

Submitted, accepted and published by:
Energy & Fuels 19 (5) (2005) 1850-1856

Impregnated CuO/Al₂O₃ Oxygen Carriers for Chemical- Looping Combustion: Avoiding Fluidized Bed Agglomeration

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

Instituto de Carboquímica (CSIC), Department of Energy and Environment, Miguel Luesma Castán 4,
50015 Zaragoza, Spain

E-mail: ldediego@icb.csic.es

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

ABSTRACT. Chemical-looping combustion (CLC) is a combustion technology with inherent separation of the greenhouse gas CO₂ that involves the use of an oxygen carrier, which transfers oxygen from air to the fuel avoiding the direct contact between them. An oxygen carrier in a CLC power plant must show high reaction rates and sufficient durability in successive cycle reactions. Furthermore, the oxygen carrier particles must not agglomerate. In order to produce materials with these characteristics different Cu-based oxygen carriers with a range of CuO content between 10 and 26 wt.% were prepared by

impregnation using alumina as support. The particles were calcined at different temperatures in the range of 550-950°C. The oxygen carriers were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and thermogravimetry (TGA). The samples were evaluated in a fluidized bed facility in order to determine their behavior in multicycle reduction-oxidation tests. A number of 100 cycles was done when the carrier did not agglomerate. The effects of metal content, calcination temperature and method of preparation on the oxygen carriers reactivity, gas product distribution, attrition rate and agglomeration were analyzed for the different oxygen carriers. It was observed that the CuO content in the oxygen carrier, the calcination temperature used in the preparation and the conversion reached by the oxygen carrier during the reduction period affected the agglomeration process. In this work, the preparation conditions to produce Cu-based oxygen carriers with high reactivities, and small attrition rates were found. Moreover, the agglomeration of these oxygen carriers in the fluidized reactor, which is the main reason adduced in the literature to reject the Cu-based oxygen carriers for the CLC process, was avoided.

1. Introduction

To reduce greenhouse gas emissions from electric power generation, the CO₂ produced from fossil fuel combustion must be captured and be made available for use or sequestration. CO₂ can be captured from the flue gas of a pulverized fuel power plant or from natural gas combined cycles, but in these cases CO₂ has a low volumetric fraction in the gas mixture (<15%) and its capture is achieved mainly by scrubbing with amine or other sorbents. Other techniques include cryogenics, membranes and adsorption. CO₂ capture would decrease the electrical efficiency of power plants¹. Besides the studies elaborated for reduction of CO₂ emissions of existing power plants, research has also began for the theoretical and practical studies of power alternatives with virtually zero emissions of pollutants².

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of the greenhouse gas CO₂. This technology involves the use of a metal oxide as an oxygen carrier, which transfers oxygen from the air to the fuel avoiding the direct contact between fuel and air. The CLC

system is made of two interconnected reactors, designated as air and fuel reactors. In the fuel reactor, the fuel gas is oxidized to CO₂ and H₂O by a metal oxide through the chemical reaction:



This 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.

Different metal oxides have been proposed in the literature as potential candidates for CLC³⁻⁵: CuO, NiO, Mn₂O₃, Fe₂O₃ and CoO. In general, these metal oxides are combined with an inert which acts as a porous binder enhancing the reactivity of the active phase and, probably, as an ionic conductor for oxygen^{6,7}. Additionally, this inactive binder increases the mechanical strength and the attrition resistance of the oxygen carrier. An oxygen carrier in a CLC power plant must show high reaction rates and conversions, resistance against carbon deposition, sufficient durability in successive cycle reactions and high mechanical strength. Furthermore, the oxygen carrier particles should not agglomerate.

Mattisson and co-workers⁸⁻¹⁰ prepared Ni-, Cu-, Co-, and Mn-based oxygen carriers on alumina support by dry impregnation and their reactivity was studied in a thermogravimetric analyzer (TGA). Moreover, these authors compared 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.¹¹ developed oxygen carriers, containing Cu, Fe, and Ni with a variety of binder materials and active metal oxide contents to be used in their Sorbent Energy Transfer System (SETS). 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. Adanez et al.¹² prepared 240 samples of potential oxygen carriers based on Cu, Fe,

Mn and Ni oxides and analyzed the effects of the chemical nature and composition of the carriers and the sintering temperature on the reactivity and mechanical strength of the carriers.

In a previous work¹³, potential Cu-based oxygen carriers for the CLC process were prepared using alumina, silica, sepiolite, titania, and zirconia as binders. The effects of oxygen carrier composition and preparation method were investigated in a TGA to develop oxygen carriers exhibiting high redox reaction rates without important changes in the chemical, structural and mechanical properties for a high number of reduction-oxidation cycles. It was observed that the oxygen carriers prepared by mechanical mixing and by coprecipitation showed an excellent chemical stability in multicycle tests, however, the mechanical properties of these carriers were seriously degraded to unacceptable levels. On the other hand, Cu-based oxygen carriers prepared by impregnation exhibited high reactivities and complete conversions in multicycle tests in TGA. In addition, the reacted particles maintained the chemical and mechanical properties of the fresh carriers, suggesting that impregnated carriers are good candidates for chemical-looping combustion processes.

