Comportamiento a alta temperatura de transportadores sólidos de oxígeno de base cobre para el proceso "chemical looping combustion"

High temperature behaviour of CuO-based oxygen carriers for chemical-looping combustion process

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Resumen

El "Chemical Looping Combustion" (CLC) es una tecnología de combustión con separación inherente del CO_2. Para escalar el proceso se necesitan materiales aptos para trabajar a alta temperatura. Se ha probado que los transportadores de base cobre cumplen los requerimientos, sin embargo se ha recomendado su trabajo a temperaturas menores de 1073 K. En este trabajo, se han desarrollado, por impregnación en diferentes soportes, dos transportadores basados en Cu. Se estudió su comportamiento a temperaturas por encima de 1073K en una unidad de CLC de 500 Wth teniendo en cuenta aspectos como: eficiencia de combustión, resistencia al desgaste, aglomeración, mantenimiento de la capacidad de transporte de oxígeno y reactividad. Problemas de aglomeración o desactivación de las partículas no se detectaron con ninguno de los TOs. Fue posible la operación estable durante más de 67 horas sólo con el TO modificado con la adición de NiO como soporte. Esta es la primera vez que un TO de base cobre, preparado por un método de fabricación comercial, se utiliza a 1173 K de temperatura en el reactor de reducción (TRR) y 1223 K en el de oxidación (TRO) y presenta buenas propiedades, abriendo nuevas posibilidades para la aplicación de materiales a base de cobre en los procesos de CLC a escala industrial.

Abstract

Chemical-Looping Combustion (CLC) is a combustion technology with inherent CO_2 separation. To scale up the CLC process materials suitable to work at high temperatures are needed. Cu-based oxygen carriers had been proved to fulfil the requirements although temperatures lower than 1073 K has been recommended. In this work, two Cu-based OCs have been developed by impregnation on different supports. The behaviour of the OCs was studied at temperatures above 1073K in a CLC continuous unit of 500 Wth taking into account aspects such as combustion efficiency, attrition, agglomeration and maintenance of the oxygen transport capacity and reactivity. Agglomeration or deactivation of the particles was never detected with neither of the oxygen carriers used. At these high temperatures, stable operation for more than 67 h was feasible only using an OC with γAl2O3 modified with NiO addition as support. This is the first time that a Cu-based OC, prepared by a commercial manufacturing method, and used at 1173 K of fuel reactor temperature (TFR) and 1223 K of air reactor temperature (TAR) exhibits such a good properties. This result opens new possibilities for the application of Cu-based materials in industrial-scale CLC processes.

1. Introduction

In order to stabilize the CO_2 concentration in the atmosphere, several measures must be taken. The Carbon Capture and Storage (CCS) is a process involving the separation of CO_2 emitted by industry and energy-related sources, and the storage for its isolation from the atmosphere over the long term. Chemical Looping Combustion (CLC) process has been suggested among the best alternatives to reduce the economic cost of CO_2 capture using gaseous fuels (Kerr, 2005) and to increase the efficiency with respect to other CO_2 capture process (Kvamsdal *et al*, 2007). In this process, CO_2 is inherently separated from other combustion products, N_2 and unused O_2, through the use of a solid oxygen carrier (OC) and thus no energy is expended for the separation.

A cornerstone in the successful development of a CLC system is the OC, which is composed of a metal oxide and a support. The OC besides having a high reactivity with the gas fuel and air during many cycles of reduction-oxidation and full fuel conversion to CO_2 and H_2O, must meet other characteristics such as low attrition, no agglomeration during fluidized bed operation, and no carbon deposition. An important aspect of the oxygen-carrier materials is the suitability to be used in continuous CLC units during long periods of time. However, the number of materials tested in this kind of units is limited, Ni-based OC conveyors being the most commonly used, followed by Cu-based OC (Adanéz *et al*, 2012).

Ni-based OC allows working at high temperatures (1173 – 1373 K) and has similar oxygen transfer capacity than Cu-based oxygen carries. Although thermodynamic restrictions make that CO and H_2 are always present in the gas outlet of the fuel reactor. In this sense Adánez *et al* (2006b) studied the behaviour of different Ni-Cu oxygen carriers using alumina as support in a batch fluidized bed working at 1123K. They found that to have a stable and low attrition rate at high temperature was necessary the existence of a minimum amount of NiO (about 4 wt. %) in the oxygen carrier to stabilize the CuO phase.

Adánez *et al* (2004) have shown that Cu-based oxygen carriers present high reaction rates and oxygen transfer capacity, and have no thermodynamic restrictions for complete fuel conversion to CO_2 and H_2O.

