2 at equilibrium. However, for NiO the thermodynamic analysis showed that there is complete CH_4 conversion but there are some CO and H_2 concentrations at equilibrium which increase

with the temperature, as shown in Figure 3. The experimental results of Figure 2 are in good agreement with this thermodynamic study.

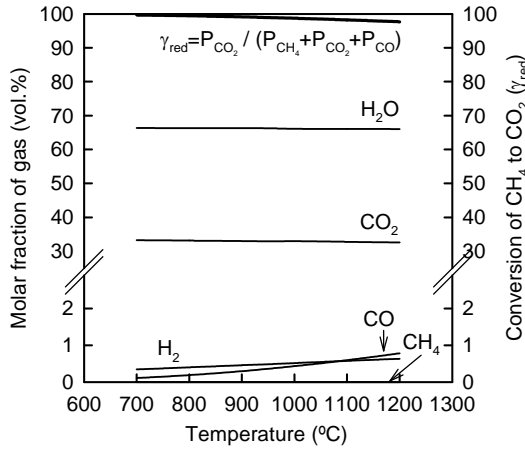
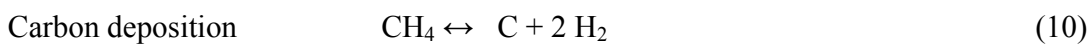
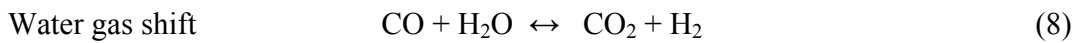
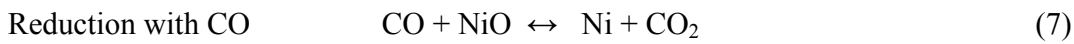
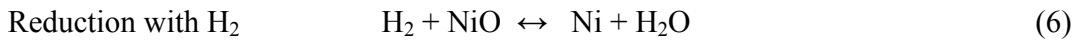
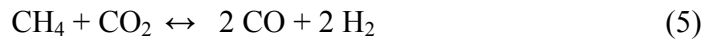
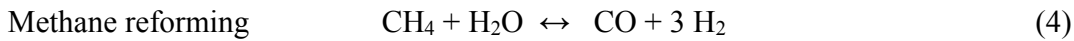


Figure 3. Thermodynamic equilibrium gas concentrations for Ni-based particles using CH₄ as fuel.

During oxidation, important amounts of CO were detected coming from the combustion of the carbon generated in the reduction period. To understand the process, it must be considered that during the reaction of NiO with CH₄ the following reactions are possible:



The Ni formed during reduction catalyzes both methane reforming²⁰ (reactions 4-5) and especially CH₄ decomposition (reaction 10). As a consequence of the CH₄ decomposition, the CH₄ concentration is modified by reaction (10) in the first part of the fixed bed reactor where most of the active phase is as metallic Ni after few seconds of reaction. Therefore, it is not possible to follow the effects of CH₄ concentration and carrier composition on the equilibrium concentrations of H₂ and CO working with CH₄ in a fixed bed reactor. However, taking into account the thermodynamic results, it is possible to assume a complete CH₄ conversion and use H₂ or CO-CO₂ as feeding gases to study the equilibrium concentrations in a fixed bed system, avoiding the disturbances due to carbon formation.

Figure 4 shows the reduction and oxidation breakthrough curves obtained in the fixed bed with the Ni₁₆- α Al oxygen carrier working with 20 vol.% H₂ or 20 vol.% CO during reduction and 4 vol.% O₂ in the oxidation. With this carrier, the H₂ and CO concentrations corresponding to the equilibrium were found during an important period of time ($t/t_0=0.7$ for H₂ and $t/t_0=0.45$ for CO) before the breakthrough point of the fixed bed. During reduction with CO, the breakthrough curve showed some kinetic limitations. After that point, H₂ and CO concentrations increased quickly and finally increased slowly due to the lower reactivity of NiAl₂O₄. This carrier showed very high oxidation reactivities as it is observed by the slopes of the plots after breakthrough. This figure also shows the breakthrough curves obtained with the Cu-based oxygen carrier, Cu₁₅- γ Al. In this case, H₂ were not measured before the breakthrough point in good agreement with the thermodynamic analysis.

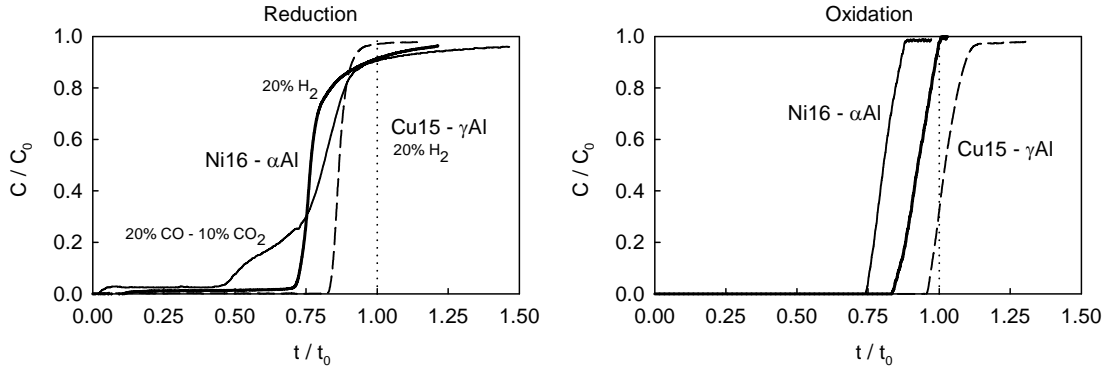


Figure 4. Fixed-bed breakthrough curves during the reduction and oxidation of the sample Ni16- α Al, and Cu15- γ Al at 950°C.

