Use of chemically and physically mixed iron and nickel oxides as oxygen carriers for gas combustion in a CLC process

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Different bimetallic Fe–Ni-based OCs have been prepared and evaluated in a TGA, a batch fluidised bed reactor, and a continuous CLC unit in order to analyse the effect of NiO content on the CLC performance when CH4 or a PSA-offgas was used as fuel. A set of experiments was conducted in continuous operation in a 500 Wth CLC unit, firstly working with a chemically mixed OC, with the iron and nickel oxides impregnated over the same alumina particle, and secondly working with a physical mixture of two impregnated Fe- and Ni-based OCs. The results were also compared with those obtained with an unmixed Fe-based OC. The effect on the combustion efficiency of different operating conditions, such as fuel composition, oxygen carrier to fuel ratio and fuel reactor temperature has been determined in the continuous unit. It was found that the use of a chemically mixed OC had a negative effect on the combustion efficiency since the formation of Fe–Ni compounds reduced the catalytic effect of Ni addition. On the other hand, a physically mixed OC with 2% of NiO increased significantly the combustion efficiency at low temperatures.

1. Introduction

Climate change is among the largest environmental, social and economic challenge currently facing mankind. In so far as climate change is concerned, there is, today, overall consensus on the need to reduce greenhouse gas emissions globally by 50% by 2050. This represents a cut of at least 80% in the industrialized world. This will mean, from now until 2050, considerable re-organization of the way in which society works (work, transport, leisure, city planning, housing, electricity production). The sectors responsible for emission – power generation, industry, transport, buildings and construction – must all prepare the transition to a low-carbon economy [1]. CO2 capture and storage technologies (CCS) have been identified as one of the options necessary to overcome the anthropogenic emissions [2]. Among the different technologies for CO2 capture, the chemical-looping combustion (CLC) process was suggested as a worthy alternative to reduce the economic cost of CO2 capture [3].

CLC involves combustion of fuels with an oxygen carrier (OC), generally a metal oxide and a binder, which transfers oxygen from the air to the fuel by means of its exchange between two different reactors, avoiding in this way the direct contact between fuel and air. In conventional combustion the flue gas stream consists of carbon dioxide, steam and mostly nitrogen. Carbon capture in this combustion involves considerable energy for separating the CO2 from the N2. In CLC, CO2 separation is simply accomplished because the flue gas stream consists only of CO2 and steam. By steam condensation, a pure CO2 stream is produced. Therefore, CLC provides a sequestration ready CO2 stream without the need for using costly gas separation techniques. Moreover, the net chemical reaction and energy release are similar to that of conventional combustion of the fuel.

A CLC system is generally composed of two interconnected fluidized bed reactors (Fig. 1) designated as air (AR) and fuel reactors (FR), where the solid metal oxide particles are circulated between the reactors. In the fuel reactor, the fuel gas (C,H,m) is oxidized to CO2 and H2O by a metal oxide (MeO) that is reduced to a metal (Me) or a reduced form of MeO. The FR is typically a bubbling or circulating bed. The metal or reduced oxide is further transferred into the air reactor where it is oxidized with air, and the material regenerated is ready to start a new cycle. The flue gas leaving the air reactor contains N2 and unreacted O2. The exit gas from the fuel reactor contains only CO2 and H2O.

A large volume of knowledge on the CLC technology has been accumulated during recent years. CLC for gaseous fuels have successfully demonstrated in different CLC prototypes in the 10–140 kWth range using oxygen carriers based on nickel, cobalt, and copper oxides [4]. Many of the studies on CLC have focused on the development of appropriate oxygen carriers able to comply with the requirements imposed by the process. Tests with around 700 different materials based...
on transition metal oxides, mixed oxides, and low-cost materials have been reported [4].

An oxygen carrier for CLC should have the following properties: high fuel conversion to CO2 and H2O; high reduction and oxidation rates; low tendency to agglomeration, fragmentation and attrition; low possibility of deactivation by carbon deposition or sulphur compounds; easy preparation to reduce costs; and it would be desired that the oxygen carrier will be environmental friendly.

Because of its low cost and environmental compatibility, Fe-based OC is considered an attractive option for CLC application. Other chemical characteristics are advantageous for the use of Fe-based oxygen carriers: low tendency to carbon deposition [5] and no risk of sulphide or sulphate formation at any sulphur containing gas concentration or operating temperature [4]. However, an important disadvantage is its low reactivity with methane [5]. But, it was observed that during the combustion of methane side reactions may occur, like the reforming reaction or the water–gas shift reaction, which generate CO and H2 gases which reacts faster with Fe-based oxygen carriers [5–7]. So, higher combustion efficiencies could be obtained increasing the reaction rate of the reforming reaction, and therefore, forcing the reaction to proceed via the intermediate products H2 and CO.

