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Title: Surface Nickel particles generated by exsolution from a perovskite structure

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Keywords: Ni particles; perovskites; exsolution process; reduction conditions; TEM

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Abstract: $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$ (with $x = 0.05$ and 0.2) perovskite oxides were successfully synthesized and its behavior under reduction atmosphere was studied. HRTEM and STEM studies, coupled to HAADF and EDX detection, allowed to evidence the Ni exsolution process to the surface of the solid and to build nano-catalytic centers. The size of these centers is independent of the reduction conditions in the range studied. The high specific surface of the raw material, its porosity and the structure defects could be responsible of the low temperature at which the exsolution process starts. The content of Ni dopants allows the control of Ni centers size on the surface and the synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.

San Luis, Argentina, February 7th, 2019.

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Editor

Dear Editor, I am pleased to submit the revised version of the manuscript entitled "Surface Nickel particles generated by exolution from a perovskite structure" by Fabiola N. Aguero, Ana M. Beltrán, María Asunción Fernández, Luis E. Cadús.

Yours Faithfully,

Dra Fabiola Nerina Aguero

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Reviewer #1: In the present study $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$ (with $x=0.05$ and 0.2) perovskite oxides were synthesized and its behavior under reduction atmosphere was studied. They claimed that the Ni exsolution to the surface of the solid built nano-centers independent on the reduction conditions. Although the idea of self-formation of Ni-nano-centers from ex-perovskite is nice idea, the present work is lack of substantial study, which is temperature programmed reduction/temperature programmed oxidation cycles. In addition to use the terminology "Ni-nano-catalytic centers", it should be tested for catalytic test reaction, which is also missed in the present study. -I suggest to carry TPR/TPO cycles and study the metallic surface area /degree of dispersion of Ni-nanoparticles if they insist to consider this work to the catalysis community.

- We have previously carried TPR/TPO cycles in order to study the nature of Ni particles generated from the perovskite structure. As we expected the results showed the reduction of Ni species from the perovskite structure and after an oxidation step the results showed only the reduction of Ni from NiO over LaAlO_3 support. These experiments also evidenced an increase of metallic Ni particle size. This study was not included in this work because the aim of this work was to study the influence of reduction variables in the generated particles size.

This kind of solids was also previously used in the steam reforming reaction and published in a previous paper. [F. N. Agüero, M. R. Morales, S. Larrégola, E. M. Izurieta, E. Lopez, L. E. Cadús. *Int. J of Hy Energ* 40(2015)15510-15520. <http://dx.doi.org/10.1016/j.ijhydene.2015.08.051>]. These solids showed to be active and stable in the studied reaction demonstrating that the efficiency of the generated Ni particles with small size from a perovskite structure was higher than that obtained from Ni particles generated from an impregnation process which presented even higher dispersion of metal particles. However, this work is focused in the study of Ni generated particles size in different conditions of synthesis. The present work provides among its highlights the perspective that it is possible to control the exsolution and therefore the size of the catalytic centers. Additionally, the smaller the Ni loads, the less the imbalance in the support structure will be. As it is mentioned in the article, this study can lay the groundwork for the design of the catalysts even used in other reactions that employ metal catalysts.

-In addition English revision is necessary

- An intense revision of the manuscript in order to check the grammar and the spelling errors have been made following the reviewer suggestions.

Reviewer #2: The authors prepared the $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$ perovskite oxides via a citrate route, investigated the Ni exsolution processes, characterized their physicochemical properties. This work contains some new results and may be

accepted for publication. However, the authors should modify their manuscript before acceptance for publication according to the following comments:

1. Why do the authors think that the Ni particles were anchored to the support? What is the evidence?

We could observed from TEM study, Figure 6 in the article that Ni particles are anchored to the support. The transition of phases are clear in the image and this is explained in the work.

Usually, the reduction gas mixture is H_2 and Ar (balance). Why do the authors use H_2 and N_2 (balance) in the reduction processes?

The balance of the reduction mixture could be done with any inert gas, N_2 is one of the gases usually used as it is Ar or He.

2. After reduction of $LaAl_{1-x}Ni_xO_3$, the lattice positions occupied by the original Ni atoms became cationic vacancies? If the perovskite oxide was changed to $LaAlO_3$ after reduction, there would be presence of La_2O_3 impurity phase.

The exolution of Ni particles certainly generates the presence of cationic vacancies. In fact after the reduction process only metallic Ni and $LaAlO_3$ phases were detected.

3. There are a large number of inappropriate English words or expressions in the manuscript. The authors should carefully polish the English of the whole manuscript.

-An intense revision of the manuscript in order to check the grammar and the spelling errors have been made following the reviewer suggestions

Surface Nickel particles generated by exsolution from a perovskite structure

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Abstract

LaAl_{1-x}Ni_xO₃ (with x= 0.05 and 0.2) perovskite oxides were successfully synthesized and its behavior under reduction atmosphere was studied. HRTEM and STEM studies, coupled to HAADF and EDX detection, allowed to evidence the Ni exsolution process to the surface of the solid and to build nano-catalytic centers. The size of these centers is independent of the reduction conditions in the range studied. The high specific surface of the raw material, its porosity and the structure defects could be responsible of the low temperature at which the exsolution process starts. The content of Ni dopants allows the control of Ni centers size on the surface and the synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.

Keywords: Ni particles, perovskites, exsolution process, reduction conditions, TEM

1. Introduction

Heterogeneous catalysis is a complex phenomenon that studies, both surface architecture of catalysts and, in many cases, the interaction of the catalytic centers with the support. Surface architecture involves size of catalytic centers, dispersion of metals and repartition between two or more metals. Stability of the catalytic centers could be strongly influenced by the interaction of the metals with the support [1]. The support could play an important role in redox processes of regeneration of the catalytic centers, in the control of deactivation process by carbon formation [2] or preventing the sintering of metallic particles [3].