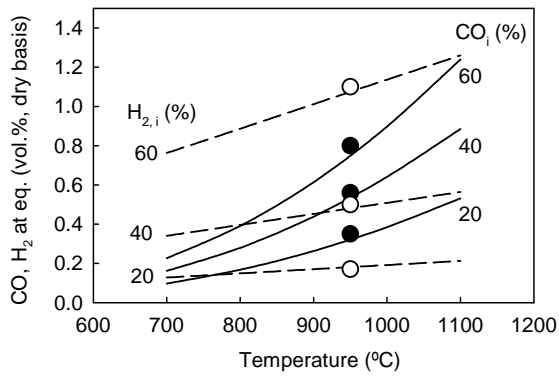


Figure 5. Thermodynamic equilibrium concentrations during Ni16- α Al reduction with different concentrations of H₂ or CO (continuous lines) and experimental results obtained in the fixed bed reactor (circles) as a function of the temperature. H₂O=0% and CO₂=10%.

The behavior before the breakthrough point was similar for all Ni-based oxygen carriers, with low CO or H₂ concentrations in the gas reactor outlet. Figure 5 shows the theoretical equilibrium concentrations at atmospheric pressure of H₂ and CO as a function of the temperature for different initial gas concentrations. It also shows the H₂ and CO concentrations measured before the breakthrough point with the Ni16- α Al oxygen carrier at 950°C and different initial gas concentrations. It can be observed a

close agreement of the experimental results with the theoretical equilibrium concentrations at the given operating conditions.

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

With Ni-based oxygen carriers prepared on γ - Al_2O_3 , CO_2 , H_2O , CO , and H_2 were formed almost immediately after introduction of CH_4 into the reactor. The CH_4 conversion was complete, although high H_2 and CO concentrations were present in the gas outlet together with CO_2 and H_2O during all the reduction period. This behavior indicated that the reduction process was mainly selective towards the formation of H_2 and CO . This behavior was similar to that found with a $\text{NiO-Al}_2\text{O}_3$ oxygen carrier prepared by freeze-granulation²¹.

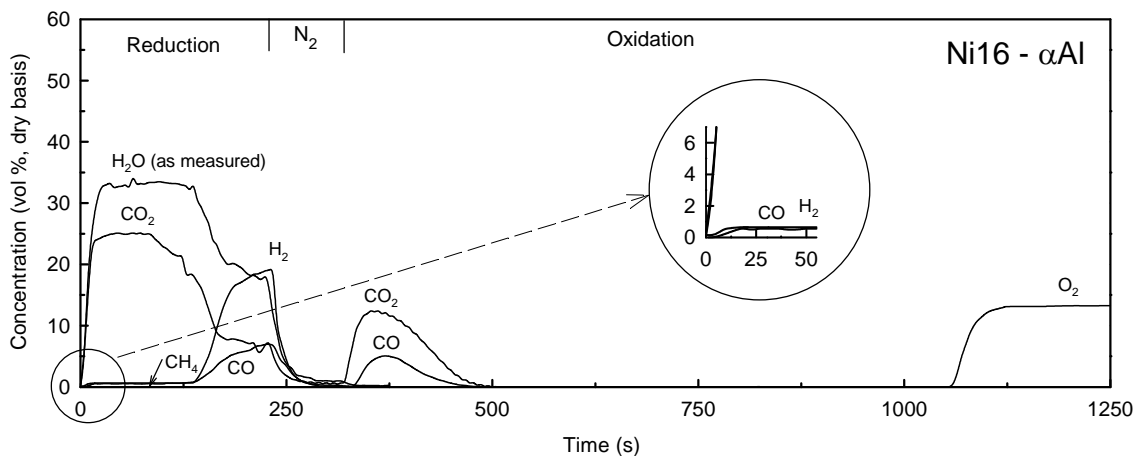


Figure 6. Gas product distribution (dry basis) obtained in the fluidized bed with the sample Ni16- α Al. H_2O concentration as measured in FTIR analyzer.

With Ni-based oxygen carriers prepared on α - Al_2O_3 (see Figure 6), CO_2 and H_2O were formed immediately after the CH_4 feeding, and no CH_4 was detected during the whole carrier reduction time.

During the first period, CO and H₂ concentration were those 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. Villa et al.¹² Cho et al.²¹ and Adánez et al.^{22,23} observed the same results working in a TGA. Villa et al.¹² suggested that the change in the product selectivity during the reduction step could be likely associated to changes in the catalyst degree of oxidation. At the beginning, the fully oxidized NiO favors the total oxidation of CH₄ (reaction 3). As the sample was reduced, the selectivity of gas product formation changes from CO₂ and H₂O to CO and H₂, possibly assisted by the occurrence of the CH₄ reforming reaction (reactions 4 and 5), catalyzed by reduced Ni active sites. It is necessary to indicate that the oxygen carrier (NiO) also oxidizes CO and H₂ (reactions 6 and 7). However, 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 oxidation and fuel reactors, the CH₄ was almost completely converted to CO₂ and H₂O. This will explain the good results obtained by Lyngfelt and co-workers^{24,25} in their 10 kW CLC pilot plant. During the oxidation period, CO and CO₂ were formed by the combustion of C generated during the reduction period. However, it was observed that the CO and CO₂ concentrations were almost zero when the reduction period was stopped at the beginning of the formation of H₂ and CO (≈200 s).

