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# Obtaining stable suspensions for washcoating in microchannels: Study of the variables involved and their effects on the catalyst



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Keywords: Perovskites Washcoating Additives Reforming Oxidation Microchannel	La <sub>0.5</sub> Ca <sub>0.5</sub> CoO <sub>3.</sub> $\delta$ and La <sub>0.9</sub> Mg <sub>0.1</sub> Al <sub>0.9</sub> Ni <sub>0.1</sub> O <sub>3.</sub> $\delta$ perovskites were prepared for ethanol oxidation reaction and for ethanol steam reforming. The perovskites were mechanically ground and suspensions were subsequently pre- pared for washcoating. The physical and physicochemical modifications introduced in the mixed oxides after suspension, and their influence on the catalytic activity, were systematically studied in the suspended solids. The deposition of catalysts in metal microchannels was performed by washcoating. The mechanical milling was carried out in a high energy ball mill followed by measurements of particle size and isoelectric point (IEP). The samples were characterized by XRD, BET, TPR, XPS, FT-IR, TGA and catalytic tests. Both catalysts showed an excellent catalytic activity and high stability. In the oxidation reaction, indications of carbonaceous residues were obtained in the sample with organic additive, and the suspension without any additive presented the best stability. The samples that were evaluated in the ethanol reforming with steam showed good catalytic activity and stability. High yield of H <sub>2</sub> was obtained and low selectivity values to CO and CH <sub>4</sub> were observed. Polyvinyl alcohol was the additive that showed the best results. The catalytic films were characterized by SEM, EDX, and

3D confocal microscopy. Their stability were studied by adhesion test.

## 1. Introduction

In recent years the use of catalysts deposited on metal surfaces has increased. There are different types of structures that are used as monolithic supports, such as monoliths, foams, meshes, microreactors, among others. A microreactor is a sub-millimeter scale structure in which a chemical reaction is developed by the physicochemical interaction of different microflows of reagents that are fed into the system [1]. The importance of microreactors lies in the intensification of the process itself [2,3]. Nowadays, the intensification of processes occupies a determining place in catalysis research and what it has been sought is the decrease in the equipments volume and the efficient use of energy. The advantages obtained with the decrease in the size of reactors and the increase in the surface-volume ratio are the decrease in the diffusional path and a notable improvement in the heat and mass transfer [4,5]. Metal microreactors are a technology with great potential application in reactors for hydrogen production. The provision of energy, either from an external agent or from an exothermic reaction that occurs simultaneously, requires the use of metallic conductive materials [6]. Catalytic oxidation (exothermic reaction) and the steam reforming reaction (endothermic reaction) of ethanol present thermal behaviors that may favor the use of reactors that combine both reactions.

Structures such as microreactors involves the implementation of new techniques for the preparation of catalysts and catalytic films. The challenge now consists in achieve the proper deposition of the active phase in the microchannels that are less than 1 mm in size. The deposited layer must be able to achieve an adequate amount of catalyst loading and it must be homogeneous and well adhered. For this aim, different techniques have been proposed, such as in situ growing, electro-deposition, anodization, chemical vapor deposition (CVD), physical vapor deposition (PVD), *etc.* However, the most commonly used technique is washcoating or immersion coating using catalyst suspensions. The quality of the deposited layer depends on the properties of the suspension, which are particle size, concentration in the suspension, use of dispersants, viscosity, temperature of the suspension and amount of depositions [7–10].

Stable suspensions (non-settleable) are obtained when the terminal velocity of the particles is very small. The stability of the washcoating suspension is governed by the Stokes Law [11]. This law proposes an equation that brings together various variables that are related by different parameters such as [12]:

• Properties of solid particles (particle size distribution, repulsion between particles, *etc.*)

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- Percentage by weight of solids in the suspension
- Additives (binders, surfactants, etc.)
- Solvent used for the suspension (water, alcohols, etc.)

The terminal velocity depends directly on the square of the particle size and the difference in density between the solid and the fluid, and inversely on the viscosity. Therefore, for a catalyst to be suspended in a particular liquid (generally water), it is convenient to reduce the particle size and increase the viscosity of the medium.

Different authors have reported that in order to obtain stable suspensions of different solids, a particle size of less than  $10 \,\mu\text{m}$  is necessary [13,14]. Particles smaller than  $3 \,\mu\text{m}$  can lead flotation and poor adhesion [15,16].

The physical modifications of the catalyst imply a drastic increase in the surface area, essentially by decreasing particle size and not by increasing porosity. This alteration of the specific surface could have, as a primary consequence, a surface with greater stress in the chemical bonds and this would lead to disturbances of the superficial energy densities, which are of great importance in the catalytic activity [17].

The preparation of a stable catalyst suspensions involves modifications of different properties in order to effectively suspend the solids. The pH is one of these properties, it can affect the surface of the catalyst both positively and negatively. A superficial electric charge is generated on the surface of the particles due to the electrical imbalance generated by the rupture of surface bonds. This generates in the solution a concentration of counterions near the surface of the particle. This concentration decreases as we move away from the particle, causing a potential difference between the surface of the particle and the bulk of the dispersant. If the particles are agglomerated by electrostatic attraction, larger agglomerates are generated that will precipitate, so it is necessary that they repel themselves to remain in suspension. The z potential is a fundamental parameter that controls the interaction of suspended particles. As this parameter is determined by the nature of the particle surface and the dispersing medium, the pH becomes more than an important value [18].

The dissolution of the catalyst or the formation of complexes with cations extracted from the solid and the modification of the valency of some of the surface elements of the catalyst can influence the catalytic performance [18,19]. Some polymeric or oligomeric species used as suspension particle stabilizers tend to deposit on the heterogeneous surface of catalysts. Then, these species block reactive access and the subsequent desorption of the product from the active sites [20]. Catalysts poisoned by carbonaceous deposits, in gas phase reactions, could be regenerated by oxidation at high temperatures [21,22]. The use of additives in the preparation of catalyst suspensions involves an exhaustively study of the possible residues that could interfere with the catalytic behavior.

This work provides an extensive and detailed systematic study of two catalysts, corresponding to different reactions, which will be later supported on the walls of metal microreactors by means of washcoating. In particular, the work consists in studying the influence on the catalytic performance of the physical modifications introduced by the decrease in the size of the particles and the physicochemical modifications introduced by the stabilizing agents of the suspension of washcoating. The work is carried out on two catalysts for different reactions but energetically complementary in their application in microreactors. On the other hand, the characterization of the catalyst layer deposited in the microchannels by washcoating is of utmost importance. The homogeneity and the adhesion are fundamental characteristics that the film must fulfill so that the structured support is applicable in catalysis.

## 2. Experimental

#### 2.1. Catalysts preparation

La<sub>0.5</sub>Ca<sub>.5</sub>CoO<sub>3- $\delta$ </sub> type perovskites for the combustion reaction were prepared by the citrate method [23]. The reagents used were La (NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (Fluka), Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (Fluka), Co(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, and monohydrate citric acid (Fluka). An aqueous solution of citric acid with a 10% excess in the cation equivalents was prepared. The aqueous solutions of metal nitrates were added to the citric acid solution and stirred for 15 min. The solution was concentrated by slowly evaporating the water in vacuum at 50 °C until a gel was obtained. This was dried at 120 °C in vacuum for 24 h and calcined for 2 h at 700 °C. The catalyst is called La<sub>0.5</sub>Ca<sub>.5</sub>Ca<sub>.5</sub>CoO<sub>3- $\delta$ </sub>.

