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CO_2 reforming of methane over $LaNiO_3$ as precursor material

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Abstract

The catalyst $LaNiO_3$ prepared by the auto-ignition method shows high activity, stability and a good resistance to carbon deposition for the CO_2 reforming of methane reaction. We have shown that during temperature increase up to 700 °C under the presence of the reactants ($CH_4 + CO_2$), the perovskite phase was transformed into Ni^0 and $La_2O_2CO_3$. Transmission electron microscopy (TEM) measurement performed after the reaction has shown that the average nickel particle size depends on the way the reaction is carried out, nickel particles are larger in the case of pre-reduced catalyst than in that of non-pre-reduced catalyst.

When using a non-reduced precursor material, the introduction of the reactant at 700 °C instead of at room temperature leads to a lower activity, whereas the nickel particle size distribution is quite similar for the two experiments. To explain the differences in the catalytic activity, we can assume that the number of accessible sites is different, consequently the way the active species are generated is a key step for the reaction.

Keywords: Catalyst; Perovskite $LaNiO_3$; Room temperature

1. Introduction

The reaction of carbon dioxide reforming of methane is a very attractive route for the conversion of two low-cost products to synthesis gas ($CO + H_2$) which can be used for the production of liquid hydrocarbons in the Fischer–Tropsch reaction [1] or in the methanol production. The reaction has been extensively studied using catalysts composed of transition metal carbides and sulfides, unsupported metals and supported group VIII metals [2–4]. Industrially, the metal of choice is nickel due to its inherent availability low cost and high activity in comparison to noble metals [5–8]. However, the main problem is the coke formation, which occurs during the reaction leading to a deactivation of the catalyst. This deactivation is especially observed in Ni based catalysts. Nevertheless, it has been shown [9] that a high metal dispersion (low metal particles size) on the support can limit the coke formation, but the main difficulty is the synthesizing of such a catalyst. The classical method to prepare a metal supported catalyst consists of impregnating the support by an aqueous solution of the metal precursor, followed by drying, calcinations and reduction. Very often, this simple method does not enable the obtention of a well-dispersed active phase as nanosized metal particles. According to the concept successfully developed by Shiozaki et al. [10], we have used the well-defined crystallized perovskite phase $LaNiO_3$ as catalyst precursor. We have already shown in a previous paper, by using a pulse technique that the perovskite phase $LaNiO_3$, as a catalyst precursor, leads to a very active catalyst for the CO_2 reforming of CH_4 [11]. The perovskite oxide phase, which was reduced by temperature programmed reduction (TPR) under hydrogen prior to the reaction leads

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to a catalyst composed of La_2O_3 and Ni^0. At 700 °C, the CH_4 and CO_2 conversion were, respectively, equal to 98 and 88% with a molar ratio $H_2/CO = 0.96$ without coke deposition.

According to these promising results we have investigated the catalytic behavior of $LaNiO_3$ previously submitted to various pre-treatments under a continuous flow of CH_4 and CO_2. The catalytic performances were then compared to the results of the physical–chemical characterizations performed before and after the reaction.

2. Experimental

2.1. Catalyst preparation

The perovskite type oxide $LaNiO_3$ was prepared by the so-called ‘‘auto-ignition method’’ [12].

Glycine ($H_2NCH_2CO_2H$) was added to an aqueous solution of La and Ni nitrates in order to attain a ratio of $NO_3^-/NH_3 = 1$. The resulting solution was slowly evaporated until a vitreous material was obtained, and then calcined at 250 °C for 1 h. During this calcination, a fast exothermic reaction occurred, yielding a formation of a powdered solid material still containing carbonaceous species. We confirmed that a calcination at 700 °C for 6 h eliminates all the remaining carbon. After reduction of the perovskite $LaNiO_3$ (Ni = 23.9 wt.%), the Ni content of the resulting catalyst varies from 24.1 wt.% (based on $Ni/La_2O_2CO_3$) to 26.5 wt.% (based on Ni/La_2O_3).