During the last years, it has been found that the combination of different oxygen-carrier materials may result in positive synergy effects, taking advantage of the favourable characteristics of each of them [4]. Different methods have been reported on literature to produce mixed oxides, such as the simple mixing [8–13], the impregnation of a second active phase onto existing particles [14] or the direct preparation of a multiple active phase material [8,9,15–24]. Considering this and in order to improve the reactivity of the Fe-based carriers with methane, some authors mixed them with a small amount of a high reactive material. Ni-based oxygen-carriers have shown very high reactivity and good performance working at high temperatures (900–1100 °C). Several investigations [25,26] found that NiO particles reacted with CH4 through CO and H2 formation, because the metallic nickel formed on the particle surface enhanced the reforming of methane. The indication that nickel catalyzes the methane reforming and the fact that iron oxide reacts fast with CO and H2, suggest that a combination of both types of oxides may show synergy effects with an increased overall rate of reaction with respect to iron. This may have great implication in terms of the cost and safety of oxygen carriers since nickel is more expensive than other metal oxides, and the use of Ni-based oxygen-carriers may require safety measures because of its toxicity.

Bimetallic oxygen carriers of Fe–Ni have been prepared by different researchers. Materials containing Ni and Fe with a spinel structure were tested in a TGA by Lambert et al. [27]. They found that impregnating NiO on a spinel material increased both oxygen-carrier capacity and reactivity of the resulting material. Lagerbom et al. [28] tested in a TGA a bimetallic Fe–Ni/Al2O3 oxygen-carrier and observed that addition of NiO to Fe2O3/Al2O3 particles improved the activity but decreased the mechanical strength. Son and Kim [22] carried out experiments in a continuous CFB using different Fe–Ni/bentonite particles. They found that the reactivity of the oxygen-carrier particles increased with increasing NiO content. The optimum ratio of NiO/Fe2O3 was found to be 3 (NiO/Fe2O3 = x75:25). In addition to mixed oxides with the spinel structure and bimetallic oxygen-carriers, other more complex metal oxides with perovskite structure have been proposed to be used as oxygen-carriers for the CLC process [29]. However, long-term chemical and mechanical properties of perovskite particles are largely unknown and further investigation with these new materials is needed to know its behaviour in continuous fluidized-bed reactors.

The addition of Ni-based particles in a bed of Fe-based particles has also been investigated. Several studies were performed with the addition of certain amount of nickel oxide using different experimental configurations as fixed bed [8], batch fluidized-bed reactor [10–12], 300 Wth circulating fluidized-bed reactor [13] and 500 Wth unit [9]. Johansson et al. [10] found that a bed of iron oxides with only 3 wt.% nickel oxide was sufficient to give a very high CH4 conversion. In addition, these researchers showed that the mixed-oxide system produced significantly more CO2 than the sum of the metal oxides that run separately, thus giving evidence of the synergy in using nickel oxide together with iron oxide. Very similar findings were also observed by Ryden et al. mixing NiO60–MgAl2O4 either in a bed of Fe2O3–MgZrO2 [12], in a bed of ilmenite [13] or waste products from the steel industry [11]. Ortiz et al. [9] reported an increase in the combustion efficiency in a continuous 500 Wth CLC prototype using PSA-offgases as fuel. Moghtaderi and Song [30] carried out a theoretical analysis of the kinetic parameters when physically mixed-metal oxides are used. No clear effect on the resulting kinetics of the mixture was achieved.

So, physical and chemical addition of Ni to a Fe-based OC has been previously investigated in the literature. However, a comparison between both Ni addition methods was never carried out before. So, this works the effects of Ni addition over a Fe-based OC that has been evaluated and compared using two different strategies: the chemical and the physical mixtures. Thus, different bimetallic OCs have been prepared by impregnation on an alumina support and evaluated in a TGA and batch fluidized bed reactor to analyse the effect of NiO content on the reactivity and gas product distribution. Moreover, a physically mixed OC, using a Fe-based and a Ni-based OC, was also evaluated in the combustion of fuel gases.
The effect of this Ni addition on the combustion efficiency was analysed in a 500 Wth CLC continuous unit using different combustion gases and operating conditions (temperature, oxygen carrier to fuel ratio and fuel composition). A first set of experiments were conducted working with a chemically mixed OC, with the iron and nickel oxides impregnated over the same alumina particle. A second set of experiments were performed working with a physical mixture of two impregnated Fe- and Ni-based OCs. The results were also compared with those obtained by the authors [31] with a highly reactive unmixed Fe-based OC developed and tested in a continuous CLC unit.

2. Experimental section

2.1. Oxygen carrier materials

The behaviour of several chemically mixed Fe-Ni oxygen carriers was analysed in this work together with a physically mixed Fe-Ni OC, using a Fe-based and a Ni-based OC. Fe-based OC was prepared by incipient wetness impregnation over commercial γ-Al2O3 (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%. The details of the preparation of NWa-155, Sasol Germany GmbH) particles of 0.1

2.2. Oxygen carrier characterization

Several techniques have been used to characterize physically and chemically the fresh and after-used oxygen carrier particles. The metal active content for the CLC process was determined by complete reduction of the sample with hydrogen in TGA at 950 °C.

The oxygen transport capacity, ROC, was calculated assuming that Fe₂O₃ is reduced to FeO-Al₂O₃ and NiO to Ni in the CLC process.

The force needed to fracture a particle was determined using a Shimpo FGN-5X crushing strength apparatus. The mechanical strength was taken as the average value of at least 20 measurements. The real density of the particles was measured with a Micromeritics AccuPyc II 1340 helium pycnometer. The surface area of the oxygen carrier was determined by the Brunauer–Emmett–Teller (BET) method by adsorption/desorption of nitrogen at 77 K in a Micromeritics ASAP-2020 (Micromeritics Instruments Inc.), whereas the pore volume was measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by powder X-ray diffractometer Bruker AXS graphite monochromator. The chemically mixed Fe-Ni oxygen carrier particles were also analysed 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.