 $\begin{array}{l} La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta} \mbox{ type perovskites for the reforming reaction} \\ were prepared also by the citrate method [24]. The reagents used were \\ La(NO_3)_3.6H_2O \ (Fluka), \ Mg(NO_3)_2.6H_2O \ (Fluka), \ Ni(NO_3)_3.6H_2O \ (Merck), \ Al(NO_3)_3.9H_2O \ (Fluka), \ and \ monohydrate \ citric \ acid \ (Merck). \\ The methodology has already been described. The solids were dried at 120 °C, in vacuum, during 24 h, and then calcined at 800 °C, for 2 h. The catalyst is called La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta}. \end{array}$ 

### 2.2. Slurries preparation and Deposition by washcoating on glass-samples

A ball milling process was carried out using a planetary ball milling (Pulverissette 6, Fritsch, Germany) equipped with cylindrical tungsten carbide (80 cm<sup>3</sup>) together with 5 mm diameter zirconia oxide balls. The dough ball-powder mass was 10:1, the rotation speed was set at 500 rpm. To identify the milled samples it is called CM for La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3. $\delta$ </sub> and NM for La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3. $\delta$ </sub>.

Suspensions were prepared with the milled catalysts and washcoating additives. The proportion was 30% w/w of catalyst in water and 6% w/w of additives. The additives used as thickeners were colloidal alumina Nyacol® (Ny) and polyvinyl alcohol (PVOH). The pH was achieved by adding nitric acid or ammonium hydroxide. The formulation and nomenclature used in this work is shown in Table 1.

The washcoating process consisted in the immersion of  $75 \times 12 \times 1$  mm size glass cores in the catalyst suspension for 1 min and then they were extracted at a constant speed of 3 cm min<sup>-1</sup>. They

## Table 1

Slurries composition and properties.

Solid symbols	Sl	Slurries Composition			Viscosity [cP]
	Catalyst [w%]	Additive [w%]	Dispersion media		
LaCa <sub>0.5</sub> Co <sub>0.5</sub> O <sub>3-δ</sub>	100	_	-	_	-
CM	100	-	-	-	-
CS1	30	-	water	4	35.1
CS2	30	6 Ny	water	4	76.9
CS3	30	6 PV	water	4	69.4
		(OH)			
CS4	30	3 Ny + 3 PV(OH)	water	4	76.4
La <sub>0.9</sub> Mg <sub>0.1</sub> Al <sub>0.9</sub> Ni <sub>0.1</sub> O <sub>3-8</sub>	100	-	-	-	-
NM	100	-	-	-	-
NS1	30	-	water	10	7.8
NS2	30	6 Ny	water	10	12.7
NS3	30	6 PV	water	10	45.5
		(OH)			
NS4	30	3 Ny + 3	water	10	41.2
		PV(OH)			

were dried at room temperature for 24 h. Then, photographs were taken for further analysis.

The viscosities of the suspensions were measured with a Rheometer viscosimeter (DV-III, Brookfield, United Kingdom). The apparent viscosity values reported were determined at 17 1/s shear rate.

## 2.3. Characterization of powders

To compare the effect of the physical and physicochemical modification introduced in the catalyst by the size reduction and during the preparation of the slurries, it was necessary to dry the different slurries for 24 h in a vacuum oven at 60 °C and calcined for 2 h at 500 °C to obtain powders. The specific surface area of the samples was calculated by the BET method from the nitrogen adsorption isotherms obtained at 77 K. A from apparatus (Gemini V, Micromeritics, USA) was used. Samples were degassed at 250 °C during 1 h. The diffraction patterns were obtained by using a difractometer (D-MAX IIIC, Rigaku, Germany) operated at 30 kV and 25 mA by Cu K $\alpha$  Nickel filtered radiation ( $\lambda$  Cu  $K\alpha 1 = 0.15418$  Å). The spectra were collected at 20 ranges of  $10^{\circ}$ –90°, at a scanning speed of 3° per minute; the crystalline phases were identified by reference to powder diffraction data. Temperature programmed reduction (TPR) was performed in a quartz U type tubular reactor using a detector TCD (SRI 110, Germany) and 100 mg and 200 mg samples were used. The reducing gas was a mixture of 5% v/v  $H_2/N_2$  at a total flow of 30 mL min<sup>-1</sup> and the temperature was increased at a rate of 10 °C/min from room temperature to 700 °C. The particle size was measured with a Particle Size (Analysette 20, Fritsch, Germany). The sample was prepared in water by adding surfactant and homogenizing in ultrasound for 10 min. The results reported as particle size correspond to the average. The isoelectric point measurements were carried out in an apparatus (System 3.0, Zeta Meter, USA) using 30 mg of dispersed sample in 10<sup>-3</sup> M KCl solution. The pH of the suspensions was modified by adding solutions of potassium hydroxide or hydrochloric acid 0.01 M. The results presented are the average of at least 20 measurements and with a maximum deviation of 3 mV. FT-IR spectra were registered by using a spectrometer (Nicolet Protegé 460, USA) in KBr pellets. The samples were diluted to 1 wt% with KBr. The spectra were the result of averaging 32 scans obtained at room temperature in a wavelength ranging from 4000 to 225 cm<sup>-1</sup>. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) experiments were performed on an equipments (DTA 50 and a TGA 51, Shimadzu, Chine).10 mg of sample were heated from ambient temperature up to 1000 °C at a heating rate of 10 °C min<sup>-1</sup> under  $50 \text{ mL min}^{-1}$  of synthetic air. X-ray photoelectron spectroscopy (XPS) data were obtained with an equipment (Multitecnic UniSpecs, UK) with a dual X-ray source of Mg/Al and a hemispheric analyzer (PHOIBOS 150, Germany). A pass energy of 30 eV and a Mg and Al anode operated at 100 W were used. The pressure was kept under  $1\times 10^{-8}$  mbar. The samples with Ni were previously reduced at 600 °C in 50 mL/min<sup>-1</sup> of 5%H<sub>2</sub>/N<sub>2</sub> stream. The samples were supported in the sample holder of the instrument, on a double-sided copper tape, and evacuated in ultra high vacuum for at least twelve hours before the readings.

## 2.4. Catalytic test

The powder catalysts from the suspensions were evaluated in the total oxidation of ethanol using a steel reactor operating at atmospheric pressure. 300 mg of active phase was used, sieved at a size of 35-50 meshes and diluted with cordierite particles of equal size in a ratio of 1:5. The feed rate was 300 mL min<sup>-1</sup>, with a load of 4000 mg C diluted in air. Reagents and products were analyzed on-line by gas chromato-graphy using a equipped (BuckScientific, Mod 910 chromatograph, USA) with a 20 M Carbowax/Chromosorb W column and flame ionization detector (FID).

The powder catalysts from the suspensions were evaluated in the ethanol reforming reaction. 150 mg of active phase and 1 g of inert (ground quartz) were used. The composition of the non-condensable fraction leaving the reactor was quantified by a GC equipment (Shimadzu, Japan) using a Carbosphere column, the reagents and condensable products were quantified by a GC cromatograph (Buck Scientific, USA) with a Porapak Q column, both with a thermal conductivity detector. The tests were carried out at 650 °C and atmospheric pressure. The water:ethanol feed ratio was 5:1 M (S/C = 2.5), with a load of  $3.3 \times 10^{-4}$  mL<sub>liq</sub>/(mg<sub>cat</sub> min) and using 50 mL min<sup>-1</sup> of He as carrier. The results shown are on a dry basis.