The catalyst 5% Ni/La_2O_3 was prepared by the wet-impregnation method using nitrate salt as the metal precursor. The nickel nitrate was dissolved in distilled water and stirred for half an hour, the appropriate weight of La_2O_3 was then added. The slurry was heated to 90 °C until the water was evaporated. The residue was then dried at 120 °C for 12 h and was subsequently heated at 500 °C under N_2 for 2 h for complete decomposition of nitrate.

2.2. Characterization

The catalysts were characterized by powder X-ray diffraction using a Siemens D-500 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV, 30 mA. The diffraction patterns were recorded in the 2θ values range 10–95° with a step size of 0.01° and 1 s per step. Transmission electron microscopy (TEM) was carried out on a Philips CM120 instrument equipped with an energy dispersive X-ray analyzer (EDX).

2.3. Temperature programmed reduction

Prior to the experiments the samples were heated at 600 °C for 2 h under argon.

Temperature programmed reduction experiments were carried out by introducing pulses of hydrogen (12 μmol H_2) every 2 min while the temperature was risen from ambient to 780 °C at the rate of 4 °C min^{-1}.

2.4. CO_2 reforming of methane

The reaction was carried out by passing a continuous flow of methane (10%), carbon dioxide (10%) and helium (80%) as carrier gas over a 50 mg (or 20 mg) catalyst bed at 700 °C, the total flow rate being equal to 100 mL min^{-1}. The temperature was increased from room temperature to 700 °C at a rate of 4 °C min^{-1} and maintained at this temperature for several hours. Different treatments of the precursor material $LaNiO_3$ were performed. $LaNiO_3$ was used without pre-treatment or after reduction under hydrogen by TPR. The temperature was increased from room temperature to 700 °C under reactant mixture or under helium.

The reaction products were analyzed by on-line mass spectrometry. The detection limit can be roughly estimated to 0.04 μmol according to the intensity of the signal measured by the MS, which corresponds to less than 1% of the total amount detected.

According to the small size of the catalyst grains (50–100 μm) and to the low specific surface area (few m^2 g^{-1}) of our samples, we expect that the reaction is not limited by transport effects.

All the catalytic experiments were performed twice.

3. Results

Before estimating the performances of the catalysts in the carbon dioxide reforming of methane, the $LaNiO_3$ perovskite was submitted to the following different pre-treatments:

- The perovskite was used without treatment prior to the reaction, the reactant being introduced at room temperature or at 700 °C.
- The perovskite was reduced by hydrogen prior to the reaction, the reactant being introduced at room temperature or at 700 °C.

3.1. CO_2 reforming of methane over $LaNiO_3$ used without treatment prior to the reaction

3.1.1. Reactants (CH_4 + CO_2) introduced at room temperature

Fifty milligrams of catalyst was heated at 600 °C under argon prior to the reaction. After cooling, an equimolar mixture of CO_2 and CH_4 was introduced while the temperature was increased to room temperature until 700 °C. Fig. 1 shows that high CH_4 and CO_2 conversions are obtained as soon as the temperature reaches 700 °C. After 15 h of reaction the CH_4 and CO_2 conversions were about 90% and the molar ratio H_2/CO was close to 1 (Fig. 1).

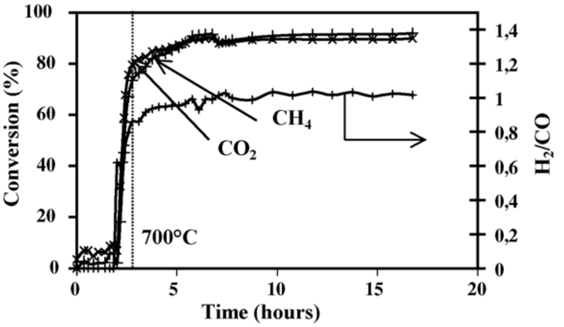

Fig. 1. Conversion of CO_2, and CH_4, molar ratio H_2/CO observed over $LaNiO_3$ during CO_2/CH_4 reforming at 700 °C as a function of time on stream. Experimental condition: no treatment of $LaNiO_3$ prior to the reaction, temperature increase under reactant.

