



NiO/Al₂O₃ oxygen carriers for chemical-looping combustion prepared by impregnation and deposition–precipitation methods

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ABSTRACT

Ni-based oxygen carriers (OC) with different NiO content were prepared by incipient wet impregnation, at ambient (AI), and hot conditions (HI) and by deposition–precipitation (DP) methods using γ -Al₂O₃ and α -Al₂O₃ as supports. The OC were characterized by BET, Hg porosimetry, mechanical strength, TPR, XRD and SEM/EDX techniques. Reactivity of the OC was measured in a thermogravimetric analyzer and methane combustion selectivity towards CO₂ and H₂O, attrition rate, and agglomeration behavior were analyzed in a batch fluidized bed reactor during multicycle reduction–oxidation tests.

XRD and TPR analysis showed the presence of both free NiO and NiAl₂O₄ phases in most of the OC. The interaction of the NiO with the alumina during OC preparation formed NiAl₂O₄ that affected negatively to the OC reactivity and methane combustion selectivity towards CO₂ and H₂O during the reduction reaction. The NiO–alumina interaction was more affected by the support type than by the preparation method used. The NiO–alumina interaction was stronger in the OC prepared on γ -Al₂O₃.

The OC were evaluated in the fluidized bed reactor with respect to the agglomeration process. OC prepared by the AI and HI methods with NiO contents up to 25 wt%, OC prepared by the DP method on γ -Al₂O₃ with NiO content lower than 30 wt%, and OC prepared by the DP method on α -Al₂O₃ with a NiO content lower than 26 wt% did not agglomerate. OC that agglomerated showed an external layer of NiO over the particles. It seems that the most important factor affecting to the formation of the external NiO layer on the OC, and so to the agglomeration process, was the metal content of the OC. The attrition rates of the OC prepared using γ -Al₂O₃ as support were higher than the ones prepared using α -Al₂O₃ as support, and in general the attrition rates of all the OC were low.

The OC prepared by AI, HI or DP methods on α -Al₂O₃ as support had appropriated characteristics to be used in the chemical-looping combustion process.

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1. Introduction

It is today generally accepted that reducing CO₂ emissions from anthropogenic sources is an urgent need for avoiding the negative effects of CO₂ on the atmosphere (greenhouse effect). One of the possibilities to achieve this goal is carbon capture and sequestration, that is, CO₂ is recovered from flue gas streams and stored. For these processes to be performed in an economically feasible way, a concentrated CO₂ stream is required. One of the approaches is the one called “chemical-looping combustion” (CLC) that combines power production with CO₂ capture in a single process. The CLC concept could be extended to the gasification of a solid fuel and to CO₂ free hydrogen production. The main advantage of CLC over conventional technologies is that direct contact between air and fuel is avoided. Therefore, CO₂ is obtained without nitrogen

dilution, avoiding costly equipment and energy consumption for separation of gases. In CLC, fuel and oxygen are contacted via an intermediate oxygen carrier (OC), a metal/metal oxide that can alternately be oxidized and reduced. A basic CLC system has two reactors, one for air and one for fuel. The OC circulates between the reactors [1].

A number of materials have been identified as suitable OC in a CLC system: metal oxides based on iron, nickel, manganese, copper or cobalt, supported on alumina, zirconia, silica, titania, or bentonite [2–13]. An OC must withstand a high number of redox cycles, both chemical and physically, in order to be used in a CLC process. In addition, other characteristics such as high oxygen transport capacity, complete fuel conversion to CO₂ and H₂O, negligible carbon deposition, good properties for fluidization (no presence of agglomeration) and easy preparation to reduce costs are also important.

To achieve low OC production costs there is a great interest in the use of commercial techniques for catalyst preparation. In the Grangemouth Capture Project (GRACE) [14], three different

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methods of preparation of OC were used: freeze-granulation, mechanical mixing followed by extrusion, and impregnation. It was found that most of the OC prepared by mechanical mixing had an unacceptable reactivity and/or mechanical properties [6]. On the contrary, OC prepared by impregnation or freeze-granulation were successfully tested in two different 10kW_{th} prototypes [15,16]. Other preparation methods have been investigated by different authors [5,17–19].

The system NiO/Al₂O₃ has been proved to be suitable for preparation of OC [5,11,18–28]. However, very few works consider the effect of the preparation method on the redox properties of the carrier. It is well known that the preparation method and the nature of the support influence the stability and activity of the nickel catalysts [29]. The metallic dispersion and the metal–support interaction are the most important characteristics of a nickel catalyst. Similar results were found for nickel-based OC. Mattison et al. [20] found that the Ni spinel (NiAl₂O₄) was present when using high calcination temperatures ($T > 800$ °C) due to the solid–solid reaction of NiO with Al₂O₃. This aluminate can react with methane in the reduction reaction of the OC, but the thermodynamic of this reaction shows a low methane conversion to CO₂ + H₂O at temperatures typical for the CLC process (gas conversion $\leq 95\%$, $T > 900$ °C). However, the conversion of methane for free NiO is always higher than 98% at these temperatures. In a previous work [30] the effect of the support on the reactivity and selectivity during methane combustion of impregnated NiO–Al₂O₃ OC was examined, using thermal and chemical modifications of the support. The OC prepared by incipient wet impregnation on γ -Al₂O₃ had low reduction reactivity and low selectivity to CO₂ and H₂O due to the strong interaction between the NiO and the alumina to form the NiAl₂O₄ compound. The OC prepared using α -Al₂O₃ had much better performance for the combustion of methane due to the weak interaction of the NiO with this thermally modified alumina. Therefore, it seems that an adequate Ni–Al OC for the CLC process should have the biggest fraction of the Ni introduced as free NiO phase instead of as the spinel form.