The goal of this work was to produce impregnated CuO/Al₂O₃ oxygen carriers with high reaction rates, high conversions, low attrition rates, and without agglomeration of solids during a high number of reduction-oxidation cycles in a fluidized bed reactor. For that, the effects of the metal content, calcination temperature, and preparation method were investigated.

2. Experimental Section

2.1. Preparation of oxygen carriers

Commercial γ -Alumina (Puralox NWA-155, Sasol Germany GmbH) particles of 0.1-0.32 mm with a density of 1.3 g/cm³ and a porosity of 55.4% was used as support to prepare, by two different impregnation methods, different samples of Cu-based oxygen carriers. In addition, a commercial catalyst supported on alumina (Aldrich Chemical Company, Inc. Cat. No. 417971) with a 13 wt.% of CuO was also analyzed for comparison purposes.

Wet impregnation. The commercial alumina particles were immersed into an excess of an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>99.5 % Merk) 1.6 M for 12 h at ambient temperature. After filtration, the oxygen carrier was dried at 60°C for 24 h and calcined in air atmosphere for 30 min at 550°C in a muffle oven to decompose the impregnated copper nitrate into insoluble copper oxide. Oxygen carriers in three different $\text{CuO}/\text{Al}_2\text{O}_3$ weight ratios (10/90, 17/83, and 21/79) were prepared by applying one, two or three successive wet impregnation+filtration+calcination steps. Finally, each carrier was calcined for 1 h at 550 or 950°C in air atmosphere.

Moreover, one oxygen carrier was prepared by wet impregnation using an almost saturated (5.4 M) aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, resulting in a copper loading of 23 wt.%, similar to the one obtained by three consecutive wet impregnations with a non-saturated solution.

In this preparation method, it was observed that the final content of the copper oxide in the oxygen carriers depended slightly on how long the filtration step was carried out.

Dry impregnation. The oxygen carriers were prepared by addition of a volume of copper nitrate solution corresponding to the total pore volume of the support particles ($0.42 \text{ cm}^3/\text{g}$). The aqueous solution was slowly added to the alumina particles, with thorough stirring at room temperature. No filtration or drying steps was required with this method. Oxygen carriers with three different $\text{CuO}/\text{Al}_2\text{O}_3$ weight ratios (10/90, 15/85, and 26/74) were prepared by one impregnation using a 3.4 M solution, and by one or two successive impregnations with a solution 5.4 M, respectively. Also in this case, the samples were calcined, in air atmosphere for 30 min at 550°C in a muffle oven, to decompose the impregnated copper nitrate into insoluble copper oxide. Finally, the oxygen carriers were calcined in air atmosphere for 1 h at the desired temperature (550, 850, and 950°C).

Table 1 shows the oxygen carriers prepared for testing in multicycle tests. The oxygen carriers are designated with the chemical symbol referred to the active metal oxide (Cu), followed by the weight CuO content, and the symbol of the support (Al). The preparation method (WI=wet impregnation, DI=dry impregnation) and the calcination temperature used in the preparation are included. For example, an oxygen carrier composed of 10 wt.% of CuO and 90 wt.% of alumina, prepared by wet impregnation

and calcined at 550°C will be designated as Cu10Al-WI-550. The commercial catalyst acting as a carrier will be designated as Cu13Al-C and no data were available about the preparation method of this carrier.

2.2. Multicycle tests

Experimental set-up. Figure 1 shows the experimental set-up used for testing the oxygen carriers. It consisted in a system for gas feeding, a fluidized bed reactor, a two ways system to recover the solids elutriated from the fluidized bed, and a gas analysis system. The gas feeding system had different mass flow controllers connected to an automatic three-way valve. This valve always forced to pass N₂ (inert) between the reducing gas and the oxidation gas to avoid explosions. The fluidized bed reactor was 0.054 m I.D. and 0.5 m height, with a 0.3 m of preheating zone just under the distributor. Two hot filters were located downstream from the fluidized bed to recover the solids elutriated from the bed during the successive reduction-oxidation cycles, which allowed us to obtain elutriation data at different times or number of cycles. The reactor had two connected pressure taps in order to measure the differential pressure drop in the bed. Agglomeration problems were detected by a sharp decrease in the bed pressure drop during operation, showing the defluidization of the bed. Different gas analyzers continuously measured the gas composition at each time. The H₂O, CO, CO₂, and CH₄ gas concentrations were measured in two infrared analyzers (FTIR and NDIR), the O₂ in a paramagnetic analyzer, and the H₂ by gas conductivity. For better data analysis, the gas concentrations versus time profiles measured were corrected for gas flow and dispersion through the sampling line and analyzers.