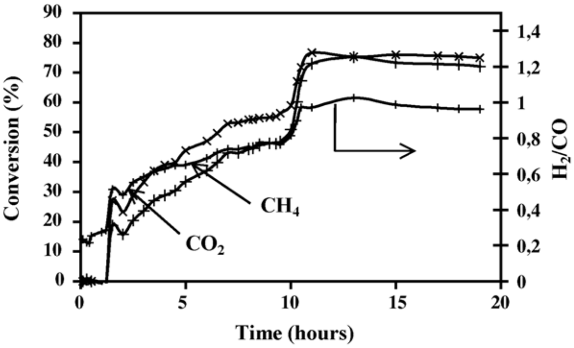

Fig. 2. Conversion of CO_2 and CH_4, molar ratio H_2/CO observed during CO_2/CH_4 reforming at 700 °C as a function of time on stream. Experimental condition: no treatment of $LaNiO_3$ prior to the reaction, temperature increase under helium.

A carbon balance close to 100%, the stability of conversions and H_2/CO ratio during the reaction confirm that a catalyst deactivation does not occur.

In order to check the stability of the catalyst the reaction was carried out for 100 h. The analysis showed that the CH_4 and CO_2 conversions were maintained close to 90%, the molar ratio H_2/CO remaining close to 1. These results show that $LaNiO_3$ as starting material leads to an active and stable catalyst for the CO_2 reforming of methane. Moreover, the molar ratio H_2/CO close to 1 and the similar conversions of CH_4 and CO_2, strongly suggest that the RWGS reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) does not proceed, since if this reaction was occurring, the H_2/CO ratio would be less than 1 and the CO_2 conversion higher than the CH_4 one.

3.1.2. Reactants (CH_4+CO_2) introduced at 700 °C

The catalyst was maintained under an inert gas (helium) during the temperature rise until 700 °C (reaction temperature). After the temperature was stabilized, the equimolar mixture of CO_2 and CH_4 was then passed through the catalyst bed. The results are shown in Fig. 2. It appears that the CH_4 and CO_2 conversions were very low during the first hours of reaction. They slowly began to increase with time on stream and seem to stabilize after 10 h of reaction. The CH_4 and CO_2 conversions were, respectively, equal to 73 and 75% with a molar ratio H_2/CO close to 1 (see Table 1).

3.2. Study of the reaction using $LaNiO_3$ reduced by hydrogen prior to the reaction

3.2.1. Reactants (CH_4+CO_2) introduced at room temperature

Metallic nickel is known to be responsible for methane activation. In order to perform the reaction with a catalyst containing a large amount of Ni^0, we have reduced the $LaNiO_3$ perovskite under hydrogen prior to the reaction. The catalyst was reduced by pulsed TPR until 780 °C. The phases present were thus Ni^0 and La_2O_3, the nickel being almost totally reduced as shown in a previous paper [11]. After the reduction step, the system was cooled down and purged by a He flow. The catalyst was then exposed to an equimolar flow rate of CH_4 and CO_2 while the temperature was increased from room temperature to 700 °C and maintained at this temperature. The results are shown in Table 1. A high CH_4 and CO_2 conversion was obtained rapidly over the reduced material showing no significant differences with the non-reduced catalyst. Nevertheless, the molar ratio H_2/CO close to 0.8 suggests that the reverse water gas shift reaction (RWGS) proceeds over this pretreated catalyst (see Table 1).