#### 2.5. Washcoating on the microchannels

The microreactors were manufactured from AISI 304 L stainless steel, in 20  $\times$  20  $\times$  2 mm plates with 20 micro-channels of 500  $\mu m.$  In the microchannels, a rough layer was previously formed by controlled oxidation [25]. This layer was coated with a thin film of alumina to generate roughness and passivate the surface [26]. The deposition of the active phase was performed by washcoating and the variables involved were studied in previous works [27-29]. The washcoating process consisted of immersing the microreactor in the catalyst suspension for 1 min and then extracting it with a Sage Instruments Model 355 equipment, at a constant speed of  $3 \text{ cm min}^{-1}$ . The excess suspension was removed by centrifugation using a centrifuge (Model 2036, Rolco, Germany), 2 min per side. The microreactors were dried for 2 h in a vacuum oven at 120 °C. One and two dives were made and calcined at 500 °C for 3 h using an oven (Model 660, Indef, Argentine). To ensure that the coating, in both the alumina and the catalyst, adheres only in the area of the microchannels, before the depositions the outer faces are covered with adhesive film. In order to subject the microreactors to temperature, the film is removed and the catalyst surfaces are left clean. This provides the adequate surface to be able to weld the units and obtain the complete microreactor. The samples were named: XB, with X = 1 and 2 corresponding to the number of loads, B = N corresponds to the reforming catalyst  $(La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta})$  and C to the oxidation catalyst ( $La_{0.5}Ca_{0.5}CoO_{3-\delta}$ ).

#### 2.6. Characterization of the film in microchannels

The adhesion of the layer deposited in the microchannels was studied by an adhesion test. The whashcoated microreactors were placed in a flask with acetone and immersed in ultrasonic vibration for 30 min, dried 1 h in a vacuum furnace at 100 °C and calcined at 500 °C for 2 h. Because the mass of the deposited solid is a very small amount in comparison with the mass of the microreactor, the mass differences cannot be appreciated. The effect of the adhesion test is studied by observation of the surface morphology with an optical microscopy. The samples subjected to adhesion tests are identified adding "TA" to the name. Scanning electron microscopy (SEM) images were obtained with a, scanning electron microscope (LEO 1450 VP, USA) provided with a Genesis 2000 energy dispersive X-ray analysis (EDAX) equipment for the quantitative analysis. Topographic 3D images of microchannels were obtained using a confocal laser scanning microscope (LEXT OLS400 0, Olympus, Japan). Ovarzún et.al. proposed that this is an alternative technique to characterize the superficial morphology and to obtain measures of thickness of superficial layers [30]. A XYZ acquisition was performed using 1 µm image scaling to cover the total height of the material and with a width of 646 µm contained in 1024 pixels (630 nm/pixel). The length of each image covered approximately 3000 µm, enough to include 4 consecutive channels of the sample. In order to construct the total image, a special mode of acquisition of the microscope called "sewing" was used, which uses the motorized plate to reposition the sample automatically, consecutively and sequentially, to

#### Table 2

Results from XRD and particle size analysis.

Sample	Crystallite size [Å]	Particle size [µm]
$\begin{array}{c} LaCa_{0.5}Co_{0.5}O_{3\cdot\delta}\\ CM\\ La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta}\\ NM \end{array}$	400 246 130 120	10 6 56 3

cover the 3000  $\mu m$  sample length. The images were acquired using (MPLAPON20XLEXT NA 0.6, Olympus, Japan) objective lens. The microchannel heights profiles were obtained from the images. The depth of the microchannel was determined from the maximum height of the microchannel wall to the minimum value of the bottom of the adjacent microchannel. The microchannel profile width was measured at a height of 150  $\mu m$  from the bottom of the microchannel. This value would correspond to 25% of the total height of the microchannel in triplicate using a cutoff value of 80  $\mu m$  along the 640  $\mu m$  microchannel.

## 3. Results

## 3.1. Milling process

The particle size of the synthesized catalysts is not adequate (see Table 2) for the preparation of stable suspension. Thus, it is necessary to carry out a grinding process until reaching the desired size. The specific surface area was used as an indirect measure of the particle size to follow the grinding process; the results are shown in Fig. 1.

The curves present an initial increase and then they stabilized around a value, as is typical of this technique. This is due to the fractionation and addition processes that occur during grinding. The specific surface increased for both catalysts from 13.5 to  $17.5 \text{ m}^2 \text{ g}^{-1}$  for La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3.6</sub> and from 9 to  $15 \text{ m}^2 \text{ g}^{-1}$  for La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3.6</sub>.

The energy transmitted in the grinding process was calculated from the equations proposed by Burgio et al. [31,32]. The results as a function of the energy dissipated ( $E_{acc}$ ) by grinding are a more useful standard reference for its reproduction than time. Under these grinding conditions the energy time relationship is linear. The energy values between 0.5 and 6 min of grinding range from  $4.72 \text{ Jg}^{-1}$  to  $57 \text{ Jg}^{-1}$ , respectively.



Fig. 1. Specific surface areas vs milling time for different catalyst. a)  $La_{0.5}Ca_{0.5}CoO_{3.6}$ ; b)  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3.6}$ .



Fig. 2. Diffraction pattern for  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  perovskite before and after milling.

## 3.2. Particle size

The particle size was measured by photosedimentography and the results are shown in the third column of Table 2. The particle size obtained from the synthesis for the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub>. $\delta$  catalyst is almost six times larger than for the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3</sub>. $\delta$  catalyst. The reduction in size was greater for the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3</sub>. $\delta$ . However, the E<sub>acc</sub> delivered by the grinding system was three times higher than for the La<sub>0.5</sub>Ca<sub>0.5</sub>CaO<sub>3</sub>. $\delta$  catalyst.

## 3.3. XRD characterization

The diffractograms of the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3. $\delta$ </sub> catalyst and the CM are shown in Fig. 2. The diffractograms coincide with the characteristic phase sheet of the base perovskite, LaCoO<sub>3</sub> (PDF 01-075-0279), indicated in Fig. 2, which is an isomorphic structure. The phase also coincides with that reported by Merino et al. [23]. No other segregated phases are observed, such as Co, La, or Ca oxides.

In the case of the reforming catalysts (Fig. 3) high crystallinity was observed and the samples were adjusted with the diffraction pattern of



Fig. 3. Diffraction pattern for  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta}$  perovskite before and after milling.



Fig. 4. TPR profile for  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  perovskites before and after milling.

Table 3

Hydrogen consumption from TPR essays of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  catalysts before and after milling.

Sample	Mass [g]	Consumption [mol]
CuO	0.05	6.291E-04
LaCa <sub>0.5</sub> Co <sub>0.5</sub> O <sub>3-8</sub>	0.10	6.051E-03
CM	0.10	5.958E-03
CuO	0.01	1.296E-04
$La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$	0.2	2.122E-04
NM	0.2	2.616E-04

the  $LaAlO_3$  pure perosvkite (PDF 01-085-1071). No diffraction lines are observed corresponding to segregated phases of La, Mg, Al or Ni oxide.

In both diffractograms an apparent loss of crystallinity observed due to the widening of the diffraction lines can be seen. Using the Scherrer equation, it can be determined for both catalysts the size of crystallite by observing decreases in size after grinding (Table 2).

## 3.4. TPR characterization

The results of temperature programmed reduction (TPR) for the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  samples compared with the milled catalyst are shown in Fig. 4, while in Table 3 the hydrogen consumptions for each of the analyzed samples are presented.

The reduction of the LaCoO<sub>3</sub> perovskite shows two stages of reduction. In literature, there is not an agreement on the reduction stages assignment. The assignations made by Taran et al. [33] indicate that the perovskite reduction includes four stages. Firstly, the formation of the oxide of the B cation and a spinel structure occurs, then, the B cation is reduced and finally La<sub>2</sub>O<sub>3</sub> and Co° are formed. On the other hand, Carvalho et al. [34] found two reduction processes: the first one corresponds to a partial reduction to give an intermediate perovskite and in the second step the sample is completely reduced to Co and La<sub>2</sub>O<sub>3</sub>. For the purpose of this work, reduction intermediate state identification

Table 4

is not relevant. The consumption of hydrogen is practically the same before and after grinding. However, grinding produces a displacement of the reduction peaks towards lower temperatures. The peak at lower temperature reaches its maximum at 70 °C less, with a strong shoulder growth. The reduction signal at higher temperatures does not change its maximum but it practically splits with a peak at a lower temperature, around 570 °C. The temperature at which reduction starts ( $T_{onset}$ ) for La<sub>0.5</sub>Ca<sub>0.5</sub>CaO<sub>3.6</sub> and CM are 100 and 80 °C, respectively.