In view of these results, it was considered of interest to analyze in a detailed way the influence of the impregnation method on the behavior of the OC. The present work investigated the impact of using different simple catalyst impregnation methods (incipient wet impregnation and deposition–precipitation) on the performance of NiO–Al₂O₃ OC in the chemical-looping combustion of methane.

1.1. Impregnation of supports

In conventional impregnation technique, deposition of the species containing the element to be deposited takes place by precipitation during drying. The drying step is critical since the impregnation solution migrates and the metal is deposited mainly where the solvent evaporates. The main drawback of the impregnation method is the limited amount of NiO that can be introduced into the support in each stage. To optimize the impregnation and to reduce the number of preparation stages, the hot impregnation method with the solution and the support at higher temperatures can be used.

Other technique proposed in the literature to increase the NiO dispersion with low interaction with the support and to prepare materials with high NiO content is the slow precipitation [31,32]. Using this technique in the deposition–precipitation method, the immobilization of the metal in the pores with a non-soluble compound before the drying step is performed. Especially with nickel the procedure is fairly straightforward. The support is loaded in a suspended solution of metal nitrate and a compound (urea, NaOH or Na₂CO₃) that is able to consume hydrogen ions is added. Usually the amount of urea is chosen to be 1.5–2.5 times the amount the-

oretically needed. The urea reaction to produce hydroxyl groups exhibits a measurable rate only at temperatures above 60 °C. The decomposition reaction is usually performed at 90 °C during 3–24 h. The amount of nickel precipitated depends on above experimental parameters. The hydrotalcite-like compounds formed in the support give a stable, homogeneous and highly dispersed metal oxides after the thermal treatment [31]. For catalysts, the Ni/NiO particle size seems to be an important factor for its activity. Smaller particle sizes provide a larger surface for reaction and hence improved catalysts reactivity. The essential difference between the deposition–precipitation method and conventional impregnation method is that for the former Ni is deposited as hydroxide in a hydrotalcite-like structure.

Two different supports (γ - and α -Al₂O₃) were used to prepare OC with the different preparation methods. The OC prepared were characterized by BET, Hg porosimetry, mechanical strength, TPR, XRD, and SEM/EDX techniques. The behavior of the different OC with respect to reactivity, selectivity, agglomeration, and attrition during multi-cycle reduction–oxidation tests of methane combustion was analyzed in a thermogravimetric analyzer (TGA) and in a batch fluidized bed facility.

2. Experimental

2.1. Preparation of OC

Two methods of synthesis, namely, deposition–precipitation (DP) and incipient wet impregnation (I) were used to prepare NiO–Al₂O₃ OC. The supported OC were prepared using Ni nitrate as metal precursor (Ni(NO₃)₂ · 6H₂O >99.5% Panreac). The materials for the support were commercial γ -Al₂O₃ (Puralox NWA-155, Sasol Germany GmbH) particles of +100–300 μ m, with a density of 1.3 g/cm³ and a porosity of 55.4%, and α -Al₂O₃ particles of +100–300 μ m, obtained by calcination of the γ -Al₂O₃ particles at 1150 °C during 2 h, with a density of 2 g/cm³ and a porosity of 47.3%.

2.1.1. Incipient wet impregnation

Two Ni-based OC were prepared by this method at ambient temperature as described in a previous work [30] using the γ -Al₂O₃ and α -Al₂O₃ as supports. The OC were prepared by addition of a volume of a saturated solution (20 °C, 4.2 M) of Ni nitrate corresponding to the total pore volume of the support particles. The aqueous solution was slowly added to the support particles, with thorough stirring at room temperature. The desired active phase loading was achieved by applying successive impregnations followed by calcination at 550 °C, in air atmosphere for 30 min, to decompose the impregnated metal nitrates into insoluble metal oxide. Finally, the carriers were sintered for 1 h at 950 °C. One OC impregnated on γ -Al₂O₃ with a NiO weight content of 21% and one OC impregnated on α -Al₂O₃ with a NiO weight content of 11% were prepared.

The main drawback of the impregnation method is the limited amount of NiO that can be introduced into the support in each stage. To reduce the number of impregnation stages, the impregnation method at hot conditions was also used.

2.1.2. Hot incipient wet impregnation

A modification of the incipient wet impregnation method was carried out by using a hot nickel nitrate solution in order to increase the solubility of the nickel nitrate. Different OC were prepared by impregnation of α -Al₂O₃ support heated at 80 °C in a planetary mixer using a saturated nickel nitrate solution at 60–80 °C (6 M). In this condition the amount of nickel deposited, in one step, over the porous support was increased compared with the impregnation method at ambient temperature (see Table 1).

Table 1
NiO content of the OC prepared on α -Al₂O₃ with different number of impregnations.

Number of incipient wet impregnations	%NiO	
	T = 20 °C	T = 70 °C
1	6	10
2	11	18
3	18	25

In the same way, the desired active phase loading was achieved by applying successive impregnations followed by calcination at 550 °C, in air atmosphere for 30 min. Finally, the carriers were sintered in a furnace for 1 h at 950 °C. Carriers with different NiO:Al₂O₃ weight ratios ranging from 10% to 25% were prepared from one to three successive impregnations.