3.2 Oxygen carriers of Ni-Cu

Thermodynamic restrictions make that CO and H₂ are always present in the gas outlet of the fuel reactor when using Ni-based oxygen carriers. These limitations could make necessary to include some process modifications to reduce the amount of non-condensable gases in the CO₂ compression and condensation stages. As it can be seen in Figure 7, the results of the thermodynamic study shows that the addition of CuO to the Ni-based oxygen carriers decreases the CO and H₂ equilibrium concentrations, allowing a higher conversion of CH₄ into CO₂ and H₂O in a CLC process.

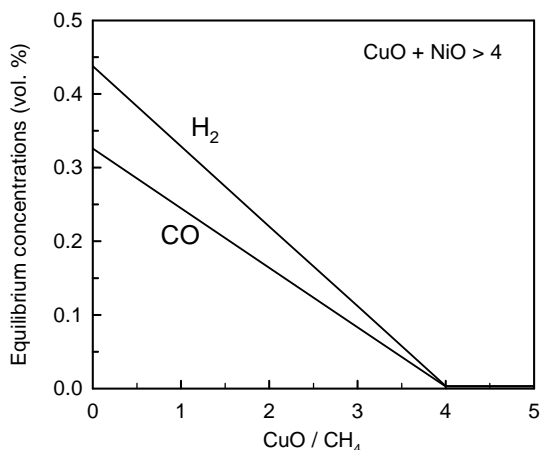


Figure 7. Equilibrium concentrations for a NiO-CuO system with CH₄ at 950 °C.

Oxygen carriers with different NiO/CuO weight ratios were prepared using α -Al₂O₃ and γ -Al₂O₃ as supports. Initially carriers with small fractions of CuO (1-4%) were prepared and tested. Figure 8 shows the TGA reactivity of these Ni-Cu oxygen carriers and that corresponding to the Ni16- α Al oxygen carrier. The addition of CuO to the Ni-based oxygen carriers prepared using α -Al₂O₃ as support decreased the reduction reactivity while the oxidation reactivity was maintained high. The type of support did not affect the results and the reactivities were similar to those obtained for the Ni-based oxygen carrier impregnated on γ -Al₂O₃.

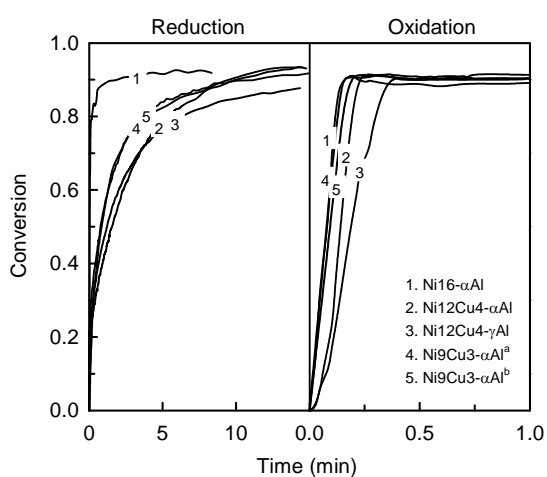


Figure 8. Effect of CuO addition on the TGA reactivity of Ni-based oxygen carriers at 950 °C. Fuel= CH₄ (15%).

These important changes in the reduction reactivity of the Ni-Cu oxygen carriers suggest structural changes in the oxygen carrier by interaction between the metal oxides or with the support. In fact, several XRD analysis carried out to the samples showed the presence of several aluminates (NiAl_2O_4 , CuAl_2O_4 , $\text{Cu}_{0.75}\text{Ni}_{0.25}\text{Al}_2\text{O}_4$) as well as the absence of free NiO (see Table 1). Thus, the reason of the decrease in the reduction reactivity due to the addition of CuO can be attributed to the loss of free NiO to form aluminates. These results agree with the work carried out by Bolt et al.¹⁹ who found that annealing conditions favored the formation of aluminates of transition metals of low valency as Cu^+ and Co^{2+} . The formation of CuAl_2O_4 spinel is fast and could increase the rate of formation of NiAl_2O_4 spinel, which decreases the reactivity of the carriers containing NiO and CuO.

In view of these results, two more oxygen carriers ($\text{Ni}_9\text{Cu}_3\text{-}\alpha\text{Al}^{\text{a}}$ and $\text{Ni}_9\text{Cu}_3\text{-}\alpha\text{Al}^{\text{b}}$) were prepared to analyze if the preparation method had any influence on the formation of these aluminates. As it can be observed in Figure 8, the reactivity of these new carriers was very similar to the carriers prepared by only one impregnation with the mixed nitrates ($\text{Ni}_{12}\text{Cu}_4\text{-}\alpha\text{Al}$), indicating that the method of preparation had no influence on the final oxygen carrier reactivity.

The behavior of the $\text{Ni}_{12}\text{Cu}_4\text{-}\alpha\text{Al}$ oxygen carrier during reduction-oxidation cycles in the fixed-bed reactor was also investigated. Figure 9 shows a comparison of the fixed bed breakthrough curves obtained with the $\text{Ni}_{16}\text{-}\alpha\text{Al}$ and $\text{Ni}_{12}\text{Cu}_4\text{-}\alpha\text{Al}$ oxygen carriers working with H_2 (20 vol.% and 40 vol.%, balance N_2) and CO (20 vol.% and 40 vol.%, 10% CO_2 , balance N_2). Two key aspects arise from these plots. The reaction capacity of the Ni-Cu oxygen carriers impregnated on $\alpha\text{-Al}_2\text{O}_3$ was lower than the original Ni-based oxygen carrier. On the other hand, the CO and H_2 concentrations measured at the gas exit before the breakthrough point with the carrier $\text{Ni}_{16}\text{-}\alpha\text{Al}$ were those corresponding to the equilibrium, while for $\text{Ni}_{12}\text{Cu}_4\text{-}\alpha\text{Al}$ these concentrations were zero (as it is highlighted in Figure 9). The breakthrough point occurs at t/t_0 values around 0.3 (for H_2) and 0.25 (for CO) indicating a low metal oxide utilization for complete CH_4 combustion to CO_2 and H_2O . To make a preliminary analysis of the NiO conversion during this period it is necessary consider that the main part of CuO present in

