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**A. Cabello, C. Dueso, F. García-Labiano, P. Gayán*, A. Abad,
L. F. de Diego, J. Adánez.**

Instituto de Carboquímica (ICB-CSIC), Department of Energy and Environment,
Miguel Luesma Castán 4, Zaragoza 50018, SPAIN.

* Corresponding author. Tel.: +34 976 733 977. Fax: +34 976 733 318. E-mail address:

pgayan@icb.csic.es (Pilar Gayán)

Performance of a highly reactive impregnated $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier with CH_4 and H_2S in a 500 W_{th} CLC unit.

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* Corresponding author. Tel.: +34 976 733 977. Fax: +34 976 733 318. E-mail address:
pgayan@icb.csic.es (Pilar Gayán)

Abstract

A synthetic Fe-based oxygen carrier prepared by impregnation using $\gamma\text{-Al}_2\text{O}_3$ as support, successfully tested for gas CLC combustion, has been now evaluated with respect to gas combustion in a 500 W_{th} CLC continuous unit when the fuel, CH_4 , contained variable amounts of H_2S .

Full gas combustion was reached at oxygen carrier-to-fuel ratio values higher than 1.5. The presence of sulfur in the fuel gas hardly affected the reactivity and combustion efficiency of the oxygen carrier, independently of the amount of sulfur in the gas stream. All the sulfur introduced as H_2S in the fuel reactor (FR) was released in the same reactor as SO_2 . Furthermore, oxygen carrier particles extracted from the CLC unit after the experimental tests with H_2S addition were

characterized by means of different techniques and no sulfur was detected in any case. The impregnated Fe-based oxygen carrier was highly reactive and sulfur resistant, and can be considered as a suitable material for CLC with gaseous fuels that contain sulfur.

Keywords: CO₂ Capture, Chemical-Looping Combustion, Iron, Oxygen Carrier, Fuel Gas, Hydrogen Sulfide.

1. Introduction

Chemical Looping Combustion (CLC) is a combustion technology where an oxygen carrier, usually a metal oxide, is used to transfer oxygen from the combustion air to the fuel, thus avoiding direct contact between air and fuel [1-2]. This technology has the advantage that CO₂ is inherently separated, thus there is no energy loss in the separation and no costs associated with gas separation equipment and operation. The solid circulates between two interconnected reactors, the fuel (FR) and the air reactor (AR). In the FR, the metal oxide reacts with the gaseous fuel to produce CO₂ and H₂O. A high concentrated CO₂ stream, ready for compression and sequestration, can be obtained condensing the steam. The oxygen carrier is oxidized again in the AR so that it is ready to start a new cycle.

In the last years, different metal oxide systems have been proposed to be used as oxygen carriers in the CLC process [2]. Among them, Fe-based oxygen carriers present several advantages such as adequate crushing strength values and a low trend towards carbon formation. Other non physical-chemical aspects, such as the cost of the oxygen carrier, the availability or its friendly environmental behavior are also advantageous with respect to other metal oxides used for the CLC process.

Iron compounds can present different final oxidation states during reduction reaction (Fe₂O₃, Fe₃O₄, FeO and Fe). The reducing gas composition and temperature are the variables that determine the

stable Fe species. For an industrial CLC system, only the transformation from hematite to magnetite ($\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$) is applicable due to thermodynamic limitations [2]. If the iron oxide is further reduced to wustite (FeO) or Fe, the CO_2 purity obtained in the FR decreased considerably since the CO and H_2 concentrations in equilibrium increase in a great extent [3]. However, when alumina or titania is present in the oxygen carrier particles, reduced compounds such as $\text{FeO}\cdot\text{Al}_2\text{O}_3$ or $\text{FeO}\cdot\text{TiO}_2$ can be formed allowing full combustion of the fuel to CO_2 and H_2O . In these conditions, a further reduction of the iron compounds is achieved in comparison with the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system [4-5].

Up to now, several natural or synthetic Fe-based oxygen carriers have been tested at lab scale (TGA and fluidized bed reactors) and small continuous CLC units for gaseous fuels [6-13]. In general, Fe-based oxygen carriers present weak redox characteristics and low combustion conversions when CH_4 is used as fuel. Nevertheless, our research group at the Instituto de Carboquímica (ICB-CSIC) developed a highly reactive Fe-based oxygen carrier prepared by the incipient hot impregnation method using Al_2O_3 as support [13]. Complete combustion efficiencies were reached at low oxygen carrier-to-fuel ratio (ϕ) values when the temperature in the FR was 1153 K. The corresponding solids inventory in the FR was around 500 $\text{kg}/\text{MW}_{\text{th}}$, which corresponds to a Fe inventory of 50 $\text{kg}/\text{MW}_{\text{th}}$. These values are the lowest referred in the literature for any kind of Fe-based oxygen carrier, both natural or synthetic.

