Performance evaluation of a Cu-based oxygen carrier impregnated onto ZrO₂ for Chemical Looping Combustion (CLC)

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Abstract

Chemical looping combustion (CLC) has been introduced as a promising technique with inherent advantages for efficient, low-cost CO₂ separation. The type of oxygen carrier employed plays a vital role in improving the overall efficiency and economic penalty of

the system. This study investigates the performance of a CuO oxygen carrier impregnated onto ZrO₂ in a continuously operated 500 W_{th} CLC unit over 30 hours of CH₄ combustion. A decrease in combustion efficiency was observed during the initial 10 hours followed by stabilization. A loss of CuO of between 13 wt% and 5 wt% was recorded during the first 5 hours of combustion before the CuO content was kept constant. This loss was due to the Cu layer peeling off the surface of particles, and the clustering and migration of CuO from internal areas to the surface and then attrited. The effect of the oxygen carrier-to-fuel ratio (ϕ) on the combustion efficiency of the impregnated Cu-based oxygen carrier was studied. In order to reach a combustion efficiency of 99%, ϕ values of 3.9 were needed. The particle attrition rate was stabilized after 30 hours of operation at 0.06%/h, and the estimated lifetime was 1500 hours of operation. XRD and TPR analyses confirmed very low interaction between CuO and the support (ZrO₂), which was unable to retain the CuO inside the particles. Therefore, the lack of interaction between the CuO and the ZrO₂ support is not positive for oxygen carrier behavior in the CLC process.

Keywords: CO₂ Capture, CLC, CuO, ZrO₂, combustion

1. Introduction

Fossil fuels are the most widely used sources of energy for electricity generation¹. Power plants burning fossil fuels are major emitters of CO₂, which is the main contributor to human-induced climate change². The use of an efficient CO₂ capture technique seems to be an interesting temporary option to allow continuation of

conventional power generation methods and to reduce anthropogenic CO₂ emissions. In a CO₂ capture and storage (CCS) system, CO₂ is captured from energy-related sources, then transported and stored at a suitable storage site where it is prevented from entering the atmosphere. Chemical looping combustion (CLC) appears to be a suitable option for a low-cost CO₂ capture³. In a CLC process, metal oxides known as oxygen carriers are used to transport oxygen from the air reactor to the fuel reactor, preventing direct contact between the air and the fuel. After fuel combustion, the spent oxygen carrier is returned to the air reactor for regeneration with O₂ for subsequent cycles. The outlet gases from the air reactor comprise N₂ and unreacted O₂. CO₂ and H₂O are formed by the complete combustion of fuel in the fuel reactor. CO₂ can be readily separated by condensing H₂O without the use of an additional CO₂ capture system. The main reactions occurring in the fuel and air reactors are as follows⁴:

where MeO represents a metal oxide, used as an oxygen carrier. Different types of oxygen carriers can be applied in a CLC process, including CuO, NiO, Mn₂O₃, Fe₂O₃, and Co₃O₄⁵. Cu-based oxygen carriers have noticeable advantages, which give them great interest for use in this work. CuO is relatively cheap, abundant, and highly reactive, and it has a high oxygen transport capacity⁶. CH₄ can be completely converted to CO₂ and H₂O in the presence of CuO⁷. In addition, both reduction and oxidation reactions are exothermic, with CuO requiring low solid flow rates in order to fulfill heat balance⁸. To enhance the reactivity, mechanical strength, and attrition resistance of CuO, oxygen carriers are commonly applied to a support. Al₂O₃ has frequently been used for this purpose in the scientific literature⁹⁻¹³.

De Diego et al.¹¹ studied the effect of synthesis conditions on the agglomeration of CuO/Al₂O₃. They found that calcination temperature and CuO content have significant effects on the agglomeration of the CuO impregnated onto γ -Al₂O₃. For particles with a CuO content of between 10 and 20 wt%, calcination temperature played an important role in the agglomeration phenomena. Particles calcined at a temperature of 850 °C or lower did not agglomerate. In another work, de Diego et al.⁹ studied the performance of a CuO oxygen carrier impregnated onto γ -Al₂O₃ with a CuO content of 14 wt% prepared at a calcination temperature of 850 °C. The prepared carrier showed satisfactory performance, and no agglomeration problems were observed. CuO, γ -Al₂O₃, and CuAl₂O₄ were detected in the XRD patterns of the fresh oxygen carrier. Formation of CuAl₂O₄ was attributed to the strong interaction between CuO and γ -Al₂O₃ in the impregnated CuO/ γ -Al₂O₃ samples, with CuO contents ranging between 15 and 26wt %¹¹. In all samples, reactivity reduced as the number of cycles increased. This reduction was ascribed to the formation of a copper aluminate during CuAl₂O₄ oxidation, causing a partial loss of free CuO and some deactivation of the carrier. However, CuAl₂O₄ is able to be reduced to Cu and CuAlO₂, providing lattice oxygen for the CLC process. The reduction in the reactivity of the oxygen carrier is caused by the difficult reoxidation of the CuAlO₂ from the reduced form. Therefore, not all the Cu will be available for the combustion in future redox cycles. This is considered to be one of the major issues when working with CuO/Al₂O₃ oxygen carriers.