Several Cu-based OC has been developed using different supports and preparation methods (Adánez *et al*, 2004; Copeland *et al*, 2002; Chuang *et al*, 2008; Johansson *et al*, 2006; Son *et al*, 2006). In the "Instituto de Carboquímica" (CSIC) has undertaken several studies using this oxygen carrier (Adánez *et al*, 2004; de Diego *et al*, 2004 y 2005; García-Labiano *et al*, 2007). A Cu-based oxygen carrier support on γ-Al_2O_3 was finally selected to test its behaviour during 200 h of continuous operation in a 10 kW$_{th}$ CLC prototype using methane as fuel at 1073 K in both fuel reactor (FR) and air reactor (AR) (Adánez *et al*, 2006a). Other works showed that the OC can fully convert syngas (Forero *et al*, 2009) or methane and no special measures should be adopted due to the presence of impurities (Gayán *et al*, 2010; Forero *et al*, 2010) when it has been carried out at 1073 K in a CLC continuous unit of 500 W$_{th.}$

In CLC, oxidation reactor exit temperature is the parameter of paramount significance for plant efficiency. The higher the oxidation temperature, the higher is the turbine inlet temperature (TIT) and hence the higher is the plant efficiency. To scale up the CLC technology information about the high temperature resistance of the oxygen carriers is needed. Agglomeration problems are particularly important working with Cu-based OC (Copeland *et al*, 2002; Cho *et al* 2004) due to the low melting temperature of the metallic Cu. There are in the literature very few works dealing with the temperature resistance of the Cu-based OC. de Diego *et al* (2005) used a CuO/γ-Al_2O_3 oxygen carrier at 1223 K in a batch fluidized bed founding that the behaviour of the oxygen carrier with respect to chemical stability and reactivity was satisfactory, although a small number of cycles were carried out. Very recently, Forero *et al* (2011) have analysed the behaviour of this oxygen carrier during long-term tests at high temperatures under

continuous operation in a CLC unit 500 W_{th}. They found that both T_{FR} and T_{AR} had a great influence on the resistance to attrition of the particles. Stable operation for more than 60 h was feasible at T_{FR} =1073 K and T_{AR} = 1173 K without agglomeration problems or deactivation of the carrier. However, an increase of 100 K in the AR temperature operation produced a reduction in the particle lifetime from 2700 to 1100 h. It was indicated that a support with a minimized interaction with the metal oxide might be useful to increase the temperature resistance of copper-based oxygen carriers.

In this paper, a Cu-based oxygen carrier was prepared by incipient wet impregnation introducing chemical pre-treatment with Ni oxide. The influence of the support on the high temperature behaviour of the two Cu-based oxygen carriers was analysed during long-term test in a 500 W_{th} CLC unit under continuous operation using methane as fuel and high temperatures both in FR, 1173 K and in AR, 1223 K. The influence of the support on the combustion efficiency, attrition rate and material agglomeration was investigated. Changes in particles with respect to reactivity, chemical composition and physical characteristic were also analysed.

2. Experimental

2.1 Preparation of oxygen carrier

The oxygen carriers were prepared by incipient wet impregnation method using CuO as active phase and γ-Al_2O_3 and NiO/γ-Al_2O_3 as supports.

Supports. Commercial γ-Al_2O_3 particles (Puralox NWa-155, Sasol Germany GmbH) of 300-500 μm with a density of 1.3 g/cm³ and a porosity of 55.4% was used as support to prepared the OC that was named as Cu-γAl and as raw material to prepare the OC named Cu-NiAl. The chemical pre-treatment consisted in precoating the support with $Ni(NO_3)_2.6H_2O$ (>99.5 % Panreac) solution. In order to minimized the environmental problems, the corresponding NiO content (3 wt.%) was achieved by applying one impregnation followed by calcination at 823 K in air atmosphere for 1 h to

decompose the impregnated nitrate.

Oxygen carriers. Cu-based OCs were prepared by the addition of a volume of saturated copper nitrate solution 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, followed by calcination at 823 K, in air atmosphere for 30 min in a muffle oven to decompose the impregnated copper nitrate into copper oxide. Finally, the oxygen carrier was stabilized in air atmosphere for 1 hour at 1123 K. Fresh and after-used samples of the oxygen carriers were physically and chemically characterized by several techniques. The main characteristics of the Cu-based oxygen carriers are showed in Table 1.