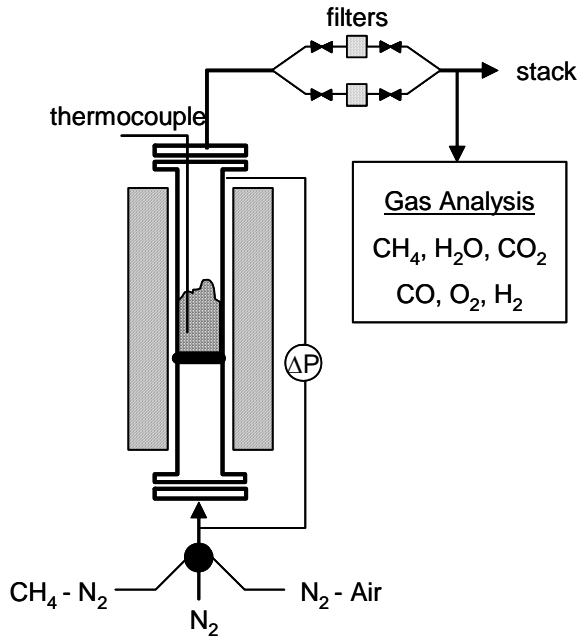
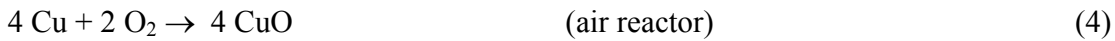
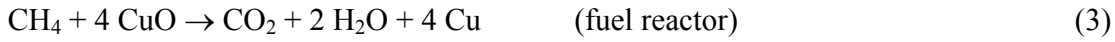


Figure 1. Experimental set-up used for multicycle tests.

Operating procedure. Batches of 200-250 g of oxygen carrier were used with a particle size of 0.1-0.32 mm. The inlet superficial gas velocity into the reactor was 0.1 m/s ($u/u_{mf} = 5-7$), both in the reduction and oxidation periods. The composition of the reducing gas was 25 vol.% CH₄ in N₂ and it was selected to avoid exceed the terminal velocity of the particles due to the increase of the gas velocity produced during the CH₄ conversion. A mixture of air with N₂ was used during oxidation with a low O₂ concentration (~ 8 vol.%). This O₂ concentration was used instead of air to avoid a large temperature increase during the exothermic oxidation reaction, since the reactor had no cooling system. The reduction periods were varied between 60 and 300 s. The oxidation periods necessary for complete oxidation varied between 900 and 1800 s. To avoid mixing of CH₄ and O₂, N₂ was introduced for 120 s after each reducing and oxidizing period. The tests were normally carried out at 800°C because at higher temperatures CuO, although stable in air atmosphere, decomposed into Cu₂O in N₂ atmosphere (with the subsequent loss of oxygen transport capacity of the carrier). Exceptionally, tests were carried out at 950°C to check the effect of this high temperature in the behavior of the carrier.

The oxygen carriers were exposed to a total number of 100 reduction/oxidation cycles, when the oxygen carrier did not agglomerate. Therefore, the oxygen carriers were evaluated in the fluidized bed reactor for a minimum time of 34 hours and a maximum of 65 hours.

Data evaluation. Reactions 3 and 4 show the main reactants and products involved in the reactions of the Cu-based oxygen carriers using CH₄ as reducing gas.



The conversions of the oxygen carriers as function of time during the reduction and oxidation periods were calculated from the gas outlet concentrations by the equations:

$$X_{red} = \int_{t_0}^{t_{red}} \frac{Q_{out}}{n_0 P_{tot}} (2P_{CO_2,out} + P_{CO,out} + P_{H_2O,out}) dt \quad (5)$$

$$X_{oxi} = \int_{t_0}^{t_{oxi}} \frac{2Q_{out}}{n_0 P_{tot}} \left(\frac{Q_{in}}{Q_{out}} P_{O_2,in} - P_{O_2,out} - 1/2P_{CO,out} - P_{CO_2,out} \right) dt \quad (6)$$

where X is the conversion of the oxygen carrier, n₀ are the moles of oxygen which can be removed from fully oxidized oxygen carrier, Q_{in} is the molar flow of the gas coming into the reactor, Q_{out} is the molar flow of the gas leaving the reactor, P_{tot} is the total pressure, P_{i,in} is the partial pressure of gas i incoming to the reactor, P_{i,out} is the partial pressure of gas i exiting the reactor, and t is the time.

The last terms in equation 6 take into account the formation of CO and CO₂ during the oxidation period due to the oxidation of C coming from the decomposition of CH₄ in the reduction period.

2.3. Characterization of oxygen carriers

The oxygen carriers were characterized before reaction and after 100 reduction-oxidation cycles. Reactivities of the prepared carriers were determined using H₂ as fuel to avoid C formation, in a TGA, CI Electronics type, described elsewhere¹²⁻¹³. The microstructures of the particles and element distribution in the solid were observed by scanning electron microscope (SEM) on a Zeiss DSM 942 microscope equipped with an Oxford Link-Isis EDX analyzer. Also, the crystalline structures of solid materials were identified by X-ray powder diffraction (XRD) from diffraction patterns between 10°-70°

2 θ using Cu K α radiation obtained with an X-ray diffractometer, Bruker AXS D8ADVANCE, equipped with a graphite diffracted-beam monochromator.