Ni based catalysts have been widely used in steam reforming reactions due to the ability of Ni particles to break the C-C bonds. However, these catalysts suffer from several limitations that hinder their further application, including sintering of Ni particles agglomeration and carbon coking [2]. Steam reforming is a structure sensible reaction [4], thus, the activity and selectivity of catalysts can be improved by controlling the size of Ni centers on the surface. This objective can be rise by decorating the surface with metal nanoparticles. Traditionally, Ni particles are loaded to the support surface by chemical or physical deposition but such nanoparticles tend to sinter [5,6]. This problem would be solved with Ni particles strongly attached to the support and with a smaller size [7]. It is probable that if Ni exsolution is made from a host structure, Ni particles will be linked to the support and will improve the resistance to sinterisation. In addition, it is necessary to

control the size of the formed Ni particles considering the synthesis and exsolution process parameters. The most relevant parameters are the catalyst treatment atmosphere and Ni composition of the catalyst precursor. It is also important to note that a relatively high specific surface area is required since this material will be used as a catalyst and this area could modify the Ni exsolution process.

Perovskite type oxides have been widely used as catalysts in several reactions. Besides, many of these oxides have been used as precursor of catalysts considering it as a host structure of cations. [8,9]. In $ABB'O_3$ mixed oxides perovskites, the exsolution process of B' is favored in comparison with B cation, on the basis of their metallic character [10-12], elements with more metallic character tends to be eliminated to the surface because the Gibbs free energy change acts as the driving force. Thus, the catalyst design could be done considering this characteristic. However, it is necessary to have a stable host structure where A and B sites remain oxidized during reduction, in order to maintain the perovskite phase as catalyst support. In literature, there are evidences of the exsolution process. Arrive *et al.* [7] worked with a $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_3$ perovskite which is used as electrode for solid oxide cell; they showed a thermogravimetric analysis in Ar/H₂ atmosphere, where a significant weight loss could be observed at 1000 °C corresponding to oxygen departures related to Ni and/or Ti cation reduction. They showed that Ni nanoparticles were obtained after a reduction process at 1200 °C. At this temperature there is an important specific surface area decrease and, then, the material is not suitable for catalysis. Thommy *et al.* [13] compared impregnation versus an exsolution process in order to improve electrocatalytic properties of $LaSrCrMnO_3$ based anodes. They showed that under hydrogen atmosphere and, in comparison to impregnation approach, exsolution does not offer significant advantages with regard to the polarization phenomena. However, the exsolution

method produces dispersed nanoparticles firmly anchored to grain surface which minimizes nanoparticles agglomeration during ageing. In a previous work, the same authors used exsolution method to improve the electrocatalytic properties of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5-x}\text{Ni}_x\text{O}_{3-x}$ [14].

There are many works in literature about obtaining metal nanoparticles highly dispersed on a support. However, there are still some questions that deserve to be responded: is it possible to achieve good results by growing up Ni particles from a host structure? Is there any influence of the parameters of the exsolution process on the final architecture of the catalytic surface? Is there any influence of the morphology of the precursor on the exsolution process?

The insights developed in this work may help to find further strategies for catalyst design. The aim is to study the parameters involved in the Ni exsolution process from a stable perovskite structure, LaAlO_3 . By this way, a higher knowledge in the design of a catalyst with defined characteristics would be reached. Even if this study has been made on a steam reforming catalyst, it could be eventually used as reference for other metallic catalyst.

2. Experimental

2.1 Catalysts preparation

$\text{LaAl}_{1-y}\text{Ni}_y\text{O}_3$ ($y = 0, 0.05, 0.2$) perovskites were prepared by the citrate method [15]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$ were dissolved in water and were added to an excess citric acid solution. The solution was slowly evaporated under vacuum in a rotavapor at 75 °C until a gel was obtained. This gel was dried in a vacuum oven, slowly increasing the temperature to 200 °C and keeping this temperature overnight, to produce a

solid amorphous citrate precursor. The resulting precursor was milled and then calcined in air at 800 °C for 2 h. The samples were named LaNi_y, with y = 0.05 and 0.2.

In order to generate Ni particles, samples were submitted to a reduction process. The reducing gas was a mixture of 5 vol % H₂/N₂, at a total flow rate of 30 mL min⁻¹. The temperature was increased from room temperature to 650 or 750 °C with a heating rate of 5, 10 or 15 °C min⁻¹ maintaining this temperature for 30 or 60 min. Table 1 summaries the conditions of the reduced samples.

2.2 Samples Characterization

2.2.1 BET Specific Surface Area Measurements (SBET)

The specific surface area of the samples was calculated by the BET method from the nitrogen adsorption isotherms obtained at 77 K. A Gemini V from Micromeritics apparatus was used.

2.2.2 X-ray Diffraction (XRD)

XRD patterns were obtained by using a Rigaku diffractometer operated at 30 kV and 25 mA by employing Cu K α radiation with Nickel filter (λ = 0.15418 nm).

2.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained with a Multitecnic UniSpecs equipment with a dual X ray source of Mg/Al and an hemispheric analyzer PHOIBOS 150. A pass energy of 30 eV and an Al anode operated at 100 W was used. The pressure was kept under 29x10⁻⁸ mbar

2.2.4 Scanning-Transmission electron microscopy (STEM)

TEM (Transmission Electron Microscopy) and STEM (Scanning-Transmission Electron Microscopy) studies were performed on a FEI Tecnai G2 F30 FEG (Field Emission Gun) microscope, equipped with a HAADF (High Angle Annular Dark Field) detector from Fischione Instruments. Images were obtained in TEM and HAADF-STEM mode at 300 kV. Compositional analyses were performed by INCA X-Max 80 silicon drift detector (SDD) for Energy-Dispersive X-Ray (EDX). In particular, STEM-EDX line profiles were acquired across the nanoparticles to confirm their composition. For TEM observations, powdery samples were homogeneously dispersed in ethanol by ultrasound and dropped on a carbon film grid.