2.1.3. Deposition–precipitation

Ni-based OC were prepared by the deposition–precipitation method by changing the pH level of a nitrate solution (following conditions of Zhao et al. [32]). Urea (Panreac) was used to induce precipitation. Predetermined concentrations of aqueous solution of nickel nitrate, depending on the desired nickel loading, was introduced into a container with a specific amount of γ -Al₂O₃ or α -Al₂O₃ suspended in a fixed amount of urea solution (urea/Ni molar ratio of 1.9). The resulting slurry was maintained with vigorous mixing at 90 °C through the aging period of 20 h. The precipitate was filtered, washed thoroughly with distilled water, and further dried at 100 °C overnight before calcinations. The calcinations were performed at 950 °C in a muffle furnace in flowing air and held for 1 h. The final metal content deposited in the sample was determined in an inductive coupled plasma ICP Jobin Yvon 2000 analyzer. It was found that around 75% of the Ni ions precipitated on the support. The theoretical maximum content of NiO in the pore volume of the γ -Al₂O₃ support was calculated to be 58 wt%. OC with different NiO:Al₂O₃ weight ratios ranging from 28% to 40% were prepared with this support. An OC with 26% of NiO was prepared using the α -Al₂O₃ as support.

Table 2 shows all the OC prepared with the two supports and the different methods. The samples were designated with the chemical symbols referred to the active metal oxide followed by the weight fraction content, and the inert used as support. The carriers prepared by deposition–precipitation method are referred as “DP” and the ones prepared by the incipient wet impregnation at ambient conditions as “AI” or as “HI” for hot impregnation. As an example, “Ni28- γ Al DP” indicates an OC with a NiO content of 28 wt%, prepared by deposition–precipitation over γ -Al₂O₃.

Table 2
Physical properties and solid crystalline phases of the fresh OC.

Sample	Method (number imp)	Apparent density (g/cm ³)	BET surface area (m ² /g)	Porosity (%)	Mechanical strength (N)	XRD phases
Ni21- γ Al AI	Ambient incipient wet impregnation (2)	1.7	83.4	50.7	2.6	γ -Al ₂ O ₃ , NiAl ₂ O ₄
Ni11- α Al AI	Ambient incipient wet impregnation (2)	2.3	8.2	42.9	5.2	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni10- α Al HI	Hot incipient wet impregnation (1)	2.3			4.5	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni18- α Al HI	Hot incipient wet impregnation (2)	2.5	7	42.5	4.1	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni25- α Al HI	Hot incipient wet impregnation (3)	2.8	5	38.5	4.8	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni28- γ Al DP	Deposition–precipitation	1.8	77.5	46.5	2.3	γ -Al ₂ O ₃ NiO, NiAl ₂ O ₄
Ni33- γ Al DP	Deposition–precipitation	2.1			2.3	γ -Al ₂ O ₃ NiO, NiAl ₂ O ₄
Ni40- γ Al DP	Deposition–precipitation	2.2			2.5	γ -Al ₂ O ₃ NiO, NiAl ₂ O ₄
Ni26- α Al DP	Deposition–precipitation	2.6	8	41.5	5.1	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄

BET area of supports: 150 m²/g for γ -Al₂O₃, 15 m²/g for α -Al₂O₃.

2.2. Characterization

Several techniques were used to characterize the fresh OC particles. The bulk density of the OC particles was calculated weighting a known volume of solid and assuming that the void was 0.45 corresponding to loosely packed bed. The mechanical strength was measured as the force needed to fracture a particle, using a Shimpo FGN-5X crushing strength apparatus. The mechanical strength was taken as the average value of at least 20 measurements.

The surface area of the OC was determined by the BET method by adsorption/desorption of nitrogen at 77 K in a Micromeritics ASAP-2020 (Micromeritics Instruments Inc.), whereas the pore volumes were measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of the crystalline phases of the OC were carried out using powder X-ray diffraction (XRD) analysis in an X-ray diffractometer Bruker AXS D8ADVANCE using Ni-filtered Cu K α radiation equipped with a graphite monochromator. Changes in morphology were determined in a scanning electron microscope (SEM) Hitachi S-3400 N. The nickel distribution in a cross section of a particle embedded in resin epoxy was determined by energy-dispersive X-ray (EDX) analysis in an EDX Rontec XFlash of Si (Li) detector.

Temperature-programmed reduction (TPR) studies were performed in an AutoChem II Micromeritics equipment, using 300 mg of the fresh OC. Each sample was heated in a 10% H₂/Ar flow (50 cm³/min) from 110 °C to 950 °C at 10 °C/min. TPR analysis was used to provide information on the reducibility of the carrier.

Table 2 shows the physical properties and the crystalline phases of fresh OC.

2.3. Reactivity tests

Reactivity tests of the OC were carried out in TGA, CI Electronics type. Detailed information about the instrument and operating procedure used can be found elsewhere [6]. For the reactivity experiments the sample was exposed to alternating reducing and oxidizing conditions. The composition of the reducing gas was: 15 vol.% CH₄, and 20 vol.% H₂O (N₂ balance). The gas used for oxidation was 100 vol.% air. To avoid mixing of combustible gas and air, nitrogen was introduced for 2 min after each reducing and oxidizing period. The experiments were carried out at 950 °C. Five cycles of reduction and oxidation were carried out to determine the reactivity of the carriers. Reactivity data were obtained in TGA tests from the weight variations during the reduction and oxidation cycles as a function of time. To convert weight data into OC conversions the involved chemical reactions were considered. The OC reactivity corresponding to the cycle 5 was used for comparison purposes.

2.4. Batch fluidized bed tests

Besides a high reactivity, another important requirement of an OC would be a high selectivity towards CO_2 and H_2O during methane combustion. In addition, good fluidization properties, which include low attrition rate and no agglomeration problems, are needed. To analyze the gas product distribution and the attrition rate existing in a fluidized bed, as well as the possible agglomeration of the solids, successive reduction–oxidation cycles in a batch fluidized bed (FB) facility were carried out.