3. Results and Discussion

Before testing the oxygen carriers in the fluidized bed facility, the reactivity of the fresh samples were analyzed in a TGA using H₂ as fuel. All the oxygen carriers showed very high reactivity independently of the preparation method, number of impregnations or calcination temperatures used in their preparation. As an example, Figure 2 shows the effect of the calcination temperature on the reactivity of the oxygen carriers.

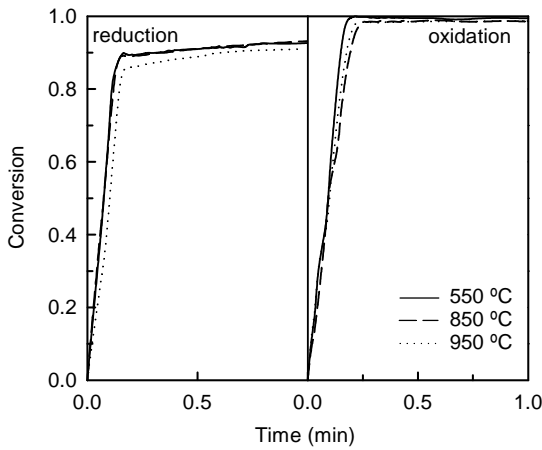


Figure 2. Effect of the calcination temperature on the reactivity in TGA of fresh Cu-based oxygen carriers. Cu15Al-DI, C_{H₂} (red)= 40 vol.%, C_{O₂} (oxid)= 21 vol.%, T=800°C.

The experiments carried out in the fluidized bed reactor allow us to know the behavior of the carriers during successive reduction-oxidation cycles. Moreover, the chemical and structural changes due to the chemical reaction, and the attrition phenomena existing in the fluidized beds can be investigated.

Figure 3 shows the outlet concentrations of CH₄, CO₂, CO, H₂, and O₂ (dry basis), in the reduction and the oxidation periods as a function of time for a typical cycle using the carrier Cu15Al-DI-850. CO₂ and H₂O were formed just immediately after the introduction of CH₄ to the reactor, and no CH₄, CO and H₂ were observed during most of the carrier reduction period, thus indicating that CH₄ conversion was

complete. Only when most of the oxygen carrier was reduced, the CH_4 concentration increased, the CO_2 and H_2O concentrations decreased, and started the formation of CO and H_2 . It has to be pointed out that complete methane conversion to CO_2 is thermodynamically limited⁵ for the oxygen carriers based on Ni and Fe (except in the transformation of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) which make that small concentrations of CO and H_2 are always present in the gas outlet of the fuel reactor. This will reduce the energetic efficiency, and will make necessary to include some process modifications to reduce the amount of non-condensable gases in the CO_2 compression and condensation stages. However, complete conversion of CH_4 without emission of CO and H_2 can be achieved using Cu-based oxygen carriers.

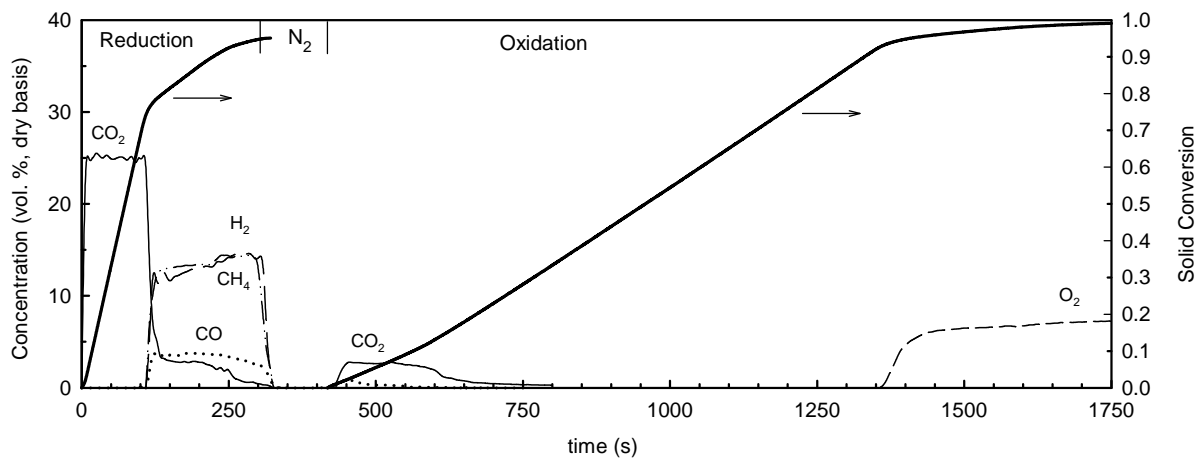


Figure 3. Typical product gas distribution in a cycle for $\text{CuO}/\text{Al}_2\text{O}_3$ oxygen carriers during multicycle testing in the fluidized bed. Cu15Al-DI-850 , $C_{\text{CH}_4(\text{red})} = 25$ vol.%, $C_{\text{O}_2(\text{oxid})} = 8$ vol.%, $T = 800^\circ\text{C}$.

