Long-lasting Cu-based Oxygen Carrier Material for Industrial Scale in Chemical Looping Combustion

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Abstract

One of the most important current objectives of the Chemical Looping Combustion (CLC) technology for gaseous fuels lies in scaling-up the aforementioned technology in the short term from 100 kW_{th} to 10 MW_{th} scale. In order to meet this challenge, the commercial availability of suitable multi ton-scale oxygen carrier materials at competitive price is needed. In this work, a Cu-based oxygen carrier prepared by the impregnation method using a commercial alumina as support, referred as Cu14γAl_Commercial, has been developed and evaluated in a 500W_{th} CLC pilot plant during the combustion of CH₄ at two different

temperatures, i.e., 800 °C and 900 °C. The outstanding results obtained in terms of both combustion efficiency and mechanical stability have shown that the Cu₁₄γAl Commercial impregnated oxygen carrier can be selected to upscale CLC technology for gaseous fuels.

Keywords: CO₂ capture; Chemical Looping Combustion; oxygen carrier; copper oxide; attrition.

1 Introduction

The application of Carbon Dioxide Capture and Storage (CCS) technologies to large fossil fuel power plants implies an increase of the cost of energy, since carbon dioxide (CO₂) capture is a highly energy intensive process. Regarding CO₂ capture, there are three approaches, designated as first generation CCS technologies, that have undergone a great development during the last decades, and some of them are today available at commercial scale. These technologies are known as pre-combustion, post-combustion and oxy-fuel combustion. However, although these processes can greatly reduce CO₂ emissions, they also result in a high energy penalty to perform the gas-separation steps involved.¹

In recent years, significant efforts are underway to develop new CO₂ capture technologies with the aim of reducing the costs associated with that process. Within these new technologies, Chemical Looping Combustion (CLC) has been suggested as one of the most promising technologies for CO₂ capture in power generation because CO₂ separation is inherent to the process, which explains its relatively lower cost.² CLC is a combustion concept where air and fuel are never mixed. Thus, the CO₂ generated is not diluted by the nitrogen (N₂) present in the air stream and, consequently, the corresponding gas-gas separation process is inherently avoided. The principle of CLC for gaseous fuels is shown in Fig. 1. Metal oxides (M_xO_y) are used to selectively transport oxygen from the air reactor to

the fuel reactor, which usually are two interconnected fluidized-bed reactors. Ideally, the fuel reactor exhaust stream only contains CO_2 and H_2O while the air reactor exhaust stream is oxygen-depleted air. This fact means that all the carbon present in the gaseous fuel can be captured as CO_2 , which is available in concentrated form after simple condensation of the steam. Furthermore, it must be highlighted that the total heat released from the CLC system is equal to the one obtained during direct combustion and, thus, the corresponding energy penalty is reduced to the CO_2 compression and purification efforts which all capture processes have in common.

Fig. 1 General scheme of the CLC process for gaseous fuels.

An oxygen carrier, which is the core part of a CLC system, is usually composed of a metal oxide and an inert material in a particulate form. The main objectives of the former are to provide a high oxygen transport capacity and to facilitate a complete conversion of the fuel to CO_2 and H_2O , whereas the inert material acts as support providing a high surface area for chemical reaction and increasing the mechanical strength and attrition resistance of the whole oxygen carrier.

Up to now, CLC technology for gaseous fuels has been successfully demonstrated with more than 4000 hours of operational experience in continuous CLC plants up to 140 kW_{th} using more than 40 different oxygen carriers.^{3,4} The next challenge is to upscale this technology from 140 kW to 10 MW since there is a promising niche application in on-field steam generation with CCS. In particular, CLC has the possibility to be applied to replace conventional CO₂ capture systems in the oil and gas industry for heat and steam generation. Successful upscaling of this technology is highly dependent on the upscaling of two aspects in parallel, namely 1) upscaling of reactor system and 2) upscaling of oxygen carrier manufacture. Most efforts are being allocated to upscale the CLC system designs to the desired power of 10 MW.⁵

In respect of the development of materials, research must be focused on providing materials with high reactivity and attrition resistance. Usually, the attrition behaviour of an oxygen carrier is determined by long-time operation in a CLC unit. Then, the lifetime of the material can be estimated. Complementary methods for the analysis of the durability of oxygen carrier particles based on “customized attrition rigs”⁶⁻⁸ have been proposed in literature. Recently, Cabello et al.⁹ have proposed a methodology based on the ASTM D5757 standard test¹⁰ to select oxygen carriers for CLC upscale related to attrition behaviour.