Cabello et al.¹³ studied the durability of a commercial CuO oxygen carrier impregnated onto γ -Al₂O₃ (Cu14 γ -Al_Commercial) over 125 hours of CH₄ combustion in a continuous CLC unit at temperatures between 800 and 900 °C. They also observed the formation of CuAl₂O₄ and the reduction of the active CuO from 13.5 wt% to 10.1 wt%. However, they found that the oxygen carrier had high reactivity and complete

combustion was obtained with oxygen carrier-to-fuel ratio (ϕ) values between 1.5–2 at 900 °C and 2–2.5 at 800 °C. To avoid the problems generated by the CuO/Al₂O₃ interaction, the use of other materials as supports has been studied. In order to block the formation of CuAl₂O₄, Gayan et al.¹⁴ analyzed the use of different Cu-based oxygen carriers for the Chemical-Looping with Oxygen Uncoupling (CLOU) process. This study found that the use of MgAl₂O₄ as a support avoids CuAl₂O₄ formation. Zhao et al.¹⁵ used molecular dynamic simulations to study the microscopic sintering properties of CuO nanograins supported on SiO₂, TiO₂, and ZrO₂, taking into account the interactions between the active component and the inner support material. They found that CuO supported on ZrO₂ showed the best sintering resistance at all the studied temperatures.

Adánez et al.⁴ performed oxygen carrier screening for the CLC process. They observed that the CuO oxygen carriers supported on ZrO₂ were highly reactive but crushing strength was low (<1N) and that they agglomerated in the TGA at temperatures higher than 900 °C. On the other hand, Moldenhauer et al.¹⁶ analyzed a Cu-based oxygen carrier with 20 wt% CuO supported on ZrO₂ prepared by spray-drying using kerosene as fuel. They obtained high reactivity with kerosene, with one fuel conversion of 99.9% achieved. However, the oxygen carrier showed a high attrition rate (0.25%/h) and agglomerated at 975°C. A further study by Gayan et al.¹⁴ analyzed an oxygen carrier with 40 wt% of CuO using ZrO₂ as inert for the CLOU process that was highly reactive and did not agglomerate at temperatures lower than 950 °C in a batch fluidized bed reactor. Mattisson et al.¹⁷ studied the behavior of CuO/ZrO₂ in a CLOU process with petroleum coke as a solid fuel. The CuO/ZrO₂ was prepared by the freeze-granulation method, and the copper content was 40 wt%. They studied the effect of temperature on the combustion efficiency in a batch fluidized bed reactor. They obtained very high

conversion rates and did not observe any problems regarding defluidization or particle agglomeration. In another work, Arjmand et al.¹⁸ used the same sample preparation method and setup to test the performance of a Cu-based oxygen carrier supported on ZrO_2 and stabilized by different materials including CaO, MgO, and CeO_2 , and using CH_4 as fuel. They reported that the CuO supported on MgO-stabilized ZrO_2 represented the best performance, and no agglomeration or defluidization was observed during CH_4 combustion.

It can be seen that ZrO_2 was used as support for Cu-based oxygen carriers mainly for CLOU process to obtain an oxygen carrier with high reactivity. Considering the previously described results, the use of a resistant ZrO_2 was considered as a support to prepare CuO oxygen carriers by impregnation. An oxygen carrier containing CuO impregnated onto ZrO_2 was prepared with a CuO concentration similar to that used in $\text{CuO}/\text{Al}_2\text{O}_3$ carriers and examined for gaseous fuel combustion owing to interest in the performance of CuO/ZrO_2 in a continuous CLC unit burning CH_4 and the study of possible interactions between the CuO and ZrO_2 . The present work analyzes the performance the impregnated CuO/ZrO_2 oxygen carrier in a 500 W_{th} continuous CLC unit over 30 hours of CH_4 combustion at 800 °C. The combustion behavior, reactivity, attrition resistance, durability, and structural evolution of the carrier were thoroughly investigated and compared with an $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ oxygen carrier.

2. Experimental

2.1. Oxygen carrier

An oxygen carrier material developed by Johnson Matthey within the SUCCESS Project¹⁹ was examined to verify its performance as an oxygen carrier for the CLC of CH₄. The oxygen carrier was prepared by incipient wetness impregnation onto a ZrO₂ support of fluidizable size (+100-300 μm) with de Diego et al.⁹. The impregnated material was calcined for 30 min at 550 °C in a muffle furnace for (NO₃)₂Cu decomposition into CuO. Finally, the oxygen carrier was calcined for 1 hour at 850 °C for stabilization. The oxygen carrier was named Cu13Zr_IP. For comparison purposes, two Cu-based oxygen carriers were used: one developed at ICB-CSIC (Cu14γAl_ICB), and another also developed by Johnson Matthey (Cu14γAl_Commercial) within the SUCCESS project¹⁹.