the fixed bed decomposes in inert atmosphere at 950 °C giving O₂ which was observed during the experimental work. Assuming that equilibrium CuO-Cu₂O was reached in the fixed bed before reaction and that all the Cu oxides reacts before than the NiO, the NiO conversion varied from 5 to 20 %.

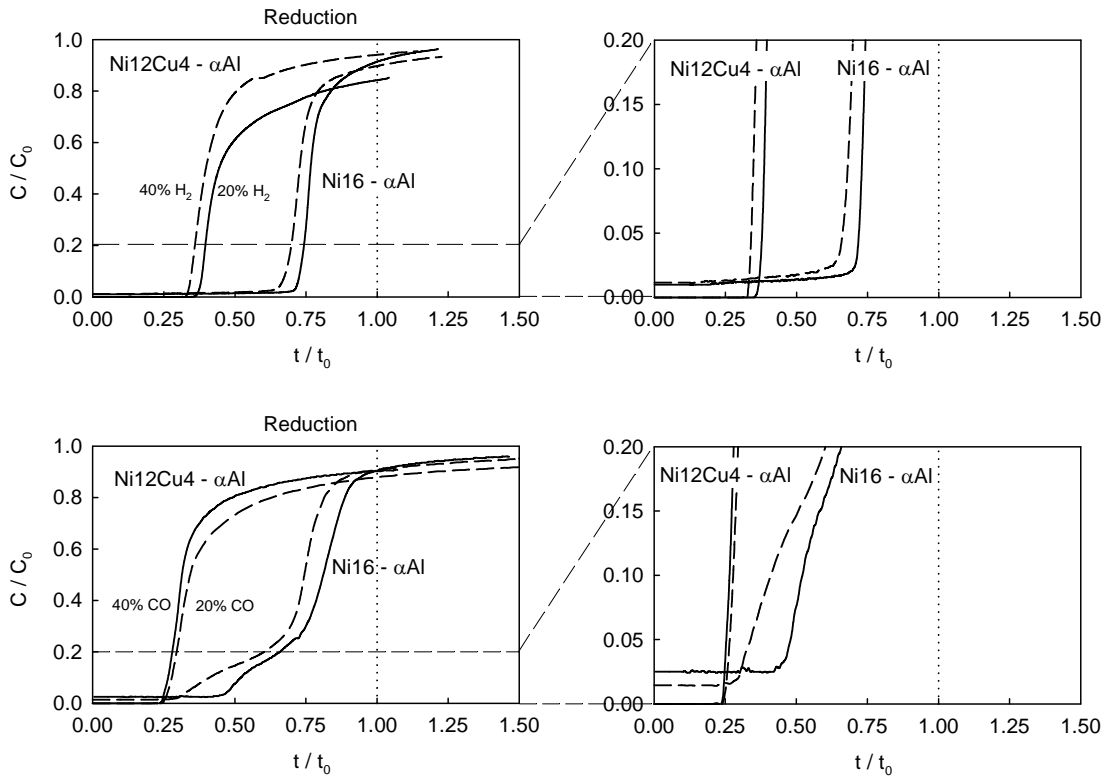


Figure 9. Effect of the CuO addition to the Ni-based oxygen carriers on the fixed-bed breakthrough curves during the reduction with H₂ or CO.

To improve the metal oxide utilization on the Ni-Cu oxygen carriers with increasing amounts of Cu were prepared by dry impregnation (Ni₈Cu₈-αAl, Ni₄Cu₁₂-αAl, Ni₁Cu₁₅-αAl). Figure 10 shows the reactivities of these oxygen carriers obtained during the reduction with H₂ in the TGA. Two steps were observed during the reduction process, one initial step with very high reactivity followed by a second step with low reactivity. The conversions reached during the first step roughly corresponded to the CuO content in the oxygen carrier, which could indicate that CuO reacts quicker and before than NiO.

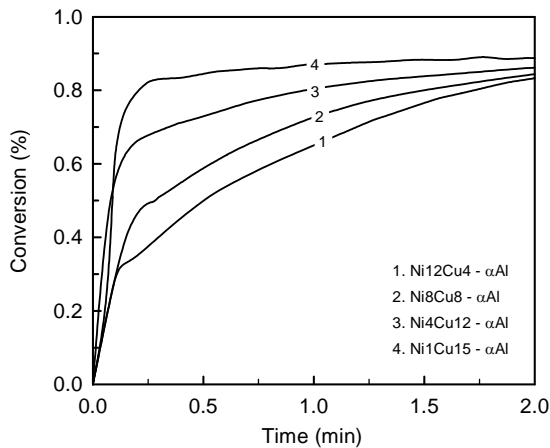


Figure 10. Effect of CuO addition on the reactivity with H₂ (20 vol. %) of Ni-Cu based oxygen carriers.