A required step for the development of an optimum oxygen carrier for the CLC process is the evaluation of its behavior in similar conditions to the ones present at industrial scale. All the previous works with Fe-based oxygen carriers have been carried out using methane, CO, or/and H_2 to simulate the composition of natural gas, syngas or PSA-off gas. However, real fuel gases at industrial scale can contain variable amounts of sulfur compounds, such as H_2S and COS. Very small amounts of H_2S (~ 20 vppm) are present in natural gas [14]. In the case of a refinery fuel gas,

the H_2S content varied depending on the site, and concentrations up to 800 vppm can be obtained. Finally, this value can be as high as 8000 vppm for raw syngas generated from coal gasification [15].

The presence of sulfur compounds can have a great influence over the design of an industrial CLC plant. Environmentally, the legislation about gaseous emissions must be fulfilled so that the sulfur released as SO_2 in the AR gas outlet stream should be lower than the legal limit value. Furthermore, sulfur can also be emitted in the FR gas outlet stream affecting in this case the quality of the CO_2 produced [16, 17].

From an operational point of view, the oxygen carrier can be poisoned by the sulfur compounds formed from the reaction between the metal oxide and sulfurous gases such as H_2S . The damage to the material can be revealed in terms of reactivity, transport capacity and combustion efficiency reduction. Formation of solid sulfur compounds depends on sulfur compound concentrations as well as temperature and pressure [3].

Thermodynamic calculations about the fate of H_2S in a CLC process have been previously conducted taking into account different metal oxides as oxygen carriers, operating conditions (temperature, pressure, and H_2S concentrations) and gaseous fuels (CH_4 , CO or H_2). Jerndal et al. [3] and Wang et al. [18] concluded that there was no risk of iron sulfide or iron sulfate formation under usual CLC process conditions in terms of temperature, concentration of sulfur-containing gases or oxygen excess. However, previous works in our research group [19, 20] found that the fate of sulfur in a CLC process could not be predicted based only with thermodynamic analyses. The thermodynamic calculations carried out by Garcia-Labiano et al. [19] regarding the effect of sulfur on Ni-based oxygen carriers predicted the absence of nickel sulfides formation at some operating conditions. However, experimental data showed that the formation of sulfides in the fuel reactor was evident even in those operating conditions selected to avoid sulfides formation according to

thermodynamics. This fact was explained according to the different gas atmosphere existing in the lower zone of the fuel reactor, which was a fluidized bed. Furthermore, Forero et al. [20] stated that, according to a thermodynamic study, the formation of copper sulfides should be avoided at oxygen carrier-to-fuel ratios (ϕ) above 1. Nevertheless, the presence of CH_4 and low concentrations of CO_2 and H_2O in the fuel reactor favored the formation of copper sulfides and the deactivation of the Cu-based oxygen carrier at $\phi = 1.3$. Moreover, other factors like kinetics of sulfur compounds can affect the sulfur gas product distribution in the CLC system predicted by thermodynamics. Finally, it is important to note that the conclusions found by Jerndal et al. [3] and Wang et al. [18] were obtained considering the pair $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ as Fe-species. In this work, alumina is used as support and hence results can be different since $\text{FeO}\cdot\text{Al}_2\text{O}_3$ specie can appears as Fe-reduced compound instead of Fe_3O_4 .

Up to now, the effect of sulfur on the performance of Fe-based oxygen carriers in continuous CLC units has not been studied yet. In this sense, more tests in continuous facilities are needed to gain an adequate understanding of the behavior and usefulness of these particles for this kind of combustion technology. The aim of this work was to test the performance of a highly reactive synthetic Fe-based oxygen carrier when the fuel, CH_4 , contained variable amounts of H_2S (up to 2000 ppm). The influence of H_2S concentration on the gas products distribution and combustion efficiency, sulfur splitting between FR and AR and oxygen carrier deactivation were investigated under continuous operation in a 500W_{th} CLC prototype. Moreover, the evolution of the oxygen carrier properties and its behavior during long-term operation was also analyzed.