Generally, the preparation methods proposed for large-scale oxygen carrier production are spray drying and impregnation.³ Concerning spray drying, relevant results have been obtained with nickel- and manganese-based oxygen carriers. The oxygen carriers based on nickel oxide were the first ones in which it was thought to upscale the CLC process for gaseous fuels as they exhibited high reactivity and low attrition rate values. In particular, very high combustion efficiency values using CH₄ as fuel as well as estimated particle lifetimes higher than 30000 hours were achieved with Ni-based oxygen carriers prepared by means of spray-drying.¹¹

However, health and environmental issues aim to minimize the use of Ni-based oxygen carriers at industrial scale due to the high toxicity of this metal. Thus, research is currently focused on the development of oxygen carriers based on other metals such as Fe, Cu and Mn. With regard to spray dried Mn-based oxygen carriers, materials based on $\text{CaMnO}_{3.8}$ perovskite present a very good performance for the CLC process with gaseous fuels in terms of reactivity and mechanical stability.^{6,12}

The impregnation method consists in depositing a solution that contains the active metal on the support. This is an easy and well-established technique that is thoroughly used for the production of catalysts at multi-ton scale. Several impregnated oxygen carriers have exhibited a good performance in terms of high reactivity towards different gaseous fuels such as CH_4 , CO or H_2 ^{4,13-20} and physicochemical stability in CLC pilot plants to burn gaseous fuels.²¹⁻³⁶ For example, Ni-, Fe- and Cu-based materials prepared by means of the impregnation method using alumina as support showed particle lifetime values of 10000, 1100 and 2500 hours, respectively.²¹⁻²³

Among the different metal oxides, copper oxide presents very suitable characteristics for the CLC process which make it one of the best candidates to be part of an oxygen carrier.³ It should be pointed out that the selection of the impregnation process as preparation method for Cu-based oxygen carriers has allowed a satisfactory use of this type of materials in CLC units with gaseous fuels. A Cu-based oxygen carrier with 14.2 wt.% CuO content, and prepared by dry impregnation using $\gamma\text{-Al}_2\text{O}_3$ as support, was evaluated during the combustion of CH_4 , syngas and light hydrocarbons in two CLC pilot plants of 500 W_{th} and 10 kW_{th} achieving a good performance in terms of combustion efficiency.^{22,30-33} Moreover, the particle lifetime inferred at 800 °C was 2500 hours, which is an adequate value that does not represent a limitation to the technology development in terms of the cost of the particles.³⁷ Nevertheless,

temperatures higher than 800°C had to be avoided in the fuel reactor in order to preserve the integrity of the particles.³³

The remarkable results previously discussed were achieved with a Cu-based oxygen carrier, designated as Cu14 γ Al_ICB, prepared at lab-scale using alumina as support. The main drawback to upscale the production of this material is that it was developed using a support not available at multi-ton scale. Therefore, suitable oxygen carrier materials at multi ton-scale and competitive price will be required to meet the challenge of upscaling CLC technology.

The main goal of this work consists in developing an impregnated Cu-based oxygen carrier with a commercial support prepared at industrial scale whose properties for the CLC process are preserved, or even improved, in relation to the ones showed by the Cu14 γ Al_ICB material. In this way, a commercial support based on γ -Al₂O₃ has been used to prepare the new impregnated Cu-based oxygen carrier, designated as Cu14 γ Al_Commercial, which has been evaluated in a continuous 500 W_{th} CLC pilot plant during CH₄ combustion tests. The effect of the temperature and the oxygen carrier-to-fuel ratio (ϕ) on the combustion efficiency has been analysed. Moreover, the evolution of the main physicochemical properties of the oxygen carrier along the operation time has been studied, focusing the interest on the attrition behaviour as well as on chemical stability of the particles.

2 Experimental

2.1 Oxygen carrier

The Cu-based oxygen carrier used in this work was manufactured by Johnson Matthey using the incipient wet impregnation technique following industrially-relevant protocols. This material was designated as Cu14 γ Al_Commercial.