2.2. Oxygen carrier characterization

The oxygen carrier was chemically and physically characterized. Oxygen transport capacity, crushing strength, jet attrition test index, particle size, pore volume, density, specific surface area, and crystalline phases were analyzed. The techniques are described by Adáñez-Rubio et al.²⁰. In Table 1 can be seen the oxygen carrier main characteristics.

Table 1. Properties of the oxygen carrier particles, fresh and used after 30 hours of CH₄ combustion in a 500 W_{th} continuous unit.

	Fresh	30-h used
Composition (wt%)	13% CuO 87% ZrO ₂	5% CuO 95% ZrO ₂
Oxygen transport capacity, R_{OC} (wt%)	2.6	1
Crushing strength (N)	1.7	1.5
Skeletal density of particles (kg/m ³)	5865	5852
AJI (%)	10.5	14.5
Porosity (%)	48.4	44.3
Specific surface area, BET (m ² /g)	4.3	3.0
XRD main phases	CuO, ZrO ₂	ZrO ₂ ; CuO amorphous

The reducibility of the Cu₁₃Zr_IP samples was determined by temperature-programmed reduction (TPR) The TPR technique was described in the following manuscript¹³.

2.3. Experimental installations

2.3.1. TGA

In order to analyze the amount of copper in the particles and the reactivity of the oxygen carrier, multiple redox cycles were carried out in a TGA, CI Electronics type, which is described by Adánez et al.⁴ The TGA measured the reactivity of the oxygen carrier with CH₄ from the variation in the sample weight as a function of time in the reduction cycles with 15% CH₄ and oxidation with air. The results of thermogravimetric analysis were obtained in conditions of control of the reaction rates by the chemical reaction as described by Adanez et al.⁴

2.3.2. 500 W_{th} continuous unit

Cu₁₃Zr_IP combustion of CH₄ performance was studied in a 500 W_{th} CLC unit at 800 °C. Fig. 1 provides a schematic diagram of the continuous unit. The CLC continuous unit consists of: Fuel and air reactors, loop seal and riser. The composition of the gases exiting from both reactors were continuously analyzed. From the fuel reactor were analyzed: O₂, CO, CO₂, H₂ and CH₄; and in the air reactor were analyzed: O₂, CO, CO₂. A detailed description of the unit can be found in Forero et al.⁷.

The total solids inventory in the continuous unit was 2.1 kg, of which 0.5 kg were in the fuel reactor. Moreover, there was a repository of 0.4 kg oxygen carrier to be added to the continuous unit when more material was needed, i.e., after circulation measurement, after extraction of particle samples, etc. All the material extracted during the operation of the continuous unit was mixed with the repository material in order to have all the material at the same grade of use. Thus, the total amount of oxygen carrier in the batch used during this study was 2.5 kg. The fuel and air reactor temperature was 800 °C during the 30 hours of continuous operation burning CH₄. The total inlet gas flow fed to the loop seal and fuel and air reactors was constant for all tests. The total gas flows in the different reactors were the following: Fuel reactor 300 LN·h⁻¹ (0.15 m/s gas velocity); primary air reactor 720 LN·h⁻¹; secondary air reactor 150 LN h⁻¹; loop seal 75 LN·h⁻¹ of N₂. CH₄ diluted in N₂ was fed as fuel.

Fig. 1. Diagram of the 500-W_{th} continuous CLC system.

2.4. Data evaluation

The oxygen carrier-to-fuel ratio, ϕ , in the 0.5 W_{th} CLC unit is calculated as follows:

$$\phi = \frac{x_{\text{CuO}} F_{\text{solids}}}{4 \cdot F_{\text{CH}_4} M_{\text{CuO}}} \quad (3)$$

where x_{CuO} is the mass fraction of copper oxide in the oxygen carrier, assuming all copper to be CuO. F_{solids} is the oxygen carrier circulation rate inside the CLC unit. M_{CuO} is the molecular weight of CuO. F_{CH_4} is the CH₄ flow fed to fuel reactor. Table 2 shows the main data for the experimental campaign performed in the 500 W_{th} continuous CLC

unit burning CH₄. In the 15 first hours of operation, in which the effect of operation time on the evolution of the Cu concentration in the oxygen carrier was analyzed, the concentration of CH₄ fed to the fuel reactor was 15 vol%, corresponding to a thermal power input of 450 W_{th} (T1).