After reduction, the carrier was regenerated by oxidation with O_2 (~ 8 vol.% of O_2 in N_2). During most of the carrier oxidation period the O_2 outlet concentration was zero because the oxygen was consumed by the oxidation of the Cu contained in the carrier particles and because the oxygen carrier oxidation was limited by the supply of O_2 to the reactor. At the end of the oxidation period, the oxygen concentration rapidly increased until 8 vol.%. A small concentration of CO and CO_2 appeared at the reactor outlet stream almost immediately after the O_2 introduction to the reactor, which was attributed to the oxidation of the carbon deposits formed in the previous reduction step. The temperature of the bed

increased only 10-20°C in the whole oxidation period due to the diluted oxygen concentration used for the experiments. Similar gas profiles were found with all the different oxygen carriers tested in the fluidized bed reactor.

3.1. Agglomeration of the carriers

Until now, the Cu-based oxygen carriers have been rejected as potential candidates for CLC as a consequence of their agglomeration^{9,11}. In this work, all the oxygen carriers prepared were evaluated in the fluidized bed reactor with respect to the agglomeration process. The behavior of the different carriers prepared in this work with respect to the agglomeration is shown in Table 1.

All the oxygen carriers with CuO contents greater than 20 wt.% (Cu21Al-WI-550, Cu21Al-WI-950, Cu23Al-WI-550, and Cu26Al-DI-550) agglomerated independently of the preparation method, the number of impregnations, or the calcination temperature used in their manufacture. In these carriers, the agglomeration always appeared at the beginning of the oxidation period, and it was detected by a sharp decrease in the bed pressure drop. Due to the sticking of the particles causing defluidization, the experiment must be stopped. However, it must be indicated that the lumps formed by sticking of the particles showed small mechanical strength and they were easily destroyed pressing with the fingers. The oxygen carriers prepared with a CuO content of 10 wt.% (Cu10Al-WI-550, Cu10Al-WI-950, Cu10Al-DI-550, Cu10Al-DI-950) never agglomerated, independently of the preparation method and the calcination temperature used. The commercial carrier (Cu13Al-C) with a CuO content of 13 wt.% did also not agglomerate.

The behavior of the carriers with an intermediate CuO content of 15 or 17 wt.% depended on the calcination temperature. Thus, those calcined at 950°C (Cu17Al-WI-950, Cu15Al-DI-950) presented agglomeration independently of the preparation method. However, those calcined at 550 or 850°C (Cu17Al-WI-550, Cu15Al-DI-550, Cu15Al-DI-850) did not agglomerate.

To understand the effects of the copper content and calcination temperature in the agglomeration process, more studies on carbon deposition and solid particle structure were carried out with some selected samples.

With the oxygen carriers that agglomerated, more tests in the fluidized bed reactor were carried out and analyzed in detail. It was observed that if the cycles had a short reduction period, where the carrier conversion (X_{red}) was lower than 50%, the oxygen carrier could be used without agglomeration problems in many cycles. As at the end of the reduction period, when the oxygen carrier conversion was high, started the formation of CO, H₂ and C, it was thought that the combustion of the C at the beginning of the oxidation period could be the responsible of the agglomeration. To investigate this fact, some cycles were carried out using H₂ as fuel gas to avoid C formation. However, the behavior of the oxygen carriers in these tests was the same as the previous using CH₄. Therefore, the C formation was rejected as responsible of the agglomeration process of the Cu-based oxygen carriers.

As the agglomeration always appeared in the oxidation period other possible explanation for this process could be related to the amount of Cu⁰ formed in the reduction period and the increase of particle temperature due to the heat generated during the exothermic oxidation taking place inside the oxygen carrier. If the temperature at any point of the particle increases up to the value near to the melting point of the metal (1085°C), the oxygen carrier could sinter. In a previous work¹⁴, the increase of temperature inside the oxygen carrier particles was calculated and it was found that this increase for the Cu-based oxygen carriers was very low (< 10°C). In addition, because the increase of temperature inside the particles is a function of the reaction rate, and therefore of the oxygen concentration, some tests using different oxygen concentrations between 2 and 15 vol.% were carried out. It was observed that the agglomeration process appeared independently of the oxygen concentration used in the tests.

As it seems that the operational conditions were not the responsible for the agglomeration process, the structural properties of the oxygen carriers were also investigated. All the Cu-based oxygen carriers were characterized before and after reaction using XRD. Moreover, some new samples were prepared at different calcination temperatures in the range of 800-1100°C only for characterization. The main results are summarized in Table 2. In addition, Table 2 shows the XRD characterization of the support after calcination in the range 550-1200°C.