Table 1 shows the main physicochemical properties corresponding to the fresh particles of this oxygen carrier. Data from fresh particles of the Cu14 γ Al_ICB oxygen carrier, as benchmark material, are included for comparison purposes.

Table 1. Properties of fresh and after-used particles of the Cu14 γ Al_Commercial oxygen carrier. Data from fresh particles of the Cu14 γ Al_ICB material are included for comparison purposes.

Oxygen carrier	Cu14 γ Al_Commercial			Cu14 γ Al_ICB
	Fresh	Used	Used	Fresh
		60 h	65 h	
		T= 800 °C	T= 900 °C	
Total CuO content (wt.%) ^a	13.8	10.1	10.0	14.2
d _p (μm)	153	151	139	225
Porosity (%)	53.0	49.1	48.7	54.8
Mechanical strength (N)	1.2	1.2	0.7	2.9
AJI (%)	3.1	2.6	46.4	4.3
XRD phases	CuO CuAl ₂ O ₄	CuO, CuAl ₂ O ₄	CuO, CuAl ₂ O ₄	CuO CuAl ₂ O ₄
	δ-Al ₂ O ₃	CuAlO ₂	α-Al ₂ O ₃	δ-Al ₂ O ₃
		δ-Al ₂ O ₃		
		α-Al ₂ O ₃		

^a determined by ICP-AES

2.2 Oxygen carrier characterization techniques

Both fresh and used oxygen carrier particles were physically and chemically characterized using different techniques with the aim of analysing the changes undergone by the Cu14 γ Al_Commercial material throughout the time of operation in the continuous CLC unit.

The reactivity and the active CuO content were determined by TGA, CI Electronics type,

described elsewhere,³⁸ whereas the total CuO content in the fresh and used samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Jobin Yvon 2000 spectrometer.

The particle size distribution of the oxygen carrier material was measured with a laser diffraction technique according to ISO 13320 Standard with a LS 13320 Beckman Coulter equipment. The porosity and pore size distribution were calculated by Hg intrusion in a Quantachrome PoreMaster apparatus. The force needed to fracture a particle was measured with a Shimpo FGN-5X dynamometer. The crushing strength value was taken from, at least, 20 measurements. The attrition resistance was determined using a three-hole air jet attrition tester ATTRI-AS (Ma.Tec. Materials Technologies Snc) configured according to the ASTM-D-5757 standard. As specified in the ASTM method, 50 g of material were tested under an air flow of 10 L min⁻¹, which supposes a jet speed of 490 m s⁻¹. The weight loss of fines was recorded after 1 h and 5 h of operation, respectively. The percentage of fines after a 5 h test is defined as the Air Jet Index (AJI). According to the ASTM method, particles with a size lower than 20 µm are considered as fines. AJI values were determined by duplicate both for fresh and used samples subjected to redox cycles at high temperature in the continuous CLC unit. The reducibility of the Cu_{1.4}Al_{1.6} Commercial samples was determined by temperature programmed reduction (TPR) experiments in a flow apparatus AUTOCHEM II from Micromeritics. Prior to the TPR experiment, the sample was flushed with Ar during 1 hour. After this pre-treatment, samples were heated at 7 °C min⁻¹ from room temperature to 1100 °C with a flow of 20 mL min⁻¹ of a mixture 10 vol.% H₂/90 vol.% Ar. XRD diffractograms were collected by a Bruker D8 Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector. The diffraction pattern was obtained over the 2θ range of 10° to 80° with a step of 0.019°. The assignation of crystalline phases was performed according to Joint

Committee on Powder Diffraction Standards. Quantitative XRD analysis was performed by Rietveld refinement using TOPAS software to obtain the amorphous phase content of the oxygen carrier particles. Finally, the microstructure of the oxygen carrier particles was studied by means of a scanning electron microscopy (SEM) system (Model ISI DS-30). This equipment was coupled to an ultrathin window PGT Prism detector for energy-dispersive X-ray (EDX) to perform elemental microanalyses.

2.3 500 W_{th} continuous CLC unit

The performance of the Cu₁₄Al₁ Commercial material for the combustion of CH₄ as fuel was evaluated in a 500 W_{th} CLC pilot plant designed and built at the Instituto de Carboquímica (ICB-CSIC). A schematic diagram of the aforementioned CLC pilot plant is shown in Fig. 2.