Table 2. Main Data of the Experimental Tests in the CLC unit

Test	T _{FR} (°C)	T _{AR} (°C)	ϕ	$\dot{m}_s$ (kg/h)	[CH ₄] (vol.%)	Power(W)
P01	800	800	3	25	15	450
P02	800	800	1.2	7.4	15	225
P03	800	800	1.6	9.8	15	225
P04	800	800	2.2	13.2	15	225
P05	800	800	3.2	19.6	15	225
P06	800	800	3.9	24.5	15	225

In the following 15 hours of operation, the effect over combustion efficiency was analyzed varying the ϕ feed a 7.5 vol% of CH₄, corresponding to an thermal power input of 225 W_{th} (T2-T6). The oxygen carrier circulation rate in series T1 was fixed at 14 kg/h, corresponding to a ϕ value of 3. In the following series (T2–T6), the circulation rate was varied between 7.4 and 24.5 kg/h in order to modify ϕ from 1.2 to 4.

The ratio between the oxygen consumed by the gas exiting from the fuel reactor and the oxygen consumed by the fuel when fully burnt to H₂O and CO₂ is defined as the combustion efficiency, η_{Comb} , calculated as follows:

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

where F_{in} and F_{out} are the molar flows at the fuel reactor inlet and outlet, respectively, and x_i is the molar fraction of the gas i . For complete combustion of the fuel in the CLC unit, the value of η_{Comb} must be 1.

3. Results and discussion

In the present work, there were 30 hours of CH_4 combustion with Cu13Zr_IP as the oxygen carrier in a 500 W_{th} continuous unit. During the first 15 hours of combustion operation, the behavior of the CuO impregnated in ZrO_2 was studied as a function of time and the evolution of its concentration in the oxygen carrier particles. In the following 15 hours of combustion, once the CuO content in the oxygen carrier was stabilized, the effect of the ϕ on combustion efficiency was studied.

3.1. Combustion behavior in the 500 W_{th} continuous unit

3.1.1. Combustion efficiency.

Oxygen carriers tend to lose active material in the first hours of operation^{9,10,13,21}. The present work analyzed the combustion efficiency of the oxygen carrier as a function of time for each hour of operation. Fig. 2 shows the evolution of combustion efficiency over time using Cu13Zr_IP as the oxygen carrier. It can be seen that by maintaining the fuel feed and solids circulation rate, combustion efficiency decreased with operating time from 99% after 1 hour of CH_4 combustion to 87.8% after 10 hours of combustion. After this time, combustion efficiency was maintained constant in the following 5 hours

of CH₄ combustion. This reduction in combustion efficiency could have been due to the loss of CuO in the oxygen carrier particles during the operation in the continuous unit.

Fig. 2. Combustion efficiency as a function of operation time in test T1. Oxygen carrier:

Cu13Zr_IP. $T_{FR} = 800\text{ }^{\circ}\text{C}$; $T_{AR} = 800\text{ }^{\circ}\text{C}$; $f_s = 14\text{ kg/h}$. $[\text{CH}_4] = 15\text{ vol\%}$.

In order to analyze and characterize the used oxygen carrier, several oxygen carrier samples were taken from the fuel and air reactors. One sample was taken every hour during the 5 first hours. After this time, one sample was taken after every 5 hours of CH₄ combustion. Several characterization tests were performed on these samples. Thermogravimetric analysis was used to determine the amount of CuO in the oxygen carrier samples, using 15 vol% H₂ as a reactant for the reduction and air during the oxidation at 950 °C. Fig. 3 shows the concentration of CuO present in the oxygen carrier particles extracted from the continuous unit during the 30 hours of continuous operation. The CuO content of the oxygen carrier particles experienced a continuous decrease at the initial 10 hours of operation, from the original 13.2 wt% to a value of 5

wt% after 5 hours of combustion. During the following 25 hours of operation, the CuO content in the particles remained constant with a value of around 5 wt%. Similar behavior had previously been observed in Cu-based oxygen carriers impregnated onto Al_2O_3 during CLC with CH_4 ^{10,13}. Cabello et al. ¹³ observed that the CuO content of a commercial oxygen carrier decreased from 13.8 wt% to 10.4 wt% (24.6% decrease) in the first 5 hours of operation, and remained stable for the following 55 hours of CH_4 combustion in the same continuous unit used in the present work. De Diego et al. ⁹ found that a Cu-based oxygen carrier prepared by impregnation lost 28.6% of the original CuO in the oxygen carrier particles (from 14 to 10 wt%) during 70 hours of combustion operation in a 10 kW_{th} continuous unit. However, the CuO content decreases in both cases were lower than those obtained in the present work, where the oxygen carrier particles lost 62.1% of the original CuO content impregnated onto the particles within 5 hours. Therefore, the use of Al_2O_3 as a support showed better behavior with respect to retention of the active phase (CuO) than ZrO_2 , which experienced a higher loss of active phase.

Fig. 3. CuO content (wt%) in the oxygen carrier samples extracted from the continuous unit during 30 hours of CH₄ combustion. Oxygen carrier: Cu₁₃Zr_IP. T_{FR} = 800 °C; T_{AR} = 800 °C.