3. Results and Discussion

The base perovskite used in this work as host structure of Ni cations is a LaAlO_3 phase (JCPDS file 31-22) with PM-3M space group and crystal planes with different polarity. In a previous work, it was demonstrated that Ni partial substitution in B position was successfully reached with a 20 % molar substitution corresponding to a Ni weight concentration of 2.5 % [16]. As it was above mentioned in the introduction section, the success in the catalyst design would be possible with a stable host structure, where A and B sites remain oxidized during reduction, in order to maintain the perovskite phase as catalyst support. The stability of the host structure was effectively proven. Figure 1 shows the XRD patterns of $\text{LaNi}_{0.2}$ before and after the reduction process ($\text{LaNi}_{0.2}\text{b}$). There are no differences between patterns. The stability of LaAlO_3 phase is clear. Evidences of the presence of other phases products of the reduction process were not found. This fact can be

explained from ΔG values calculated with HSC Chemistry 5.1 program. This program calculates the ΔG values considering the reduction atmosphere, the temperature and the cations involved (Figure 2). La and Al oxides are thermodynamically stable under reduction conditions. La and Al oxides have $\Delta G > 0$ at the simulated reduction conditions while nickel oxide is easily reducible. These data show that it is possible to imagine the exsolution of Ni in order to decorate the surface in a controlled manner.

There is another factor that can contribute Ni to overcome the energy barrier to arise the surface. Perovskites type solids are not homogeneous. In fact, Lanthanum based perovskites catalysts show a La/B cation atomic ratio determined from XPS higher than 1 [17]. Some authors have found that the stress and electronics effects could be responsible of difference in the concentration of dopant atoms at the surface with respect to the bulk [18]. This inhomogeneous concentration of the dopant atoms could help to drive the exsolution process. In addition, this particularity could aid to obtain isolated clusters of Ni strongly anchored to the support, the LaAlO_3 perovskite. When the exsolution process starts, the concentration of dopant atoms increases at the vicinity of the surface [19]. A XPS study of perovskites after and before the reduction process could be useful to see this phenomenon. Actually, results showed in Table 2 indicate that after reduction the Ni/(La+Al) atomic ratio increases from 0.04 to 0.09 for $\text{LaNi}_{0.2}$ and the Ni/Al atomic ratio increases from 0.06 to 0.13. These data indicate that Ni migrates to the surface enriching it, considering that XPS is a surface characterization of the most external layer of atoms. It is expected that Ni nanoparticles grow from the perovskite structure. This growth process starts when a nucleation center is obtained. But this process could take place both at the surface and in the bulk of the host material. According to Oh et al. [20] it is expected the nucleation of

particles on the surface rather than in the bulk due to a smaller energy strain. The nucleation center could be responsible of an increase in the growth rate due to a hydrogen spill over generated on it. In addition, XRD pattern does not show any line corresponding to Ni diffraction. It is possible that Ni-nanoparticles are very small and well-dispersed on the support surface as it is expected.

In order to obtain further information regarding the exsolution process and the formation of Ni-nanoparticles, a systematic TEM study was carried out, including HRTEM, HAADF-STEM and EDX-STEM. This TEM study was performed to address four issues: 1) morphological characterization of the catalyst and localization of the expected Ni-nanoparticles; 2) influence of the reduction temperature, reduction time and heating rate on the nanoparticle size; 3) influence of the composition of Ni on the exsolved nanoparticles size; and finally: 4) Interaction of Ni-nanoparticles on the surface.

Morphology of the catalyst and localization of the expected Ni-nanoparticles.

Figure 3 shows HAADF-STEM images of the catalyst LaNi_{0.2} (a) before and (b), after reduction for LaNi_{0.2}b. It is worth to mention that contrast on HAADF-STEM is proportional to $t \cdot Z^n$, where t represents the specimen thickness crossed by the electron beam and Z is the averaged atomic mass of the material that interacts with the electron beam, with n ranging between 1.6 and 1.9 in most cases [21]. Therefore, the observed black areas should correspond to the presence of large pores, which are clearly observed in a wide range of sizes in the calcined sample.

Perovskites in this work were synthesized by the citrate method that provides solids with relatively high specific surface area (SSA), around $7 \text{ m}^2\text{g}^{-1}$ (Table 2) in comparison to that obtained from ceramics methods with high calcination temperatures, generally higher than

1000 °C. The exsolution process in this work was made at lower temperatures than those reported in several studies of solid oxide fuel cells materials. In those papers [7,21] specific surface area are not reported but the high calcination and reduction temperatures are indicative of a sintered material with small specific surface area. The SSA obtained for perovskites in this work is explained on the basis of a porous material, as it is clearly observed by TEM (for example, see Fig. 3-5). The porosity of sample would favor the Ni exsolution process due to the presence of high stress and electronics effects in a surface boundary. The stress at the surface could aid the exsolution process by a decrease of the driving force necessary to start it. Intrinsic properties such as surface features, mechanical stress and related strains [20] and the presence of defects as oxygen vacancies and dislocations [22,23] could have an impact in the nucleation sites. This agrees with what we explained in a previous paper about the presence of oxygen vacancies in the LaAlO_3 base perovskite, that reveals high content of Os/Ol ratio and high temperatures reduction signals [16]. The morphology of the samples after reduction was also studied by HAADF-STEM (Fig. 3b), showing the same porous morphology. Ni-nanoparticles are expected to be in such reduced samples. The contrast on HAADF-STEM images may help to identify the Ni-nanoparticles. However, in this case, it is not so straight forward because, on one hand, there were Ni-metal nanoparticles ($Z = 28$) and, on the other hand, LaAlO_3 (average $Z \approx 19$). Furthermore, Ni-nanoparticles are supported on the perovskite. Considering all these aspects, in principle, Ni-nanoparticle may present a slightly brighter contrast than the perovskite. In fact, it has been possible to identify in HAADF images some brighter particles which may correspond to Ni-nanoparticles, as it is marked by an arrow in Fig. 3b. The presence of Ni in these nanoparticles have been confirmed by acquiring EDX-STEM line profiles across them. This strategy of analyses (EDX-STEM profiles) has been

employed to investigate all the catalysts of this work, as it will be shown in the next sections.