The experimental set-up for testing the OC consisted of a system for gas feeding, a FB reactor, a two ways system to recover the solids elutriated from the FB, and a gas analysis system [33]. The FB reactor, 54 mm D.I. and 500 mm height, is electrically heated by a furnace. The reactor had two connected pressure taps in order to measure the differential pressure drop in the bed. Agglomeration problems could be detected by a sharp decrease in the bed pressure drop during operation, causing defluidization of the bed. Two hot filters located downstream from the FB recovered the solids elutriated from the bed during the successive reduction–oxidation cycles, which allowed obtaining elutriation data at different times or number of cycles. Different gas analyzers continuously measured the gas composition at each time. The CO , CO_2 and CH_4 were determined in an infrared analyzer (in dry basis, after water condensation), the O_2 in a paramagnetic analyzer, and the H_2 by gas conductivity. An FTIR analyzer, Temet CX4000, measured the H_2O concentration. For better data analysis, the gas concentrations profiles were corrected for gas flow dispersion through the sampling line and analyzers. The correction was done using a method of deconvolution, taking into account the distribution of the residence time of the gas in the system [34].

The experiments were carried out at 950°C , with an inlet superficial gas velocity into the reactor of 0.1 m/s, and using ~ 300 g of OC. The composition of the gas was 25 vol.% CH_4 in N_2 during reduction and 10–15 vol.% O_2 in N_2 during oxidation. The reduction periods were varied between 120 and 300 s. The oxidation periods necessary for complete oxidation varied between 450 and 1500 s. To avoid mixing of CH_4 and O_2 , nitrogen was introduced for 2 min after each reducing and oxidizing period. The OC were exposed to a total number of 100 reduction/oxidation cycles when it was possible.

3. Results and discussion

3.1. OC characterization

Table 2 shows the apparent density, BET surface area, porosity, mechanical strength, and crystallite phases in the fresh OC. OC prepared using $\gamma\text{-Al}_2\text{O}_3$ as support had higher BET surface area and porosity and lower density and mechanical strength than the OC prepared using $\alpha\text{-Al}_2\text{O}_3$, independently of the method used for preparation. The specific surface areas and porosities of the OC were lower than the corresponding to the alumina support. The differences between the OC were mainly due to the differences between the supports. $\alpha\text{-Al}_2\text{O}_3$ support was obtained by calcinations of $\gamma\text{-Al}_2\text{O}_3$ at high temperature (1150°C during 2 h). During this process the BET surface area and porosity of the original support decreased and the density and mechanical strength increased by sintering. In any case, all the OC prepared in this work were hard, having crushing strengths between 2.3 and 5.2 N. Although, a straight correlation between crushing strength and attrition rate has not been found, a high crushing strength of the particles is needed in a continuous chemical looping process to prevent fragmentation and attrition of the particles.

XRD patterns obtained showed the formation of aluminum spinel compounds in all of the OC. The presence of a spinel phase was

expected due to the high calcination temperature of the OC (950°C) [35]. The results showed that the proportion of nickel surface compound to free nickel oxide depends on the support and the preparation method used.

By one hand, the sample prepared by AI on $\gamma\text{-Al}_2\text{O}_3$ had all the impregnated NiO reacted to NiAl_2O_4 . By the other hand, all samples prepared with $\alpha\text{-Al}_2\text{O}_3$ had free NiO (see Table 2), independently of the method used for preparation, since the interaction between the metal oxide and the support was reduced using the $\alpha\text{-Al}_2\text{O}_3$ support [30]. Finally, the samples prepared by deposition–precipitation method had free NiO independently of the support used. This can be due to the formation of Feitknecht compound [29] before the calcinations step of the OC. The presence of this brucite type hydroxide layers were determined by XRD analysis of the dried samples before calcination. Although the Feitknecht compound disappeared after the calcination stage, the metal stability and interaction with the support was influenced.

TPR analysis were performed to determine the number of reducible species available in the OC and to find the temperature at which the reduction of these species occurs. Fig. 1 shows the different spectra measured for the samples. In line with literature data [36,37] the complex TPR spectra showed a H_2 consumption peak in the $400\text{--}600^\circ\text{C}$ temperature range and a high temperature peak near $800\text{--}1000^\circ\text{C}$. The peak in the temperature range of $400\text{--}600^\circ\text{C}$ is attributed to the reduction of Ni^{2+} in the NiO phase, and its complexity likely ascribed to the presence of different sized for NiO crystallites [36]. The high temperature peak is associated with the reduction of Ni^{2+} in NiAl_2O_4 . In this sense, TPR profiles are consistent with XRD data which indicate the presence of both NiO and NiAl_2O_4 phases in most of the oxygen carriers. It is also clear from the TPR results that both the preparation method and specially the support affect to the reducibility of the carriers. OC prepared by incipient wet impregnation of $\gamma\text{-Al}_2\text{O}_3$ showed a predominant single peak at temperatures higher than 750°C , which indicates the absence of bulk oxides on the support and an abundance of the nickel spinel phase, which was also determined by XRD analysis. OC samples prepared by deposition–precipitation using the same support, $\gamma\text{-Al}_2\text{O}_3$, showed a low temperature peak and a high temperature peak, indicating the presence of free NiO and NiAl_2O_4 . The high reduction peak at 940°C of this sample indicates a strong metal–support interaction. All OC prepared using the $\alpha\text{-Al}_2\text{O}_3$ as support had two reduction zones with similar characteristics, independently of the preparation method used. The two reduction zones are indicative of the presence of both phases NiO and NiAl_2O_4 in the OC as it was also measured in the XRD analysis.