2. Experimental section

2.1 Oxygen carrier material

A synthetic Fe-based oxygen carrier prepared by impregnation, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier, has been used in this work. Commercial $\gamma\text{-Al}_2\text{O}_3$ (Puralox NWA-155, Sasol Germany GmbH) particles

of 0.1–0.32 mm, with density of 1.3 g/cm³ and porosity of 55.4 % were selected as support. The oxygen carrier was prepared impregnating the support heated at 353 K in a planetary mixer with a saturated iron nitrate solution [Fe(NO₃)₃·9H₂O] at 333–353 K (3.8 M). The volume of solution added corresponded to the total pore volume of the support particles. This solution was slowly added to the alumina particles with thorough stirring at hot temperature (353 K). The material resulting from the first impregnation was calcined at 823 K in air atmosphere for 30 min to decompose the impregnated metal nitrate into the metal oxide. Finally, after the second impregnation, the oxygen carrier was sintered in a furnace at 1223 K for 1 h. The main physical and chemical properties of this oxygen carrier can be found in Gayán et al. [13].

2.2 Oxygen carrier characterization

Several techniques have been used to physically and chemically characterize both fresh and after-used oxygen carrier particles. The reactivity of the particles was determined by TGA. The force needed to fracture a particle was determined using a Shimpo FGN – 5X crushing strength apparatus. The crushing strength was obtained as the average value of at least 20 measurements. The attrition resistance was determined using a three-hole air jet attrition tester, ATT-100M, configured according to ASTM-D-5757-95 [21]. As specified in the ASTM method, 50 g of material, in this case fresh and used samples, were tested under 10L/min of air flow. The weight loss of fines was recorded at 1 h and 5 h of time on stream, respectively. The percentage of fines after a 5 hours test is the Air Jet Attrition Index (AJI). According to the ASTM method, particles with a size lower than 20 µm are considered as fines. The identification of crystalline chemical species was carried out by powder X-Ray Diffraction (XRD) in a Bruker AXS D8 Advance, equipped with monochromatic beam diffracted graphite, using Ni-filtered “Cu Kα” radiation. On the other hand, the reducibility of the oxygen carrier particles was determined by temperature-programmed reduction (TPR) experiments in a flow apparatus AUTOCHEM II from Micromeritics. Finally, the oxygen carrier particles were also analyzed in a scanning electron microscope (SEM) ISI DS-130 coupled to an

ultra thin window PGT Prism detector for energy-dispersive X-ray (EDX) analysis in order to determine the microstructure and to carry out an elemental microanalysis.

2.3 Reactivity of the oxygen carrier

Reactivity tests of fresh and after-used particles were carried out in a TGA, CI electronics type, described elsewhere [22]. The reactivity of the oxygen carrier was determined with CH₄ as reducing gas. All the reactivity tests were carried out at 1223 K and at atmospheric pressure. The gas composition was 15 vol. % CH₄, and 20 vol. % H₂O was added to avoid carbon formation by CH₄ decomposition during reduction reaction. Finally, nitrogen was used to balance. For oxidation reaction, pure air was used as reacting gas. After weight stabilization, the experiment was started by exposing the oxygen carrier to three alternating reducing and oxidizing cycles.

The conversion of solids for the reduction reaction was calculated as:

$$X_r = \frac{m_{ox} - m}{R_{OC} \cdot m_{ox}} \quad (1)$$

m_{ox} being the mass of the fully oxidized solids, m the instantaneous mass of the sample and R_{OC} the oxygen transport capacity for the transformation between Fe₂O₃ and FeO·Al₂O₃. The conversion of the oxidation reaction was calculated as $X_o = 1 - X_r$.

2.4 ICB-CSIC-g1 facility

A schematic diagram of the 500 W_{th} chemical-looping combustion prototype used for the experimental tests is shown in Figure 1. This facility was composed of two interconnected fluidized-bed reactors, a riser for solid transport, a solid valve to control the solids fed to the FR, a loop seal and a cyclone. This design allowed the variation and control of the solid circulation flow rate between both reactors.

The FR (1) and the AR (3) are two bubbling fluidized-beds (0.05 m i.d.) with a bed height of 0.1 m. The AR was followed by a riser (4) of 0.02 m i.d. and 1 m height. A further description of this CLC prototype is present elsewhere [19, 20].

To study the effect of sulfur on the oxygen carrier, the CLC pilot plant included two mass flow controllers for H_2S and H_2 . Small amounts of H_2 (up to 1 vol. %) were fed together with H_2S to avoid the decomposition of H_2S in the feeding lines. Furthermore, the gas lines downstream the FR were heated by electrical resistances in order to avoid steam condensation and H_2SO_4 formation. A nondispersive infrared (NDIR) analyzer (Siemens Ultramat U22) was used to detect the SO_2 concentrations obtained at the AR gas outlet stream. To analyse the FR gas outlet stream, a gas chromatograph (Varian 3400-CX GC) equipped with a PORAPAK-Q packed column for chromatographic separation and a sulfur-specific flame photometric detector (FPD) was used. In this way, it was possible the detection of the different gaseous sulfur compounds that could appear in the FR as H_2S , SO_2 , COS , CS_2 , etc. The chromatograph was calibrated in the range of 0-1500 vppm for H_2S and 0-2000 vppm for SO_2 .