From the reduction profiles (Fig. 4) of the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> catalyst, information about the nature of the Ni species in the perovskite can be obtained. The sample La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3. $\delta$ </sub> shows a wide signal at the range of 300–500 °C with a maximum at 446 °C, and two signals above 500 °C. In LaNiO<sub>3</sub> perovskites, it has been reported that the first two peaks are assigned to the reduction of LaNiO<sub>3</sub> to La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub> and then to La<sub>2</sub>NiO<sub>4</sub>. The third broad peak corresponds to the reduction of La<sub>2</sub>NiO<sub>4</sub> to Ni and La<sub>2</sub>O<sub>3</sub> [35,36].

The NM sample shows a shift in the reduction signals, they are shifted at lower temperatures and the signal intensity increases. It is observed that the consumption of hydrogen in NM is greater than  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$ . The higher hydrogen consumption could be due to a higher proportion of Ni<sup>3+</sup> species instead of Ni<sup>2+</sup> or a higher proportion of easily reducible species [29,37].

## 3.5. Zeta potential analysis

The isoelectric point value is at a pH 9 for  $La_{0.5}Ca_{0.5}Ca_{0.5}CoO_{3-\delta}$ , and about 6 for  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$ . A pH far from this point should be selected to ensure the stability of the particles in suspension.

This value for the suspensions was set at pH 4 by adding HNO<sub>3</sub> for the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> catalyst and pH 10 for the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> catalyst with the addition of ammonium hydroxide. The solvent medium must be selected taking into account the potential dissolution of the perovskite or the formation of complexes with cations extracted from the perovskite. The selected solvents meets the stated requirement.

We also determined Zeta potential of alumina particles to understand possible interaction. In this case the isoelectric point is about at pH 5.

## 3.6. X-ray photoelectron spectroscopy (XPS)

In both samples, the O1s spectra whose main peak was observed between 528–531 eV were analyzed. The deconvolution led to two components, one of low energy and another of high one. In the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3.8</sub> sample the low energy peak (529.8–530.1 eV) is attributed to the lattice oxygen (O<sub>L</sub>) and the high energy peak (5313 eV) is assigned to the adsorbed oxygen (O<sub>ads</sub>) on the surface of the catalyst which are indicators of surface vacancies. In the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3.8</sub> sample the low energy peak is at 528.6 eV and the high energy peak is at 530.6 eV. The results of the O<sub>ads</sub>/O<sub>L</sub> ratio are shown in Table 4.

#### 3.7. Slurry properties

Polyvinyl alcohol has been selected as additive due to its organic character, and alumina as an inorganic colloidal thickener. A

Catalyst	$O_{ads}/O_L$	La/Co	Ni/La + Mg + Al	Mg/La + Ni + Al
$\begin{array}{l} La_{0.5}Ca_{0.5}CoO_{3\cdot\delta}\\ La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta} \end{array}$	0.54 0.15	1.13	0.048 (0.05) <sup>a</sup>	0.01 (0.05) <sup>a</sup>

<sup>a</sup> Values between brackets correspond to nominal ones.

#### Table 5

Specific surface areas of  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta}$  and  $La_{0.5}Ca_{0.5}CoO_{3\cdot\delta}$  powders.

Sample	$La_{0.5}Ca_{0.5}CoO_{3-\delta}$	CM	CS1	CS2	CS3	CS4
$\begin{array}{c} S_{BET}^{\  \  a} \ [m^2 \ g^{-1}] \\ S_{BET}^{\  \  b} \ [m^2 \ g^{-1}] \end{array}$	13.5	17.8 15.3	19.1 19.2	28.2 20.2	15.1 17.3	25.5 18.3
Sample	$La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3\cdot\delta}$	NM	NS1	NS2	NS3	NS4
S <sub>BET</sub>	9	14.1	16.6	17	16.1	19.8

<sup>a</sup> specific surface areas  $[m^2 g^{-1}]$  before catalytic test.

<sup>b</sup> specific surface areas  $[m^2g^{-1}]$  after 1 h 30 min under reaction at 650 °C.

pseudoplastic behavior was observed in all the suspensions of the catalysts according to the viscosity values, which is typical of suspensions [29]. The apparent viscosities shown in Table 5 were measured at shear stresses similar to those used during the washcoating technique, involving the extraction of the microreactor at 3 cm min<sup>-1</sup>.

## 3.8. Washcoating in glass-sample

Once the suspensions are stable, it is necessary to make a morphological observation of the covering. To do this, the stability of the suspensions and their covering power were studied by means of visual observation, by performing washcoating on glass cores as a washcoating test. A good adhesion of the active phase on the surface can be estimated.

The CS1 and NS3 suspensions are those that presented a film with greater homogeneity and load (Fig. 5). In the suspensions that both additives were present, agglomerations were observed and the  $NS_2$  suspension presented, particularly, a low load.

To study the effect it causes on the physical and physicochemical properties of a solid, being suspended in a liquid, it is necessary to eliminate the dispersant. Therefore the suspensions are dried and calcined.

## 3.9. Specific surface area

The solids obtained from the catalyst suspensions and their respective additives show higher  $S_{BET}$  than the ground base catalyst. NS1, NS2 and NS3 have a similar surface area, which is 15% larger than the one of the ground base catalyst. NS4 shows an increase of the  $S_{BET}$  of the order of 30%.

The specific surface areas of the CSx post-suspension catalysts were also measured after the drying and calcinations. At the same time, in Table 5, the results for this surface after reaction at 650 °C are shown, to observe the effects that could cause on the catalyst the necessary working temperature by its coupling with the reforming reaction. The catalyst with the largest surface area is CS2, containing 6% alumina, followed by CS4 containing 3% alumina. The specific surface for CS3 is somewhat smaller than that of CM. After the reaction at 650 °C the specific surface areas of CSx decreases but all remain above CM. CS1 shows some stability.

## 3.10. TGA

Table 6 shows the values of mass loss obtained by TGA. At low temperatures the loss of mass is attributed to dehydration but in all the



Fig. 5. Washcoating on glass-samples for the different catalyst slurries.

Table 6TGA of milled catalyst and its slurries after and before catalytic test.

Sample	Total Weight loss (w%)	600-700 °C weight loss (w%)
СМ	3.84	2
CS1	3.5	1.2
CS2	4.83	1.17
CS3	6.9	3.79
CS4	4.63	3.04
CS1p	3.65	1.83
CS2p	3.8	1.06
CS3p	3.99	1.3
CS4p	3.65	0.86

samples an abrupt fall is observed in the range of 600–700  $^\circ$ C, being the highest fall for the CS3 and CS4 suspensions.

## 3.11. FT-IR

In Fig. 6 the FT-IR spectra of the CM catalyst samples before and after the reaction are observed. The CS1 and CS2 samples have a very weak signal at  $1500-1490 \text{ cm}^{-1}$  wave length, whereas the CS3 and CS4 samples have an intense signal, corresponding to the presence of carbonaceous species.

#### 3.12. Catalytic activity

#### 3.12.1. Combustion

Table 7 shows the temperatures in which the 50% and 80% conversions of ethanol ( $T_{50}$ ,  $T_{80}$ ) were reached. All samples of the dried suspensions and the ground catalyst showed slightly higher activity than the original catalyst. In order to confirm the stability of the samples prepared for combustion in a possible thermal coupling with the reforming reaction that occurs at temperatures above 600 °C, all samples were re-evaluated after being subjected to an ethanol combustion reaction at 650 °C for 90 min. All the samples, the ground catalyst, CM, and the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> original catalyst showed a deactivation of between 30 and 40 °C.



7

#### Table 7

Catalytic test for  $La_{0.5}Ca_{0.5}CoO_{3\cdot\delta}$  catalyst before and after milling and different slurries.