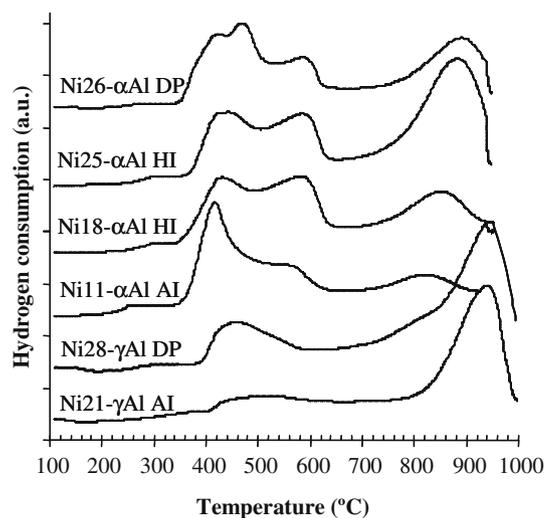


Fig. 1. H_2 -TPR profiles of the fresh OC prepared by different methods.

3.2. OC reactivity

Reactivity data were obtained in TGA tests from the weight variations during the reduction and oxidation cycles as a function of time. The TGA experiments allowed to analyze the reactivity of the OC under well-defined conditions, and in the absence of complex fluidizing factors such as those derived from particle attrition and interphase mass transfer processes.

The OC reactivity corresponding to the cycle 5 was used for comparison purposes. Fig. 2 shows the conversion versus time curves for the samples prepared by the incipient wet impregnation and deposition–precipitation methods using both supports (γ - and α - Al_2O_3). As can be seen, the Ni-based OC prepared on γ - Al_2O_3 showed lower reduction reactivity than the OC prepared on α - Al_2O_3 . This lower reduction reactivity of the OC prepared on γ - Al_2O_3 was due to the higher formation of NiAl_2O_4 species that are more difficult to reduce (see TPR results). It can also be observed that the carrier prepared on γ - Al_2O_3 by the deposition–precipitation method had higher reduction reactivity than the one prepared by incipient wet impregnation. This improvement was due to the presence of the NiO specie in this carrier, as it was determined by XRD and TPR results.

All the samples prepared with α - Al_2O_3 as support, independently of the method used, had a very high reduction reactivity, because the interaction between the metal and the support was reduced using the alumina thermally pre-treated [30]. However, the conversion reached by the OC prepared by deposition–precipitation method was lower than the one reached by the OC prepared by incipient wet impregnation.

All the OC exhibited very high reactivity during oxidation reaction and this reactivity was hardly affected by the preparation method or support type used.

3.3. OC behavior in batch fluidized bed

Reduction–oxidation multicycle tests were carried out in a batch fluidized bed to determine the gas product distribution and to analyze the fluidization behavior of the OC with respect to the attrition and agglomeration phenomena in similar conditions to those existing in a CLC process.

3.3.1. Gas product selectivity

In a previous work [30] the behavior of the OC prepared by incipient wet impregnation at ambient temperature was analyzed.

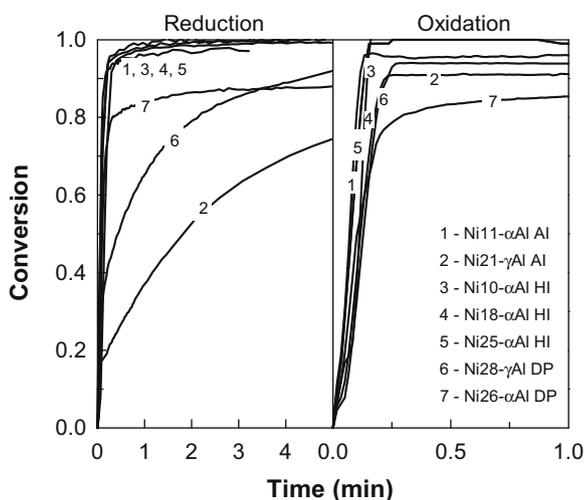


Fig. 2. Effect of preparation method on the reactivity of the Ni-based OC. $T = 950^\circ\text{C}$.

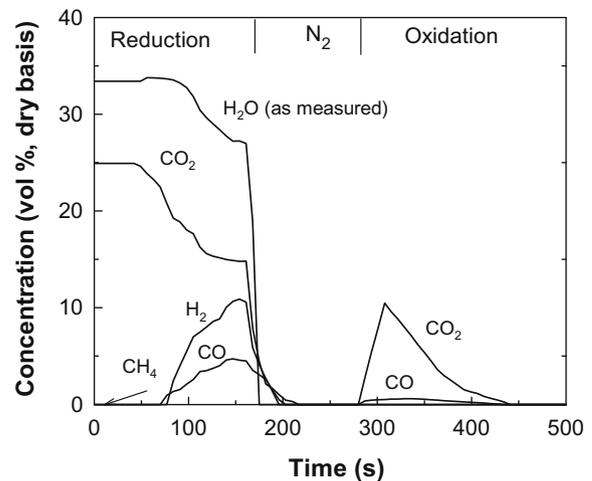


Fig. 3. Typical gas product distribution (dry basis) measured during a reduction–oxidation cycle in the batch fluidized bed working with Ni18- α Al HI. H_2O concentration as measured in an FTIR analyzer.

It was found that with the OC prepared on γ - Al_2O_3 , Ni21- γ Al AI, the CH_4 combustion was mainly selective towards the formation of H_2 and CO, and with the OC prepared on α - Al_2O_3 , Ni11- α Al AI, the CH_4 was almost completely converted to CO_2 and H_2O .