2.2 CLC continuous unit of 500 Wth

Fig. 1 show a schematic diagram of the reactor system, located at "Instituto de Carboquímica" (CSIC). The facility used in this study is a CLC continuous unit of 500 Wth composed of two interconnected fluidized bed reactors. Detailed information about the prototype and operating procedure used can be found elsewhere (Forero *et al*, 2009).
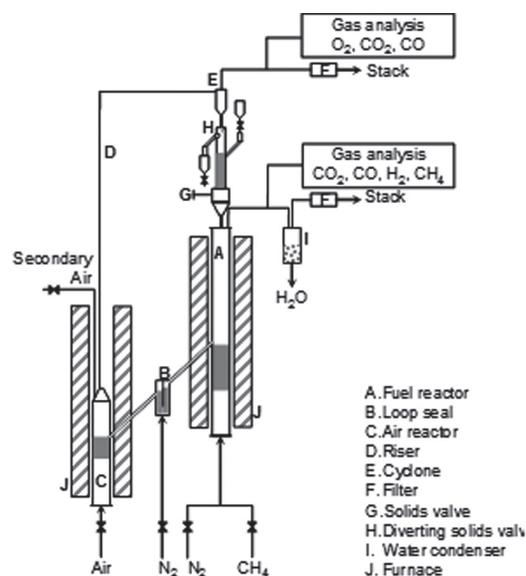
Figure 1. Schematic diagram of the Chemical-Looping Combustion continuous unit of 500 Wth.

Table 1. *Properties of the fresh and used Cu-based OCs.*

	Cu-γAl		Cu-NiAl	
	Fresh	Used-29h	Fresh	Used-67h
CuO content, xCuO (wt%)	14.2	13	12.8	10.6
Oxygen transport capacity Ro,OC (%)	2.86	2.62	2.57[a]	2.13[a]
Porosity (%)	50	58	54	45
Specific surface area BET (m2/g)	91.3	6.8	91.4	4.9
Bulk density (g/cm3)	1.7	1.5	1.6	2.1
Crushing strength (N)	2.9	0.6	3.1	2.0
Crystalline phases, particles from AR	CuO $CuAl2O4$ $\gamma Al2O3$	CuO $CuAl_2O_4$ αAl_2O_3	CuO $CuAl_2O_4$ $NiAl_2O_4$[b,c] γAl_2O_3	CuO $CuAl2O4$ $NiAl_2O_4$[b,c] αAl_2O_3
Crystalline phases, particles from FR filter		Cu CuO Cu_2O $CuAl_2O_4$ αAl_2O_3		Cu CuO Cu_2O $CuAl_2O_4$ αAl_2O_3
Crystalline phases, particles from AR filter		CuO $CuAl_2O_4$ $CuAlO_2$ αAl_2O_3		CuO $CuAl_2O_4$ $NiAl_2O_4$[b,c] αAl_2O_3

[a] NiO as inert. [b] Minor amount [c] Identified by TPR

The solid inventory in the plant was about of 1.2 kg of OC. The fuel gas in the FR was methane diluted in nitrogen and air was used as fluidizing gas in the AR. The inlet gas flow and gas velocity used were the same used in a previous work (Forero *et al*, 2011).

2.3 Combustion tests

Long-term CLC tests under different operating conditions were carried out at high temperature both in the FR (T_{FR} = 1173 K) as in the AR (T_{AR} = 1223 K) using Cu-based oxygen carriers and methane as fuel. FR and AR temperatures were kept constant during overall operation for each test using the same batch of oxygen carrier particles. The duration of the tests were fixed to be long enough to analyze the effect of temperature on the physical and chemical characteristics of the particles and make a reliable estimation of the particle lifetime at those conditions. The tests with Cu-γAl should be early stopped due to operational problems caused by the amount of fines generated. More than 67 h in hot conditions were carried out in tests with Cu-NiAl where operation of the plant was possible.

The oxygen carrier to fuel ratio (ϕ) was defined by Ec. (1), where F_{CuO} is the molar flow rate of the copper oxide and F_{CH_4} is the inlet molar flow rate
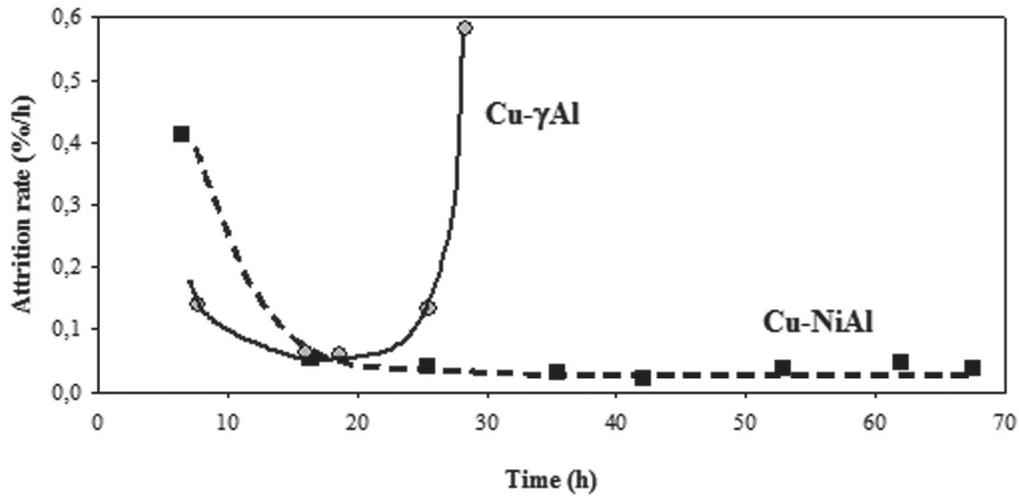
Figure 2. *Effect of the oxygen carrier to fuel ratio on the combustion efficiency of two Cu-based OCs.*
T_{FR}= 1173 K , T_{TAR}= 1223 K. ○ *Cu-γ Al.* ■ *Cu-NiAl. Values indicate the solids inventory per MW, m*FR*
(kg/MWth).