Effect of the reduction conditions on the Ni-nanoparticle size

The influence of the reduction temperature, heating rate and reduction time in the nanoparticle size was studied. Figure 4 shows STEM-HAADF images, in which representative Ni-nanoparticles have been detected for LaNi_{0.2} samples after different reduction conditions. Particle size was measured on STEM-HAADF images, after identifying the Ni signal in the EDX line profile. The corresponding line profiles along one nanoparticle clearly show the strong increase of the Ni signal over them. Table 3 shows the results of Ni-nanoparticles average sizes obtained as a function of reduction treatment conditions. It can be observed that Ni-nanoparticles size practically does not change in the studied reduction conditions range. They are not completely round and their size is around 20 nm. Gao *et al.* [19] also studied the influence of reduction variables in Ni-nanoparticle size from a La_{0.4}Sr_{0.4}Sc_{0.9}Ni_{0.1}O_{3- δ} perovskite material. They found that at higher reduction time, higher particles size was observed. However, the curves of particle size as a function of reduction time became asymptotic at higher reduction time. In this work, the effect of low reduction time was studied considering the need to obtain the minimum particle size. Moreover, it must be considered the feasibility to carry out the reduction pre-treatment in the catalytic process. For this reason, the experiments were carried out under constant concentration of hydrogen conditions, 5 vol. % H₂/N₂. Reduction temperatures were chosen considering TPR results trying to avoid a sinterization of catalyst. Probably, at these reduction conditions, only part of bulk Ni²⁺ has been transformed into Ni-metal at the

surface, although the main part was still in the perovskite structure. It is clearly observed that there is not a parametric sensibility of Ni-particle size in the range studied.

Ni concentration in the host structure

It is possible that the maximum size of Ni-nanoparticles depends on total amount of Ni atoms in the bulk material. In fact, Gao *et al.* have suggested, by DFT calculations, that the total amount of Ni could be a reasonable factor limiting the maximum size of the nanoparticles [19]. As it was above discussed, the size of particles does not depend on the reduction conditions used in this work. To prove the effect of Ni content on the host structure a LaNi_{0.05} perovskite was synthesized, reduced and observed by HRTEM and STEM. Figure 5 shows a STEM-HAADF image, together with the corresponding EDX-STEM line profile, of a representative Ni-nanoparticle located on the perovskite surface for the reduced LaNi_{0.05} sample. Already from the line profile along the nanoparticle it is clear, in comparison to Fig. 4, that nanoparticles are smaller. The estimated average value from the study of several nanoparticles is also included in Table 2. We found that the size of Ni centers on the surface is almost proportional to the Ni content. A quarter of Ni dopants gives centers that are almost a quarter smaller than those observed for LaNi_{0.2b}.

Interaction of Ni-nanoparticles with the surface

Figure 6 shows a HRTEM image of a representative small Ni-nanoparticle attached to the main bulk of the perovskite for the reduced LaNi_{0.2b} sample. The lattice space of the perovskite bulk is clearly visible and the Filtered Fourier Transform (FFT) of the marked area shows spots corresponding to {010} planes of the crystalline structure of the LaAlO₃

base phase. The small Ni-nanoparticle appears anchored to the perovskite, also showing a crystalline structure, as seen in the HRTEM image and the FFT pattern. Nanoparticles are not round, instead, they appeared faceted to some extent. The analysis of the FFT patterns indicates that Ni-nanoparticles can be oxidized to NiO on the surface as it may be expected due to the air exposure.

As it has been demonstrated by the STEM-EDX line profile analyses, the concentration of Ni in the nanoparticle is significantly higher than that on the host material. It is possible that the growth results from the diffusion of Ni^{2+} ions to the nanoparticle followed by the reduction to Ni metal. The Ni metal could activate hydrogen spill over to accelerate the process of reduction. As a result Ni-nanoparticles can be strongly anchored at the bulk perovskite grains, which would be very beneficial for their stability in reaction conditions.

4. Conclusions

$\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$ perovskite oxides (with $x = 0.05$ and 0.2) were successfully synthesized and its behavior under reduction atmosphere was studied. HRTEM and HAADF-STEM studies, coupled to EDX detector, allowed evidencing the Ni exsolution process to the surface of the oxides to build nano-catalytic centers. The size of these centers did not depend on the reduction conditions for the studied range. This range was limited in order to obtain a material suitable for catalysis from the point of view of the morphology and the specific surface area.

The high specific surface of the raw material, its porosity and the structure defects could be responsible of the low temperature at which the exsolution process starts. The content of Ni dopants allows the control of Ni centers size on the surface and the synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.

Therefore, this study could give certain information about the design of nano-materials that could be used as catalysts for several reactions. In general, reactions in which metals particles with small nanoparticle size, highly dispersed and well anchored on a support, are necessary.

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Table captions.

Table 1: Conditions of the reduced samples.

Table 2: XPS of samples before and after the reduction treatments. S_{BET} results.

Table 3: Ni particle mean size values determined by TEM analysis as a function of reduction conditions and Ni content.