3.2.2. Reactants (CH_4+CO_2) introduced at 700 °C

After the reducing treatment, the catalyst was maintained under He until the temperature reached 700 °C, at which the

Table 1
CH_4, CO_2 conversion, H_2/CO ratio, phases detected by XRD after 15 h of reaction, average nickel particle size determined by TEM after reaction

Catalyst	Conversion (%)		Molar ratio H_2/CO	XRD analysis at the end of the reaction	Average Ni particle size (nm)
	CH_4	CO_2			
$LaNiO_3$ introduction of CH_4–CO_2 at room temperature	90	87	≈1	$La_2O_2CO_3$	21
$LaNiO_3$ introduction of CH_4–CO_2 at 700 °C	73	75	≈1	$La_2O_2CO_3$	19
Reduced catalyst introduction of CH_4–CO_2 at room temperature	90	90	≈0.8	$La_2O_2CO_3$	27
Reduced catalyst introduction of CH_4–CO_2 at 700 °C	50	60	≈0.6	$La_2O_2CO_3$	35

$CH_4/CO_2/He = 10/10/80$, catalyst weight = 50 mg, flow = 100 mL min^{-1}, $T = 700$ °C.

Table 2
CH_4, CO_2 conversion, H_2/CO ratio, after 15 h of reaction over $LaNiO_3$ and 5% Ni/La_2O_3 introduction of the reactant at room temperature

Catalyst	Conversion (%)		Molar ratio H_2/CO
	CH_4	CO_2	
$LaNiO_3$	41	57	0.69
5% Ni/La_2O_3	43	58	0.68

$CH_4/CO_2/He = 10/10/80$, catalyst weight = 20 mg, flow = 100 mL min^{-1}, $T = 700\,^{\circ}C$.

mixture of CH_4 and CO_2 was introduced. The conversions of CH_4 and CO_2 slowly increased during the first 5 h of reaction, until they reached a plateau, where the conversions and the molar ratio H_2/CO remained constant (see Table 1).

3.3. CO_2 reforming of CH_4 over 5% Ni/La_2O_3

A catalyst composed of metallic nickel supported on lanthanum oxide was compared to the $LaNiO_3$ starting material. The nickel amount (5%) was chosen to avoid having a too large nickel loading which could lead to a poor dispersion of the Ni^0 particles and then a low catalytic activity [7]. The contact time was changed by decreasing the amount of catalyst (20 mg against 50 mg for the preceding experiments), in order to be far from the thermodynamic equilibrium.

The reaction was carried out by following the procedure leading to the best catalytic performances, i.e. introduction of the reactants at room temperature and rise of temperature under reactants. The catalytic results are gathered in Table 2. The catalytic performances appeared similar for the two catalysts. For both catalysts (5% Ni/La_2O_3 and $LaNiO_3$), the carbon dioxide conversion is higher than the methane conversion and the molar ratio H_2/CO is close to 0.7 showing that the reverse water gas shift reaction easily proceeds when the residence time decreases (space velocity: 3×10^5 mL h^{-1} g^{-1}). Carbon deposit was not detected on the catalyst even after 15 h on stream.

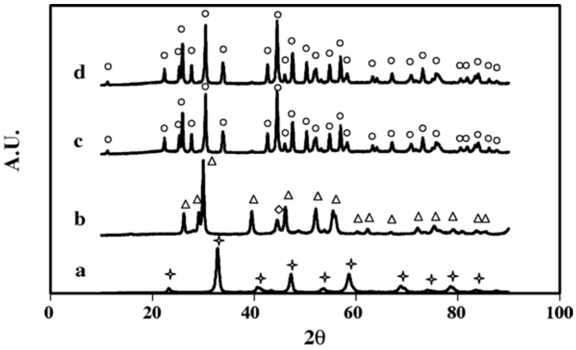

Fig. 3. XRD analysis of the material before reaction (a), after reduction by TPR (b), after reaction at 700 °C: non-reduced catalyst + introduction of reactants at room temperature (c), catalyst reduced by TPR + introduction of reactants at 700 °C (d). (△) La_2O_3, (◇) Ni, (○) $La_2O_2CO_3$, (✦) $LaNiO_3$.