of the CH_4 in the FR. A value of $\phi = 1$ corresponds to the stoichiometric CuO amount needed for a full conversion of the fuel to CO_2 and H_2O:

$$\phi = \frac{F_{CuO}}{4F_{CH_4}} \qquad (1)$$

The effect of the oxygen carrier to fuel ratio, ϕ on the combustion efficiency was carried out varying the fuel concentration. It must be pointed out, that although during the first 10 h of operation the experiments were carried out at different power inputs. The remaining operation time was carried out at constant operating conditions corresponding to those of complete combustion of methane.

The combustion efficiency (Ec. (2)) was defined as the ratio of the oxygen consumed by the gas leaving the FR to that consumed by the gas when the fuel is completely burnt to CO_2 and H_2O.

$$\eta_c = \frac{(2x_{CO_2} + x_{CO} + x_{H_2O})_{out} \; F_{out}}{(4x_{CH_4})_{in} \; F_{in}} \; 100 \qquad (2)$$

where F_{in} is the molar flow of the inlet gas stream, F_{out} is the molar flow of the outlet gas stream, and x_i is the molar fraction of the gas *i* corresponding to the inlet or outlet.

Attrition and/or fragmentation of particles were analyzed during continuous long-term tests. Attrition rate (*A*), was defined by Ec. (3), where w_f is the weight of elutriated particles < 40 μm during a period of time, w_t is the weight of total solids inventory and Δt is a period of time during the particles were collected

$$A = \frac{w_f}{w_t . \Delta t} 100 \qquad (3)$$

3. Results and discussion

The results are presented analyzing the influence of the oxygen carrier to fuel ratio on the combustion efficiency and on the behavior of OCs.

3.1 Combustion efficiency

During the first 10 h of operation the experiments were carried out varying the fuel flow but keeping the solids circulation rate approximately constant (≈ 8.5 kg/h). Fig. 2 shows the effect of the oxygen carrier to fuel ratio, ϕ, on the combustion efficiency when the power input changed in the range of 500–780 Wth at T_{FR} = 1173 K and T_{AR} = 1223 K with two OCs. Therefore, as the fuel flow increased, the ϕ ratio and the solids inventory in the

FR per MW_{th} of fuel gas, m^*_{FR}, decreased. In both cases, 280 kg/MW_{th} to achieved full conversion of methane is necessary at low φ values (φ > 1.2). This result showed the high reactivity of the OCs, independently of the support used.

3.2 Oxygen carrier behaviour

Besides full combustion, other aspects like agglomeration, attrition, reactivity, and oxygen carrier properties should be considered to evaluate the behaviour of the different oxygen carriers during tests at high temperature. However, in spite of that the high operation temperatures used in the experiments, agglomeration or defluidization of the reactors (FR or AR) were never detected. These results are very relevant for the future use of Cu-based materials as oxygen carrier for CLC technology taking into account the high temperatures used in the tests (T_{FR}=1173 K, and T_{AR}=1223 K).

3.2.1 Attrition rates

Attrition rate is a useful measure to estimate the lifetime of particles. Fig. 3 shows the evolution with time of the attrition rate during the operation in the CLC continuous unit of 500 W_{th} with both OCs. The generation of fine particles was high at the beginning of the operation for two OCs. Later, the attrition rate due to the internal changes produced in the particles by the successive reduction and oxidation cycles during operation presented different behaviour depending on the OC.