In the fresh oxygen carriers calcined below 800°C, no reaction between copper oxide and alumina was observed independently of the preparation method and the CuO content. At 850°C, CuO formed CuAl_2O_4 by solid state reaction with Al_2O_3 and the carrier contained mixtures of CuO and CuAl_2O_4 . At 950°C all CuO reacted to form CuAl_2O_4 . So, we could conclude that in the fresh carriers the formation of aluminium spinel compounds (CuAl_2O_4) increased with increasing the calcination temperature. Other authors^{8,9,15-17} also found similar results.

In addition, it was found that in the fresh carriers calcined at 1000°C the $\gamma\text{-Al}_2\text{O}_3$ partially transformed to $\alpha\text{-Al}_2\text{O}_3$. This phase transition was completed at 1050°C. However, in samples of $\gamma\text{-Al}_2\text{O}_3$ without CuO, formation of $\alpha\text{-Al}_2\text{O}_3$ was not observed up to calcination temperatures of 1150°C¹⁸ (see Table 2). In this case the $\gamma\text{-Al}_2\text{O}_3$ transformed first to $\theta\text{-Al}_2\text{O}_3$, increasing the $\theta\text{-Al}_2\text{O}_3$ content with increasing the calcination temperature, and the $\theta\text{-Al}_2\text{O}_3$ transformed to $\alpha\text{-Al}_2\text{O}_3$. At 1150°C the entire sample was as $\alpha\text{-Al}_2\text{O}_3$. So, it seems that the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$, apparently via the formation of $\theta\text{-Al}_2\text{O}_3$, was accelerated by the presence of CuO in the oxygen carriers. After reaction (100 cycles, 800°C), the particles calcined at 550 and 850°C showed the same composition independently of their calcination temperature. In the samples calcined at 950°C, independently of the Cu content of the oxygen carrier, formation of CuAlO_2 was observed after reaction. These solid phase transitions and copper aluminate formation could affect to the oxygen carrier properties, as it is shown in Table 1. The density of the oxygen carriers before and after reaction was measured and included in Table 1. The density of the fresh particles calcined at 950°C was slightly higher than the calcined at lower temperatures. Moreover, an increase in the density of the oxygen carriers was also measured after reaction for all samples.

Some samples of different copper concentration and calcination temperature, fresh and after 100 cycles, were analyzed by SEM-EDX. The particles calcined at 950°C had a little more heterogeneous structure than the calcined at 850 and 550°C. On the other hand, the particles with different copper concentration but calcined at the same temperature had similar structure. Moreover, a uniform

distribution of the CuO inside the particle was found in all the samples. Figure 4, shows as an example, a SEM-EDX picture of a particle cross section of the sample Cu15Al-DI-850.

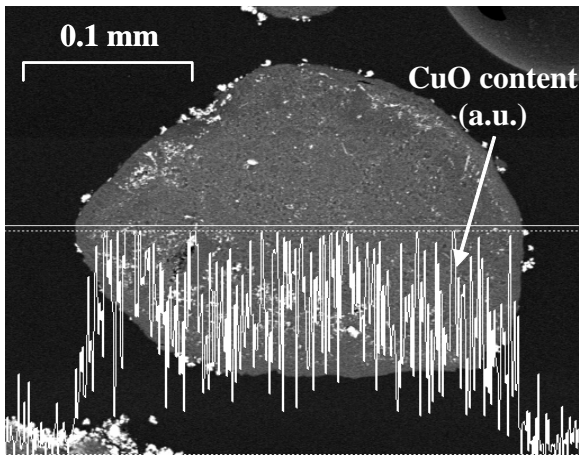


Figure 4. CuO distribution in the cross section of a particle of the oxygen carrier Cu15Al-DI-850 determined by EDX.

After the analysis carried out, no clear reasons to explain the different behavior of the Cu-based oxygen carriers with respect to agglomeration process have been found. However, based on the experimental results of this work, a range of conditions (CuO content, calcination temperature and reduction conversion) to use Cu-based oxygen carriers in a CLC process avoiding the agglomeration has been found.

3.2. Attrition rates

In addition to the agglomeration problems, 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.

In this work, the oxygen carriers that did not agglomerate, (Cu10Al-WI-550, Cu10Al-WI-950, Cu10Al-DI-550, Cu10Al-DI-950, Cu17Al-WI-550, Cu15Al-DI-550, Cu15Al-DI-850, and Cu13Al-C), were tested during 100 reduction-oxidation cycles at 800°C to analyze the effect of the number of cycles on their attrition rate and reactivity.

Figure 5 shows the attrition rates measured with the different oxygen carriers, prepared by wet and dry impregnation methods. The attrition rate was 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.

Moreover, in Figure 5, it can be seen, the effect of the calcination temperature and the preparation method on the attrition rate. An increase in the calcination temperature produced a decrease on the attrition rate. On the other hand, the effect of the preparation method on the attrition rate was very small, being the attrition rate in the wet impregnated particles slightly higher than in the dry impregnated particles. The commercial particles had a behavior very similar to the carriers Cu17Al-WI-550 and Cu15Al-DI-550.