Fig. 2 shows that combustion efficiency continued to decrease after the CuO concentration of 5 wt% in the particles was reached (5 h). This continuous decrease could be attributed to the use of the repository of particles. In fact, not all the particles in the batch had the same CuO composition during the first 5 hours. Therefore, the combustion efficiency found between 5 and 10 hours was higher than the combustion efficiency that would have been achieved had all the particles had a 5 wt% concentration of CuO. At 10 hours, all the solids used in this work, i.e., initially inside the CLC unit (2.1 kg) and in the repository (0.4 kg) were used in the CLC unit, and a homogeneous composition could be assumed.

As the CuO content decreased, the ϕ also decreased (eq. (3)). With a concentration of CuO of 5 wt% in the oxygen carrier particles, considering the amount of CH₄ fed and the oxygen carrier circulation rate used, the ϕ value was around 1. This value was 2.6 times lower than the initially used. In the following 5 hours of CH₄ combustion the combustion efficiency was stabilized due to the CuO of the oxygen carrier particles was stable.

3.1.2. Effect of the oxygen carrier-to-fuel ratio.

After 15 hours of continuous operation, the CuO content of the particles was stabilized. In the following 15 hours of CH₄ combustion, the effect of ϕ on combustion efficiency

was analyzed. For low CuO contents (5 wt%) in the oxygen carrier and at the maximum circulation flow rate (25 kg/h), it was necessary to use low CH₄ concentration (7.5 vol%) to obtain high ϕ values. To determine combustion efficiency, mean gas concentrations taken during 1 hour of continuous combustion in steady state were used. Small deviations with time were found (± 0.1). The flow rates of the circulating solids were stable, and two measurements were used to calculate the oxygen carrier-to-fuel ratio. Fig. 4 shows the effect of the ϕ on combustion efficiency with the Cu13Zr_IP oxygen carrier. It can be seen that combustion efficiency increased from 92.6% at ϕ of 1.2 to 99% for one ϕ value of 3.9. Fig. 4 also shows a comparison with the combustion efficiency obtained with other CuO oxygen carriers impregnated onto Al₂O₃. Cu13Zr_IP showed slightly lower combustion efficiency than that found with a Cu-based oxygen carrier impregnated onto γ -alumina with 14 wt% CuO (Cu14 γ Al_ICB)¹⁰, tested in a 10 kW_{th} continuous unit at the ICB-CSIC. Moreover, the Cu13Zr_IP also showed lower combustion efficiency than a commercial Cu-based oxygen carrier impregnated onto γ -alumina (Cu14gAl_Commercial)¹³. Cabello et al.¹³ found that Cu14gAl_Commercial had high reactivity, achieving complete combustion of CH₄ with an ϕ of between 2 and 2.5. At these ϕ values, Cu13Zr_IP reached combustion efficiency values of around 98%. According to Fig. 4, the use of Cu13Zr_IP will require oxygen carrier-to-fuel ratios higher than 3 in order to achieve complete combustion of the fuel.

Fig. 4. Effect of the ϕ on combustion efficiency with the Cu13Zr_IP oxygen carrier in tests T2-T6. $T_{FR} = 800^{\circ}\text{C}$; $T_{AR} = 800^{\circ}\text{C}$. For comparison, data are plotted for Cu14 γ Al_Commercial¹³ and Cu14 γ Al_ICB¹⁰.

The reactivity of these oxygen carriers was measured in the TGA with H_2 at 800°C for comparison. Fig. 5 shows the reduction curves for the Cu13Zr_IP and Cu14 γ Al_Commercial¹³ oxygen carriers at similar operating times burning CH_4 in the continuous CLC unit. It can be seen that the reactivity was higher for the Cu13Zr_IP even after 30 hours of combustion. Furthermore, it can be seen that the reactivity of both oxygen carriers with H_2 was stable with the time of CH_4 combustion. Therefore, the difference in reactivity of both oxygen carriers was not responsible for the lower combustion efficiency obtained in the continuous CLC unit using Cu13Zr_IP as the oxygen carrier.

Fig. 5. Reduction conversion curves with H₂ (15 vol%; N₂ to balance) at 800 °C for Cu13Zr_IP at different times of operation in the continuous unit (15, 20, and 30 hours).

For comparison data are plotted for Cu14γAl_Commercial (22 and 41 hours of operation in the same continuous CLC unit)¹³.

In regard to CuO inventory in the fuel reactor, with 5 wt% CuO in the stabilized Cu13Zr_IP oxygen carrier, the CuO inventory in the fuel reactor was 120 kg CuO/MW_{th}. In the case of the Cu14γAl_Commercial oxygen carrier at the lower CH₄ inlet concentration in the fuel reactor, there was a CuO inventory in the fuel reactor of between 90 and 120 CuO/MW_{th}¹³. Therefore, in the present work the fuel reactor was burning CH₄ with similar CuO inventories as those used by Cabello et al. Because it was observed that oxygen carrier reactivity was not responsible for the difference in the combustion efficiency obtained with both oxygen carriers, and that the CuO inventory in the fuel reactor was similar with both oxygen carriers, the effect of the fuel concentration fed to the fuel reactor was analyzed.