The continuous CLC unit consists of two bubbling fluidized bed reactors, the fuel reactor and the air reactor, interconnected by a loop seal, a riser for solids transport, a solids valve to control the solids circulation rate between both reactors, a cyclone, a diverting solids valve to take samples from the air reactor, a small deposit to take samples from the fuel reactor and two filters to collect the elutriated fines during the process. This facility also has on-line gas analysers to get continuous data of gas composition at the fuel reactor and air reactor outlet streams. A more detailed description of the 500 W_{th} continuous CLC system can be found elsewhere.²¹

Fig. 2. Schematic diagram of the 500 W_{th} continuous CLC system (ICB-CSIC-g1 facility).

2.4 Testing conditions

Two experimental campaigns were performed in the CLC facility with the Cu₁₄γAl₁ Commercial oxygen carrier. The total solids inventory used in the system for both test series was 1.2 kg, of which 0.3 and 0.4 kg were in the fuel and air reactors, respectively. The first experimental campaign consisted of 60 hours of continuous operation working at a temperature of 800 °C both in the reduction and oxidation reactor. The second one was conducted at a temperature of 900 °C in both reactors and lasted for 65 hours. A new batch of fresh particles was used in each of these test series.

The inlet gas flows fed to the fuel reactor, loop seal and air reactor were maintained constant for all the tests. The gas flow fed to the fuel reactor was 170 LN h^{-1} , which corresponded to an inlet gas velocity of 0.1 m s^{-1} . The bottom loop seal was fluidized with N_2 (45 LN h^{-1}). The air flow fed to the air reactor was divided into the primary air (720 LN h^{-1}), added at the bottom bed, and the secondary air (150 LN h^{-1}), added at the top of the bubbling bed to help particle entrainment in the riser.

A mixture of CH_4 and N_2 was used as fuel to analyse the behaviour of the Cu14 γ Al_Commercial material for the CLC process. N_2 acted as diluting agent. The main operating conditions and data corresponding to the tests performed in the $500 \text{ W}_{\text{th}}$ continuous CLC system are shown in Table 2.

Table 2. Main operating conditions corresponding to the tests carried out in the $500 \text{ W}_{\text{th}}$ continuous CLC system with the Cu14 γ Al_Commercial oxygen carrier.

Test	CH_4 (vol.%)	T_{FR} (°C)	T_{AR} (°C)	f_s (kg/h)	ϕ	Power (W_{th})	Solids inventory (kg/MW)
T1	20	800	800	14.3	2.6	338	888
T2	25	800	800	14.4	2.1	423	709
T3	30	800	800	13.6	1.6	508	590
T4	40	800	800	13.1	1.2	677	443
T5	20	900	900	11.0	2.0	338	888
T6	25	900	900	11.0	1.6	423	709
T7	30	900	900	11.0	1.3	508	590
T8	40	900	900	11.0	1.0	677	443

The oxygen carrier-to-fuel ratio, ϕ , which is defined as the ratio between the flow of oxygen supplied by the oxygen carrier and the oxygen needed to stoichiometrically react with the fuel

flow, is calculated by Equation 1 as follows:

$$\phi = \frac{F_{Cu}}{4 \cdot F_{CH_4}} \quad (1)$$

where F_{Cu} is the molar flow rate of copper present in the oxygen carrier in any form, i.e., CuO, Cu₂O, Cu, CuAl₂O₄ and CuAlO₂, calculated from the corresponding solids circulation rate in the CLC unit, f_s , and F_{CH_4} is the inlet molar flow rate of CH₄ in the fuel reactor.

In both test series, conducted at 800 °C (T1-T4) and 900 °C (T5-T8) respectively, the effect of the oxygen carrier-to-fuel ratio, ϕ , on the combustion efficiency was evaluated varying the concentration of CH₄ in the gaseous stream fed to the fuel reactor from 20 to 40 vol. %, whereas the solids circulation rate, f_s , was maintained approximately constant. The range of CH₄ concentration values used in this work corresponds to an input thermal power between 338 and 667 W.