In this work, the gas product distribution obtained during CH_4 combustion with the OC prepared by the hot incipient wet impregnation and by the deposition–precipitation methods was analyzed. Fig. 3 shows the typical gas product distribution measured with an OC prepared by HI on α - Al_2O_3 , Ni18- α Al HI. CO_2 and H_2O were formed immediately after the CH_4 feeding and no CH_4 was measured during all the reduction period, thus indicating that CH_4 conversion was complete and mainly selective towards CO_2 and H_2O , (CO and H_2 concentrations were those corresponding to the thermodynamic equilibrium of $\text{NiO}-\text{CH}_4$ at the reaction temperature). Only when most of the OC was reduced, the CO_2 and H_2O concentrations decreased and the formation of CO and H_2 increased. In the oxidation period, CO_2 and CO were formed by the combustion of C generated in the reduction period by CH_4 decomposition. Very similar gas product distributions were found for all the samples prepared by hot incipient wet impregnation method with different nickel content, Ni10- α Al HI and Ni25- α Al HI. Moreover, this gas product distribution was very similar to that found for the carrier prepared by AI on α - Al_2O_3 , Ni11- α Al AI.

Figs. 4 and 5 show the gas product distributions measured during the reduction reaction with the OC prepared by the deposition–precipitation method, using γ - Al_2O_3 and α - Al_2O_3 as supports. With the OC prepared on α - Al_2O_3 , Ni26- α Al DP, the gas product distribution was similar to that obtained with the OC prepared by hot incipient wet impregnation, Ni18- α Al HI, which showed a high CH_4 combustion selectivity towards the formation of CO_2 and H_2O during most of the reduction period. With the OC prepared on γ - Al_2O_3 , Ni28- γ Al DP, the CH_4 conversion was complete but the selectivity to CO_2 and H_2O was poor. The reduction time with full CH_4 conversion to CO_2 and H_2O was negligible, and high H_2 and CO concentrations were present in the gas outlet together with CO_2 and H_2O during all the reduction period. This behavior indicated that the formation of NiAl_2O_4 affects negatively to the methane combustion selectivity towards CO_2 and H_2O , since the rate of oxygen release by NiAl_2O_4 is slower than the one of NiO . As a consequence less oxygen was available for the full oxidation of H_2 and CO .

A comparison of the gas product distributions measured during the reduction–oxidation multicycle tests with the Ni-based OC prepared by DP, AI and HI methods showed that the methane

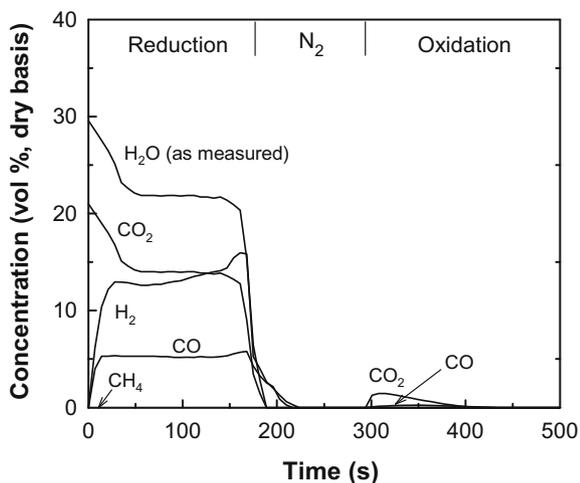


Fig. 4. Typical gas product distribution (dry basis) measured during a reduction-oxidation cycle in the batch fluidized bed working with Ni28- γ Al DP. H₂O concentration as measured in an FTIR analyzer.

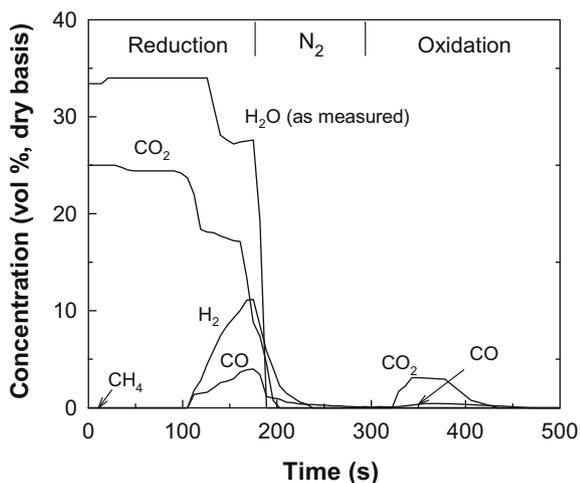


Fig. 5. Typical gas product distribution (dry basis) measured during a reduction-oxidation cycle in the batch fluidized bed working with Ni26- α Al DP. H₂O concentration as measured in an FTIR analyzer.

combustion selectivity during the reduction reaction strongly depended on the OC support, being the preparation method and/or

the total metal oxide content of the OC of lower relevance. OC with high content of free NiO had high reactivity and also high methane combustion selectivity to CO₂ and H₂O. The interaction of the NiO with the alumina formed NiAl₂O₄ that affected negatively to the methane combustion reactivity and selectivity towards CO₂ and H₂O during the reduction reaction.

3.4. Agglomeration and attrition behavior

The multi-cycle tests carried out in the batch fluidized bed were useful to determine the fluidization behavior of the OC with respect to the attrition and agglomeration phenomena.

All the OC prepared were evaluated in the fluidized bed reactor with respect to the agglomeration process. It was found that the OC prepared by the Al (Ni21- γ Al Al and Ni11- α Al Al) and HI (Ni10- α Al HI, Ni18- α Al HI, and Ni25- α Al HI) methods, with NiO contents up to 25 wt%, never agglomerated. The OC prepared by the DP method on γ -Al₂O₃ with a NiO content lower than 30 wt% (Ni28- γ Al DP) did not agglomerate, however, those prepared with NiO contents higher than 30 wt% (Ni33- γ Al DP and Ni40- γ Al DP) agglomerated, indicating that the NiO content affected the agglomeration behavior of the OC. This result is analogous as the one found in a study of the agglomeration behavior of the Cu-based OC prepared by impregnation [33], where it was found that the CuO content affected the agglomeration behavior of the OC. When the OC agglomerated, the tests must be stopped due to the sticking of the particles causing defluidization. Finally, the OC prepared by the DP method on α -Al₂O₃ with a NiO content of 26 wt% (Ni26- α Al DP) presented a small agglomeration. This OC formed small lumps by sticking of the particles. These lumps had small mechanical strength and were easily destroyed by the fluidization process because did not cause defluidization. Fig. 6 shows SEM images of fresh and after-used particles of this OC. As can be seen, the particles looked agglomerated after being used.