2.3. Reactivity tests in TGA

The reactivity of the different oxygen carriers was determined in a TGA, Cl electronics type, described elsewhere [33]. For the experiments, the oxygen carrier was loaded in a platinum basket and heated to the set operating temperature in air atmosphere. After weight stabilization, the experiment was started by exposing the oxygen carrier to alternating reducing and oxidizing conditions. To avoid mixing of combustible gas and air, nitrogen was introduced for 2 min after each reducing and oxidizing period.

The reactivity of the oxygen carrier was determined with different reducing gases: CH₄, CO and H₂ at different temperatures. The gas composition was 15 vol.% of the reducing gas. In the experiments with CH₄, 20 vol.% H₂O was introduced to avoid carbon formation by methane decomposition. Steam was incorporated to the gas stream by bubbling

| Table 1 | Main characteristics of the oxygen carriers. |
|---------|---------------------------------------------|
|         | Fe15-WM | Fe15Ni2-CM | Fe15Ni5-CM | Fe15Ni12-CM | Ni18-WM |
| Fe₂O₃ (wt.%) | 15.2 | 15.5 | 14.9 | 14.2 | – |
| NIO (wt.%) | – | 2 | 5 | 12.3 | 18 |
| Oxygen transport capacity (%) | 1.5 | 2 | 2.5 | 4.1 | 3.9 |
| Crystalline strength (N) | 2.5 | 1.8 | 2.0 | 2.7 | 4.1 |
| Real density (g/cm³) | 3.9 | 3.9 | 3.8 | 4.2 | 4.3 |
| Porosity (%) | 50.5 | 51.8 | 48.4 | 45.6 | 42.5 |
| Specific surface area, BET (m²/g) | 39.1 | 44.2 | 56.3 | 19.9 | 7.0 |

| XRD | Fresh | TGA Oxidation | Reduction | Batch Oxidation | Reduction | CLC facility |
|----|------|---------------|-----------|---------------|-----------|-------------|
| α-Al₂O₃, Fe₂O₃ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| NiAl₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| NiO | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| NiAl₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |
| α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ | NiFe₂O₄ | α-Al₂O₃, Fe₂O₃, NiFe₂O₄ |

| a | Determined by TGA. |
| b | Including Fe and Ni contents. |
| c | Minor amounts. |
through a water containing saturator at the selected temperature to reach the desired water concentration. Similarly, 20 vol.% \( \text{CO}_2 \) was introduced together with CO to avoid carbon formation by the Boudouard reaction. In all cases, nitrogen was used to balance. For oxidation reaction, 100% air was used as reacting gas. The effect of temperature on the reactivity of the OCs was evaluated using the different fuel gases at 830 and 950 °C. The conversion of solids for the reduction reaction was calculated as:

\[
X_i = \frac{m_{\text{ox}} - m}{R_{\text{OC}} m_{\text{ox}}}
\]

being \( m_{\text{ox}} \) the mass of the fully oxidized solids, \( m \) the instantaneous mass of the sample and \( R_{\text{OC}} \) the oxygen transport capacity of solids for the transformation between \( \text{Fe}_2\text{O}_3 \) and \( \text{FeAl}_2\text{O}_4 + \text{NiO}/\text{Ni}, \) given in Table 1.

The conversion for the oxidation reaction was calculated as \( X_o = 1 - X_i \).

### 2.4. Fluidized bed reactor

Several reduction–oxidation multicycles were carried out in a batch fluidized bed reactor to know the gas product distribution during reaction and the fluidization behaviour of the carrier. The experimental set-up has been described elsewhere [31].

The tests were carried out at 950 °C with an inlet superficial gas velocity into the reactor of 10 cm/s. The composition of the gas was 25 vol.% \( \text{CH}_4 \) in \( \text{N}_2 \) during reduction and 10–15 vol.% \( \text{O}_2 \) in \( \text{N}_2 \) during oxidation. The reduction periods were varied between 60 and 300 s. The oxidation periods necessary for complete oxidation varied between 0.1 and 0.3 mm.

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

**Reduction**

\[
X_{\text{red}} = \frac{\int_{t_0}^{t_f} Q_{\text{out}}}{t_f - t_0} \left( 2P_{\text{CO}_2,\text{out}} + P_{\text{CO},\text{out}} + P_{\text{H}_2,\text{O},\text{out}} \right) dt
\]