The combustion efficiency, η_c , is defined as the ratio of oxygen consumed by the gas leaving the fuel reactor to that consumed by the gas when the fuel is completely burnt to CO₂ and H₂O. This parameter can be expressed as follows:

$$\eta_c = 1 - \frac{(x_{CO} + x_{H_2} + 4 \cdot x_{CH_4})_{out} \cdot F_{out}}{(4 \cdot x_{CH_4})_{in} \cdot F_{in}} \quad (2)$$

where F_{in} and F_{out} are the molar flows at the inlet and outlet of the fuel reactor, respectively, and x_i is the molar fraction of the gas i . A value of parameter η_c close to 1 indicates that almost full combustion conditions have been achieved in the CLC unit.

3 Results and discussion

3.1 Oxygen carrier performance during CH₄ combustion in CLC

The behaviour of the Cu14γAl_Commercial oxygen carrier was evaluated in the 500 W_{th}

continuous CLC system with the aim of determining if this material was a good candidate to upscale CLC technology for gaseous fuels. In a first step, 60 hours of continuous operation were conducted at 800 °C, both in the fuel and air reactors, to analyse the combustion efficiency and the particle integrity of the selected material. Fig. 3 (a) shows the combustion efficiency of this Cu-based oxygen carrier as a function of the oxygen carrier-to-fuel ratio, ϕ , used in the CLC unit. This material presented a good behaviour obtaining complete CH₄ combustion at ϕ values around 1.5 – 2.0. The corresponding solids inventories used in these tests are shown in Table 2. However, it was previously determined that the oxygen carrier-to-fuel ratio (ϕ) had more influence on the combustion efficiency (η_c) than the solids inventory. In addition, complete combustion could be obtained with lower solids inventory values.³⁹

In a second step, a new batch of this material was used to analyse its performance at a higher temperature, i.e., 900 °C. As a whole, 65 hours of continuous operation were conducted at these conditions without operational problems, such as agglomeration or defluidization. Fig. 3 (b) shows the effect of the oxygen carrier-to-fuel ratio (ϕ) on the combustion efficiency (η_c) at high temperature. The results were excellent, even better than the ones obtained at 800 °C, since higher combustion efficiencies were achieved at low ϕ values, which indicated that an increase of the operating temperature in the CLC unit was clearly beneficial. The performance of the Cu₁₄Al₁Commercial material tested at 800 °C and 900 °C was also compared with the one presented by the reference material at these conditions and the results were very similar.^{22,33}

An adequate oxygen carrier to upscale CLC technology must present not only a good behaviour for fuel combustion, but also a high particle lifetime. The particle lifetime of an oxygen carrier can be experimentally determined in a CLC unit based on its corresponding attrition rate. The experimental attrition rate as a function of the operation time was

determined by collecting and weighing the particles elutriated from the reactors. The particles collected in the filters with a size higher than 45 μm were returned to the system. Thus, attrition rate, A ($\% \text{ h}^{-1}$), is defined through the following equation:

$$A = \frac{m_f}{m_t \cdot \Delta t} \cdot 3600 \cdot 100 \quad (3)$$

where m_f is the mass of elutriated particles with a particle size lower than 45 μm during a particular period of time, Δt (expressed in seconds), and m_t is the total mass of solids in the CLC plant.

Fig. 3. Effect of the oxygen carrier-to-fuel ratio on the combustion efficiency with the Cu14 γ Al_Commercial oxygen carrier. (a) $T_{FR} = 800^\circ\text{C}$, $T_{AR} = 800^\circ\text{C}$, (b) $T_{FR} = 900^\circ\text{C}$, $T_{AR} = 900^\circ\text{C}$. Cu14 γ Al_ICB oxygen carrier is taken as reference material.^{22,33}

As can be observed in Fig. 4 (a), the attrition rate of the Cu14 γ Al_Commercial material tested at 800 °C was high ($\sim 0.25 \% h^{-1}$) during the first hours of operation due to rounding effects in the oxygen carrier particles, but it progressively decreased until a constant value was reached. Thus, the attrition rate was quickly stabilized at $0.02 \% h^{-1}$.