Testing conditions.

The total solids inventory in the system was 1.2 kg approximately, of which 0.3 and 0.5 kg were in the FR and AR, respectively. A total operation time of 75 h at hot conditions, 50 of them were with sulfur addition, was carried out using the same batch of oxygen carrier particles. The temperatures in the AR and FR were always kept constant at about 1223 K and 1173 K respectively. The inlet gas flow in the FR was 170 $\text{L}_\text{N}/\text{h}$ (0.1 m/s) for all the tests. Air was used as fluidizing gas in the AR, which was divided into the primary air, added from the bottom bed (720 $\text{L}_\text{N}/\text{h}$), and the secondary air, added at the top of the bubbling bed to help particle entrainment in the riser (150 $\text{L}_\text{N}/\text{h}$). Nitrogen was also used to fluidize the bottom loop seal (37.5 $\text{L}_\text{N}/\text{h}$).

The fuel gas was a stream containing CH_4 , different amounts of H_2S and N_2 to balance. H_2S concentrations used in the different tests (750, 1300 and 2000 vppm) were calculated with respect to the total inlet gas flow in the FR, i.e., 170 $\text{L}_\text{N}/\text{h}$. Three different experimental tests series were carried out within the scope of this work. Table 1 shows a summary of the main variables used in each test. Combustion test 1 is a reference test without sulfur addition. In tests 2-4, it was

determined the effect of the H₂S content on the behavior of the Fe-based material working at high oxygen carrier-to-fuel ratios ($\phi = 1.9$). Finally, tests 5-9 were carried out at low oxygen carrier-to-fuel ratios ($\phi < 1.4$) using two different H₂S concentrations to analyze the effect of sulfur when CH₄ was not completely converted.

The oxygen carrier-to-fuel ratio (ϕ) was defined by Eq. (2), as:

$$\phi = \frac{F_{Fe_2O_3}}{4 \cdot F_{CH_4}} \quad (2)$$

Where $F_{Fe_2O_3}$ is the molar flow rate of Fe₂O₃ and F_{CH_4} is the inlet molar flow rate of CH₄ in the FR. This parameter can be defined as the ratio between the oxygen supplied and the oxygen needed to stoichiometrically react with the fuel flow. As the H₂S and H₂ concentrations are practically negligible in relation to the CH₄ concentration fed to the CLC system, it can be considered that a value of $\phi = 1$ corresponds to the stoichiometric relation between Fe₂O₃ and CH₄ in reaction (3).

In reaction (3) iron aluminate (FeO·Al₂O₃) is the Fe-reduced compound allowing complete combustion of the gaseous fuel to CO₂ and H₂O. In this sense, when hematite, Fe₂O₃, is supported over alumina particles, the oxygen transport capacity of the oxygen carrier is increased by three times in comparison with the transformation from hematite to magnetite (Fe₂O₃ – Fe₃O₄) [13].

The combustion efficiency (η_c) has been defined as the ratio of oxygen consumed by the gas leaving the FR to that consumed by the gas when the fuel is completely burnt to CO₂ and H₂O. So, the η_c gives an idea about how the CLC operation is close or far from the complete combustion of the fuel, i.e., $\eta_c = 100\%$.

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

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 . It must be considered that the H_2S combustion process had a very small relevance in the η_c values since the amount of H_2S fed was very low in relation to CH_4 .

3. Results

3.1 Thermodynamic calculations

Several thermodynamic studies regarding the fate of sulfur with Fe-based oxygen carriers have been previously carried out [3, 18]. These thermodynamic studies were conducted without taking into account the formation of $FeO \cdot Al_2O_3$ as a reduced iron phase when alumina is used as support.

Therefore, a thermodynamic study was now carried out using the HSC Chemistry 6.1 [23] software to determine the fate of sulfur when a Fe_2O_3/Al_2O_3 oxygen carrier was used. This program finds the most stable phase combination and seeks the phase composition where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant pressure and temperature.