**Oxidation**

\[
X_{\text{ox}} = \frac{\int_{t_0}^{t_f} 2Q_{\text{out}}}{t_f - t_0} \left( \frac{Q_{\text{in}}}{Q_{\text{out}}} P_{\text{O}_2,\text{in}} - P_{\text{O}_2,\text{out}} - 1/2P_{\text{CO}_2,\text{out}} - P_{\text{CO},\text{out}} \right) dt
\]

\[
Q_{\text{out}} = \frac{Q_{\text{in}} \left( 1 - P_{\text{O}_2,\text{in}} \right)}{1 - P_{\text{CO}_2,\text{out}} - P_{\text{CO},\text{out}} - P_{\text{O}_2,\text{out}}}
\]

where \( X_i \) is the conversion of the oxygen carrier, \( Q_{\text{in}} \) is the molar flow of the gas coming into the reactor, \( Q_{\text{out}} \) is the molar flow of the gas leaving the reactor, \( P_{\text{out}} \) is the total pressure, \( P_{\text{in}} \) is the partial pressure of gas \( i \) entering to the reactor, \( P_{\text{in}} \) is the partial pressure of gas \( i \) exiting the reactor, \( n_0 \) are the moles of oxygen which can be removed from fully oxidized oxygen carrier, and \( t \) is the time. The last terms in Eq. (4) take into account the formation of \( \text{CO} \) and \( \text{CO}_2 \) during the oxidation period due to the oxidation of C coming from the decomposition of \( \text{CH}_4 \) in the reduction period.

The back-mixing in the system, which was illustrated by the transient changes in gas concentration during the first seconds of reaction, was considered in order to obtain the actual concentration of the gases in the bed. The correction was done using a method of deconvolution that takes into account the gas residence time distribution in the system [34].

### 2.5. ICB-CSIC-g1 facility

Fig. 2 shows a schematic diagram of the continuous atmospheric CLC facility used in this work, which was designed and built at Instituto de Carboquimica (ICB-CSIC). The pilot plant was basically composed of two interconnected fluidized-bed reactors—the air and fuel reactors, a riser for solids transport from the air reactor to the fuel reactor, a solid valve to control the solids flow rate fed to the fuel reactor, a loop seal and a cyclone. This design allowed the variation and control of the solid circulation flow rate between both reactors.

In the FR (1) the oxygen carrier particles are reduced by the fuel. Reduced oxygen carrier particles overflowed into the AR (3) through a U-shaped fluidized bed loop seal (2), to avoid gas mixing between fuel and air. The oxidation of the carrier took place at the AR. Secondary air could be introduced at the top of the bubbling bed to help particle entrainment. \( \text{N}_2 \) and unreacted \( \text{O}_2 \) left the AR passing through a high-efficiency cyclone (5) and a filter (9) before the stack. The oxidized solid particles recovered by the cyclone were sent to a solids reservoir setting the oxygen carrier ready to start a new cycle. In addition, these particles avoid the leakage of gas between the FR and the riser. The regenerated oxygen carrier particles returned to the FR by gravity from the solids reservoir through a solids valve (7) which controlled the solids circulation flow-rate entering the FR. A diverting solids valve (6) located below the cyclone allowed the measurement of the solids flow rates at any time. Fine particles produced by fragmentation/attrition in the plant were recovered in the filters that were placed downstream of the FR and AR. The gas outlet streams of the FR and AR were drawn to respective on-line gas analysers to get continuous data of the gas composition. Detailed information about this experimental facility was described elsewhere [31].

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**Fig. 2.** Schematic diagram of the ICB-CSIC-g1 facility.
The gas composition of the PSA-offgas was determined to a steam reforming process coupled with a CLC system (SR-CLC) in order to know the potential of the materials as oxygen carriers for and a simulated PSA-offgas stream. The PSA-offgas was used in the bottom loop seal (37.5 Nl h⁻¹ OC (Fe15-WM)).

The effect of NiO addition on a Fe-based OC was analysed working with both fuels, methane and a simulated PSA-offgas stream. The PSA-offgas was used in order to know the potential of the materials as oxygen carriers for a steam reforming process coupled with a CLC system (SR-CLC) [31,35]. The gas composition of the PSA-offgas was determined to be 12 vol.% of CH₄, 18 vol.% of CO₂, 25 vol.% de H₂ and 45 vol.% of CO₂ taken from the final report of CACHT project (FP VI-019972) [36].

Table 2 shows a summary of the different operating conditions used in the experiments conducted with both fuels. In the test series of experiments carried out with both fuels, the fuel reactor temperature, the fuel flow, the solids circulation rate and the power of the plant varied.

The oxygen carrier-to-fuel ratio (ϕ) was defined by Eq. (6), as:

\[ \phi = \frac{F_{\text{Fe}_2\text{O}_3 \times \text{NiO}}}{F_{\text{Fuel}}} \]  

\( F_{\text{Fe}_2\text{O}_3 \times \text{NiO}} \) being the molar flow rate of the iron and nickel oxide and \( F_{\text{Fuel}} \) is the inlet molar flow rate of the fuel in the FR. Parameter \( b \) is the stoichiometric coefficient of the fuel gas mixture, calculated in Eq. (7) as:

\[ b = \frac{4x_{\text{CH}_4} + x_{\text{CO}} + x_{\text{H}_2}}{x_{\text{CH}_4} + x_{\text{CO}} + x_{\text{H}_2}} \]  

Thus, the oxygen carrier-to-fuel ratio (ϕ) was defined as the ratio between the oxygen supplied and the oxygen needed to stoichiometrically react with the fuel flow. A value of the ϕ ratio equal to unity means that the oxygen supplied by the solids is exactly the stoichiometric oxygen to fully convert the fuel gas to CO₂ and H₂O.