The Cu-γAl presented an abrupt increase of the generation of fines after 20 h of operation resembling that the particles had chunked. The amount of fines was too high and forced to stop operation in the plant. With Cu-NiAl OC the system was running satisfactorily around 67 h, with a stable and low value of the attrition rate (0.04 %), giving an estimation of the particle lifetime around 2700 h. This value is comparable to the one calculated for a CuO-γAl$_2$O$_3$ oxygen carrier during 100 h of operation in a 10 kW CLC pilot plant, although working at lower temperatures (1073 K) in both reactors (de Diego *et al*, 2007). Therefore, an increase of 100 K in the T_{FR} and 150 K in T_{AR} can be done without a detrimental effect on the particle lifetime when chemical pre-treatment was used in the
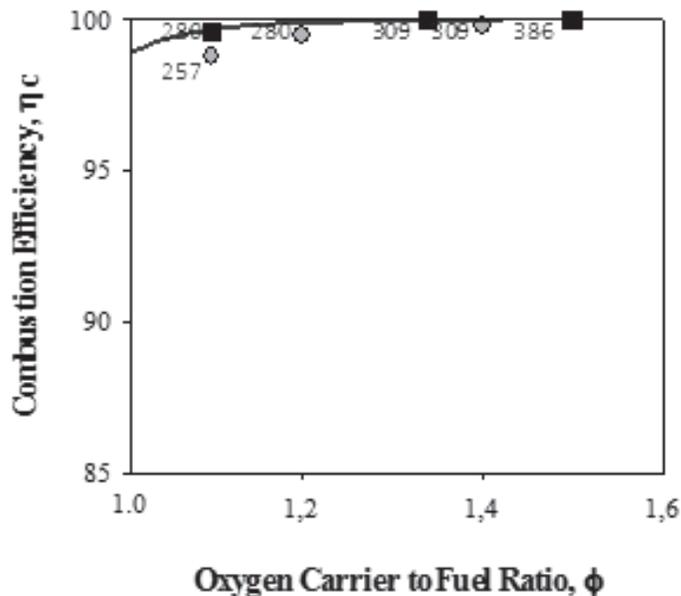
Figure 3. *Attrition rates vs. time of two Cu-based OCs. TFR= 1173 K, TAR= 1223 K. ○Cu-γAl. ■Cu-NiAl*
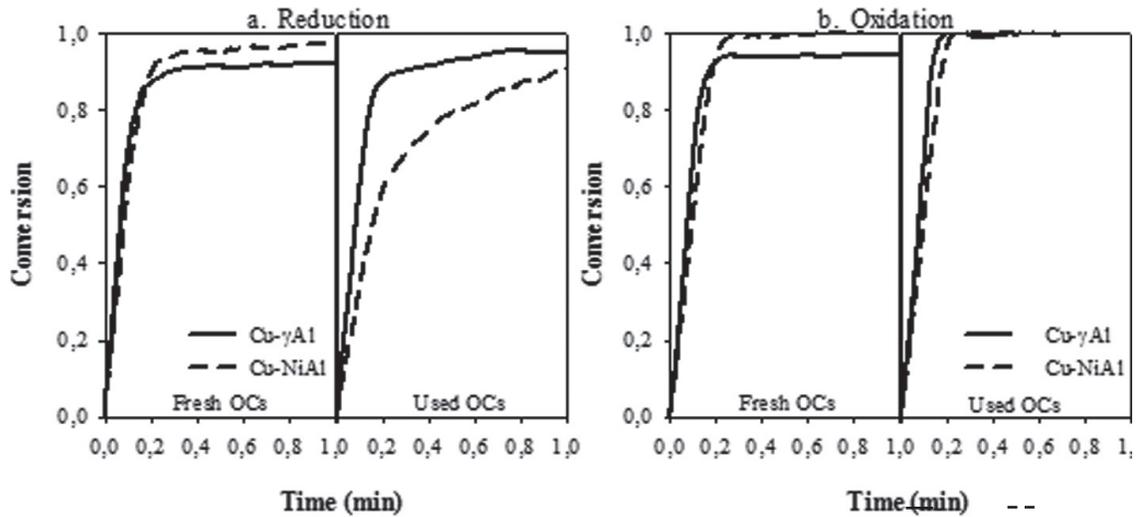
Figure 4. *Solid conversion vs. time curves in TGA for a) reduction and b) oxidation reactions of fresh and after-used Cu-based OCs particles. Reduction: CH4 = 15%, H2O = 20%, N2 = 65%. Oxidation: air. T=1073 K. Cu-γAl. Cu-NiAl.*

preparation of the modified support to obtain Cu-NiAl OC.

3.2.2 Reactivity

The CuO content (x_{CuO}) reduction measured for OCs during the operation in the CLC plant (see Table 1) produced a decrease in the oxygen transport capacity ($R_{o,OC}$) of the OCs and might be changes in the reactivity. However, in spite of the reduction in the oxygen transport capacity, full combustion efficiency for $\phi > 1.2$ were always reached in the CLC continuous unit during operation. Fig. 4 shows the conversion curves obtained in TGA at 1073 K, using a mixture of 15 vol %CH4, 20 vol % H2O, and 65 vol % N2 in the fresh oxygen carrier and in samples taken at the end of the different tests, corresponding also to different operation times.