The calculations were conducted considering CH_4 as fuel, H_2S concentrations up to 5000 vppm and operating temperatures from 973 K to 1273 K. Figure 2 shows the thermodynamic equilibrium of the compounds existing in the FR at 1173 K as a function of the oxygen present in this reactor, that is, as a function of the oxygen carrier-to-fuel ratio, ϕ . The values were expressed as the volumetric percentage of gas composition for methane combustion and the mass percentage of sulfur species present in the products in relation to the methane and sulfur fed into the system, respectively. Regarding the equilibrium gas composition, it can be observed that at ϕ values above 1, complete combustion of CH_4 to CO_2 and H_2O was achieved. In these conditions, Fe_2O_3 and $FeO \cdot Al_2O_3$ were the only iron species present. If the parameter ϕ was decreased below 1, unreacted H_2 and CO appeared reaching their maximum values when the equilibrium $Fe-FeO \cdot Al_2O_3$ was found. In that case, CO_2 and H_2O were not present in the gas equilibrium and CH_4 appeared as an unreacted gas. The CH_4 concentration at equilibrium increased at very low ϕ values when hematite was fully

reduced to metallic iron. Regarding the sulfur species present in the thermodynamic equilibrium, the unique stable sulfur compound in the FR was SO_2 when $\phi \geq 1$. At sub-stoichiometric conditions, different solid and gaseous sulfur species can appear depending on the amount of oxygen present in the system. Only working at very low oxygen carrier-to-fuel ratios ($\phi < 0.1$), a stable solid sulfur compound, $\text{Fe}_{0.877}\text{S}$, could be formed when elemental Fe exists. The thermodynamic calculations made at different temperatures and H_2S concentrations showed similar results.

In order to understand in a better way the results shown in Figure 2, a compilation of all the possible reactions regarding a Fe-based oxygen carrier that reacts with CH_4 and H_2S is shown, both in the FR and AR.

Using CH_4 as gaseous fuel and Fe_2O_3 impregnated over Al_2O_3 as oxygen carrier, the overall reaction in the FR is given by Eq. (3). CO and H_2 can appear by partial oxidation reaction between CH_4 and the Fe-based oxygen carrier.

Both compounds can later react with the oxygen carrier by the following ways:

When the fuel gas contains H_2S , the number of chemical reactions that can be carried out in the FR increases. At ϕ values above 1, the main reaction that takes place is the one that involves the iron oxide with the H_2S in order to form SO_2 through equation (8).

Thermodynamic calculations showed that $\text{Fe}_{0.877}\text{S}$ was the only stable iron sulfide that could be formed when elemental Fe exists in the equilibrium.

The reduced oxygen carrier particles are transported to the AR where the following reactions can take place. Firstly, the iron aluminate is oxidized to hematite:

Furthermore, the iron sulfide that comes from the FR can react with the oxygen added in the AR to $FeSO_4$ or Fe_2O_3 with SO_2 release.

As the temperature in the AR of a CLC unit is always higher than 973 K, it would be supposed that the iron sulfide would be released in this reactor in form of SO_2 .

3.2 Effect of H_2S on the combustion efficiency

To determine the behavior of the oxygen carrier in atmospheres that contain sulfur, several tests were carried out in the 500 W_{th} CLC prototype under continuous operating conditions using a mixture of CH_4 and H_2S as fuel gas. Reactivity, combustion efficiency, agglomeration, and sulfur splitting between reactors were analyzed. As it was previously mentioned, concentrations up to 2000 vppm of H_2S were used in the fuel stream fed to the FR.

Figure 3 summarizes the main results obtained during the experimental work showing the gas concentration of the different compounds measured at the outlet streams of the FR and AR. In this Figure, tests 1-4 with high oxygen carrier-to-fuel ratio values ($\phi = 1.9$) are presented. The combustion of the CH_4 was complete to CO_2 and H_2O . Furthermore, it was also observed that the gas concentration profiles were not affected by the presence of H_2S in the system independently of

the H_2S concentration introduced. As it was predicted from the thermodynamic calculations, all the sulfur introduced as H_2S in the FR was oxidized to SO_2 . H_2S , COS and CS_2 were not detected in any case at the outlet of the FR. The concentrations of CO_2 and SO_2 measured in dry basis in the FR were a bit lower than the CH_4 and H_2S concentrations fed into the system due to the small dilution produced by the N_2 flowing from the loop seal into the FR. Moreover, neither CO_2 nor CO was detected in the AR gas stream, which indicated the absence of gas leakage between reactors and no carbon formation in the FR. Finally, it is important to highlight that SO_2 was never detected at the outlet of the AR. The operation of the prototype was very stable for a long period of time even in those cases where high amounts of H_2S were added (1300 and 2000 vppm).

In tests 5-9, at which the oxygen carrier-to-fuel ratios were close to stoichiometry conditions, CO_2 concentration was lower than that corresponding to full fuel combustion and some unconverted CH_4 appeared while CO and H_2 concentrations were very low in all cases (< 0.2 vol. %). It must be pointed out that a ϕ value higher than 1.5 at 1153 K was determined in a previous work [13] to obtain full combustion of CH_4 in this facility with the oxygen carrier material. The addition of different amounts of H_2S to the gaseous fuel stream caused a negligible effect on the CO_2 and CH_4 concentrations at the outlet stream from the FR.