Figs. 7a and b show SEM images of fresh particles embedded in resin, cut, and polished. The former corresponds to an OC that did not agglomerate, Ni18- α Al HI, and the later to an OC that agglomerated, Ni33- γ Al DP. As can be seen, the OC that agglomerated showed an external layer of NiO over the particles that could favors the sticking of the particles. The outer shell of NiO was also corroborated by EDX analysis. SEM-EDX line profiles revealed two high peaks of Ni corresponding to the external shells of the fresh particles.

SEM images and EDX line profiles were also carried out to after-used particles that agglomerated. Fig. 8 shows a SEM image and a EDX line profile of used particles of Ni33- γ Al DP embedded in resin, cut, and polished. It clearly shows that the NiO layer deposited

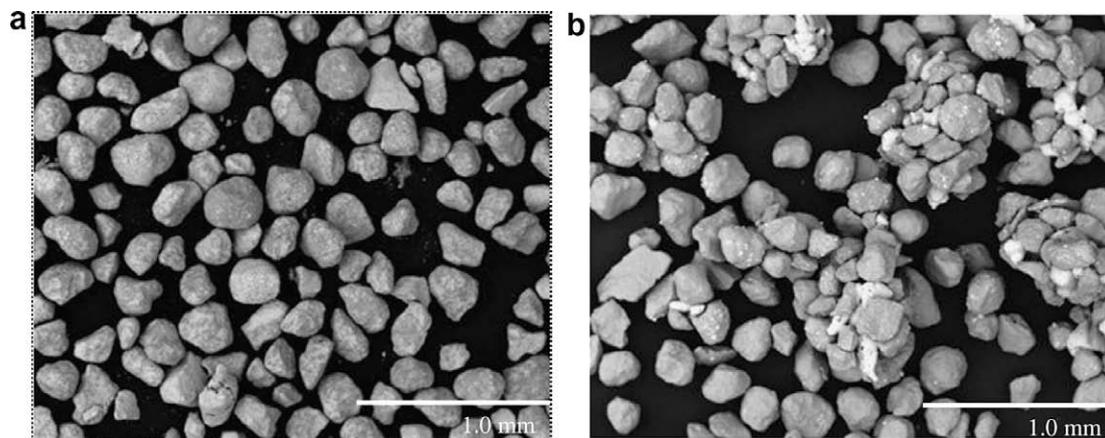


Fig. 6. SEM images of the OC fresh and used particles of Ni26- α Al DP: (a) SE (secondary electrons) image of fresh particles. (b) SE image of used particles.

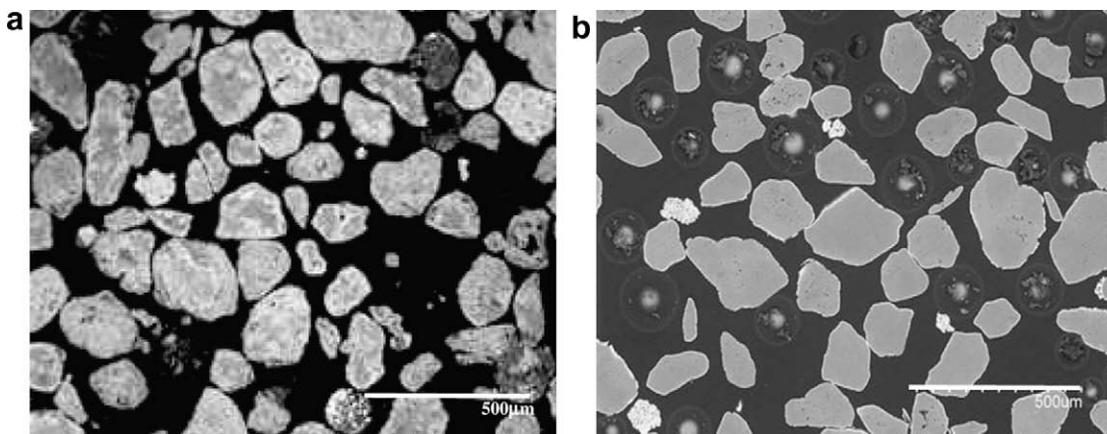


Fig. 7. SEM images of the cross sections of the fresh OC particles: (a) Ni18- α Al HI; (b) Ni33- γ Al DP

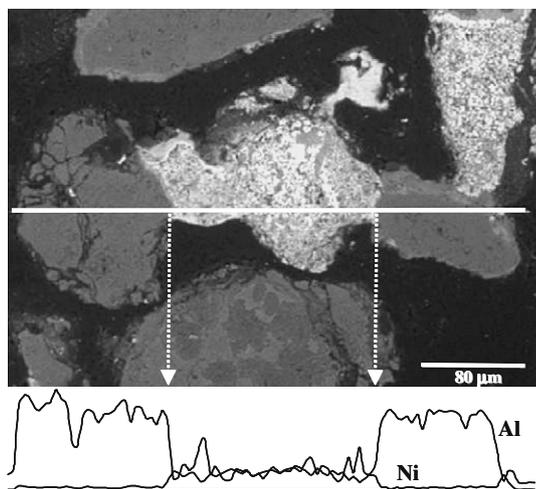


Fig. 8. SEM-EDX line profiles of Ni and Al in a cross section of used particles of Ni33- γ Al DP.