4. Catalyst characterization

4.1. XRD analysis

XRD analyses were performed after reaction in order to observe the modification of the active phase during the reaction. Fig. 3 shows that the perovskite phase $LaNiO_3$ (Fig. 3a) was not maintained after the reduction treatment under hydrogen (Fig. 3b), the only phases detected being

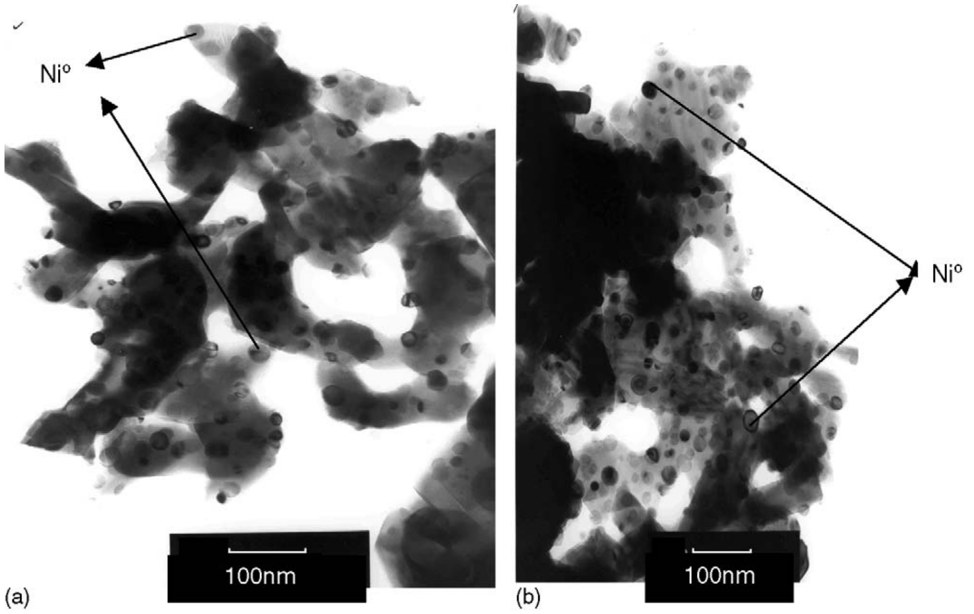

Fig. 4. TEM image of the catalyst at the end of the reaction: (a) $LaNiO_3$ reduced by TPR prior to the reaction + introduction of the reactant at room temperature and (b) $LaNiO_3$ without reduction + introduction of the reactant at room temperature.

metallic nickel and lanthanum oxide (La_2O_3). Independently of the treatment, after the reaction the only phase detected was lanthanum oxycarbonate $La_2O_2CO_3$ (Fig. 3c and d) showing that a phase transformation of the perovskite takes place during the reaction.

4.2. *Characterization by electron microscopy*

TEM investigation was performed after 15 h of reaction, the reactant being introduced at room temperature. With or without reduction of $LaNiO_3$ prior to the reaction, no significant differences were observed between the two pictures (Fig. 4), spherical particles of metallic Ni being clearly visible. The Ni particles were observed together with a phase corresponding probably to the lanthanum oxycarbonate $La_2O_2CO_3$.

Several authors have suggested the possibility of the covering of nickel particles by lanthanum oxide or oxycarbonate, but here we have not observed any indications for such covering [6].

The Ni particles sizes were measured by TEM analysis. The particle size distribution after reaction is given in Fig. 5. The data in the figure are normalized to 100 particles, while 210–250 particles were considered for the TEM analysis. For the catalyst reduced by TPR prior to the reaction, the diameter of the particles ranges between 4 and 56 nm when the reactants are introduced at room temperature, and between 4 and 64 nm when the reactants are introduced at 700 °C. For the non-reduced starting material the particle size is between 4 and 36 nm when the reactants are introduced at room temperature and between 4 and 44 nm when the reactant are introduced at 700 °C. The average Ni particle size is higher on the pre-reduced material (Table 1) than on the non-reduced catalyst. This result could be explained by the sintering of the nickel particles during the reduction of $LaNiO_3$ at high temperature (780 °C).