Sample	$T_{80}^{a}$	$S_{100} \operatorname{CO_2^b}$	T <sub>80</sub> <sup>c</sup>	$S_{100} \operatorname{CO_2}^d$	$\Delta T_{80}$
CS1	188	231	221	264	33
CS2	188	232	213	251	25
CS3	200	220	221	260	21
CS4	182	221	225	261	43
LaCa <sub>0.5</sub> Co <sub>0.5</sub> O <sub>3-8</sub>	202	234	240	291	38
CM	198	236	215	270	17

<sup>a</sup> Temperature [°C] to reach 80% of ethanol conversion.

<sup>b</sup> Temperature [°C] to reach 100% CO<sub>2</sub> selectivity.

 $^{\rm c}$  Temperature [°C] to reach 80% of ethanol conversion after 1 h30 min catalytic test at 650 °C.

 $^d\,$  Temperature [°C] to reach 100% CO\_2 selectivity after 1 h30 min catalytic test at 650 °C.

## 3.12.2. Steam reforming of ethanol

Fig. 7 shows the conversion of ethanol data and selectivity to  $H_2$ , CH<sub>4</sub>, CO and CO<sub>2</sub> of the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> post-suspension catalysts, after being dried and calcined at 500 °C.

The samples were very active and stable for at least 9 h. Total ethanol conversion was observed, in all cases, with acceptable  $H_2$  yields, low selectivity to CO and very low to CH<sub>4</sub>. In any case the presence of acetaldehyde, ethane or ethylene was detected.

All the samples showed good yields. The NS3 sample showed the highest selectivity value to H<sub>2</sub> (70%) during the reaction time, with values of selectivity to carbon monoxide of 18%, and a very low selectivity to methane (1%). Meanwhile, the other catalysts showed values similar to the original reference catalyst. All the catalysts showed better selectivity to hydrogen than the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> original catalyst. A decrease in the selectivity to CO and CH<sub>4</sub> is observed.

## 3.13. Scanning Electron Microscopy (SEM)

Once the catalyst is deposited, it is necessary to observe the homogeneity of the film. The SEM micrographs with 12 X, 1 K X and 4 K X magnification (Fig. 8) show the deposition of the XC and XN catalysts in the microchannels. In both catalysts, with 1 and 2 charges, the surface observed is homogeneous and without channel obstruction. With 2 charges an obvious greater coverage is observed. By means of semiquantitative EDX analysis, it was possible to analyze the composition of the different surface morphologies (Tables 8 and 9). The depth of the microanalysis is approximately 5 µm, so the values obtained are approximations. In Fig. 8 the different sectors studied with microanalysis are indicated with letters. In the sample 1C, a partial covering of the surface by the particles of what would be the Co catalyst is observed. The EDX microanalysis (Table 8) indicates that zone designated B it would correspond to the combustion catalyst while zone C would be the surface with alumina previously deposited on the channel. A high percentage of Fe is observed in zone A. Probably the lowest coverage with a catalyst load does not cover the large iron spheres product of the superficial thermal pretreatment. In the photomicrograph (Fig. 8) with 4kX the combustion catalyst is observed as an agglomerate of variable particle sizes between 3 and 5 µm formed by spherical particles of regular size less than 1 µm. After two catalyst loads, better coverage is evidenced. This can be deduced from the microanalysis where the greater composition of Co and La is observed compared to zone B of sample 1C. You can also see growths rich in Fe and Cr that are obtained previously in the surface treatment in zone E. In the case of the reforming catalyst, as in Sample 1C, it can be seen areas that the catalyst could not cover. This area, marked as F, shows in the microanalysis (Table 9) a greater percentage of Fe and Al, as expected. In zone G, the decrease of these two cations and the percentage increase in Ni, La and Mg corresponding to the presence of reforming catalyst is observed.





With 2 active phase loads, similar results are obtained as in XC samples. They present more catalyst and a greater coverage. There are also indications of the spherical growths generated during the pretreatment of de metallic surface. In zone I the growth is rich in Fe and Cr, metals that obviously are not provided by the catalyst.

## 3.14. Adherence test

Fig. 9 shows SEM images with 12X increases of the samples with adhesion test (TA). No significant detachments or changes in surface morphology are observed.

## 3.15. 3D Images with confocal microscope

Fig. 10 shows the 3D image of the microchannels. Although the images of all the samples are similar, they are useful for observing the surface morphology and mainly verify that the deposited layer is homogeneous and does not generate accumulations that obstruct the microchannel. This technique allows to take heights and distances from the images. By difference, the film thicknesses can be estimated. Table 10 presents the results obtained from distances taken at three different heights as detailed in the image. When comparing the distances between ridges with the base sample A (microchannel only with alumina) it is observed that they have decreased in all samples with both catalysts. This would be giving information about the thickness of the film. The 1C sample compared to the base A in the zone closest to the bottom (a) shows a decrease in the distance of  $112 \,\mu m$ , while in the heights (b) and (c) the values are around 65 µm. The film thickness, then, can be estimated at 66 µm at the bottom of the microchannel decreasing as we ascend the wall to about 32 µm in thickness. In 1 N sample in height (a) the distance has decreased to 106 µm, while in zone (b) and (c) the values are similar, 103 and 98 µm, respectively. This gives us a uniform film with thickness value around  $50\,\mu m \pm 6\,\mu m$ .

With 2 catalyst loads the 2 N sample shows a predictable behavior, where the film thickness increased to  $60 \,\mu m \pm 2 \,\mu m$ . But 2C sample shows an unusual behavior since the film thickness decreased to  $34 \,\mu m$  at the bottom of the microchannel and  $45 \,\mu m$  at the walls, values much smaller than in the sample with 1 load.

This characterization technique also allows to obtain the value of the roughness, Ra. The value of Ra is an arithmetical measure of the absolute values of the height roughness peaks (Zi) (Fig. 10). An increase in roughness is observed with the increase in the load of combustion catalyst and the opposite occurs with the reforming catalyst

## 4. Discussion

The catalysts used in this work were selected for their excellent characteristics of structural stability and catalytic performance. The  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  catalyst was studied by Merino et al. [23]. This perovskite was synthesized by the citrate method. This method ensures to obtain homogeneous solids with high surface areas. The incorporation of Ca<sup>2+</sup> cation in the structure of the perovskite generates an unbalanced electronic system, that is, an increase in oxygen vacancies, an increase in the oxidation states of Co<sup>3+</sup> to Co<sup>4+</sup> and/or the production of anionic vacancies. By means of X-ray photoelectron spectroscopy (XPS) Merino et al. [23] obtained the superficial atomic ratios. The La/ Co ratio was the double that the one calculated theoretically, suggesting an enrichment of the solid surface with La. This is in agreement with the results shown in Table 4. The  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  catalyst emerges from a meticulous study of the design of the catalyst that lies in the need to find an active and selective one with high stability in the steam reforming reaction of ethanol. To avoid the deactivation of the catalyst it is necessary to obtain Ni particles with small domainns, with a high dispersion in a support with alkaline characteristics. In addition, the ability of the perovskite structure to incorporate several cations in a random way generates islands enriched in different cations. The controlled destruction by a reduction step of the perovskite tends to move the most reducible metal, in this case Ni, to the surface and generate small particles. Agüero et al. [24] corroborated the arrangement of the different Ni species on the catalyst surface after the reduction step by means of XPS. The atomic ratio of n(Ni)/n(La + Mg + Al) was similar to the value of the LaMgNi perovskite, which would indicate that the Ni ejection to the surface is reached in a controlled manner. This is in line with the results obtained in this work (Table 4). The same trend is observed with the Mg/(La + Ni + Al) ratio. It results in a catalyst with excellent yields and stability in the reaction time [24].