Fig. 4. Attrition behaviour of the Cu14 γ Al_Commercial oxygen carrier tested in the 500 W_{th} CLC unit. (a) T_{FR} = 800 °C, T_{AR} = 800 °C, (b) T_{FR} = 900 °C, T_{AR} = 900 °C. Cu14 γ Al_ICB oxygen carrier is taken as reference material.^{22,33}

This stabilized value is taken to estimate the corresponding value of particle lifetime. The particle lifetime of an oxygen carrier, LT (h), can be estimated from the attrition rate through Equation 4:

$$LT(h) = \frac{100}{A} \quad (4)$$

This attrition rate value implied an estimated particle lifetime of 5000 hours, which was two times higher than the particle lifetime inferred for the reference material.²²

The high attrition rate showed by the Cu14 γ Al_Commercial material during the first hours of operation caused a significant copper loss in the oxygen carrier particles, as can be clearly observed in Fig. 5. However, the total copper oxide content was rapidly stabilized at 10.1 wt.% throughout the time of operation. The active copper oxide content present in the oxygen carrier particles was also determined by TGA.

Fig. 5. Total copper oxide content versus time of operation for the Cu14 γ Al_Commercial oxygen carrier tested in the 500 W_{th} continuous CLC system at 800 °C. Cu14 γ Al_ICB oxygen carrier is taken as reference material.³⁰

The copper oxide content values calculated from TGA technique were almost identical to the total content values, indicating that the remaining copper oxide could be reduced with the

gaseous fuels. In this point, it must be highlighted that the remaining metal oxide content was high enough to obtain very satisfactory results in terms of combustion efficiency, as was shown in Fig. 3. Comparing this total copper oxide content profile with the one obtained for the Cu-based reference material, it can be stated that the Cu14 γ Al_ICB oxygen carrier had a smoother but similar copper loss.

The attrition rate was also experimentally determined in the continuous CLC unit at 900 °C to evaluate if an increase of the temperature affected on the mechanical integrity of the Cu14 γ Al_Commercial material. The attrition rate profile showed in Fig. 4 (b) confirmed that the increase of the temperature in the fuel and air reactors was clearly detrimental for the performance of this oxygen carrier. Initially, the attrition rate followed a similar tendency to the one found for the same material operating at 800 °C, i.e., the amount of elutriated fines collected in the filters of the CLC unit was very high during the first hours of operation but it was rapidly stabilized at a very low value ($< 0.02 \text{ \% h}^{-1}$). However, the attrition rate started to increase in a great extent after 45-50 hours of operation. Finally, after 65 hours, it was decided to stop the experimentation. At that moment, the attrition rate reached a value of $0.22 \text{ \% h}^{-1}$, which indicated that the corresponding particle lifetime of this oxygen carrier was lower than 450 hours. This behaviour was similar to that shown by the Cu14 γ Al_ICB material, see Fig. 4 (b).

Based on the previous results achieved with the Cu14 γ Al_Commercial oxygen carrier regarding combustion efficiency and attrition resistance, it can be stated that it presented an excellent performance for the CLC process at 800 °C, even better than the reference material. On the other hand, when the CLC unit was operated at 900 °C, the oxygen carrier exhibited an excellent behaviour for CH₄ combustion, but an inadequate mechanical integrity.

3.2 Oxygen carrier characterization

In this section, fresh and used particles of the Cu14 γ Al_Commercial and Cu14 γ Al_ICB oxygen carriers were analysed by means of different characterization techniques to understand why the former exhibited better properties for the CLC process than the latter considering that the amount of metal oxide, the type of support (γ -Al₂O₃), and the preparation method were similar for both materials.

3.2.1 Reactivity of the oxygen carrier

The notable performance shown by the Cu14 γ Al_Commercial material regarding CH₄ combustion efficiency can be explained based on both the ability of copper oxide to completely burn the fuel to CO₂ and H₂O and the high reaction rate exhibited by the oxygen carrier particles.

Fig. 6 illustrates the reduction conversion (X_r) versus time curves both for fresh and used particles extracted from the air reactor of the CLC pilot plant at different times of operation during the combustion tests performed at 800 °C. The data correspond to the third reduction cycle obtained in the TGA equipment. Fresh sample exhibited a high reduction rate reaching an 80 % of the reduction conversion in less than 10 seconds. As can be observed, the reaction rate barely changed throughout the 60 hours of continuous operation.

Fig. 6. Reduction conversion vs time curves for the Cu14 γ Al_Commercial material at different times of operation in the CLC unit (0, 9, 22, 41 and 60 h) during the combustion tests performed at 800 °C. Reducing agent: 15 vol.% H₂ (N₂ to balance). T = 800 °C.