Table 1. Conditions of the reduced samples

Sample	Reduction Conditions		
	T (°C)	Heating rate (°C/min)	t (min)
LaNi _{0.2} a	650	15	30
LaNi _{0.2} b	650	15	60
LaNi _{0.2} c	750	5	30
LaNi _{0.2} d	750	15	30
LaNi _{0.05b}	650	15	60

Table 2. XPS of samples before and after the reduction treatments. S_{BET} results.

Sample	XPS Results		S_{BET} (m ² /g)
	Ni/(La+Al)	Ni/Al	
LaNi _{0.2} b	0.09	0.13	
LaNi _{0.2}	0.04	0.06	7.4
LaNi _{0.05} b	0.06	0.10	
LaNi _{0.05}	0.05	0.10	6.3

Table 3. Ni particle mean size values determined by TEM analysis as a function of reduction conditions and Ni content.

Sample	Reduction Conditions			Ni Particle Mean size (nm)
	T (°C)	B (°C/min)	t (min)	
LaNi _{0.2} a	650	15	30	18.5
LaNi _{0.2} b	650	15	60	20
LaNi _{0.2} c	750	5	30	22
LaNi _{0.2} d	750	15	30	22
LaNi _{0.05} b	650	15	60	6

Figure captions

Figure 1: X-Ray diffraction patterns obtained for calcined samples.

Figure 2: Gibbs free energy for the reduction of La, Al and Ni oxides to corresponding metals in H₂. Generated by the HSC chemistry software. The reaction was considered as $1/xM_xO_y + y/xH_2(g) = M + y/xH_2O(g)$.

Figure 3: STEM images of the samples: a) LaNi_{0.2} and b) LaNi_{0.2b}

Figure 4: STEM images and EDX-STEM profiles of sample LaNi_{0.2} after different reduction conditions (a-d) according to Table 1. The arrow indicates the direction along which the EDX profile was acquired over the particle.

Figure 5: STEM image and EDX-STEM profile taken over the particle (along the arrow direction) for the LaNi_{0.05b} sample. Inset: detail of the EDX profile.

Figure 6: HRTEM image of sample LaNi_{0.2b}. Insets: HRTEM detail of the Ni-nanoparticle and FFT of two marked areas on the Ni-nanoparticle and the perovskite.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Surface Nickel particles generated by exsolution from a perovskite structure

(Note: The corrections included in the revised version were of English language)

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Abstract

LaAl_{1-x}Ni_xO₃ (with x= 0.05 and 0.2) perovskite oxides were successfully synthesized and its behavior under reduction atmosphere was studied. HRTEM and STEM studies, coupled to HAADF and EDX detection, allowed to evidence the Ni exsolution process to the surface of the solid and to build nano-catalytic centers. The size of these centers is independent of the reduction conditions in the range studied. The high specific surface of the raw material, its porosity and the structure defects could be responsible of the low temperature at which the exsolution process starts. The content of Ni dopants allows the control of Ni centers size on the surface and the synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.

Keywords: Ni particles, perovskites, exsolution process, reduction conditions, TEM

1. Introduction

Heterogeneous catalysis is a complex phenomenon that studies, both surface architecture of catalysts and, in many cases, the interaction of the catalytic centers with the support. Surface architecture involves size of catalytic centers, dispersion of metals and repartition between two or more metals. Stability of the catalytic centers could be strongly influenced by the interaction of the metals with the support [1]. The support could play an important role in redox processes of regeneration of the catalytic centers, in the control of deactivation process by carbon formation [2] or preventing the sintering of metallic particles [3].

Ni based catalysts have been widely used in steam reforming reactions due to the ability of Ni particles to break the C-C bonds. However, these catalysts suffer from several limitations that hinder their further application, including sintering of Ni particles agglomeration and carbon coking [2]. Steam reforming is a structure sensible reaction [4], thus, the activity and selectivity of catalysts can be improved by controlling the size of Ni centers on the surface. This objective can be rise by decorating the surface with metal nanoparticles. Traditionally, Ni particles are loaded to the support surface by chemical or physical deposition but such nanoparticles tend to sinter [5,6]. This problem would be solved with Ni particles strongly attached to the support and with a smaller size [7]. It is probable that if Ni exsolution is made from a host structure, Ni particles will be linked to

the support and will improve the resistance to sinterisation. In addition, it is necessary to control the size of the formed Ni particles considering the synthesis and exsolution process parameters. The most relevant parameters are the catalyst treatment atmosphere and Ni composition of the catalyst precursor. It is also important to note that a relatively high specific surface area is required since this material will be used as a catalyst and this area could modify the Ni exsolution process.

Perovskite type oxides have been widely used as catalysts in several reactions. Besides, many of these oxides have been used as precursor of catalysts considering it as a host structure of cations. [8,9]. In $ABB'O_3$ mixed oxides perovskites, the exsolution process of B' is favored in comparison with B cation, on the basis of their metallic character [10-12], elements with more metallic character tends to be eliminated to the surface because the Gibbs free energy change acts as the driving force. Thus, the catalyst design could be done considering this characteristic. However, it is necessary to have a stable host structure where A and B sites remain oxidized during reduction, in order to maintain the perovskite phase as catalyst support. In literature, there are evidences of the exsolution process. Arrive *et al.* [7] worked with a $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_3$ perovskite which is used as electrode for solid oxide cell; they showed a thermogravimetric analysis in Ar/H₂ atmosphere, where a significant weight loss could be observed at 1000 °C corresponding to oxygen departures related to Ni and/or Ti cation reduction. They showed that Ni nanoparticles were obtained after a reduction process at 1200 °C. At this temperature there is an important specific surface area decrease and, then, the material is not suitable for catalysis. Thommy *et al.* [13] compared impregnation versus an exsolution process in order to improve electrocatalytic properties of $LaSrCrMnO_3$ based anodes. They showed that under hydrogen atmosphere and, in comparison to impregnation approach, exsolution does not offer

significant advantages with regard to the polarization phenomena. However, the exsolution method produces dispersed nanoparticles firmly anchored to grain surface which minimizes nanoparticles agglomeration during ageing. In a previous work, the same authors used exsolution method to improve the electrocatalytic properties of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5-x}\text{Ni}_x\text{O}_{3-x}$ [14].