The conversion level of the oxygen carrier was calculated for the reduction and oxidation reactions as:

$$X_{red} = \frac{m_\infty - m}{m_\infty \; R_{o,o} \; x_{CuO}}$$ (4)

$$X_\alpha = 1 - \frac{m_\infty - m}{m_\infty \; R_{o,o} \; x_{CuO}}$$ (5)

where m is the actual mass of sample, m_{ox} is the mass of the sample fully oxidized.

After-used Cu-γAl maintained their high reactivity. Cu-NiAl OC presented a decrease in the reduction reactivity; which is attributed mainly to the loss of the CuO content (see Table 1). Although it could be due to the presence of $NiAl_2O_4$, whose reactivity is lower than that of NiO (Adánez *et al*, 2009; Dueso *et al*, 2010, Dueso *et al*, 2012) is not clearly noticed an increase in this compound, as discussed later. However, the used particles were fully reduced below 60 s, and showed very high oxidation reactivities, indicating that particles maintain its high reactivity after operation at high temperatures in the CLC unit.

3.2.3 Characterization of Cu-based oxygen carriers

To analyze the results obtained regarding the effect of the support on the behaviour of the particles at high temperature, physical and chemical properties of the oxygen carrier particles coming from the AR, and from fines recovered in the filters at the FR and AR outlet streams were compared to those of fresh particles. Table 1 shows the main properties of the different materials after used in the CLC continuous unit of 500 W_{th} during long-term tests.
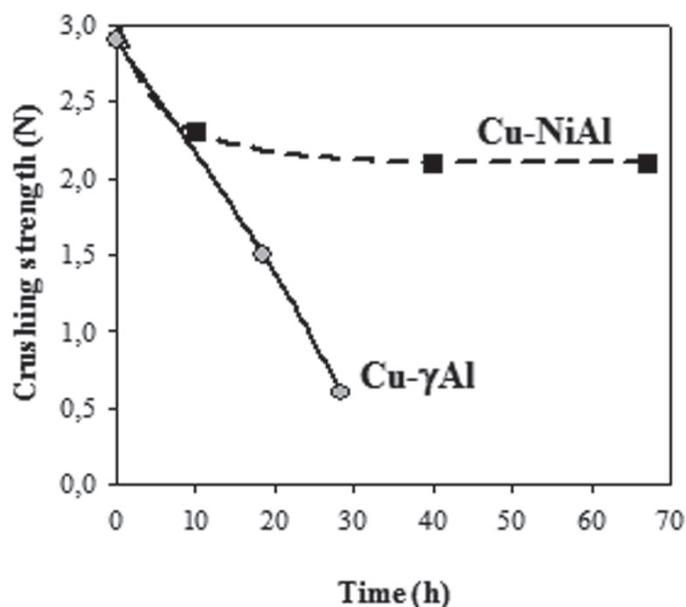
Figure 5. *Crushing strength evolution of the two Cu-based OCs.*
◉ *Cu-γAl.* ■ *Cu-NiAl.*

Porosity. The chemical pre-treatment of the γAl_2O_3 to produce $NiOAl_2O_4$ (6 %) hardly affected the pore size distribution of γAl_2O_3. At the end of the tests, the pore size distribution of the samples had changed considerably with respect to the fresh particles with the full disappearance of 12 nm pores. Changes in porosity are related with changes in the oxygen carrier bulk density, consequently the Cu-γAl presented a minor decrease of this characteristic and Cu-NiAl presented an increased.

Specific surface area. The BET specific surface area of two used OCs decreased due to that thermal sintering occurred inside the particles due to the high operational temperatures used in FR and AR.

Crushing strength. Fig. 5 shows the effect of the support on the crushing strength at different operation times from samples extracted from the AR. Cu-γAl OC presented a fast and important decrease of this property, with a value of less than 1N after 25 h of operation. However, Cu-NiAl OC had a smooth decrease, with a value of 2.1 N at the end of operation at high temperature. Therefore, the initial values of the crushing strength of the OC particles are not a suitable characteristic to evaluate the particle lifetime in the process.

Crystalline phases. Powder XRD patterns of the fresh carriers, shown in Table 1, revealed the presence of CuO, and $\gamma\text{-}Al_2O_3$ as the main crystalline phases for fresh OCs. The interaction of copper with the support is revealed through the formation of copper aluminate, $CuAl_2O_4$. $NiAl_2O_4$ are also present in the corresponding OCs.