3.2.2 Air Jet Index (AJI)

The evolution of the attrition resistance of the oxygen carrier particles during the CH₄ combustion tests was also analysed by means of the determination of the Air Jet Index (AJI). Samples were extracted from the CLC pilot plant at different times of operation during the experimental campaigns conducted at 800 °C and 900 °C. The remarkable result regarding attrition rate obtained with the Cu14 γ Al_Commercial at 800 °C, see Fig. 4 (a), was also corroborated by means of the attrition resistance tests performed to fresh and used particles according to the ASTM-D-5757 standard. The AJI for the fresh oxygen carrier particles was 3.1 %, which is a noteworthy value taking into account that materials with an AJI of 5 % or below are considered appropriate for their use as oxygen carrier in a CLC process, according to the selection criteria given in the work of Cabello et al.⁹

Fig. 7. Evolution of the Air Jet Index (AJI) throughout the time of operation in the continuous CLC facility for the Cu₁₄γAl_Commercial oxygen carrier tested at 800 °C and 900 °C.

In addition, this low value was maintained throughout the time of operation in the continuous CLC unit, see Fig. 7. In this regard, the AJI took a value of 2.6 % for the oxygen carrier particles extracted from the air reactor of the CLC facility at the end of the experimental campaign.

The fact that this parameter was maintained at a very low and almost constant value suggested that the thermal and chemical stresses suffered by the particles during operation in the CLC process did not affect their attrition behaviour. Moreover, if other physical properties of the oxygen carrier particles, such as density, crushing strength and particle size distribution (PSD), are also maintained roughly constant along the time of operation, there is a high degree of confidence that the oxygen carrier particles will preserve an adequate mechanical integrity during a period of time corresponding to the particle lifetime predicted by the attrition rate experimentally determined.⁹ In this case, the values of density, porosity and PSD

corresponding to the oxygen carrier particles extracted from the CLC unit after 60 hours of operation barely changed with respect to the ones showed by fresh material, see data from Table 1 and Fig. 8, respectively.

Unlike tests performed at 800 °C, in which the AJI remained approximately constant over time, the fact of operating at higher temperature produced a steady increase in this parameter reaching a value of 46.4 % after 65 hours of operation, see Fig. 7. This result is shown in accordance with the inadequate attrition value measured in the pilot plant experimentally. In this case, the mechanical resistance was highly deteriorated due to the considerable increase of the thermal and chemical stresses underwent by the particles of this Cu-based oxygen carrier. This deterioration was also reflected in a decrease of both the crushing strength and the size distribution of the Cu₁₄γAl_Commercial particles, as can be clearly observed in Table 2 and Fig. 8.

Fig. 8. Particle size distribution (PSD) of the Cu₁₄γAl_Commercial oxygen carrier at different times of operation and testing conditions.

3.2.3 XRD analyses

Fig. 9 shows the XRD patterns corresponding to fresh and used samples of Cu₁₄γAl_Commercial and Cu₁₄γAl_ICB oxygen carriers as well as the assignation of phases present in each sample. Used samples refer to oxygen carrier particles extracted from the air reactor at the end of the corresponding experimental campaigns performed at 800 °C and 900 °C. Quantitative analyses of the Cu-based phases, as well as the amorphous phase content in the samples, have been also determined from Rietveld refinement. Regarding the fresh materials, it was concluded that the amount of free CuO was higher in the Cu₁₄γAl_Commercial oxygen carrier than in the Cu₁₄γAl_ICB oxygen carrier. In contrast, fresh particles of the reference material presented a higher amount of CuAl₂O₄. Previous research works performed at ICB-CSIC demonstrated that both CuO and CuAl₂O₄ could be considered as active copper-based species for CLC process since they were able to react with different gaseous fuels.^{19,20,30}

Fig. 9 XRD patterns of (a) fresh and (b) used particles of the Cu14 γ Al_Commercial and Cu14 γ Al_ICB oxygen carriers tested at 800 °C and 900 °C.

In both materials, δ -Al₂O₃ was detected as support. This fact implies that the support used to prepare both oxygen carriers, i.e., γ -Al₂O₃, underwent a phase change during the calcination process. Finally, the quantitative XRD analyses also concluded that the amorphous phase content in the Cu14 γ Al_Commercial particles was higher than in the particles of the benchmark material (37 wt.% vs 32 wt.%), see Table 3. The amorphous phase content was reduced in the used oxygen carrier particles of both materials due to the high temperature operation in the CLC units. This reduction degree was much more pronounced on the Cu14 γ Al_Commercial particles tested at 900 °C. In this point, it should be mentioned that the

amorphousness decrease was mainly produced during the first 10 hours of continuous operation in the CLC units.