There are many works in literature about obtaining metal nanoparticles highly dispersed on a support. However, there are still some questions that deserve to be responded: is it possible to achieve good results by growing up Ni particles from a host structure? Is there any influence of the parameters of the exsolution process on the final architecture of the catalytic surface? Is there any influence of the morphology of the precursor on the exsolution process?

The insights developed in this work may help to find further strategies for catalyst design. The aim is to study the parameters involved in the Ni exsolution process from a stable perovskite structure, LaAlO_3 . By this way, a higher knowledge in the design of a catalyst with defined characteristics would be reached. Even if this study has been made on a steam reforming catalyst, it could be eventually used as reference for other metallic catalyst.

2. Experimental

2.1 Catalysts preparation

$\text{LaAl}_{1-y}\text{Ni}_y\text{O}_3$ ($y = 0, 0.05, 0.2$) perovskites were prepared by the citrate method [15]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$ were dissolved in water and were added to an excess citric acid solution. The solution was slowly evaporated under vacuum in a rotavapor at 75 °C until a gel was obtained. This gel was dried in a vacuum oven, slowly increasing the temperature to 200 °C and keeping this temperature overnight, to produce a

solid amorphous citrate precursor. The resulting precursor was milled and then calcined in air at 800 °C for 2 h. The samples were named LaNi_y, with y = 0.05 and 0.2.

In order to generate Ni particles, samples were submitted to a reduction process. The reducing gas was a mixture of 5 vol % H₂/N₂, at a total flow rate of 30 mL min⁻¹. The temperature was increased from room temperature to 650 or 750 °C with a heating rate of 5, 10 or 15 °C min⁻¹ maintaining this temperature for 30 or 60 min. Table 1 summaries the conditions of the reduced samples.

2.2 Samples Characterization

2.2.1 BET Specific Surface Area Measurements (SBET)

The specific surface area of the samples was calculated by the BET method from the nitrogen adsorption isotherms obtained at 77 K. A Gemini V from Micromeritics apparatus was used.

2.2.2 X-ray Diffraction (XRD)

XRD patterns were obtained by using a Rigaku diffractometer operated at 30 kV and 25 mA by employing Cu K α radiation with Nickel filter (λ = 0.15418 nm).

2.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained with a Multitecnic UniSpecs equipment with a dual X ray source of Mg/Al and an hemispheric analyzer PHOIBOS 150. A pass energy of 30 eV and an Al anode operated at 100 W was used. The pressure was kept under 29x10⁻⁸ mbar

2.2.4 Scanning-Transmission electron microscopy (STEM)

TEM (Transmission Electron Microscopy) and STEM (Scanning-Transmission Electron Microscopy) studies were performed on a FEI Tecnai G2 F30 FEG (Field Emission Gun) microscope, equipped with a HAADF (High Angle Annular Dark Field) detector from Fischione Instruments. Images were obtained in TEM and HAADF-STEM mode at 300 kV. Compositional analyses were performed by INCA X-Max 80 silicon drift detector (SDD) for Energy-Dispersive X-Ray (EDX). In particular, STEM-EDX line profiles were acquired across the nanoparticles to confirm their composition. For TEM observations, powdery samples were homogeneously dispersed in ethanol by ultrasound and dropped on a carbon film grid.

3. Results and Discussion

The base perovskite used in this work as host structure of Ni cations is a LaAlO_3 phase (JCPDS file 31-22) with PM-3M space group and crystal planes with different polarity. In a previous work, it was demonstrated that Ni partial substitution in B position was successfully reached with a 20 % molar substitution corresponding to a Ni weight concentration of 2.5 % [16]. As it was above mentioned in the introduction section, the success in the catalyst design would be possible with a stable host structure, where A and B sites remain oxidized during reduction, in order to maintain the perovskite phase as catalyst support. The stability of the host structure was effectively proven. Figure 1 shows the XRD patterns of $\text{LaNi}_{0.2}$ before and after the reduction process ($\text{LaNi}_{0.2b}$). There are no differences between patterns. The stability of LaAlO_3 phase is clear. Evidences of the presence of other phases products of the reduction process were not found. This fact can be

explained from ΔG values calculated with HSC Chemistry 5.1 program. This program calculates the ΔG values considering the reduction atmosphere, the temperature and the cations involved (Figure 2). La and Al oxides are thermodynamically stable under reduction conditions. La and Al oxides have $\Delta G > 0$ at the simulated reduction conditions while nickel oxide is easily reducible. These data show that it is possible to imagine the exsolution of Ni in order to decorate the surface in a controlled manner.

There is another factor that can contribute Ni to overcome the energy barrier to arise the surface. Perovskites type solids are not homogeneous. In fact, Lanthanum based perovskites catalysts show a La/B cation atomic ratio determined from XPS higher than 1 [17]. Some authors have found that the stress and electronics effects could be responsible of difference in the concentration of dopant atoms at the surface with respect to the bulk [18]. This inhomogeneous concentration of the dopant atoms could help to drive the exsolution process. In addition, this particularity could aid to obtain isolated clusters of Ni strongly anchored to the support, the LaAlO_3 perovskite. When the exsolution process starts, the concentration of dopant atoms increases at the vicinity of the surface [19]. A XPS study of perovskites after and before the reduction process could be useful to see this phenomenon. Actually, results showed in Table 2 indicate that after reduction the Ni/(La+Al) atomic ratio increases from 0.04 to 0.09 for $\text{LaNi}_{0.2}$ and the Ni/Al atomic ratio increases from 0.06 to 0.13. These data indicate that Ni migrates to the surface enriching it, considering that XPS is a surface characterization of the most external layer of atoms. It is expected that Ni nanoparticles grow from the perovskite structure. This growth process starts when a nucleation center is obtained. But this process could take place both at the surface and in the bulk of the host material. According to Oh et al. [20] it is expected the nucleation of

particles on the surface rather than in the bulk due to a smaller energy strain. The nucleation center could be responsible of an increase in the growth rate due to a hydrogen spill over generated on it. In addition, XRD pattern does not show any line corresponding to Ni diffraction. It is possible that Ni-nanoparticles are very small and well-dispersed on the support surface as it is expected.