The behavior of these oxygen carriers was also tested in the batch FB. Figure 11 shows the results obtained with the oxygen carrier Ni12Cu4- α Al. In this case, CO₂ and H₂O were formed immediately after CH₄ feeding and no CH₄ was observed during the reduction period. In contrast to the happened with the Ni16- α Al oxygen carrier, the CO and H₂ concentrations were zero during the initial part of the reduction period. Later, the 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. Thus, it was concluded that with the addition of CuO to the Ni-based oxygen carriers impregnated on α - or γ -Al₂O₃, a full conversion of CH₄ to CO₂ and H₂O can be reached during a part of the reduction period. The time of this period with zero emissions of CO and H₂ increased with increasing the CuO content in the oxygen carrier. However, it seemed that the NiO utilization before CO and H₂ appearance was low.

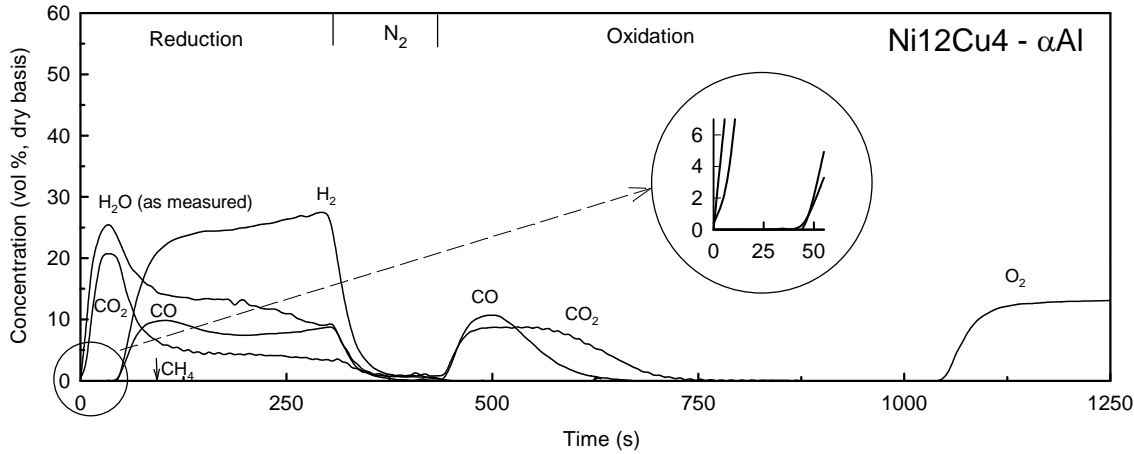


Figure 11. Gas product distribution (dry basis) obtained in the fluidized bed with a Ni-Cu based oxygen carrier. H₂O concentration as measured in FTIR analyzer.

Two parameters were determined by analysis of the gas product distribution during reduction in FB: X_{CO_2} represents the MeO conversion to CO₂ before the CO and H₂ appearance in the gas stream, and X_T represents the overall MeO conversion obtained in the test. Table 2 shows the values of these parameters for the Ni-Cu oxygen carriers as well as the concentrations corresponding to thermodynamic equilibrium for a simultaneous reaction of CuO and NiO with CH₄ in a closed system.

Table 2. Parameters obtained from FB tests and equilibrium concentrations.

Oxygen carrier	X_T^a	X_{CO_2}	Equilibrium concentration at 950 °C	
			H ₂	CO
Ni16- α Al	58	--	0.44	0.33
Ni12Cu4- α Al	42	16	0.33	0.24
Ni8Cu8- α Al	57	38	0.22	0.16
Ni4Cu12- α Al	79	61	0.11	0.08
Ni1Cu15- α Al	87	67	0.027	0.02
Cu15- α Al	93	70	0	0

a- 300 g of oxygen carrier, 950 °C, 25 % CH₄, 0.1 m/s, 300 s of reduction time.

It was observed that the MeO conversion before CO and H₂ generation increased with increasing the CuO content in the oxygen carrier. It is important to indicate that the CO and H₂ concentrations were zero during this period of time. However if the equilibrium for a uniform mixture of both metal oxides in a closed system is fulfilled, CO and H₂ concentrations should be different to zero, as it is indicated in Table 2. Only if CuO is the unique reacting metal oxide during this period it is possible to reach zero emissions of CO and H₂. As it was previously mentioned, TGA results indicated a two-step reaction with low reaction rates for the second one, which would correspond to the Al₂O₄Ni reduction.

To confirm what metal oxide reacts before or if there is a simultaneous reaction of both metal oxides, a sample was taken from the FB corresponding to the period of full conversion to CO₂ during the reduction process of the Ni₈Cu₈- α Al oxygen carrier (X = 38%). XRD analysis (see Table 1) indicated the presence of metallic Cu, however no metallic Ni was found. This indicates that CuO is initially used for the reaction with CH₄, and explains the zero concentrations measured at the gas outlet stream.

In the previous section, it was found the positive effect on the CO and H₂ equilibrium concentrations of the addition of CuO to the Ni-based oxygen carriers prepared by dry impregnation on alumina supports. However, these new materials showed a decrease in their reactivity. It is well known in the literature that small amounts of some salts can change the material properties with respect to their reactivity or catalytic activity by changes in their internal structure. They may be present as separate phases or combined with Al₂O₃ as aluminate or spinel phases^{26,27}. Basic metal oxides, such as K₂O and La₂O₃ are often incorporated into steam reforming catalysts to provide operational advantages resulting from lower support acidity, higher nickel dispersion, and better steam activation.^{28,29} To improve the reactivity of the oxygen carriers, salts of K₂O and La₂O₃ were added in several amounts to the Ni-Cu oxygen carriers.

However, the reduction reactivities of the Ni-Cu oxygen carriers did not improve with the addition of K or La, and were lower than the original Ni-based oxygen carrier, Ni₁₆- α Al. The behavior of these modified oxygen carriers was also analyzed in the FB, but only small changes were observed in the gas product distribution, indicating that the addition of K and La salts has not a significant effect on the CO and H₂ emissions.