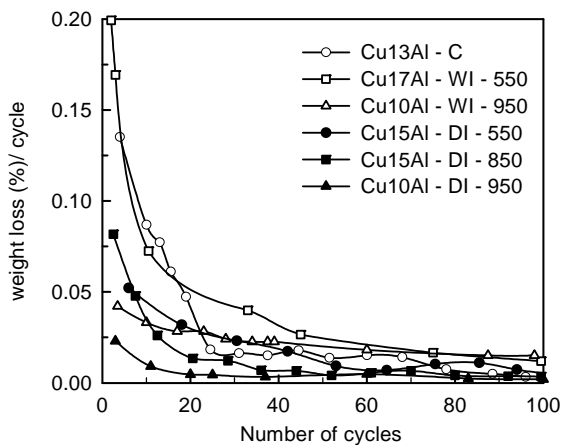


Figure 5. Attrition rates of the oxygen carriers in multicycle tests in a fluidized bed.

An important fact was that the attrition rates did not change appreciably from the cycle 50 to the cycle 100, with a mean attrition rate of 0.01%/cycle ($< 0.02\%/h$ in our tests) or even lower for some oxygen carriers (Cu10Al-DI-950, Cu15Al-DI-850). Assuming this value as a measure of the steady-state attrition of the carrier particles, this leads to a lifetime of the particles of 10000 cycles (5000 h in our

tests). This particle lifetime implies a particle cost of less than 1 Euro/ton CO₂ captured¹⁹ which makes this new technology economically competitive in comparison with other CO₂ capture technologies.

3.3. Effect of number of cycles on reactivity

As commented before, in every cycle the carrier undergoes important chemical and structural changes at high operating temperature and, consequently, it could be expected substantial changes in the reactivity of the oxygen carriers with the number of cycles. In a previous work¹³, it was observed that Cu-based oxygen carriers prepared by impregnation exhibited high reactivity and excellent chemical stability during the multicycle tests in a TGA. In this section, the reactivity of the carriers in multicycle tests was analyzed in a fluidized bed reactor.

Figure 6 shows the outlet CO₂ gas concentrations as a function of time for different cycles of the Cu₁₅Al-DI-850 oxygen carrier. The concentration-time curves obtained in the fluidized bed reactor were almost coincident revealing that the carrier reactivity was not affected substantially by the number of cycles in use. Similar results were observed with the other carriers.

The reactivity of the oxygen carrier before and after 100 cycles in the fluidized bed was also analyzed in a TGA using H₂ as fuel gas. As can be seen in Figure 7, the reactivities of fresh and after reaction oxygen carriers were high and not affected by the number of cycles, corroborating the results observed in the fluidized bed reactor. It was concluded that the Cu-based oxygen carriers that did not agglomerate have also high reactivity and good chemical stability during multicycle reduction-oxidation tests in the fluidized bed reactor at 800°C.

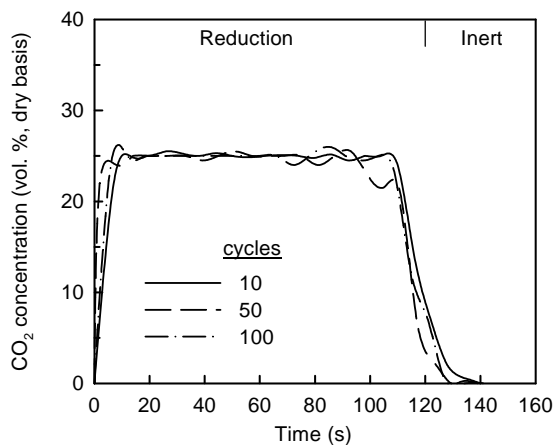


Figure 6. Effect of number of reduction-oxidation cycles on CO₂ gas exit concentration in different cycles (10-50-100) for the oxygen carrier Cu15Al-DI-850. C_{CH₄} = 25 vol.%, T = 800°C.

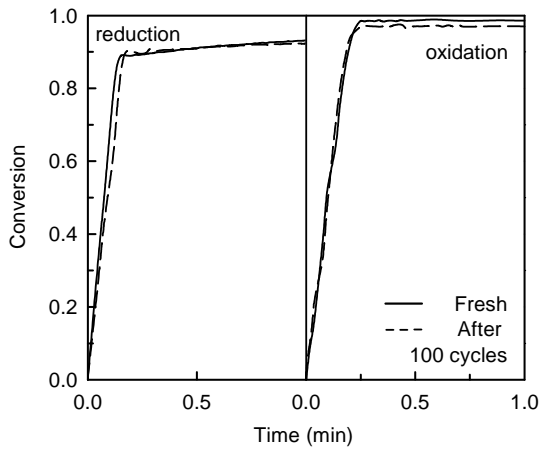


Figure 7. Reactivity in TGA of the oxygen carriers before and after 100 cycles. Cu15Al-DI-850, C_{H₂}(red) = 40 vol.%, C_{O₂}(oxid) = 21 vol.%, T = 800°C.