Powder XRD analysis of samples extracted from the AR and collected at the outlet of the AR and FR streams at the end of each long-term test are also showed in Table 1. The powder XRD patterns of the used samples revealed the transformation of the γ-Al2O3 to $\alpha\text{-}Al_2O_3$ in both OCs as a most stable phase at high temperature, explaining the observed evolution of the textural properties of the used particles. A new copper aluminate, $CuAlO_2$, was detected in used particles of Cu-γAl. Reduced CuO phases, Cu_2O and Cu, were detected in all the samples collected in the filter at the outlet of the FR. Oxidized compounds of copper (CuO and copper aluminates) were only found in the samples coming from the AR and from the AR filter, verifying that the oxygen carrier reached always full oxidation state in the AR. As it can be seen, similar crystallite compounds to the fresh OCs particles were detected in the corresponding used samples. This fact
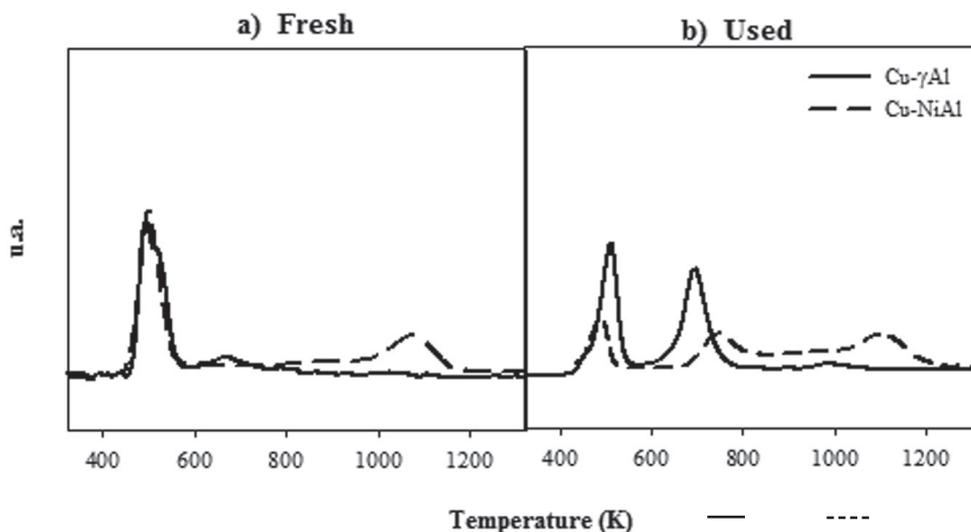
Figure 6. *H2-TPR profiles of the fresh and after-used Cu-based OCs.* Cu-γAl. Cu-NiAl.

revealed that the attrited material is composed both of copper compounds and of support. A possible cause of the low attrition found in Cu-NiAl OC could be the absence of a new phase ($CuAlO_2$) found in used samples when Cu-γAl OC is used as found in previous work (Forero *et al*, 2011).

Temperature-programmed reduction. The identification of the formation of $NiAl_2O_4$ in the fresh and after used Cu-NiAl particles should be carried out by TPR analysis due to XRD technique only detects crystalline phases with content higher of 5 %. Therefore, TPR analyses of fresh and used particles of the different OCs were performed to determine the reducible species and the temperature at which the reduction of these species occurs. Fig. 6 shows the different TPR profiles measured for the fresh and after used OCs particles. The TPR spectra showed several H_2 consumption peaks. The peak in the temperature range of 473–573 K is attributed to the reduction of dispersed and bulk CuO species (Luo *et al*, 2005). The peak in the temperature range of 623–773 K is attributed to the reduction of $CuAl_2O_4$ (Luo *et al*, 2005). The peak in the temperature range of 650 – 900 K is attributed to the reduction of Ni^{2+} in the free NiO phase (Dueso *et al*, 2010) . The reduction of $CuAlO_2$ phase has a high temperature peak around 1033 K (Artizzu *et al*, 1999). The high temperature peak at 1073–

1273 K is associated with the reduction of Ni^{2+} in $NiAl_2O_4$ (Li y Chen, 1995).

Similar profiles were measured for the different OCs both fresh and after used. Fresh OCs presented a main peak corresponding to the reduction of CuO compound. After used OCs presented two main peaks attributed to CuO and $CuAl_2O_4$ reductions and a minor peak around 973 K corresponding to $CuAlO_2$ phase (Artizzu *et al*, 1999). In this sense, TPR profiles are consistent with XRD data which indicate the presence of both CuO and $CuAl_2O_4$ as main phases in most of the samples and a minor existence of $CuAlO_2$ compound. It is worth noting that these three compounds are highly reactive. The presence of $NiAl_2O_4$ in the Cu-NiAl OC was revealed by the high temperature peak characteristic of the reduction of this phase in both fresh and after-used particles. Although, in after-used particles a peak between 650- 900 K appears indicating the presence of NiO, which is more reactive than $NiAl_2O_4$ (Adanéz *et al*, 2009), is not consistent with that observe in reactivity. Possibly the amounts are very low that not have influence in reactivity of this oxygen carrier. The chemical pre-treatment of the γAl_2O_3 with NiO to form partially the stable $NiAl_2O_4$ structure in the Cu-NiAl OC could help to increase the temperature resistance of the particles and to reduce the attrition rate of this OC.