3.2.1 Mixing particles of Ni-based and Cu-based oxygen carriers.

Ni-based oxygen carriers impregnated on α -alumina showed the highest reduction reactivity and also in a previous work¹⁷ it was found that Cu-based oxygen carriers impregnated on alumina had a very high reactivity. So, a new test at 950°C was carried out in the fluidized bed facility mixing oxygen carrier particles of Ni₁₆- α Al and Cu₁₅- γ Al in the same NiO/CuO weight ratio as the carrier Ni₁₂Cu₄- α Al.

Figure 12 shows the results obtained in the fluidized bed with these mixed carriers. A comparison between the results obtained in this test and those obtained with the carrier Ni₁₂Cu₄- α Al (Figure 11) shows a similar gas product distribution. However, with the mixed carrier particles, the time during the reduction period in which the CH₄, CO and H₂ concentrations were zero was higher because of the higher reactivity of Ni₁₆- α Al and Cu₁₅- γ Al oxygen carriers. However, multicycle tests carried out at 950 °C in FB showed that Cu-based oxygen carrier particles were destroyed after 35 cycles, which eliminates the possibility of use of a mixture of both carriers at high temperatures. To use the CuO capability to reduce CO and H₂ emissions, that is to finish the combustion obtained with the Ni-based oxygen carriers, it would be necessary to use a new reactor located downstream the fuel reactor operating at a maximum temperature of 850 °C.

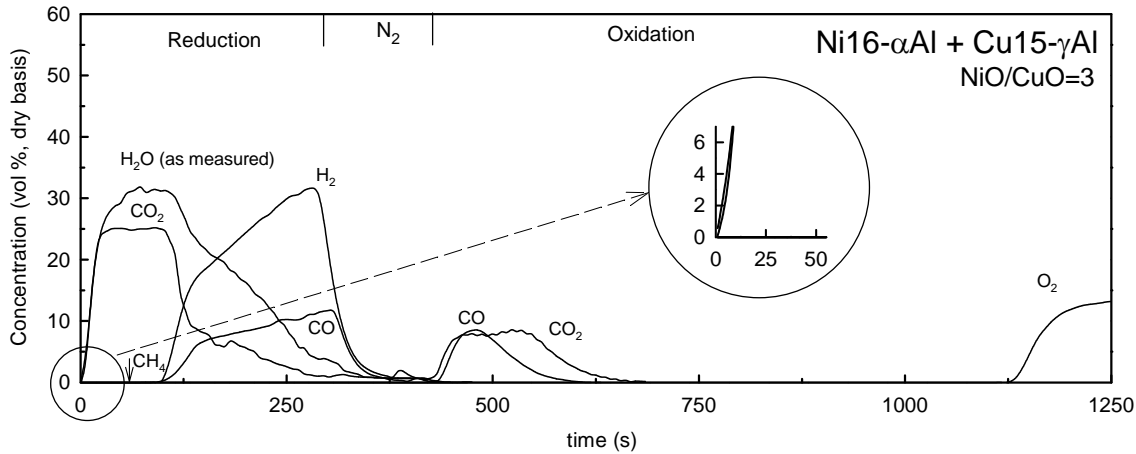


Figure 12. Gas product distribution (dry basis) obtained in fluidized bed with Ni16- α Al and Cu15- γ Al oxygen carriers mixed with the same NiO and CuO weights as Figure 10. H₂O concentration as measured in FTIR analyzer.

3. Attrition and agglomeration behavior

It is important that oxygen carriers maintain high reactivity and particle integrity for many cycles of oxidation and reduction. 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. Figure 13 shows the attrition rate of several oxygen carriers tested as a function of the number of reduction/oxidation cycles.

The attrition rates were higher in the first cycles due to the rounding effects on the particles and to the fines stuck to the particles during preparation. Later, the attrition rates due to the internal changes produced in the particles by the successive reduction and oxidation processes decreased reaching low attrition rate values. The mean attrition rate obtained from cycle 30 to 100 was lower than 0.01%/cycle for the majority of the oxygen carriers. Assuming this value as a measure of the steady-state attrition rate of the carrier particles, the lifetime of the particles will be higher than 10000 cycles. This good behavior with respect to attrition is not strange considering that the alumina used as support in the

catalyst manufacture industry for use in fluidized beds at similar conditions to those existing in a CLC process. Figure 13 also shows the oxygen carriers that were destroyed after multi-cycle testing.

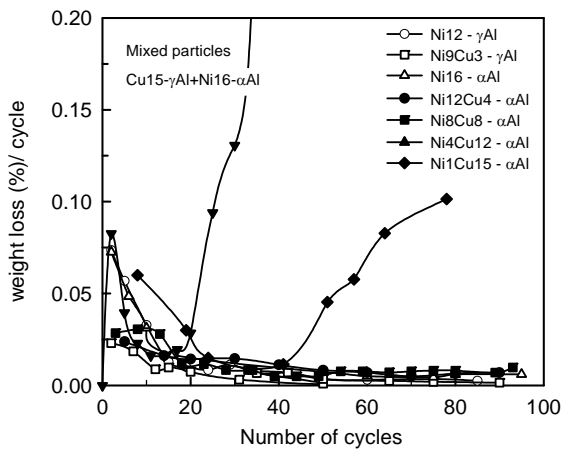


Figure 13. Attrition rates of several Ni-based oxygen carriers prepared by impregnation.