The first treatment that receives the catalyst, in order to prepare a suspension suitable for washcoating, is grinding. Grinding is the method used to reduce particle size. The novelty of this work is the use of a planetary ball mill, which is considered a high energy mill. The energy parameter accumulated includes ball impact energy, ball impact frequency, grinding time and mass of the solid to grind [31]. La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> and La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> perovskites presented different behavior against milling for size reduction. This can be attributed to their intrinsic and physical characteristics, such as elasticity and fragility. The more refractory the material is, the greater its fragility is and so the possibility of reaching an increase in S<sub>BET</sub> due to a decrease in size. During grinding there is a compromise between speed of addition (plastic shock) and fracture speed (inelastic shock) so that the particle size is stabilized around a characteristic value for each



Fig. 8. SEM micrographs of sample 1C, 2C, 1 N y 2 N with increases of 12x, 1Kx and 4Kx.

material under these grinding conditions. To be able to achieve a  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  perovskite with half of the particle size of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  perovskite it was necessary to triplicate the grinding time and thereby triplicate the energy transmitted in the process of grinding.

Fig. 1 graphically shows a direct effect of milling on the increase of the surface area. In the case of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  perovskite the

increase in the specific surface area was faster and higher with less  $E_{cum}$  compared to the  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  perovskite. It can be concluded that with energy dispersions of  $3.2\times10^5\,J\,g^{-1}$  and  $9.8\times10^5\,J\,g^{-1}$  for  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$ , respectively, optimal conditions for washcoating are reached. Although reactive grinding is widely used for synthesis [32], in the grinding of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  perosvkites the only

Table 8

XC microanalysis, Wt%.

10 0 11			-	10	CU
A 1C 23.7 0.4   B 1C 23.9 3.2   C 1C 22.6 48.6   D 2C 11.8 0.2   E 2C 26.9 6.2   stoichiometric 24.4	0.3 29.2 0.2 21.2 6.5 10.2	1.1 22.6 1.6 34.6 10.2 35.4	2.5 1.5 5.6 0.5 3.6	70.7 5.5 20.5 1.4 37.7	1.3 14 1 30.4 8.8 30

Table 9
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XN microanalysis, Wt%

AN IIICIOallaiysis	s, WVL%0.						
Ро	0	Al	Mg	La	Cr	Fe	Ni
F1N	34.5	30.7	0.7	2.4	1.8	27.6	2.5
G 1 N	13.7	9.1	1,1	42.1	9.2	14.1	10.7
H 2 N	23.4	16.7	1.8	54.5	0.2	0.7	2.8
I 2 N	15.7	1.7	0.3	8.7	31.1	35.6	6.8
stoichiometric	23.3	11.8	1.9	60.8			2.8

observable effect is the physical transformation, without evidence of the formation of a new detectable phase. In Fig. 2 and Fig. 3, a widening of the XRD diffraction lines for both catalysts can be observed, which can be attributed to the reduction of the crystalline sizes as a sample of the energy accumulation in the crystalline structure (Table 2). Barroso Quiroga et al. [32] reported the shift of the particle size distribution curves. The mechanical energy that is transferred to the sample is stored in the form of defects in the structure [17]. The decrease in size produces an increase in the specific surface area and its main consequence is the increase in crystalline tensions. This increase in the surface area has resulted in an increase in stress and electronics effects. The crystallite size (Table 2) of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  catalyst decreases by almost 40%, while the one of the  $La_{0,9}Mg_{0,1}Al_{0,9}Ni_{0,1}O_{3\text{-}\delta}$  catalyst only 7%. This may be due to the ceramic behavior of  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$ due to the presence of Ca. On the other hand, the  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3-\delta}$  catalyst has a rather plastic behavior, so the reduction of crystallite is more difficult. The presence of the Ca earth alkaline species in the  $La_{0.5}Ca_{0.5}CoO_{3.\delta}$  perovskite could justify its refractory character, whereas in the  $La_{0.9}Mg_{0.1}Al_{0.9}Ni_{0.1}O_{3.0}\delta$  perovskite all species are metallic [38].

It is important to take into account that when the particle size becomes smaller, the superficial defects play an important role in the properties of the materials [39,40]. The increase of the specific surface is accompanied by the generation of new adsorption centers that could be able to catalyze the activation of the chemisorbed hydrogen. In fact, this is reflected in the decrease of the reduction temperature by TPR for both catalysts (Fig. 4). Although for the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  catalyst the consumption of hydrogen was not modified (Table 3), the shift of the reduction temperature towards lower values, after milling, would corroborate that there are not composition and crystalline structure modifications, the physical modifications of the surface alter the redox behavior of the catalyst. In the case of LaAlNiO<sub>3</sub> perovskite after grinding a greater reducibility is observed, measured by the hydrogen consumption (Table 3). Grinding produces a reduction in size, in an atmosphere without oxygen supply, and is generally accompanied by a reductive process [41]. Therefore, an increase in Ni<sup>3+</sup> species can be ruled out. The larger reaction surface for the hydrogen could favor a deeper reduction of the perovskite and a more generalized Ni reduction that is in the LaAlO3 structure.

The physical modification resulting from the reduction in size has consequences on the redox behavior of the catalyst. Also on the characteristics of the surface resulting from the modifications of the structural stresses.

When considering surface interactions additives will play a fundamental role. Additives may be used to promote slurry stability. Longchain surfactants containing hydrophilic and hydrophobic groups, for instance, adsorbs on the catalyst surface leading to steric stabilization of the slurry. Thickeners that increase the viscosity can also be used; inorganic colloids (alumina, silica, etc.) or organic compounds (polyvinyl alcohol, polyvinylpirrolidone, ammonium methacrylate, etc.) are examples of these common additives [12]. Therefore, the necessity to achieve a stable suspension requires the use of compounds that could modify the physicochemistry of the surface. In fact, once the desired particle size is achieved, it is necessary to study the other variables involved in the stability, such as pH, solids concentration and viscosity. Assuming that the particles in the suspension do not interact with each other, the stability would only depend on the content of solids, being the interaction greater as the concentration of solids increases [41]. Agüero et al. [37] have determined that the best concentration of solids is 30% w/w. However, more than one catalyst load is necessary to achieve a greater amount of active surface phase. The greater load is achieved with a higher number of dives in a more diluted suspension.

The particles are also affected by the pH of the medium. This is an important variable since the polarization of the particles surface controls their interactions. The isoelectric point measured by Zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the Zeta potential indicates the degree of the electrostatic repulsion between adjacent particles, with similar charge, in the dispersion. For molecules and particles that are small enough, a high Zeta potential will confer stability, that is, the dispersion will resist aggregation. When the potential is low, the attractive forces can exceed this repulsion and the dispersion can break and flocculate. Therefore, colloids with high Zeta potential (negative or positive) are electrically stabilized, while colloids with low Zeta potential tend to coagulate or flocculate. A value of 40 mV ensures a good stability [42]. Therefore, the pH value of the suspensions must be sufficiently far from the value of the isoelectric point of the solid. This would ensure that the particles repel each other and cannot agglomerate and thus precipitate. The isoelectric points of the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and  $La_{01}Mg_{0.1}Al_{0.9}NO_{3-\delta}$  catalysts are found in the pH values of 9 and 6, respectively. Taking into account what was previously described, the values of pH of 4 and 10 were then selected for the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3-δ</sub> and La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3-δ</sub> catalysts, respectively, which are at a value of 40 mV. The pH modification is achieved by the addition of acids or bases. However, the medium pH must be selected taking into account the potential dissolution of the perovskite or the formation of complexes with cations extracted from the perovskite. Whatever the choice, there will be modifications in the physicochemistry of the catalytic surface. In the case of La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3-δ</sub> perovskite, the Ni can form stable ammonium complexes at pH 10. Yet, a perovskite itself is an extremely stable system [37], Ni is found in a very low concentration and is not available outside the structure. It is for these reasons that the alkaline medium is supposed to be suitable for work. On the other hand, in the  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  perovskite, the Co could undergo an extraction by an acid medium. In this particular case, this possibility is ruled out because in an acid pH Co is stable only as  $Co^{2+}$  and in the perovskite it is in a set +3/+4, so it would need the presence of a reducer for its extraction. The reduction of the Co perovskite would present a reddish tint that was not observed later in the suspension [43]. Therefore, for both systems it is estimated that the possibilities of modifications of the solids with the proposed conditions have been minimized. For the suspension with alumina (Nyacol) it is also important to know the isoelectric point, since it will be an additive and it must be in the presence of the catalysts at the selected pH. Nyacol is far from its isoelectric point and has Zeta potential values close to 30 mV. At pH 10 both Z potential of NM and the alumina are negative, while at pH 4 both CM and alumina are positive. This would limit the agglomeration between particles because they have the same charge and could explain the behavior of suspensions with alumina as an



Fig. 9. SEM micrographs of sample 1CTA, 2CTA, 1 NTA y 2 NTA with increases of  $12 \times$  .

additive in terms of viscosity and homogeneity.