In order to obtain further information regarding the exsolution process and the formation of Ni-nanoparticles, a systematic TEM study was carried out, including HRTEM, HAADF-STEM and EDX-STEM. This TEM study was performed to address four issues: 1) morphological characterization of the catalyst and localization of the expected Ni-nanoparticles; 2) influence of the reduction temperature, reduction time and heating rate on the nanoparticle size; 3) influence of the composition of Ni on the exsolved nanoparticles size; and finally: 4) Interaction of Ni-nanoparticles on the surface.

Morphology of the catalyst and localization of the expected Ni-nanoparticles.

Figure 3 shows HAADF-STEM images of the catalyst LaNi_{0.2} (a) before and (b), after reduction for LaNi_{0.2}b. It is worth to mention that contrast on HAADF-STEM is proportional to $t \cdot Z^n$, where t represents the specimen thickness crossed by the electron beam and Z is the averaged atomic mass of the material that interacts with the electron beam, with n ranging between 1.6 and 1.9 in most cases [21]. Therefore, the observed black areas should correspond to the presence of large pores, which are clearly observed in a wide range of sizes in the calcined sample.

Perovskites in this work were synthesized by the citrate method that provides solids with relatively high specific surface area (SSA), around $7 \text{ m}^2\text{g}^{-1}$ (Table 2) in comparison to that obtained from ceramics methods with high calcination temperatures, generally higher than

1000 °C. The exsolution process in this work was made at lower temperatures than those reported in several studies of solid oxide fuel cells materials. In those papers [7,21] specific surface area are not reported but the high calcination and reduction temperatures are indicative of a sintered material with small specific surface area. The SSA obtained for perovskites in this work is explained on the basis of a porous material, as it is clearly observed by TEM (for example, see Fig. 3-5). The porosity of sample would favor the Ni exsolution process due to the presence of high stress and electronics effects in a surface boundary. The stress at the surface could aid the exsolution process by a decrease of the driving force necessary to start it. Intrinsic properties such as surface features, mechanical stress and related strains [20] and the presence of defects as oxygen vacancies and dislocations [22,23] could have an impact in the nucleation sites. This agrees with what we explained in a previous paper about the presence of oxygen vacancies in the LaAlO_3 base perovskite, that reveals high content of Os/Ol ratio and high temperatures reduction signals [16]. The morphology of the samples after reduction was also studied by HAADF-STEM (Fig. 3b), showing the same porous morphology. Ni-nanoparticles are expected to be in such reduced samples. The contrast on HAADF-STEM images may help to identify the Ni-nanoparticles. However, in this case, it is not so straight forward because, on one hand, there were Ni-metal nanoparticles ($Z = 28$) and, on the other hand, LaAlO_3 (average $Z \approx 19$). Furthermore, Ni-nanoparticles are supported on the perovskite. Considering all these aspects, in principle, Ni-nanoparticle may present a slightly brighter contrast than the perovskite. In fact, it has been possible to identify in HAADF images some brighter particles which may correspond to Ni-nanoparticles, as it is marked by an arrow in Fig. 3b. The presence of Ni in these nanoparticles have been confirmed by acquiring EDX-STEM line profiles across them. This strategy of analyses (EDX-STEM profiles) has been

employed to investigate all the catalysts of this work, as it will be shown in the next sections.

Effect of the reduction conditions on the Ni-nanoparticle size

The influence of the reduction temperature, heating rate and reduction time in the nanoparticle size was studied. Figure 4 shows STEM-HAADF images, in which representative Ni-nanoparticles have been detected for LaNi_{0.2} samples after different reduction conditions. Particle size was measured on STEM-HAADF images, after identifying the Ni signal in the EDX line profile. The corresponding line profiles along one nanoparticle clearly show the strong increase of the Ni signal over them. Table 3 shows the results of Ni-nanoparticles average sizes obtained as a function of reduction treatment conditions. It can be observed that Ni-nanoparticles size practically does not change in the studied reduction conditions range. They are not completely round and their size is around 20 nm. Gao *et al.* [19] also studied the influence of reduction variables in Ni-nanoparticle size from a La_{0.4}Sr_{0.4}Sc_{0.9}Ni_{0.1}O_{3- δ} perovskite material. They found that at higher reduction time, higher particles size was observed. However, the curves of particle size as a function of reduction time became asymptotic at higher reduction time. In this work, the effect of low reduction time was studied considering the need to obtain the minimum particle size. Moreover, it must be considered the feasibility to carry out the reduction pre-treatment in the catalytic process. For this reason, the experiments were carried out under constant concentration of hydrogen conditions, 5 vol. % H₂/N₂. Reduction temperatures were chosen considering TPR results trying to avoid a sinterization of catalyst. Probably, at these reduction conditions, only part of bulk Ni²⁺ has been transformed into Ni-metal at the

surface, although the main part was still in the perovskite structure. It is clearly observed that there is not a parametric sensibility of Ni-particle size in the range studied.