According to the experimental work herein carried out, the Cu-based OCs developed can be used at T_{FR}=1173 K and T_{AR}=1223 K without agglomeration problems or deactivation of the carrier with a complete combustion of the fuel working at oxygen carrier to fuel ratios above ≈1.2, which corresponds to a solid circulation rate of ≈4.0 kg s^{-1} per MW$_{th}$. Being the maximum circulation rate of solids about 16 kg s^{-1} per MW$_{th}$ 41, the optimal operation conditions (ϕ> 1.2) could be easily reached in an industrial CLC system using Cu-based oxygen carriers.

The OC prepared using NiO/γAl$_2$O$_3$ as support can be used at T_{FR}=1173 K and T_{AR}=1223 K without any operational problems. Operational cost related with the oxygen carrier renovation should be taking into account. High attrition rates will decrease the particle lifetime increasing the cost of the CLC process. It can be seen that Cu-NiAl OC had a low attrition rate and the highest particle lifetime (2700 h) even working at high temperatures. As can be inferred from these results, an increase of 100 K in the T_{FR} and 150 K in T_{AR} can be done with the same replacement of the material that working at 1073 K in both reactors with the CuO-γAl$_2$O$_3$ OC.

In addition, Cu-based OC had been rejected as best candidate for the CLC process due to its agglomeration problems and its restricted operational temperatures. The results found in this work show that Cu-based OC can be used at higher temperatures than referred before without any operational problems. This is the first time that a Cu-based OC, prepared by a commercial manufacturing method, and used at 1173K in the FR and 1223 K in the AR exhibits such a good properties (high reactivity together with high mechanical durability and absence of agglomeration). This result opens new possibilities for the application of Cu-based materials in industrial-scale CLC processes.

Nevertheless, the OC developed in this work with high temperature resistance contains a low amount of NiO (3 wt.%). Some drawbacks are derived from this NiO content, an expensive metal oxide with important health and environmental hazards.

By the one hand, the use of NiO, more expensive than CuO, would increase the costs of the oxygen carrier manufacture. By the other hand, it would be necessary a waste management analysis of this OC due to the environmental risks of Ni. Although in a previous work (García-Labiano *et al*, 2007), it was found that the solid waste generated in a CLC process working with CuO-γAl$_2$O$_3$ OC can be classified as a stable nonreactive hazardous waste acceptable at landfills for nonhazardous wastes, the presence of a small fraction of NiO or NiAl$_2$O$_4$ in the residue would required more detailed studies.

4. Conclusions

Two Cu-based oxygen carriers have been developed by impregnation on different supports (γAl$_2$O$_3$ and NiO/γAl$_2$O$_3$). The supports were prepared by chemical modifications of commercial γAl$_2$O$_3$ with the aim of reduce the interaction with the metal oxide. The influence of the support on the high temperature behaviour of the Cu-based oxygen carriers was analyzed during long-term test in a 500 W$_{th}$ CLC unit under continuous operation using methane as fuel and high temperatures both in FR, 1173 K and in AR, 1223 K. The behaviour of the OCs on the process performance was evaluated taking into account important aspects such as: combustion efficiency, resistance to attrition, fluidization behaviour (no presence of agglomeration) and maintenance of the oxygen-carrying capacity and reactivity.

Complete fuel combustion was reached at ϕ > 1.2 with both OCs. Moreover, in spite of the high temperatures used in the tests, agglomeration or defluidization of the bed were never detected in reducing or oxidation conditions with any of the OCs used in this work.

Cu-γAl OC had an abrupt increase of the attrition rate resembling that the particles had chunked. Cu-NiAl OC had a low and stable attrition rate after 67 h of operation at high temperature, maintaining its structural integrity and original homogeneity. The presence of NiAl$_2$O$_4$ in the Cu-NiAl OC structure could help to avoid the sintering process of Cu

inside the particles and to reduce the attrition rate of this OC. It was concluded that a Cu-based OC prepared using γAl_2O_3 as support modified with a small NiO addition is adequate to operate without attrition or agglomeration problems in the CLC process at high temperature.

The initial values of the crushing strength of the OC particles are not a suitable characteristic to evaluate the particle lifetime in the process.

This is the first time that a Cu-based OC, prepared by a commercial manufacturing method, and used at 1173K in the FR and 1223 K in the AR exhibits such a good properties: high reactivity together with high mechanical durability and absence of agglomeration. This result opens new possibilities for the application of Cu-based materials in industrial-scale CLC processes.

5. Acknowledgements

6. References

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