To analyse the effect of the ϕ ratio, the experiments were carried out varying the flow of the fuel, but maintaining roughly constant the solids circulation flow-rate in each set of experiments. To maintain the total flow of gas entering to the fuel reactor, the corresponding flow of nitrogen was added in every case. Under all operating conditions, the ratio of the constituent gases of the PSA off-gas, i.e. CH₄, H₂, CO, CO₂ was maintained constant. When the flow of the fuel was varied, the air to fuel ratio, the solids inventory per MWth (\( m_{\text{FF}} \)) and the gas concentration were varied simultaneously.

To analyse the effect of FR temperature on combustion efficiency the experiments were carried out at two different FR temperatures, 830 and 880 °C.

To evaluate the behaviour of the oxygen carrier during the combustion tests, the combustion efficiency (\( \eta_c \)), defined in Eq. (8), was used as a key parameter. The combustion efficiency (\( \eta_c \)) was defined as the ratio of the oxygen consumed by the gas leaving the FR to that consumed by the gas when the fuel is completely burnt to CO₂ and H₂O. So, the ratio gives an idea about how the CLC operation is close or far from the full combustion of the fuel, i.e. \( \eta_c = 100\% \).

\[ \eta_c = \frac{\left(2x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2}\right)_{\text{out}} - \left(2x_{\text{CO}_2} + x_{\text{CO}}\right)_{\text{in}}}{\left(4x_{\text{CH}_4} + x_{\text{CO}} + x_{\text{H}_2}\right)_{\text{in}}} \times 100. \]  

\( F_{\text{in}} \) being the molar flow of the inlet gas stream, \( F_{\text{out}} \) the molar flow of the outlet gas stream, and \( x_i \) the molar fraction of the gas in the inlet or outlet gas stream.

| Test | Fuel gas (vol.%) | \( T_{\text{FR}} \) | \( F_i \) (kg/h) | \( \phi \) | Power (Wth) |
|------|----------------|------------------|----------------|---------|-------------|
| PSA-1 | 100.0 | 830 | 13.4 | 2.4 | 436 |
| PSA-2 | 72.1 | 830 | 13.4 | 3.3 | 317 |
| PSA-3 | 57.5 | 830 | 13.4 | 4.2 | 249 |
| PSA-4 | 41.1 | 830 | 13.4 | 5.8 | 181 |
| PSA-5 | 100.0 | 880 | 13.4 | 2.4 | 436 |
| PSA-6 | 72.1 | 880 | 13.4 | 3.3 | 317 |
| PSA-7 | 57.5 | 880 | 13.4 | 4.4 | 238 |
| PSA-8 | 41.1 | 880 | 13.4 | 6.2 | 169 |

The total solids inventory in the system was about 1.2 kg of solid material. The temperature in the air reactor was always kept constant at about 950 ± 15 °C. The inlet flow of fuel was 170 Nl h⁻¹, which corresponds to an inlet gas velocity in the fuel reactor of 10 cm s⁻¹. The inlet air flow in the AR was 720 Nl h⁻¹ as primary air, (46 cm s⁻¹ at 900 °C), and 150 Nl h⁻¹ as secondary air. Nitrogen was used to fluidize the bottom loop seal (37.5 Nl h⁻¹).
3. Results and discussion

The behaviour of several chemically mixed Fe–Ni oxygen carriers was analysed in this work together with a physically mixed Fe–Ni OC, using a Fe-based and a Ni-based OC.

Table 1 shows the physical and chemical characteristics of the fresh OCs. As it can be seen, the NiO content affects the properties of the materials. The higher the NiO content, the higher the density and mechanical strength of the oxygen carriers prepared by impregnation and the lower the porosity and the superficial area.

XRD patterns of the fresh oxygen carriers showed the phase transformation of the alumina support during the calcination step and the formation of nickel aluminium spinel (NiAl2O4) and nickel ferrite (NiFe2O4) compounds for the nickel oxide. Moreover, in Fig. 3 SEM images of the fresh chemically mixed Fe–Ni OC particles are shown. The oxygen carrier particles exhibited an irregular shape, since impregnation of porous alumina particles has been carried out. The iron and nickel distributions inside the particles were also analysed by EDX in some particles embedded in resin epoxy, cut, and polished. A uniform distribution of iron and nickel through the particles was found.

3.1. Reactivity in TGA

The different samples of chemically mixed OCs were first characterized by TGA, in order to know their reactivity with different fuel gases (CH4, H2 and CO), since methane and PSA-offgas (a mixture of H2 + CO + CH4) were used as fuel in the continuous unit. The influence of the temperature was also studied.

For Fe-based oxygen carriers, different reduction reactions are possible depending on the reducing gas composition and temperature. For the data presented here, it was assumed that the weight variations observed in the TGA were mainly associated with the transformation Fe2O3/FeO·Al2O3. This assumption was confirmed by the results obtained by the XRD patterns, as it can be seen in Table 1, which shows that the final reduced form in the experiments carried out using CH4 was the form FeO·Al2O3.

Fig. 3 shows the reduction and oxidation reactivities at 950 °C using CH4 as reduction gas and air for oxidation for the chemically mixed OCs, together with the Fe15-WM and the Ni18-WM OCs for comparison purposes. As it can be seen, the effect of Ni addition on the bimetallic OC is negative, as higher amount of Ni in the mixed OC implies lower reactivity of the OC. These results can be explained by the formation of a Fe–Ni spinel compound in the bimetallic OCs with lower methane reactivity than the corresponding to Fe2O3 and NiO [37], as it could be seen in Table 1. XRD patterns show the formation of NiFe2O4 in the oxidation state and FeNi3 in the reduced state in all the bimetallic OCs. This fact may lead to a solid conversion higher than 1, since it was assumed that the total iron content is reduced only to FeO·Al2O3 using CH4 as fuel gas.