The combustion efficiency, η_c , reached in the CLC unit was used as comparison parameter to evaluate the behavior of the oxygen carrier during the different tests carried out. Figure 4 shows the effect of the oxygen carrier-to-fuel ratio on the combustion efficiency for each test. As it can be observed, there were no significant differences with respect to the results obtained by Gayán et al. [13] working with the same oxygen carrier in the absence of H_2S . In this sense, it can be concluded that the presence of H_2S in the fuel gas (Tests 2-9) hardly affected the combustion efficiency, independently of the amount of sulfur present in the fuel stream.

Regarding the oxygen carrier-to-fuel ratio value needed to obtain full fuel combustion, it can be stated that a ϕ value of 1.5 is a low value that permits to fulfill the mass and energy balances in the CLC system. Furthermore, this oxygen carrier-to-fuel ratio value is similar to those found for other Cu- and Ni-based oxygen carriers for CH₄ combustion [24, 25].

Sulfur mass balances made in the CLC system at the different tests are summarized in Table 2. These balances were carried out by integration the SO₂ concentration present at the gas outlet stream of the FR since the emission of unreacted H₂S in the FR or SO₂ in the AR was never detected in any test. Furthermore, although SO₃ could not be measured continuously, thermodynamic analyses carried out at usual CLC operating conditions demonstrated that the presence of SO₃ was almost negligible in the FR, and for that reason the influence of this compound on the sulfur mass balances was not considered. Sulfur balances closed in a range of ± 5 wt. % in all cases, which can be attributed to experimental errors, indicating the absence of a noteworthy iron sulfides formation in the FR. However, a deeply characterization of used oxygen carrier particles extracted from the CLC unit was made in order to corroborate these results.

Finally, it can be highlighted that a smooth operation of the CLC unit was achieved during the 75 hours of experimental work, and operational problems, such as corrosion, were never found due to the presence of H₂S in the CLC plant.

3.3 Characterization of the oxygen carrier.

3.3.1 Mechanical integrity and tendency for agglomeration

The mechanical integrity of the fresh and used material was evaluated by different methods. First, the crushing strength of the fresh particles was measured in a dynamometer as 1.5 N. This value dropped up to 0.9 N for oxygen carrier particles taken out from the CLC unit after 75 h of operation. This value is lower to the one reported by Gayán et al. [13] due to a longer operation time (75 h vs 46 h). Also, the attrition index of the fresh particles was determined by the ASTM-D-

5757-95 method as 4.7 %. Materials with AJI values below 5 % are generally considered suitable for use in a transport reactor in the catalyst industry [26]. However, this value increased up to 12.8 % for the particles extracted from the CLC unit at the end of the experimental work. This increase can be due to the drop of the crushing strength that the particles underwent during its long-term operation inside the CLC unit.

Moreover, an attrition rate was experimentally determined during the CLC process. Particles elutriated from both reactors were recovered in the cyclones and filters and weighted to calculate the attrition rate. Those particles whose size was lower than 40 μ m were considered as attrited particles. The attrition rate measured of the Fe₂O₃/Al₂O₃ oxygen carrier during these experimental tests was similar to the one obtained by Gayán et al. [13] with the same Fe-based oxygen carrier but without H₂S addition. In both cases, the attrition rate was high during the first hours as a consequence of the rounding effects on the irregularities of the particles and because of the fines stuck to the particles during the preparation. Finally, the attrition rate of the Fe₂O₃/Al₂O₃ oxygen carrier was stabilized at approximately 0.09 wt. %/h, giving a particle lifetime of 1100 h.

Finally, it is important to point out that during the 75 h of operation at hot conditions in the CLC unit, the oxygen carrier particles never showed agglomeration or defluidization problems in spite of the H₂S fed.

3.3.2 Oxygen carrier reducibility

Fresh and after-used samples were also analyzed by TPR technique in order to study the reducibility of the Fe₂O₃/Al₂O₃ oxygen carrier. Figure 5 illustrates the TPR profiles corresponding to the fresh sample and the samples extracted from the AR and FR of the CLC plant after Test 1 and Test 9. These tests correspond to the reference test without sulfur addition and the last test with H₂S addition in this experimental work, respectively. In this way, the effect of sulfur on the reducibility of the Fe-based oxygen carrier could be evaluated. The TPR profile corresponding to commercial pure Fe₂O₃ particles was also included for comparison purposes.