Table 3. Amorphous phase quantification of both fresh and used Cu14 γ Al_Commercial and Cu14 γ Al_ICB oxygen carrier particles and the corresponding support materials obtained from XRD data.

	Cu14 γ Al_Commercial	Cu14 γ Al_ICB	γ Al_Commercial	γ Al_ICB
Fresh	37.0	32.0	37.8 ^a	33.8 ^a
Used (800°C)	33.0	26.0	36.4 ^b	32.3 ^b
Used (900°C)	12.0			

a) 1 h, 850 °C in furnace; b) 24 h, 800 °C in furnace.

In order to find the source of the varying degree of amorphousness of these oxygen carriers, XRD analyses were carried out to the corresponding alumina-based materials used as supports. These supports were calcined at two different conditions. On the one hand, the supports were calcined 1 hour at 850 °C, being this heat treatment the one used during the preparation process of the fresh oxygen carriers. On the other hand, the supports were calcined 24 hours at 800 °C, thus simulating a long-term operation in a continuous CLC plant. The obtained results are also shown in Table 3. At both calcination conditions, the degree of amorphousness was higher in the alumina from which the Cu14 γ Al_Commercial material was developed than in the alumina from which the reference material was prepared. This result indicated that the amorphousness of the oxygen carrier was mainly provided by the alumina-based material used as support. Therefore, it can be concluded that a higher degree of amorphousness in the support of a Cu-based oxygen carrier prepared by means of the impregnation method produces a higher amount of free CuO in the oxygen carrier particles

because the support presents a lower degree of interaction with the active metal oxide avoiding the formation of a relevant amount of CuAl_2O_4 . This fact could be beneficial with respect to the mechanical resistance of the oxygen carrier considering that both CuO and CuAl_2O_4 are highly reactive compounds with gaseous fuels. Finally, it should be pointed out that the amorphousness decrease detected in the oxygen carriers is due to the presence of copper since, if there is no copper, the amorphousness of the support is maintained roughly constant over time.

3.2.4 Temperature programmed analyses

Temperature programmed reduction (TPR) analyses were performed to fresh and after-used samples of the $\text{Cu}_{14}\gamma\text{Al}$ _Commercial and $\text{Cu}_{14}\gamma\text{Al}$ _ICB oxygen carriers tested at 800 °C and 900 °C to evaluate the reducibility of these materials, and, specifically, the interaction degree between the active metal oxide, i.e., CuO , and the two different alumina-based materials used as supports.

Fig. 10 shows the TPR profiles of the analysed samples. Fresh and after-used oxygen carrier particles of both materials tested at 800 °C exhibited two reduction peaks at low temperature and a broad band at about 700 °C. The peaks obtained at low temperature could be assigned to the reduction CuO -like species. These peaks have been also described as small Cu^{+2} domains and CuO clusters.⁴⁰ The well resolved peaks in the TPR patterns of the samples seemed to indicate that these CuO species could be assigned to clusters and not to small Cu^{+2} domains. As can be observed in this Figure, mainly in the fresh samples, these low-temperature peaks were higher for the $\text{Cu}_{14}\gamma\text{Al}$ _Commercial oxygen carrier, which implied that the amount of free CuO in the particles of this material was higher than in the particles of the reference material, which agrees with the XRD analyses. Moreover, the band found at 700 °C could be attributed to the reduction of CuAl_2O_4 . In this case, this band was more noticeable in the TPR

profiles corresponding to the Cu₁₄γAl_ICB oxygen carrier which was also corroborated by the XRD results.

Fig. 10. TPR profiles of (a) fresh and (b) after-used particles of the Cu₁₄γAl_Commercial and Cu₁₄γAl_ICB oxygen carriers tested at 800 °C and 900 °C.

Moreover, it must be pointed out that the TPR profile corresponding to the fresh sample of the benchmark material showed a small band at about 350 °C, which did not appear for the Cu₁₄γAl_Commercial oxygen carrier. The band observed at this temperature may indicate that Cu⁺² was reduced to Cu⁺¹ in the form of CuAlO₂ due to the greater degree of interaction