Ni concentration in the host structure

It is possible that the maximum size of Ni-nanoparticles depends on total amount of Ni atoms in the bulk material. In fact, Gao *et al.* have suggested, by DFT calculations, that the total amount of Ni could be a reasonable factor limiting the maximum size of the nanoparticles [19]. As it was above discussed, the size of particles does not depend on the reduction conditions used in this work. To prove the effect of Ni content on the host structure a LaNi_{0.05} perovskite was synthesized, reduced and observed by HRTEM and STEM. Figure 5 shows a STEM-HAADF image, together with the corresponding EDX-STEM line profile, of a representative Ni-nanoparticle located on the perovskite surface for the reduced LaNi_{0.05} sample. Already from the line profile along the nanoparticle it is clear, in comparison to Fig. 4, that nanoparticles are smaller. The estimated average value from the study of several nanoparticles is also included in Table 2. We found that the size of Ni centers on the surface is almost proportional to the Ni content. A quarter of Ni dopants gives centers that are almost a quarter smaller than those observed for LaNi_{0.2b}.

Interaction of Ni-nanoparticles with the surface

Figure 6 shows a HRTEM image of a representative small Ni-nanoparticle attached to the main bulk of the perovskite for the reduced LaNi_{0.2b} sample. The lattice space of the perovskite bulk is clearly visible and the Filtered Fourier Transform (FFT) of the marked area shows spots corresponding to {010} planes of the crystalline structure of the LaAlO₃

base phase. The small Ni-nanoparticle appears anchored to the perovskite, also showing a crystalline structure, as seen in the HRTEM image and the FFT pattern. Nanoparticles are not round, instead, they appeared faceted to some extent. The analysis of the FFT patterns indicates that Ni-nanoparticles can be oxidized to NiO on the surface as it may be expected due to the air exposure.

As it has been demonstrated by the STEM-EDX line profile analyses, the concentration of Ni in the nanoparticle is significantly higher than that on the host material. It is possible that the growth results from the diffusion of Ni^{2+} ions to the nanoparticle followed by the reduction to Ni metal. The Ni metal could activate hydrogen spill over to accelerate the process of reduction. As a result Ni-nanoparticles can be strongly anchored at the bulk perovskite grains, which would be very beneficial for their stability in reaction conditions.

4. Conclusions

$\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$ perovskite oxides (with $x = 0.05$ and 0.2) were successfully synthesized and its behavior under reduction atmosphere was studied. HRTEM and HAADF-STEM studies, coupled to EDX detector, allowed evidencing the Ni exsolution process to the surface of the oxides to build nano-catalytic centers. The size of these centers did not depend on the reduction conditions for the studied range. This range was limited in order to obtain a material suitable for catalysis from the point of view of the morphology and the specific surface area.

The high specific surface of the raw material, its porosity and the structure defects could be responsible of the low temperature at which the exsolution process starts. The content of Ni dopants allows the control of Ni centers size on the surface and the synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.

Therefore, this study could give certain information about the design of nano-materials that could be used as catalysts for several reactions. In general, reactions in which metals particles with small nanoparticle size, highly dispersed and well anchored on a support, are necessary.

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Table captions.

Table 1: Conditions of the reduced samples.

Table 2: XPS of samples before and after the reduction treatments. S_{BET} results.

Table 3: Ni particle mean size values determined by TEM analysis as a function of reduction conditions and Ni content.

Table 1. Conditions of the reduced samples

Sample	Reduction Conditions		
	T (°C)	Heating rate (°C/min)	t (min)
LaNi _{0.2} a	650	15	30
LaNi _{0.2} b	650	15	60
LaNi _{0.2} c	750	5	30
LaNi _{0.2} d	750	15	30
LaNi _{0.05b}	650	15	60

Table 2. XPS of samples before and after the reduction treatments. S_{BET} results.

Sample	XPS Results		S_{BET} (m ² /g)
	Ni/(La+Al)	Ni/Al	
LaNi _{0.2} b	0.09	0.13	
LaNi _{0.2}	0.04	0.06	7.4
LaNi _{0.05} b	0.06	0.10	
LaNi _{0.05}	0.05	0.10	6.3

Table 3. Ni particle mean size values determined by TEM analysis as a function of reduction conditions and Ni content.

Sample	Reduction Conditions			Ni Particle Mean size (nm)
	T (°C)	B (°C/min)	t (min)	
LaNi _{0.2} a	650	15	30	18.5
LaNi _{0.2} b	650	15	60	20
LaNi _{0.2} c	750	5	30	22
LaNi _{0.2} d	750	15	30	22
LaNi _{0.05} b	650	15	60	6

Figure captions

Figure 1: X-Ray diffraction patterns obtained for calcined samples.

Figure 2: Gibbs free energy for the reduction of La, Al and Ni oxides to corresponding metals in H₂. Generated by the HSC chemistry software. The reaction was considered as $1/xM_xO_y + y/xH_2(g) = M + y/xH_2O(g)$.

Figure 3: STEM images of the samples: a) LaNi_{0.2} and b) LaNi_{0.2b}

Figure 4: STEM images and EDX-STEM profiles of sample LaNi_{0.2} after different reduction conditions (a-d) according to Table 1. The arrow indicates the direction along which the EDX profile was acquired over the particle.

Figure 5: STEM image and EDX-STEM profile taken over the particle (along the arrow direction) for the LaNi_{0.05b} sample. Inset: detail of the EDX profile.

Figure 6: HRTEM image of sample LaNi_{0.2b}. Insets: HRTEM detail of the Ni-nanoparticle and FFT of two marked areas on the Ni-nanoparticle and the perovskite.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

***Graphical Abstract**

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Ni-nanoparticle strongly anchored to the LaAlO₃ support.

Highlights

Perovskites behaviour under reducing atmosphere were studied.

Ni exsolution process to surface build nano-catalytic centers.

The size of Ni particles is independent on the reduction conditions in the range studied.

The content of Ni dopants allows the control of Ni centers size at the surface.

The synthesis method provides Ni-nanoparticles strongly anchored to the resultant support.