On the other hand, the use of Cu-based oxygen carriers in the CLC process has been rejected for some researchers by the agglomeration problems that present this type of oxygen carriers.^{14,16} For this reason, special attention was taken to analyze the agglomeration behavior of the Ni-Cu oxygen carriers during cyclic reduction/oxidation process in the FB reactor. It is important to indicate that it was not found any agglomeration problem with any Ni-Cu oxygen carrier tested. These results agree with those found in a previous work¹⁷ where agglomeration can be avoided in any oxygen carrier prepared by impregnation if the Cu content was below 10-15 wt.%, as it was the case of the oxygen carriers prepared for this work.

4. Discussion

Different oxygen carriers of Ni-Cu have been prepared to reduce the CO and H₂ emissions produced during a CLC process working with Ni-based carriers. The tests carried out in batch fluidized bed with these oxygen carriers showed the existence of an initial reduction period with full conversion to CO₂ and H₂O, that is, with zero emissions of CO and H₂. This time depended on the CuO content of the oxygen carrier. From TGA reactivity tests and XRD analysis of partially reduced samples obtained in

batch fluidized bed tests it was concluded that the CuO present in the oxygen carrier reacts before the NiO and that the NiO utilization during this period was low.

However, in a fluidized bed reactor with perfect mixing of solids, as it is the fuel reactor in a CLC process, it is not possible to get zero CO and H₂ emissions because there are particles with a broad distribution of MeO conversions inside. The CO and H₂ emissions obtained in a CLC process could be decreased working with Ni-Cu oxygen carriers with increasing CuO contents. However, to work at high temperatures (above 950 °C) it is necessary the existence of a minimum amount of NiO in the oxygen carrier (about 4%) to stabilize the material.

To completely eliminate the low CO and H₂ concentrations obtained at the outlet of the dense phase of the fuel reactor working with Ni-Cu oxygen carriers it would be necessary an additional reaction step. This could be obtained with the use of a two-stage fluidized bed for the fuel reactor. Calculations obtained from the reactivity data obtained with H₂ in TGA showed that the residence time of the solids in the upper fluidized bed necessary to eliminate the low CO and H₂ concentrations coming from the lower fluidized bed would be low.

On the other hand, as the possibility of use a physical mixture of a Ni- α Al and Cu- α Al oxygen carriers at 950 °C is not acceptable due to the physical destruction of Cu- α Al, to use the Cu- α Al capability to reduce the CO and H₂ emissions obtained in a CLC process working with Ni-based oxygen carriers, it would be necessary the use of an additional reactor located downstream the fuel reactor operating at a maximum temperature of 850 °C.

5. Conclusions

NiO- α -Al₂O₃ oxygen carriers prepared by dry impregnation showed very high reactivities both during reduction and oxidation reactions. The conversion of CH₄ with these oxygen carriers was complete although the equilibrium concentrations of CO and H₂ were obtained at the gas outlet of the reactor.

The addition of CuO to the Ni-based oxygen carriers allows the full conversion of CH₄ to CO₂ and H₂O in the batch fluidized bed reactor during a period of the reduction time. TGA and XRD studies of partially reduced Ni-Cu oxygen carriers indicated that CuO was used for the reduction reaction before NiO. During this initial period, equilibrium concentrations of CO and H₂ were zero because only reacts the CuO and there is not presence of reduced Ni.

However, to take advantage of the capability of these Ni-Cu oxygen carriers to reduce the CO and H₂ emissions in a continuous CLC system, a two-stage fluidized bed would be necessary. Oxygen carriers with increasing amounts of CuO allowed to increase the metal oxide fraction used for the complete combustion to CO₂. The presence of more than 4 % of NiO in the oxygen carrier stabilized the CuO phase and allowed to work at 950 °C with high metal oxide utilization for complete CH₄ combustion.

The use of salts of K and or La in the preparation of the Ni-Cu oxygen carriers did not produce any improvement in their behavior during CLC testing. The attrition rate of the all carriers prepared by impregnation on alumina was low, and no agglomeration problems were observed with any of the Ni-Cu oxygen carriers.

ACKNOWLEDGMENT

This research was carried out with financial support from the CCP (CO₂ Capture Project), Project subcontract No. C006 under DOE contract No. DE-FC26-01NT411145 and the Spanish Ministry of Education and Science (Project CTQ2004-04034)

REFERENCES

1. Ritcher, H.; Knoche, K. Reversibility of combustion process. In Efficiency and Costing; Second Law Analysis of Process; Gaggioli, R.A. Ed.; ACS Symp. Ser. **1983**, 235, 71-86.
2. Mattisson, T.; Lyngfelt, A. Capture of CO₂ using Chemical-Looping Combustion. In *Scandinavian-Nordic Section of Combustion Institute*, **2001**.
3. Ishida, M.; Jin, H. A novel combustor based on chemical-looping reactions and its reaction kinetics. *J. of Chem. Eng. of Japan* **1994**, 27, 296-301.
4. Ishida, M.; Jin, H. A novel chemical-looping combustor without NO_x formation. *Ind. Eng. Chem. Res.* **1996**, 35, 2469-2472.
5. Wolf, J.; Anheden, M.; Yan, J. Comparison of nickel- and iron-based oxygen carriers in chemical looping combustion for CO₂ capture in power generation. *Fuel* **2005**, 84, 993-1006.
6. Ishida, M.; Jin, H.; Okamoto, T. A fundamental study of a new kind of medium material for chemical-looping combustion. *Energy&Fuels* **1996**, 10, 958-963.
7. Ishida, M.; Jin, H.; Okamoto, T. Kinetic behavior of solid particles in chemical-looping combustion: suppressing carbon deposition in reduction. *Energy&Fuels* **1998**, 12, 223-229.
8. Jin, H.; Okamoto, T.; Ishida, M. Development of a novel chemical-looping combustion: synthesis of a looping material with a double metal oxide of CoO-NiO. *Energy&Fuels* **1998**, 12, 1272-1277.
9. Jin, H.; Okamoto, T.; Ishida, M. Development of a novel chemical-looping combustion: Synthesis of a solid looping material of Ni/NiAl₂O₄. *Ind. Eng. Chem. Res.* **1999**, 38, 126-132.
10. Jin, H.; Ishida, M. Reactivity study on natural-gas-fueled chemical-looping combustion by a fixed-bed reactor. *Ind. Eng. Chem. Res.* **2002**, 41, 4004-4007.