The Fe15-WM and the Ni18-WM OCs had been previously confirmed as high oxygen carriers for fuel gases (CH4, H2 and CO) [31,32], as it can be seen in Fig. 4.

In spite of the formation of Fe–Ni compounds, the oxidation reactivities for all the bimetallic OC were high and very similar to the Fe15-WM OC, as it can be seen in Fig. 4.

The effect of the fuel gas was analysed for the bimetallic OCs using H2 and CO in the TGA. Fig. 5 shows the reduction and oxidation conversions versus time curves obtained using H2 as reacting gas, and air for the oxidation at 950 °C and for the Fe15-WM. As it can be seen, very high reactivities were obtained with all carriers. It must be pointed out that using H2 different reduction states can be reached depending on the ratios H2O/H2 used [38]. In the TGA conditions used

Fig. 3. SEM–EDX images of the chemically mixed Fe–Ni oxygen carrier particles; a) Fe15Ni2-CM; b) Fe15Ni5-CM; c) Fe15Ni12-CM.

Fig. 4. Effect of NiO addition on the reactivity of the different oxygen carriers at 950 °C. Reduction: 15%CH4 + 20% H2O. Oxidation: air.
in this work, reduction up to Fe⁰ could be reached. Comparing with the values obtained with CH₄ as reacting gas, it can be seen that higher reactivity was obtained working with H₂ with all carriers.

Fig. 6 shows the reactivity curves for the mixed OCs and for the Fe₁₅-WM, using CO as reacting gas at 950 °C. Similar results to CH₄ were obtained for the effect of Ni content on the reactivity: higher NiO content implies lower reactivity of the mixed OC. Comparing Figs. 4, 5 and 6, it can be seen that the highest reactivities were obtained with H₂ as reacting gas, followed by CH₄. The lowest reactivities were observed working with CO as reacting gas. These results agree with the ones obtained by Abad et al. [38] and Dueso et al. [39], who found the highest reactivities working with H₂ and the lowest with CO using Ni-based oxygen carriers. In all cases, lower reactivities were achieved with those OCs with higher Ni contents.

The effect of temperature on the reactivity of the OCs was evaluated using the different fuel gases at 830 and 950 °C. Fig. 7 shows the reactivities obtained with CH₄ as reacting gas at the low temperature for all the bimetallic OCs. As it can be seen comparing Figs. 4, 5 and 6, it can be seen that the highest reactivities were obtained with Fe₁₅Ni₂-CM, Fe₁₅Ni₅-CM, and Fe₁₅Ni₁₂-CM. The results obtained were compared with the one achieved working with the Fe-based OC without mixed, Fe₁₅-WM, at similar conditions.

3.2. Oxygen carrier behaviour in batch fluidized bed

Several reduction–oxidation multicycles were done with the chemically mixed oxygen carriers in the batch fluidized bed reactor, using CH₄ as reducing gas, to determine the gas product distribution and to analyse the fluidization behaviour of the oxygen carriers with respect to agglomeration phenomena. The carriers tested were the Fe₁₅Ni₂-CM, Fe₁₅Ni₅-CM, and Fe₁₅Ni₁₂-CM. The results obtained were compared with the one achieved working with the Fe-based OC without mixed, Fe₁₅-WM, at similar conditions.

Fig. 8 shows the outlet product gas distribution for a typical reduction period of 2 min working with the chemically mixed OCs and with the Fe₁₅-WM at 950 °C using CH₄ as fuel in the batch fluidized bed reactor. It was found, in all cases, a first period of full conversion of CH₄, where CO₂ and H₂O were formed just immediately after the introduction of the reducing gas to the reactor. After this first period, CO₂ and H₂O concentrations begin to decrease as a result of the decrease of the oxygen transference rate. Because of this, the CH₄, CO and H₂ concentrations start to increase because to the oxygen carrier is unavailable to convert fully CH₄ into CO₂ and H₂O, and the partial oxidation of methane takes place. In this period, it can be observed that as NiO content in the bimetallic OC increases, the CH₄ concentration at the outlet of the reactor decreases, due to the capacity of the Ni active sites to catalyze the reforming reaction of methane. Thus, the selectivity of methane reaction to CO₂ + H₂O increased as Ni content increases in the oxygen carrier increases. Small amounts of nickel oxide (<5 wt.%) in the OC are sufficient to fully convert all the methane inlet flow. Similar results were found during the whole batch experiments indicating that the OC maintains its reactivity during cycling operation.

The multi-cycle tests carried out in the batch fluidized bed reactor were useful to determine the fluidization behaviour of the oxygen carrier with respect to the agglomeration phenomena. Although a high degree of conversion was reached in the cycling tests, neither of the bimetallic OCs show any agglomeration behaviour during operation. These results agreed with previous works carried out in continuous operation using the unmixed OC Fe₁₅-WM, and other Fe-based materials [7,31,42] where the absence of agglomeration in the use of Fe-based materials for the CLC process was established.