Abad et al.²² studied the effect of oxygen carrier reactivity on the minimum oxygen carrier inventory needed in the fuel reactor to burn different gaseous fuels. The equations used in that work were able to be used to calculate the minimum oxygen carrier needed in the fuel reactor as a function of the inlet fuel concentration. Table 3 shows the minimum oxygen carrier inventory needed in the fuel reactor to completely burn the CH₄ to CO₂ and H₂O for different inlet fuel concentrations. Calculations were made using kinetic data and equations from Abad et al.²² for a Cu-based oxygen carrier with 10 wt% CuO and using γ -Al₂O₃ as support. It can be seen that when the CH₄ inlet concentration ([CH₄]_{inlet}) decreases, the gas expansion factor ($\Delta\epsilon_g$) and the mean concentration of CH₄ in the fuel reactor ([CH₄]_{mean}) also decreases. These variations in key factors cause the minimum oxygen carrier inventory needed to obtain complete combustion of the fuel to increase from 52 kg/MW_{th} with 100% CH₄ to 128 kg/MW_{th} when only 7.5 vol% of CH₄ is fed in. This effect was due to the difference in the driving force when considering mean CH₄ concentration in the fuel reactor as a function of the inlet CH₄ concentration. Thus, the greater the driving force, the faster the kinetics of the combustion reaction between the fuel and oxygen carrier, and the lower the inventory of oxygen carrier needed to obtain the same combustion efficiency.²²

Table 3. Minimum oxygen carrier inventories to achieve 99.9% combustion of CH₄. Kinetic data and equations used for calculations taken from Abad et al.²².

[CH ₄] _{inlet} (vol%)	$\Delta\epsilon_g$ (-)	[CH ₄] _{mean} (vol%)	m _{FR} (kg/MW _{th})
100	2	13.2	52
30	1.6	4.4	78
7.5	1.15	1.3	128

Where m_{FR} is the inventory of oxygen carrier in the fuel reactor. As regards Cu14 γ Al_Commercial, CH₄ concentration varied between 20 and 40 vol%¹³, while the concentration of CH₄ fed in the case of Cu13Zr_IP was 7.5 vol%. Therefore, although the reactivity of both oxygen carriers was similar, the lower combustion efficiency obtained in the continuous CLC unit for Cu13Zr_IP with respect to Cu14 γ Al_Commercial can be explained by the lower concentration of CH₄ fed to the fuel reactor.

3.1.3 Attrition during combustion

The attrition rate of the oxygen carrier was studied during combustion operation in the 500 W_{th} continuous CLC unit. Particle lifetime can be calculated experimentally through the attrition rate measured in the continuous CLC unit. Attrition rate is calculated as a function of the weight of particles collected with a size lower than 45 μ m elutriated from fuel and air reactors. The attrition rate, A (%/h), is calculated by:

$$A = \frac{m_f}{m_t \Delta t} \cdot 100 \quad (5)$$

where m_f is the mass of elutriated particles with a size lower than 45 μ m recovered during Δt (hours), and m_t is the total mass of solids in the continuous CLC unit. Fig. 6 shows the attrition rate obtained for the Cu13Zr_IP oxygen carrier during 30 hours of CH₄ combustion in the 500 W_{th} continuous CLC unit. It can be seen that the attrition rate was high at 5 and 10 hours of operation (0.52 %/h and 0.38 %/h, respectively). After 15 hours of combustion, the attrition rate decreased to values near 0.1 %/h, although these values were still high. After 30 hours of operation the attrition rate value decreased to 0.06 %/h. This attrition rate value is 1.6 times higher than that obtained by

Adánez et al.¹⁰ for a Cu-based oxygen carrier prepared by impregnation using γ -Al₂O₃ as the support, and 3 times higher than that of a commercial Cu-based oxygen carrier also impregnated onto γ -Al₂O₃¹³.

Fig. 6. Evolution of the attrition Jet Index (AJI) with operating time for the Cu13Zr_IP oxygen carrier in the 500W_{th} continuous CLC unit.

The attrition rate value obtained in the continuous CLC unit made is possible to calculate the oxygen carrier particle lifetime, LT (h), as follows:

$$LT(h) = \frac{100}{A} \quad (6)$$

The lifetime estimated through attrition rate has a value of 1500 hours of operation. This value is lower than the values obtained for other Cu-based oxygen carriers prepared by impregnation onto γ -Al₂O₃, which showed values of 2500 hours¹⁰ and 5000 hours¹³, respectively. The high attrition rate observed during the first hour of operation is associated with the high loss of CuO from the oxygen carrier particles in the elutriated material, as seen in Figure 3. Based on the results obtained in the continuous CLC unit

regarding attrition rate, combustion efficiency, and CuO loss, the use of ZrO₂ as a support for Cu-based oxygen carriers does not improve on the performance of CuO/ γ -Al₂O₃ oxygen carriers for the CLC of CH₄, and improvement of the oxygen carrier is needed.