TEM analysis has been performed over the 5% Ni/La_2O_3 catalyst before reaction. Some particles appear to be aggregated, the nickel particle size being comprised between 11 and 42 nm, whereas the agglomerates size is 150 nm × 90 nm.

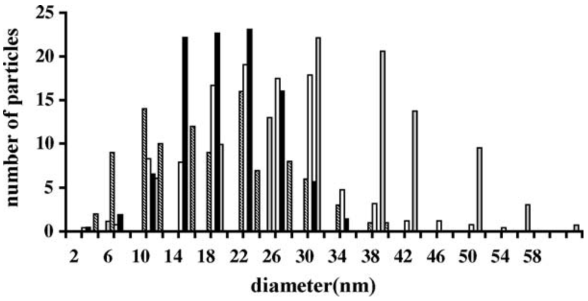

Fig. 5. Particle size distribution determined from TEM measurements after 15 h of reaction. Black: non-reduced catalyst + introduction of the reactant at room temperature; hatched: non-reduced catalyst + introduction of the reactant at 700 °C; white: $LaNiO_3$ reduced by TPR prior to the reaction + introduction of the reactant at room temperature; grey: $LaNiO_3$ reduced by TPR prior to the reaction + introduction of the reactant at 700 °C. The data are normalized to a total of 100 particles.

5. Discussion

The carbon dioxide reforming of methane was performed using the perovskite type catalyst $LaNiO_3$ as precursor material. The perovskite phase was rapidly modified while the temperature was increased from room temperature to 700 °C under a stoichiometric mixture of CH_4 and CO_2. The reduction properties of methane lead to the formation of metallic nickel and lanthanum oxide [13,14], while carbon dioxide easily adsorbs at the surface of the basic La_2O_3 to form oxycarbonate species [7,15]. The catalyst thus obtained is highly active, the CH_4 and CO_2 conversion being equal to 90% with a molar ratio H_2/CO close to 1 while the space velocity was as high as 1.2×10^5 mL h^{-1} g^{-1}. Moreover, no side reactions were observed as carbon deposition or RWGS commonly observed when using lanthanum and nickel based catalyst [15,16]. These results suggest that under these experimental conditions, the thermodynamic equilibrium was reached according to the value of the standard free energy calculated at 700 °C ($\Delta G^{\circ}_{973\,\mathrm{K}} = -16\,\mathrm{kJ\,mol^{-1}}$) [17,18].

We have shown that the catalyst was extremely stable: no deactivation was detected within a period of 100 h, the CH_4 and CO_2 conversion remaining at 90% with a molar ratio H_2/CO close to 1. Such a high stability has been already observed for Ni/La_2O_3 catalyst by Zhang et al. but only for low conversion (about 30%), a significant deactivation occurring for higher conversion [7,16].

The catalytic performances of $LaNiO_3$ as starting material have been compared (Table 2) to those obtained with our reference catalyst 5% Ni/La_2O_3 [7,16]. The CH_4 and CO_2 conversion and the molar ratio H_2/CO are approximately the same while the nickel amount is significantly different. This result suggests that only a small proportion of the reduced nickel is accessible to the reactants at the surface of the catalyst obtained by the reduction of the perovskite $LaNiO_3$.

The nature of the crystallographic phases on our catalysts was determined by XRD analysis after 15 h of reaction. With or without pre-treatment, the only phase detected was the $La_2O_2CO_3$ hexagonal phase. Nevertheless, the results show that the catalyst activity was lower when the reactant feed is introduced at 700 °C instead of performing the increase of temperature under reactants (see Table 1). During the rise of temperature under reactants, two important steps proceed: the reduction of Ni^{3+} to Ni^0 and consequently the formation of La_2O_3 on which the CO_2 adsorption leads to the formation of $La_2O_2CO_3$. The formation of $La_2O_2CO_3$ seems to be a key step for the reaction as it has been pro-posed by different authors [7,19,20], some of them have suggested that the lanthanum carbonate could prevent the nickel phase to be deactivated by coke formation [21–23].