11. Ryu, H. J.; Bae, D. H.; Jin, G. T. Effect of temperature on reduction reactivity of oxygen carrier particles in a fixed bed chemical-looping combustor. *Korean J. of Chem. Eng.* **2003**, 20, 960-966.
12. Villa, R.; Cristiani, C.; Groppi, G.; Lietti, L.; Forzatti, P.; Cornaro, U.; Rossini, S. Ni based mixed oxide materials for CH₄ oxidation under redox cycle conditions. *J. of Molecular Catalyst A: Chemical* **2003**, 204-205, 637-646.
13. Mattisson, T.; Jardnas, A.; Lyngfelt, A. Reactivity of some oxides supported on alumina with alternating methane and oxygen- Application for chemical-looping combustion. *Energy&Fuels* **2003**, 17, 643-651.
14. Cho, P.; Mattisson, T.; Lyngfelt, A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* **2004**, 83, 1215-1225.
15. Mattisson, T.; Johansson, M.; Lyngfelt, A. Multicycle reduction and oxidation of different types of iron oxide particles- application to Chemical-Looping Combustion. *Energy&Fuels* **2004**, 18, 628-637.
16. Copeland, R.; Alptekin, G.; Cesario, M.; Gershanovich, Y. Sorbent Energy Transfer System (SETS) for CO₂ separation with high efficiency. *The 27th Int. Techn. Conference on Coal Utilization&Fuel systems.* **2002**, Clearwater, Florida, USA.
17. de Diego, L. F.; Gayán, P.; García-Labiano, F.; Celaya, J.; Abad, A.; Adánez, J. Impregnated CuO/Al₂O₃ oxygen carriers for chemical-looping combustion: avoiding fluidized bed agglomeration. *Energy&Fuels* **2005**, 19, 1850-1856.
18. Adánez, J.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad A. Selection of oxygen carriers for chemical-looping combustion. *Energy&Fuels* **2004**, 18, 371-377.

19. Bolt, P.H.; Habraken, F.H.P.M.; Geus, J.W. Formation of Nickel, Cobalt, Copper, and Iron aluminates from α - and γ -Alumina-supported oxides: a comparative study. *J. of Solid State Chemistry* **1998**, 135, 59-69.
20. Hou, K.; Hughes, R. The kinetics of methane steam reforming over a Ni/ α -Al₂O catalyst. *Chem. Eng. Sci.* **2001**, 82, 311-328.
21. Cho, P, Mattisson T. Lyngfelt A., Carbon Formation on Nickel and Iron Oxide-Containing Oxygen Carriers for Chemical-Looping Combustion. *Ind. Eng. Chem Res.* 2005, 668-676.
22. Adánez, J.; García-Labiano, F.; de Diego, L.F.; Gayán, P.; Celaya, J.; Abad, A. Characterization of oxygen carriers for chemical-looping combustion. *7th International Conference on Greenhouse Gas Technology*, Vancouver, Canada, **2004**. Paper 91.
23. Adánez, J.; García-Labiano, F.; de Diego, L.F.; Gayán, P.; Abad, A.; Celaya, J. Development of oxygen carriers for chemical-looping combustion. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results form the CO₂ Capture Project*. Thomas, D., Benson, S. Eds.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 1, Chapter 34.
24. Lyngfelt, A.; Kronberger, B.; Adánez, J.; Morin, J.-X.; Hurst, P. The GRACE project. Development of oxygen carrier particles for chemical looping combustion. Design and operation of a 10 kW chemical looping combustor. *7th International Conference on Greenhouse Gas Technology*, Vancouver, Canadá, **2004**. Paper 132.
25. Lyngfelt, A.; Thunman, H. Construction and 100 h of operational experience of a 10 kW Chemical-Looping Combustor. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results form the CO₂ Capture Project*. Thomas, D., Benson, S. Eds.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 1, Chapter 36.

26. Richardson, J.T.; Turk, B.; Twigg, M.V. Reduction of model steam reforming catalysts: effect of oxide additives. *Applied. Cat. A: General* **1996**, 148, 97-112.
27. Horiuchi, T.; Sakuma, K.; Fukui, T.; Kubo, Y.; Osaki, T.; Mori, T. Suppression of carbon deposition in the CO₂-reforming of CH₄ by adding basic metal oxides to a Ni/Al₂O₃ catalyst. *Applied. Cat. A: General* **1996**, 144, 111-120.
28. Osaki, T.; Mori, T. Role of potassium in carbon-free CO₂ reforming of methane on K-promoted Ni/Al₂O₃ catalysts. *J. of Catalysis* **2001**, 204, 89-97.
29. Martínez, R.; Romero, E.; Guimon, C.; Bilbao, R. CO₂ reforming of methane over coprecipitated Ni-Al catalysts modified with lanthanum. *Applied. Cat. A: General* **2004**, 274, 139-149.