In the CLC process increasing the inlet gas temperature in the gas turbine increases the efficiency of the process. For this reason, a multicycle test (20 cycles) was carried out at 950°C in the fluidized bed facility using the Cu15Al-DI-850 oxygen carrier. The behavior of this oxygen carrier at 950°C with respect to chemical stability and reactivity was very satisfactory during the test, in spite of the high temperature used. The gas product distribution was similar to the tests at 800°C although some CuO decomposition during the inert period after oxidation reaction was observed. The high temperature did not affect negatively to the agglomeration process of the oxygen carrier.

4. Conclusions

Different CuO/Al₂O₃ oxygen carriers, prepared by wet and dry impregnation methods with a range of CuO content between 10 and 26 wt.%, were analyzed in a fluidized bed facility during 100 reduction-oxidation cycles using CH₄/N₂ as fuel to determine the gas product distributions at the exit of the fluidized bed reactor, the attrition rates, and specially their behavior with respect to the agglomeration process.

It was found that CuO/Al₂O₃ oxygen carriers with a CuO content lower than 10 wt.% never agglomerated in the fluidized bed, and the CuO/Al₂O₃ oxygen carriers with a CuO content greater than 20 wt.% always agglomerated. This phenomenon was independent of the preparation method and the calcination temperature used in their manufacture. On the other hand, the behavior of CuO/Al₂O₃ oxygen carriers with an intermediate CuO content (15-17 wt.%) depended on the calcination temperature used in their preparation. Those calcined at 950°C agglomerated and those calcined at temperatures lower than 850°C did not agglomerate.

The attrition rate, due to the internal changes produced in the particles by successive reduction-oxidation cycles in the fluidized bed, was low for almost all of the CuO/Al₂O₃ oxygen carriers. This attrition rate decreased with increasing the calcination temperature used in the preparation of the carriers.

The reactivity of the oxygen carriers, during the reduction and oxidation reactions, was high and it was not affected by the number of cycles carried out in the fluidized bed. In addition, complete CH₄ conversion to CO₂ and H₂O during most of the reduction period was obtained.

The excellent properties of the CuO/Al₂O₃ oxygen carriers prepared with the conditions that avoid the agglomeration problems suggest that these materials are good candidates for a CLC process.

ACKNOWLEDGMENT

This research was carried out with financial support from the Spanish Ministry of Education and Science (Project PPQ-2001-2111) and the European Coal and Steel Community (Project 7220-PR125).

Table 1. Physical properties of the fresh and reacted oxygen carriers.

Sample	Number of impregnations	Solution concentration (mol/l)	Apparent density (g/cm ³)		Agglomeration
			Fresh	After 100 cycles	
Cu10Al-WI-550	1	1.6	1.4	1.7	No
Cu10Al-WI-950	1	1.6	1.8	2.0	No
Cu17Al-WI-550	2	1.6	1.4	1.7	No
Cu17Al-WI-950	2	1.6	1.8	-	Yes
Cu21Al-WI-550	3	1.6	1.4	-	Yes
Cu21Al-WI-950	3	1.6	1.8	-	Yes
Cu23Al-WI-550	1	5.4	1.5	-	Yes
Cu10Al-DI-550	1	3.4	1.5	1.7	No
Cu10Al-DI-950	1	3.4	1.8	2.0	No
Cu15Al-DI-550	1	5.4	1.4	1.7	No
Cu15Al-DI-850	1	5.4	1.4	1.7	No
Cu15Al-DI-950	1	5.4	1.8	-	Yes
Cu26Al-DI-550	2	5.4	1.5	-	Yes
Cu13Al-C	-	-	1.5	1.6	No

Table 2. Phases of the support and the different oxygen carriers identified by XRD.

Calcination temperature (°C)	Support	CuO impregnated on γ -Al ₂ O ₃	
		Fresh	After 100 cycles at 800 °C
550	γ -Al ₂ O ₃	CuO, γ -Al ₂ O ₃	CuO, CuAl ₂ O ₄ , γ -Al ₂ O ₃ , α -Al ₂ O ₃
800	γ -Al ₂ O ₃	CuO, γ -Al ₂ O ₃ ,	
850	γ -Al ₂ O ₃	CuO, CuAl ₂ O ₄ , γ -Al ₂ O ₃	CuO, CuAl ₂ O ₄ , γ -Al ₂ O ₃ , α -Al ₂ O ₃
950	γ -Al ₂ O ₃ , θ -Al ₂ O ₃	CuAl ₂ O ₄ , γ -Al ₂ O ₃	CuO, CuAl ₂ O ₄ , CuAlO ₂ , γ -Al ₂ O ₃ , α -Al ₂ O ₃
1000	γ -Al ₂ O ₃ , θ -Al ₂ O ₃	CuAl ₂ O ₄ , γ -Al ₂ O ₃ , α -Al ₂ O ₃	
1050	γ -Al ₂ O ₃ , θ -Al ₂ O ₃	CuAl ₂ O ₄ , α -Al ₂ O ₃	
1100	γ -Al ₂ O ₃ , θ -Al ₂ O ₃	CuAl ₂ O ₄ , α -Al ₂ O ₃	
1150	α -Al ₂ O ₃		

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