Once the reactivity and selectivity to CH₄ combustion of the different bimetallic OCs have been determined in the TGA and in the batch fluidized bed a few conclusions can be drawn. By one hand, the higher Ni content in the chemically mixed FeNi OCs, the lower CH₄, and CO reactivity. On the other hand, the selectivity to full conversion of methane increases as Ni content increases due to the catalytic effect of the reduced nickel. According to this, the chemically mixed FeNi OC, Fe₁₅Ni₁₂-CM, was selected to evaluate its behaviour
in the continuous unit, since it has shown a high reactivity with hydrogen, methane, and CO, at 950 °C and full conversion of CH₄ was reached in the fluidized bed facility during reduction periods.

3.3. Test in ICB-CSIC-g1 facility

The effect of Ni addition on the combustion efficiency was analysed in the 500 Wth CLC continuous unit using the unmixed Fe-OC, the chemically mixed Fe–Ni OC and the physically mixed Fe–Ni OC. A first set of experiments were conducted working with a chemically mixed OC, with the iron and nickel particles impregnated over the same alumina particle. A second set of experiments were performed working with a physical mixture of two impregnated Fe- and Ni-based OCs. Moreover, these results were compared with those obtained in the same facility using an unmixed Fe-based OC, Fe15-WM, described in detail in a previous work [31].

As it was commented above, the Fe15Ni2-CM OC was selected for the continuous CLC facility experiments. A total of about 38 h at hot conditions, of which 32 corresponded to combustion conditions were conducted in the facility with the bimetallic oxygen carrier. Experiments were performed with CH₄ and a simulated PSA-offgas as gas fuels for comparison purposes. The effect of the oxygen carrier-to-fuel ratio and the fuel reactor temperature on the combustion efficiency, ϕ, was analysed.

The gas product concentrations of the fuel and air reactors were measured by on line analysers. These gas concentrations were used to make carbon, hydrogen and oxygen mass balances over the whole reactor system. For better comparison, the results are presented in N₂ free dry basis. CO and CO₂ concentrations at the outlet of the AR were never detected in any test. Thus, no losses in CO₂ capture were produced by carbon transfer to the AR, reaching 100% CO₂ capture in the process.

Fig. 9a) shows the effect of ϕ on the combustion efficiency using the Fe15Ni2-CM as oxygen carrier, working with CH₄ as fuel at 830 °C and at 880 °C. As it can be observed full combustion of the fuel was reached at ϕ values higher than 4 working at 830 °C. An important effect of the temperature can be seen also, especially at low ϕ values.

Fig. 10a) shows the gas product distribution measured at the outlet of the FR in these tests. High CH₄ and low CO and H₂ concentrations were measured at low ϕ values for both temperatures, 830 and 880 °C, when CH₄ was used as fuel, indicating a negligible catalytic effect of Ni present in the Fe15Ni2-CM OC. An increase in the oxygen carrier to fuel ratio produced an increase in the conversion of methane as more oxygen is available for combustion of the fuel.

3.3.1. Effect of the fuel composition

A simulated PSA-offgas stream (a mixture of CH₄, CO, and H₂) was also used as fuel in the CLC continuous unit in order to prove the feasibility of the Fe15Ni2-CM oxygen carrier for a SR-CLC process. Fig. 9b) shows the effect of ϕ on the combustion efficiency using the Fe15Ni2-CM as oxygen carrier, working with PSA-offgas as fuel at 830 °C and at 880 °C. Full combustion of the fuel working at 880 °C can be reached at ϕ values higher than 4. An important effect of the fuel reactor temperature on the combustion efficiency was found, as CO is present in the PSA-offgas and this OC had a slow reactivity as gas fuels for comparison purposes. The effect of the oxygen carrier-to-fuel ratio and the fuel reactor temperature on the combustion efficiency, ϕ, was analysed.

The gas product distribution measured at the outlet of the FR in these tests. High CH₄ and low CO and H₂ concentrations were measured at low ϕ values for both temperatures, 830 and 880 °C, when CH₄ was used as fuel, indicating a negligible catalytic effect of Ni present in the Fe15Ni2-CM OC. An increase in the oxygen carrier to fuel ratio produced an increase in the conversion of methane as more oxygen is available for combustion of the fuel.

3.3.2. Effect of Ni addition on a Fe-based OC

In order to analyse the effect of Ni addition on the behaviour of Fe-based OC, a second set of experiments were performed working with a physical mixture of two impregnated Fe- and Ni-based OCs, Fe15Ni2-PM. The results were compared with those obtained in the first set of experiments, the chemically mixed Fe15Ni2-CM OC, and also with previous obtained with unmixed Fe-based OC, Fe15-WM [31]. It was added the necessary amount of Ni18-WM to obtain a
mixed OC with a similar percentage of Ni than the chemically mixed OC. A total of about 56 h at hot conditions, of which 50 corresponded to combustion conditions were carried out in the facility using the Fe15Ni2-PM oxygen carrier.