The fresh sample exhibited three different hydrogen consumption peaks. The first peak at 683 K could be attributed to the reduction of isolated Fe_2O_3 units on the surface of the support to Fe_3O_4 with weak interaction with the support. The second peak at 985 K was attributed to the transition from Fe_3O_4 to FeO . This reduction process took place at higher temperature than that for commercial Fe_2O_3 (see Table 3), suggesting that the alumina had a stabilizing effect on the FeO metastable phase formed during reduction. Finally, the third peak corresponding to the last reduction step, the transition from FeO to Fe^0 , took place at 1132 K. This third peak could not be attributed to the spinel formation ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) because the reduction temperature was not as high as necessary to reduce the spinel.

The samples extracted from the AR and FR in tests 1 and 9 showed very similar TPR patterns which indicated that the reducibility of the material was not affected by the presence of sulfur in the feeding gas. Regarding the samples taken from the AR, the first H_2 consumption peak had a lower area than the one which corresponded to the reduction process from Fe_2O_3 to Fe_3O_4 . Furthermore, this peak was shifted to a higher temperature (760 K approximately) than that corresponding to the fresh sample, indicating that the interaction between the iron phases and the support was higher as the number of reduction-oxidation cycles in the continuous CLC unit was increased. The intensity of the second peak (~ 970 K) was higher than the one that corresponded to the fresh sample. Nevertheless, the intensity of the third step of reduction (a shoulder for both AR samples) was lower. This result could be explained in terms of that the reduction process $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ took place continuously, as it has been reported elsewhere [27].

In the samples taken from the FR it was observed a continuous H_2 consumption up to a temperature close to 1173 K, when a small peak-shoulder could be found. This TPR profile could be indicative of the presence of different Fe phases in the samples. Thus, the reduction of Fe_2O_3 to Fe_3O_4 was combined with the presence of Fe_3O_4 and iron aluminate ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) on the samples. This continuous reduction process can be found described by Ren-Yuan et al. [28]. Finally, the peak-

shoulder that appeared at a higher temperature (around 1173 K) could indicate the reduction of $\text{FeO} \cdot \text{Al}_2\text{O}_3$ to elemental Fe. The iron aluminate compound was only measured from TPR analysis carried out to FR-samples, as in TPR results of fresh and samples collected from the AR was not measured. Thus, it can be concluded that the iron aluminate was formed during the CLC reduction process in the FR. This result confirms experimentally, as in the work conducted by Gayán et al. [13], that the presence of alumina in the oxygen carrier particles allowed the reduction of the Fe_2O_3 up to Fe^{+2} , in the form of $\text{FeO} \cdot \text{Al}_2\text{O}_3$, obtaining complete conversion of the gaseous fuel to CO_2 and H_2O when the oxygen carrier-to-fuel ratio was high enough ($\phi \geq 1.5$). Furthermore, the presence of iron aluminate in the samples extracted from the FR after each experimental test was also determined by X-ray diffraction (XRD) analyses. In order to avoid the oxidation of these samples, the oxygen carrier particles were cooled in N_2 to room temperature previously to be tested. Figure 7 shows the powder XRD patterns of fresh and used particles extracted after 75 h of operation both from FR and AR.

3.3.3 Oxygen carrier reactivity

Figure 6 shows the conversion versus time curves obtained both for the fresh material and the samples extracted from the CLC plant after Test 2 and Test 9. The data correspond to the third cycle of reduction-oxidation in the TGA. These three samples exhibited very similar reactivity both for reduction and oxidation, corroborating that the oxygen carrier reactivity was hardly affected by the presence of sulfur in the fuel gas.

3.3.4 Oxygen carrier structure

Sulfur mass balances for each experimental test closed in a range of ± 5 wt. %. The objective in this section is to verify, by means of different characterization techniques, the presence, or not, of sulfur in the oxygen carrier particles extracted from the CLC unit after the experimental tests with H_2S addition. These analyses would confirm that those minor differences in the closure of the sulfur balances were due to experimental errors.

From the powder XRD patterns it was concluded that there was no detection of any crystalline phase that contained sulfur in the structure of the particles, both extracted from the AR and the FR in any experimental test (see Figure 7). However, it is important to take into account that crystalline phases present in the samples with a mass percentage lower than 5 wt. % cannot be detected by means of XRD technique.

Oxygen carrier particles were also analyzed by SEM-EDX in order to check if sulfur was formed in the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier during tests with sulfur addition. Figure 8 illustrates a SEM image of a cross-section of oxygen carrier particle after 75 h of operation inside the CLC prototype. It can be stated that sulfur was not detected in the particles, neither inside nor in the external surface.

The characterization of this Fe-based material confirmed that no sulfur was detected in any of the used samples indicating that the small deviations in the sulfur mass balances showed in Table 2 can be attributed to experimental errors. Therefore, the oxygen carrier was capable of burning all the H_2S to SO_2 without the formation of iron sulfides.