The pH value is not the only responsible for controlling the stability of the suspension by peptization-flocculation, so it is the viscosity, since it decreases the sedimentation rate of the particles. The low viscosities allow to obtain highly adherent and homogeneous coatings but with low solid loads. Therefore, in order to obtain a homogeneous coating, numerous coating layers are required. On the contrary, high viscosity values will allow a high specific load per coating, with a lower homogeneity (possible accumulations and, in the limits, blocking of channels) resulting in less adherent coatings.

On the other hand, to promote the stability of the suspension by viscosity modification, additives can be used. The long chain of surfactants containing hydrophilic and hydrophobic groups for example, is adsorbed on the surface of the catalyst leading to the steric stabilization of the suspension [44]. Thickeners that increase viscosity may also be used [1,7]. However, it should be considered that surfactants, thickeners and other additives can present competitive and synergistic mechanisms, making it difficult to predict early the behavior of such

complex mixtures. What is certain is that all functional groups of additives and pH control compounds can alter the physicochemistry of the surface of the catalyst.

The optimum viscosity ranges from 5 to 30 cP as proposed by several authors [44–46]. However, the non-Newtonian character of suspensions with high solids content makes it difficult to compare the viscosity values obtained at different cutting speeds. The rheological properties are controlled mainly by the solid content of the suspension and the peptization step (pH and additives) [47]. But, as mentioned above, the role of additives (organic or inorganic) is complex and produces synergistic or competitive effects in the process variables.

Fig. 5 shows the photographs of glass-sample which is useful as reference [37]. In the deposition on control glasses the CM catalyst adheres better and uniformly without any additive. Meanwhile, the NM catalyst has better homogeneity when it contains polyvinyl alcohol in the suspension. Nevertheless, homogeneity is not enough to decide the best working condition, besides this, the physicochemical modifications induced by the use of additives and pH regulators must be evaluated.



Fig. 10. Image of microchannels with 3D confocal microphotography.

## Table 10 Measurements of microchannel width and roughness of the base samples with alumina, XC and XN, $\mu$ m.

Muestra	а	b	с	Ra
A <sup>a</sup>	439	500	536	1.7
1C	327	431	472	3.5
2C	371	451	495	4.1
1 N	333	397	438	4.6
2 N	318	371	416	3.5

<sup>a</sup> Alumina covered microchannel.

The evaluation of the modifications of the catalytic performance can help to clarify if there are physicochemical modifications in the catalyst. In the oxidation reaction, all the samples exceed the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3.</sub> $\delta$  catalyst, evaluated from the T<sub>80</sub> (Temperature at which the conversion is 80%) (Table 6). The physical and physicochemical treatments evidently improve the activity.

The increase in the specific surface area, due to the milling effect, of around  $4 \text{ m}^2 \text{g}^{-1}$  (Table 3), can be a factor that improves the activity. However, the increase in the reducibility that facilitates redox behavior in a stable chemical environment, such as that offered by a perovskite, seems to be the determining factor in the improvement of the catalytic performance. The reducibility shown in TPR would be indicating two stages of reduction, although each peak could represent more than one stage [23]. There is a first stage of reduction between 350-450 °C and another approximately at 600 °C. In CM the shift to lower temperatures is more marked. The T<sub>onset</sub> in the reduction profiles corresponding to  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$  and CM show that grinding has a positive effect on the reducibility of the system. These values are generally higher in all the catalysts subjected to suspensions with respect to CM. When the performance results of the catalyst in the suspensions are observed, the sequence is CS4 > CS1catalytic = CS2 > CM > CS3 >  $La_{0.5}Ca_{0.5}CoO_{3-\delta}$ . The results indicate that although the observed homogeneity is similar in all the samples, in CS3 the activity is disadvantaged. The activity of the other suspensions is higher than the CM one, CS4 and CS1-CS2 samples show a very similar activity. CS1 has the advantage of being only a suspension in water without additives. It is probable that the polyvinyl alcohol leaves residues after the drying and calcination of the suspensions. If this is the case, through TGA and FT-IR, susceptible carbonaceous species should be identified, as well as, bonds detectable by FT-IR. By thermogravimetric analysis of the ground catalyst and its suspensions, nitrogenous, carbonaceous or adsorbed or deposited water can be observed. For this reason, TGA essays were carried out and Table 6 shows the values of mass loss obtained by analytical technique.

At low temperatures the loss of mass is attributed to dehydration but in all the samples an abrupt fall is observed in the range of 600–700 °C, being the highest fall for the CS3 and CS4 suspensions.

The TGA signal shows a mass loss in stages at low temperatures, most of the mass loss is attributed to dehydration and evaporation of the volatile organic components.

At high temperatures (above 600 °C) it can be assigned to decomposition of impurities from  $Co_3O_4$  to CoO [48]. However, it cannot be discarded that they are the remains of carbonates of the introduced organic species. For the same purpose, measurements were made by FT-IR.

In Fig. 6 the infrared spectra of the CM catalyst samples before and after reaction are observed. The CS3 and CS4 samples have an intense signal, corresponding to the presence of carbonaceous species. The CS1 and CS2 samples have a very weak signal at that wavenumbers. The common denominator among them is the polyvinyl alcohol as additive. In fact, these FT-IR analyses reveal the presence of carbonates, identifying the characteristic vibrational modes in 866, 1504-1492, 711 cm<sup>-1</sup> [49]. Evidently, the calcination conditions were not sufficient to eliminate the carbonaceous residues. Since it is desired to use this catalyst in a reactor that works in an autothermal manner, the catalyst must be able to work at temperatures of the reforming reaction, that is 650 °C, and remains stable in the oxidation reaction. Under this condition, the sublimation of volatile Cr compounds is not expected. This is due to the thermal treatment of the steel of the microreactor was carried out in a more extreme condition, in terms of temperature and humidity, for its corrosion than the operational catalytic reaction condition. The La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> catalyst has a calcination temperature of 700 °C, higher than the proposed working temperature. Merino et.al. did not report the sublimation of metal cations when working in these

conditions [23]. When evaluating in the oxidation of ethanol, the catalyst that has been used in the suspension and subjecting it to the extreme condition of 650 °C for one hour, the following sequence of catalytic activity was observed: CS2 > CM > CS1 = CS3 > CS4  $> La_{0.5}Ca_{0.5}CoO_{3-\delta}$ . This sequence shows that there is an eventual deactivation by thermal effect, which allows to determine that the catalyst that is less deactivated by the effect of the additives and the working temperature is CS3. Although the alumina could occlude the catalyst in its matrix, the Al<sub>2</sub>O<sub>3</sub> catalyst mixture is clearly morphologically stable and does not affect the available catalyst surface for the reaction. This deactivation in the catalyst when it is subjected to other suspension media can be due to its sintering caused by the temperature and the absence of a stable matrix such as alumina. In fact, this is what is observed in the S<sub>BET</sub> post-reaction results shown in Table 5, the specific surface areas of CSx decreases but all remain above CM. Those solids that in the suspension had Nyacol had a higher specific surface area. After the heat treatment at 650 °C this specific surface noticeably decreases.