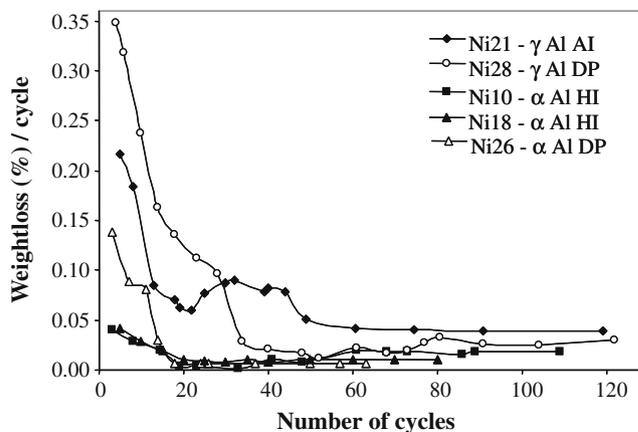


Fig. 9. Attrition rates of Ni-based OC prepared with different methods and supports.

over the external surface of the particles favored the sticking of the particles, forming agglomerates. It seems that the most important factor affecting to the formation of the external NiO layer, and so to the agglomeration process, was the metal content of the OC. The agglomeration increased with increasing the metal content. In addition, some influence of the support type and preparation method was also observed. The carrier Ni26- α Al DP presented a small agglomeration, however, the carrier Ni25- α Al HI, that had almost the same NiO content, and the carrier Ni28- γ Al DP, with higher NiO content, did not agglomerate. The different behavior could be due to the more uniform distribution of the NiO over the support obtained using the HI method than the DP method, and the more uniform distribution of the NiO over the γ -Al₂O₃ than over the α -Al₂O₃ due to the higher porosity and specific area.

The attrition rate of the OC is another important parameter to be accounted as a criterion for using a specific OC in a fluidized bed reactor. High attrition rates will decrease the lifetime of the particles increasing the cost of the CLC process.

Fig. 9 shows the attrition rates measured with the different OC. Similar trends to those observed in a previous work using OC prepared by AI were found [30]. The attrition rates were usually higher in the first cycles due to the rounding effects on the irregularities of the particles and because of the fines stuck to the particles during their preparation. After 20–40 cycles of reaction, the attrition rates of the OC decreased and were almost constant. The attrition

rates of the OC prepared using γ -Al₂O₃ were always higher than the ones measured with the OC prepared using α -Al₂O₃ as support, due to the higher mechanical strength of this last support. The effect of the preparation method on the OC attrition rate was observed in the first cycles of reaction, with higher attrition rates in the OC prepared by the DP method. It seems that the preparation steps of precipitation and filtration are responsible of these higher attrition rates. However, after 20–40 cycles the differences between the attrition rates of the different OC were less noticeable. In general, the attrition rates were low, showing that the internal changes produced in the particles by the successive reduction and oxidation cycles did not affect to the mechanical properties of the OC. The presence of holes or cracks was not evidenced in SEM micrographs of the surface of the fresh and after-used OC particles.

The results obtained in this work suggest that OC prepared by AI, HI or DP methods on α -Al₂O₃ support are suitable to be used in a CLC process. As the DP method is highly time-consuming (long precipitation times, filtration and drying stages are needed) and the particles with high nickel contents could agglomerate in the fluidized bed, the HI method seems to be more suitable to produce cheap OC. The HI method using α -Al₂O₃ as support allowed the production, in an easy way, of OC with high metal content, high reactivity, and high selectivity towards CO₂ and H₂O. Moreover, low attrition rates were measured and no agglomeration problems were detected working with these OC in the fluidized bed facility.

4. Conclusions

Ni-based oxygen carriers were prepared by incipient wet impregnation at ambient, hot conditions and deposition–precipitation methods using γ -Al₂O₃ and α -Al₂O₃ as supports.

It was found that the interaction of the NiO with the alumina during OC preparation formed NiAl₂O₄ decreasing the content of free NiO in the OC. This fact affected negatively to the OC reduction reactivity and methane combustion selectivity towards CO₂ and H₂O. The NiO–alumina interaction was higher in the OC prepared on γ -Al₂O₃ than in the OC prepared on α -Al₂O₃, and so, Ni-based OC prepared on α -Al₂O₃ showed higher reactivity and methane combustion selectivity towards CO₂ and H₂O than OC prepared on γ -Al₂O₃, independently of the method used for the OC preparation.

Most of the OC prepared did not agglomerate during multi-cycle tests in a batch fluidized bed. The OC that agglomerated showed an external layer of NiO over the surface of the particles that favored the sticking of the particles. Although some influence of the support type and preparation method was observed, the most important factor affecting to the formation of the external NiO layer on the OC, and so to the agglomeration process, was the metal content of the OC. The agglomeration of the OC particles increased with increasing the metal content of the OC.

The attrition rates of the OC prepared using γ -Al₂O₃ as support were higher than the ones measured using α -Al₂O₃ as support, and in general the attrition rates of all the OC were low.

The OC prepared by AI, HI or DP methods on α -Al₂O₃ as support are suitable to be used in the CLC process. As the DP method is highly time-consuming and the particles with high nickel contents agglomerated in the fluidized bed, the HI method seems to be the most suitable to produce cheap oxygen carriers. This method allowed the production of OC with high metal content, high reactivity, high selectivity towards CO₂ and H₂O, low attrition rate, and without agglomeration problems in the fluidized bed facility.

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