4. Conclusions

A synthetic Fe-based oxygen carrier prepared by impregnation using $\gamma\text{-Al}_2\text{O}_3$ as support was evaluated with respect to gas combustion in a 500 W_{th} CLC continuous unit when the fuel, CH_4 , contained variable amounts of H_2S (up to 2000 ppm).

The presence of H_2S in the fuel gas hardly affected the reactivity of the oxygen carrier and the combustion efficiency of the fuel gas, independently of the amount of sulfur present in the fuel stream. Full gas combustion conditions were achieved at $\phi > 1.5$ operating at temperatures of 1173 K and 1223 K in the FR and AR respectively. In addition, all the sulfur fed with the fuel gas was released as SO_2 in the flue gas from the FR. No sulfur was detected in the used samples extracted from the CLC unit after an exhaustive characterization of the oxygen carrier particles.

Some environmental considerations regarding sulfur presence in the different outlet streams of an industrial CLC unit that operated with this Fe-based oxygen can be drawn. Firstly, as the SO_2

emissions released from the AR were non-existent, there would be no difficulty to fulfill the legislation about gaseous emissions in power plants. On the other hand, all the sulfur fed into the system was released as SO_2 in the flue gas from the FR. This could mean important consequences with respect to the quality of the CO_2 ready for sequestration that should be taken into account. The necessity of treatment of the flue gas downstream the FR would depend on the purity requirements of the liquefied CO_2 to be transported, compressed and stored. Currently, there is no legislation about restrictive contaminant contents in CO_2 for transport and storage, and much uncertainty exists about these limits [17].

On the basis of the experimental results obtained in this work, it can be concluded that the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier presents an optimal behavior for the combustion of methane with hydrogen sulfide in the CLC prototype since this oxygen carrier was not susceptible to be poisoned by sulfur showing a very good reactivity and combustion efficiency when the fuel contained variable amounts of H_2S .

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Figure Captions

Figure 1. Schematic diagram of the ICB-CSIC-g1 facility.

Figure 2. Thermodynamic equilibrium as a function of parameter ϕ . Fuel gas: CH₄; H₂S: 5000 vppm; T_{FR} = 1173 K. Figure 3. Gas product distribution obtained at the outlet of AR and FR during different tests.

Figure 4. Effect of the presence of H₂S in the fuel gas on the combustion efficiency for different oxygen carrier-to-fuel ratios, ϕ . Numbers correspond to tests given in Table 1. For comparison reasons, tests carried out by Gayán et al. [13] have been added.

Figure 5. TPR profiles of commercial Fe₂O₃ and Fe₂O₃/Al₂O₃ oxygen carrier particles, fresh and used particles extracted from the AR (left) and FR (right).

Figure 6. TGA reactivity of fresh and after used particles. Reducing gas composition: 15 vol. % CH₄, 20 vol. % H₂O and N₂ to balance. Oxidizing gas composition: pure air. T = 1223 K.

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Tables

Table 1. Operating conditions used during experiments with H₂S in the CLC facility.

Table 2. Mass balance of sulfur for each test.

Table 3. Position of peaks for TPR analyses.

Test	CH ₄ conc. (vol. %)	H ₂ S in (vppm)	F _s (kg/h)	ϕ	Power (W _{th})	Accumulated combustion time (h)
1	30	0	16	1.9	507	4
2	30	2000	16	1.9	507	10
3	30	1300	16	1.9	507	18
4	30	750	16	1.9	507	20
5	30	1300	12.0	1.4	507	26
6	30	1300	9.4	1.1	507	34
7	30	1300	8.5	1.0	507	42
8	30	2000	11.2	1.3	507	48
9	30	2000	10.3	1.2	507	54

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	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
ϕ	1.9	1.9	1.9	1.4	1.1	1.0	1.3	1.2
H ₂ S fed (vppm)	2000	1300	750	1300	1300	1300	2000	2000
Sulfur distribution (%)								
In	100	100	100	100	100	100	100	100
Out gas FR	95.8	97.4	102.3	98.5	96.2	94.9	97.7	95.3
Out gas AR	0	0	0	0	0	0	0	0

Table 2. Mass balance of sulfur for each test.

Sample	T (K) reduction		
Commercial Fe ₂ O ₃	673	898	1106
Fresh sample	683	985	1132
Test 1 AR	753	969	1105
Test 1 FR	Continuous H ₂ consumption		1175
Test 9 AR	762	971	1105
Test 9 FR	Continuous H ₂ consumption		1171

Table 3. Position of peaks for TPR analyses.