3.2. Oxygen carrier characterization

Cu13Zr_IP oxygen carrier samples extracted from the continuous CLC unit were analyzed to ascertain the evolution of the main particle characteristics. In order to observe the evolution of the CuO impregnated onto the ZrO₂, one sample was taken every hour during the first 5 hours of operation, after which time one sample per reactor was taken after every 5 hours of operation. A total of 17 samples were taken and analyzed.

3.2.1. CH₄ reactivity of the oxygen carrier

As shown in section 3.1, the oxygen carrier experienced a high loss of the CuO in its composition, from 13.2 wt% to 5 wt%, in around 5 hours of continuous operation. It was therefore necessary to know whether this loss of active material affected the reactivity of the oxygen carrier particles with the fuel. Fig. 7 shows the reduction curves obtained in the TGA at 800 °C using 15 vol% CH₄ as fuel for samples taken at different operation times in the continuous CLC unit. It can be observed that the oxygen carrier particles presented high reactivity and that the sample reached the maximum conversion in less than one minute in the TGA. Comparing these results with those obtained using H₂ as fuel in the TGA (Fig. 5), it can be seen that the oxygen carrier particles are much more reactive with H₂ than with CH₄, reaching maximum conversion in around 10

seconds. The reactivity of the samples with CH₄ did not change during 30 hours of CH₄ combustion, even though there was a large decrease in the CuO content during the first 5 hours of operation.

Fig. 7. Reduction conversion curves with CH₄ (15 vol%; N₂ to balance) at 800 °C for Cu13Zr_IP at different times of operation in the continuous unit.

3.2.2. Air jet index

One important parameter for oxygen carrier characterization is attrition, which can be also characterized in cold conditions using the Air Jet Index (AJI) attrition test. Samples extracted every 5 hours of continuous operation were analyzed to show the evolution of the AJI value with operating time in the continuous unit burning CH₄. The AJI value for fresh particles was 10%, which was higher than the reference value considered as acceptable for fluid catalytic cracking (FCC) catalysts (AJI ≤ 5%)²³, see Fig. 8. This value can be seen to have undergone a significant increase in the first 5 hours of operation, associated with the loss of CuO, see Fig. 3. This increase can be also

observed in the attrition rate measured recovering the elutriated material from the continuous unit. The AJI value changed with combustion time, reaching values near 12% at 15 hours, although one slight increase was observed at 30 hours, which could indicate that particle integrity was decreasing. This trend does not agree with the attrition rate found during continuous unit operation, indicating that there is no direct relation between both parameters.

Fig. 8. Attrition Jet Index (AJI) evolution with operating time for the Cu13Zr_IP oxygen carrier in the 500 W_{th} continuous CLC unit.

3.2.3. XRD analyses

Fig. 9 shows the XRD patterns of the fresh (Figure 9(a)) and used Cu13Zr_IP oxygen carrier particles after 30 hours of CH₄ combustion (Figure 9(b)). In the fresh particles, Fig. 9(a), what appears to be crystalline phases of the oxygen carrier active phase (CuO, blue peaks) and the support (ZrO₂, red peaks) can be seen. However, the peaks of crystalline CuO were not detected in the used particles. Only the presence of ZrO₂ was

detected, see Fig. 9(b). However, CuO contents higher than 5% were always present in the particles, as determined by thermogravimetric analysis. Thus, the lack of CuO phase in the particles could be attributed to the fact that the CuO present in the particles after 30 hours of operation would have become amorphous CuO.

Fig. 9. XRD patterns of (a) fresh and (b) used Cu₁₃Zr_IP oxygen carrier particles after 30 hours of CH₄ combustion.

3.2.4. Temperature programmed reduction (TPR)

TPR was carried out with fresh and 30-hour used samples of the Cu13Zr_IP oxygen carrier and a sample of Cu13gAl_Commercial¹³ to evaluate the reducibility of these materials. Fig. 10 shows that the main peak was obtained at temperatures as low as 214 °C and 218 °C for fresh and used particles of Cu13Zr_IP, respectively. The peaks found at these low temperatures are related to the reduction of CuO species, specifically to small and well-dispersed Cu²⁺ entities²⁴. Moreover, both Cu13Zr_IP samples showed one small peak at 140 °C. Anderson et al. related this secondary peak to larger CuO clusters that are easily reduced²⁴. These results show that in both Cu13Zr_IP oxygen carrier samples, the CuO was well dispersed in the particles, although large CuO clusters were found. Both peaks were detected at temperatures 30–40 °C lower than the peaks found by Anderson et al.²⁶.