It is interesting to note that in the CS1 sample there is no modification of the BET specific surface area, which would indicate a certain structural stability. When observing the temperature to reach 100% selectivity to CO<sub>2</sub> (Table 7), it presents modifications. However, in general, all the catalysts that were subjected to suspensions present better performance than the CM catalyst.

The observations in glass presented in Fig. 5 show that the depositions of NM solid, dispersed in the different suspensions with additives, have different behavior than the CM catalyst. The most homogeneous suspension is observed with PVOH, whose viscosity was the highest and whose value is near CS1 viscosity.

In the case of the La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> catalyst, that is tested in the reforming reaction, different results than the ones of the La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> catalyst are observed. In Fig. 7 the data of ethanol conversion, selectivity to H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> of the catalysts obtained from the suspensions, the original catalyst and the grinding one, are presented. Grinding did not significantly modify the catalytic activity. Only a decrease in the selectivities to CO and CH<sub>4</sub> was observed. The presence of acetaldehyde, ethane or ethylene in no case was detected.

Although the reduction in size due to the effect of grinding was necessary to obtain an adequate particle size, clearly this treatment did not have a negative effect on the performance of the catalyst. The greater reducibility, TPR, shown by the catalyst after grinding does not decisively influence its catalytic performance, but it could be the cause of the decrease in the CH<sub>4</sub> yield. La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3- $\delta$ </sub> has a different behavior than that used in combustion because the Ni works in the reduced state. The greater reducibility only influences the speed of *in situ* formation of Ni catalytic centers but not their catalytic performance. Based on the results obtained, preparing the suspension with the organic additive, polyvinyl alcohol, results in homogenous catalyst layers without appreciable modification in the catalytic activity.

Once selected the conditions in which the suspensions of the catalysts are stable and selecting the suspensions that present better characteristics, that is, better coverage and better catalytic performance, the washcoating is carried out in the stainless steel microchannels. The selected suspensions are CS1 and NS3. As stated above, the goal of the washcoating technique is to obtain a well-adhered catalyst and to form a homogeneous film on the surface. For the film to meet these requirements, the different variables involved in the stability of the suspension were studied. However, the preparation of the surface of the monolithic support, in this case the stainless steel microreactors, also plays an important role. This surface was thermally treated to generate roughness and alumina was deposited as a surface passivant [27].

The homogeneity of the catalyst film was observed by SEM micrographs (Fig. 8). For both, the reforming and oxidation catalyst, the deposition was effective. In both cases, 1 and 2 charges, the observed surface is homogeneous without channel obstruction. Along the microchannels the morphology is maintained, so it can be affirmed that the washcoating deposition is effective in the whole extension of the microreactor. Also, the catalyst film apparently appears to be well adhered to the metal surface. The adhesion of the catalyst is an important factor to be taken into account, since in real conditions, the catalysts for the combustion or reforming reactions, work in rigorous conditions. In Fig. 9 the SEM images of the samples with adhesion test (TA) are observed. No landslides are observed, or areas without catalyst. Obviously, the deposited layer for both the oxidation catalyst and the reforming catalyst, have an excellent adherence.

Fig. 8 shows the images with increases of 1Kx and 4Kx. In these images it can be seen a greater coverage of active phase with the increase in catalyst loading. This is corroborated with the EDX microanalysis (Table 8 and 9). Spherical growth rich in Fe is also observed. These growths are the product of the thermal treatment and it is probable that a single catalyst load will not be enough to cover them [27,28].

In the photomicrograph of Fig. 8 the combustion catalyst presents an agglomerate of variable particle sizes of between 3 and  $5\,\mu m$  but after two catalyst loads (2C, Fig. 8) a better coverage is evidenced. In the case of reforming catalyst, a similar behavior is observed.

By analyzing three-dimensional images with confocal microscopy, the film thickness can be estimated. Fig. 9 shows the 3D image of the microchannels. The film deposited on the microchannels does not have the same thickness in the walls of the microchannel as in the bottom, although they are kept along. Both the CSx samples and the NSx samples showed a decrease in thickness as we moved away from the bottom of the channel, although this effect is more marked for the CSx samples. Comparing the NS1 and NS2 samples it can be seen that the film thickness is homogenous throughout the microchannel, presenting approximately 10 µm of thickness more with the increase in catalyst load. 1C and 2C samples show a clear difference in catalyst thicknesses. While it is expected that the catalyst film increases with the load, it is not observed in this case. This can be due to three factors, the difference in the original size of the microchannel due to machining, the previously deposited alumina thickness variation, or a redissolution of the catalyst in the suspension. The best distribution of the catalyst on the surface of the microchannel for the NSx samples can be attributed to the smaller size of particle.

Another very interesting fact that this characterization technique allows us to obtain is the value of the roughness, Ra. In general, this variable is treated with images, but the technique allows obtaining a numerical value. The value of Ra is calculated from the Z heights as shown in the Fig. 10. An increase in the roughness is observed with the increase in load of the combustion catalyst and the opposite occurs with the reforming catalyst. This can also be assigned to the different sizes of the catalyst particles. Larger particle size greater roughness while smaller the particle, the smoother the surface.

It is clear that the characterization of the catalyst layer is neither simple nor exact. However, this work contributes to subsequent studies relating to the catalytic performance of the microreactor and its stability in the system.

In general, in order to achieve a well-adhered and stable supported catalyst system, it is necessary to systematically study each system separately. To follow a sequence of steps that ensure the success of the deposition is essential.

## 5. Conclusion

The study carried out with two different perovskites applied to two different reactions has shown that there are physical changes that modify their behavior against different characterization techniques. However, these modifications do not necessarily affect the catalytic performance, for which the characteristics of the reaction must be taken into account.

The physicochemical variables of the catalyst surface are influenced by the use of solvents and additives. The  $Al_2O_3$  gels, although they can occlude part of the catalyst in their bulk matrix resulting in a decrease in activity, show no loss of activity. The alumina matrix appears to morphologically stabilize the catalyst. The hydrocarbons can generate carbonaceous residues that, depending on the catalyst and the reaction in which they are used, can be more or less efficiently eliminated. The physical modification induced by the milling favors the catalytic activity, both by the increase of the specific surface area and by the improvement of the reducibility. The latest, in the case of combustion reactions, is translated into a better redox behavior of the catalyst.

Regarding the additives, and in the particular cases of this work, different behaviors were observed according to the solid in contact. For La<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>3.8</sub> catalyst, carbonaceous residues remain mainly in the suspension with the organic compound (polyvinyl alcohol) and this is reflected in lower catalytic activity. In contrast, the catalyst suspended only in water is highly efficient in homogeneous coverage and stability after working in reaction at 650 °C. This result is significant since it is not necessary to introduce additives in the washcoating suspension; there is less possibility of inferring in the characteristics of the catalyst. For the case of La<sub>0.9</sub>Mg<sub>0.1</sub>Al<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3-δ</sub> perovskite the results are different. The catalyst in suspension with an organic additive, such as the polyvinyl alcohol, resulted in a stable suspension, high homogeneity of the catalytic film and no appreciable changes in the catalytic activity. Both catalysts were successfully deposited on the surface of the metal microchannels. No obstructions or accumulations of catalyst were observed. The effective film thickness can be estimated, the catalyst with smaller particle size was more homogeneous along the microchannel. The stability of the film was excellent in severe working conditions.

## **Declaration of Competing Interest**

There is no conflict of interest. If accepted, the article will not be published elsewhere in the same form, in any language, without the written authorization of the Publisher

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