According to Table 1, it seems that the simultaneous reduction of nickel and oxycarbonate formation is of paramount importance to avoid the RWGS reaction and obtain a H_2/CO ratio close to 1.

When the perovskite $LaNiO_3$ was reduced by TPR prior to the reaction, the catalyst was thus composed of metallic nickel and lanthanum oxide [11]. The reduction step did not change the CH_4 and CO_2 conversions, a high activity is obtained, but the molar ratio H_2/CO was close to 0.8 (instead of 1) resulting from the occurrence of the RWGS reaction.

The reduction of $LaNiO_3$ followed after cooling by a temperature increase until the reaction temperature (700 °C) under helium leads to a poor activity with a molar ratio equal to 0.6.

The RWGS reaction appears to be favored over the reduced material when the methane conversion is the lowest. These results are in accordance with the thermodynamic calculations which show that the RWGS reaction can proceed at low CH_4 conversion leading to a CO_2 conversion higher than the CH_4 one and a H_2/CO ratio less than 1, whereas at high conversion, close to the thermodynamic equilibrium values, the amount of H_2 converted to H_2O by the RWGS reaction is rather low, the CH_4 and CO_2 conversions being then similar with a H_2/CO ratio close to 1 [24].

In order to measure the particles sizes, TEM measurements were performed after several hours of reaction. When the catalyst was not reduced before to be in contact with reactant feed, the average nickel particles size was the smallest with a size close to 20 nm. The pre-reduced catalysts present higher average particles size (27–35 nm), the highest size being observed when the reactant feed is introduced directly at the reaction temperature. Moreover, the particles size histogram (Fig. 5) shows that the distribution of the sizes is narrower for the non-reduced catalysts than for the pre-reduced ones. The biggest particles detected have a diameter of 36 nm for the catalysts not reduced before the reaction, whereas for pre-reduced catalysts the biggest particles size reaches 56 nm. This difference could be attributed to the sintering of the nickel particle due to the treatment under hydrogen at 780 °C for the pre-reduced catalysts.

Without reducing treatment under H_2 before the reaction, the average nickel particle size is approximately the same ($\approx$20 nm) regardless of the temperature at which the reactant feed was introduced (room temperature or 700 °C), whereas the catalytic activity is significantly different. It is generally expected that the better the dispersion of nickel the higher is the catalytic activity [25]. The differences observed in our experimental conditions could result from the accessibility of the reactants to the nickel particles, some of them being probably embedded in the lanthanum oxide or oxycarbonate support and then inaccessible to the reactants. This point will be investigated by the measurement of metallic sites at the surface of the catalyst using hydrogen chemisorption.

6. Conclusion

The use of the perovskite $LaNiO_3$ as a catalyst precursor gives good performances for the reaction of carbon dioxide reforming of methane. The best catalytic performances were obtained without pre-treatment of the perovskite when the reactants are introduced at room temperature. The CH_4 and CO_2 conversion were, respectively, equal to 90 and 87% with a H_2/CO molar ratio equal to 1, the catalytic activity remaining stable for more than 100 h.

The oxycarbonate phase is formed during the reaction at 700 °C whatever the $LaNiO_3$ treatment before the reaction.

The reduction step of the perovskite under hydrogen before the reaction leads to a sintering of the nickel particles, on which the reverse water gas shift reaction can occur, the higher the particle size, the more favored is the RWGS reaction.

The perovskite $LaNiO_3$ used as promoter material allows an active and selective catalyst to be obtained. The high activity can be attributed to the high dispersion of the nickel particles obtained by the reduction under reactant. Nevertheless, the lower activity obtained when the reactants are introduced at 700 °C, despite the high dispersion of the nickel particles, can be explained by the amount of accessible nickel particles. Thus, a high dispersion of metallic nickel at the surface of the catalyst is necessary for a high activity but is not sufficient.

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