Fig. 10. TPR profiles of fresh and used oxygen carrier particles of Cu13Zr_IP and Cu14γAl Commercial.

On the other hand, the low temperature peak for the fresh Cu14gAl_Commercial particles divides into two at 185 °C, with a shoulder at 208 °C. Moreover, this sample shows two small peaks, at 340 °C and 720 °C, respectively, which are associated with the formation of copper aluminate with different Cu species: Cu^+ (CuAlO_2 , at 340 °C) and Cu^{2+} (CuAl_2O_4 , at 720 °C)¹³.

Fig. 10 also shows that for both samples of Cu13Zr_IP no peaks were detected other than those associated with the CuO. Therefore, this confirms the very low interaction of CuO with the support (ZrO_2).

3.2.5. SEM characterization

Fresh and used Cu13Zr_IP oxygen carrier particles were analyzed by SEM-EDX to examine the changes in the structure during continuous CLC operation in the 500 W_{th} CLC unit. Fig. 11 shows the evolution of the external and internal structure of the oxygen carrier particles for fresh and used particles at different operating times. It can be observed that CuO was homogeneously distributed inside the fresh particles of the oxygen carrier, with a thin CuO layer on the surface, Fig. 11(a,b). After 1 hour of CH₄ combustion, the external layer of CuO started to come away from the oxygen carrier particle surface, but still remained joined to the particle, Fig. 11 (c, d). Sintering of CuO crystals began inside the particle. After 2 hours of operation, the external layer of CuO disappeared, with this Cu elutriated and decreasing the CuO content of the particles from 13.2 to 10.5 wt%. At the same time, the CuO inside the particles formed large agglomerates that migrated to the particle surface, where they were easily attrited and lost, Fig. 11(e,f).

BSE Cross section particle image

BSE particle imagen

Fig. 11. SEM images of Cu₁₃Zr_IP particles: BSE cross section of a particle (left) and BSE image of a particle (right) after different hours of CH₄ combustion in the

continuous CLC unit: (a), (b) Fresh particles; (c),(d) 1 h; (e), (f) 2 h; (g), (h) 3 h; (i), (j) 4 h; (k), (l) 5 h; (m), (n) 10 h; (o), (p) 30 h.

During the following hour, the Cu inside the particles continued to migrate to the surface, from where it was attrited, decreasing the CuO content in the particles to 7.5 wt%, Fig. 11 (g, h). After 4 hours of operation, Large agglomerates of CuO inside some of the particles that could migrate to the surface, and big cracks started to appear between these Cu agglomerates and the surface, Fig. 11 (i, j). Fig. 11 (k, l) shows that after 5 hours of operation, the large agglomerates broke the particles, while grains of Cu started to disappear on the surface. The CuO content in the particles was reduced to 5 wt%. After 10 hours of operation, the CuO agglomerates inside and outside the particles, Fig. 11 (m, n), had disappeared. The CuO remaining in the particles was homogenously distributed in the particle (inside and outside). Finally, Fig. 11 (o, p) shows that the remaining Cu inside the particle started to agglomerate again after 30 hours of operation but did not seem to migrate to the surface. On the surface, the distribution of Cu is homogenous and equal to that of the particles after 10 hours of CH₄ combustion.

In conclusion, it can be deduced from the SEM-EDX analysis that the Cu can migrate more easily inside the ZrO₂ support than in the Al₂O₃ because of the interaction of CuO with Al₂O₃ that retains more the CuO inside the particles. Therefore, the lack of interaction between the CuO and the ZrO₂ support is not positive for oxygen carrier behavior in the for CLC process.

4. Conclusions

The behavior of a CuO-based oxygen carrier impregnated onto ZrO₂ was studied in a 500 W_{th} continuous CLC unit over 30 hours of CH₄ combustion. Complete combustion of CH₄ to CO₂ and H₂O was achieved. In the first 5 hours of combustion, the oxygen carrier experienced an important loss of CuO by attrition (from 13.2 wt% to 5 wt%). However, the oxygen carrier reactivity remained stable even with the loss of oxygen transport capacity.

SEM-EDX analysis showed that the high loss of CuO was due to the sintering and migration of CuO crystals from the inside of the particle to the surface, where these crystals were easily attrited and lost. After 10 hours of continuous operation, the CuO content in the oxygen carrier particles was stabilized, and the CuO content in the fines decreased to values near those of the oxygen carrier composition.

Therefore, Cu can migrate more easily when ZrO₂ is used as support than when γ -Al₂O₃ is used, owing to no intermediate species being formed between the active phase and the support, which is able to retain the CuO inside the particles. Thus, the lack of interaction between the CuO and the ZrO₂ support is not positive for the behavior of the oxygen carrier in the CLC process. Moreover, the lifetime of Cu13Zr_IP was estimated to be 1500 hours, so it will be necessary to improve the oxygen carrier properties in regard to the CuO loss, and to improve resistance to the attrition.

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