Fig. 11(a) and (b) shows a comparison of the combustion efficiency as a function of the $\phi$ value using the three different OCs, i.e. Fe15Ni2-PM, Fe15Ni2-CM and Fe15WM, using CH$_4$ as fuel at 830 and 880 °C, respectively. As it could be seen no substantial improvement of the combustion efficiency was reached working with the chemically mixed bimetallic oxygen carrier, Fe15Ni2-CM, in respect to the results obtained with the Fe-based oxygen carrier without mixing, Fe15-WM. It can be seen that higher combustion efficiencies were obtained working at 830 °C with the Fe15Ni2-PM in respect to the ones obtained with the Fe15-WM. Small differences between the combustion efficiencies values were observed at 880 °C. Fig. 12 shows the effect of the oxygen carrier to fuel ratio on gas product concentration at the exit of the FR, using CH$_4$ as fuel, at 830 °C, working with Fe15Ni2-PM. As it can be observed lower values of CH$_4$ and higher H$_2$ and CO concentrations were detected at the outlet of FR with the physically mixed material in respect to the ones obtained with the Fe15Ni2-CM, confirming the effect of NiO on the methane reforming when Ni is not bounded in the same particle.
3.3.2.1. Effect of the fuel composition. Fig. 13 shows a comparison of the combustion efficiency as a function of $\phi$ using the three different materials (Fe15-WM, Fe15Ni2-CM and Fe15Ni2-PM) as oxygen carrier, working with PSA-offgas as fuel, at 830 °C and at 880 °C, respectively. Comparing with the results obtained using CH$_4$ as fuel it can be seen that higher combustion efficiency can be obtained working with CH$_4$ as fuel, due to the catalytic effect of Ni and the low reactivity of Ni with CO. It can be observed the similar combustion efficiencies for the physically mixed carrier and the Fe-based OC without mixed. Full combustion of the fuel was reached with these OCs at $\phi$ values of 2.5 at 880 °C. It can be also observed that the lowest values of the combustion efficiency were achieved working with the bimetallic oxygen carrier Fe15Ni2-CM at both temperatures.

3.4. Discussion

According to the results obtained with the Fe15Ni2-CM using CH$_4$ or PSA-offgas as fuels, it could be said that worse results were obtained at both temperatures with the chemically mixed OC. Therefore, no improvement of the combustion efficiency was detected working with the chemically mixed OC in respect to the results obtained with a Fe-based OC without mixed. The formation of mixed compounds like the awaruite (FeNi$_3$) or the trevorite (NiFe$_2$O$_4$) which could hinder the catalytic effect of Ni could be the cause of the poor results achieved with the Fe15Ni2-CM OC, as it could be seen in experiments conducted in TGA, where it was determined that the higher Ni content in the oxygen carrier the lower the reactivity of the carrier.

According to the results obtained with the physically mixed OC a positive effect was only measured when methane was used as fuel at low temperatures due to a Ni catalytic effect. Similar combustion efficiencies were found to respect with the results obtained with the Fe-based OC without mixed working with PSA-offgas.

The use of a specific OC has important implications for a CLC system. The reactivity of the solids determines the solids inventory in the system and the operating conditions needed. Table 3 shows the required values of $\phi$ and solid inventories in the FR, $m_{FR}^*$, to reach full combustion of the fuel, working with the different bimetallic OCs tested in the continuous 500 W$_{in}$ unit at 830 and 880 °C, using CH$_4$ and PSA-offgas as fuels.

As it can be observed, using CH$_4$ as fuel, the highest solid inventory needed was obtained for the chemically mixed OC. A very low solid inventory (600 kg/MW) is required with the physically mixed OC at 880 °C.

Using PSA-offgas as fuel, higher solid inventories are needed with the chemically mixed OC, due to the formation of Ni based compounds, NiFe$_2$O$_4$ and NiAl$_2$O$_4$, with a slower reactivity.

The considerable improvement of the combustion efficiency achieved working with the physically mixed OC at low temperature, and the limited improvement obtained working with the chemically mixed OC at any temperature, can be explained by the fact that in the physical mixture of Fe–OC and Ni–OC, the Ni–OC particles not only act as a catalyst but also as an oxygen carrier, providing bulk oxygen for the reactions with methane. The highest amount of oxygen transported, the lowest solid inventory is required to reach full combustion of the fuel.

4. Conclusions

The effect of Ni addition over a Fe-based OC has been evaluated and compared using two different strategies: the chemical and the
physical mixtures. Thus, different bimetallic OCs have been prepared with the iron and nickel oxides impregnated over the same alumina support particle. Moreover, a physically mixed OC, using a Fe-based and a Ni-based OCs, was also evaluated in the combustion of fuel gases. The effect of this Ni addition on the combustion efficiency was analysed in a 500 kWθ CLC continuous unit using methane and a PSA-offgas as fuel gases at different operating conditions.

It was found that the use of a chemically mixed Fe–Ni OC had a negative effect on the combustion efficiency compared to the results obtained with an unmixed Fe-based OC since the formation of Fe–Ni compounds reduced the catalytic effect of Ni addition. However, the addition of 2 wt.% of NiO by a physical mixture of an impregnated OC can improve significantly the combustion efficiency of methane at low temperatures.

A considerable reduction of the solid inventories needed to reach full CH₄ or PSA-offgas combustion was measured working with the Fe15Ni2-PM OC. In conclusion, in order to improve the behaviour of a Fe-based OC via NiO addition is preferable to mix physically a Ni-based OC and a Fe-based OC, with each metal supported on different particles, instead of the chemical addition by impregnation of NiO on Fe-based OC particles, supporting both metals on the same particle.

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