Dry reforming of methane over Ni perovskite type oxides

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Abstract

$La_{1-x}Sr_xNiO_3$ perovskite type oxides were synthesized by the auto combustion method and tested as catalysts precursors in the dry reforming of methane with CO_2 to syngas at 700 °C and 1 atm. In order to understand the catalyst behavior, the reaction was studied by a pulse technique using a CH_4/CO_2 ratio close to one. The solids were characterized by X-ray diffraction (XRD), BET surface area, temperature-programmed reduction and oxidation (TPR-TPO) and scanning electronic microscopy (SEM). XRD analysis showed that reduction of the perovskites proceeds through formation of intermediate species to obtain Ni^0, La_2O_3 and SrO. $LaNiO_3$ showed the higher activity among the studied perovskites while La_2NiO_4 was not active for the reaction. It was observed that catalytic activity was Sr content dependent, following the order: $LaNiO_3 > La_{0.6}Sr_{0.4}NiO_3 > Ni$ (5%)/$La_2O_3 > La_{0.9}Sr_{0.1}NiO_3$. During reaction, nickel remained as Ni^0 while $SrCO_3$ and $La_2O_2CO_3$ phases are formed which improved methane reforming and the regeneration of the La_2O_3 phase. The lack of carbon formation is attributed to the presence of these phases.
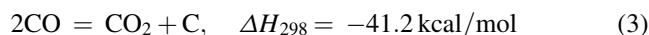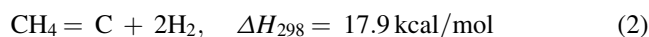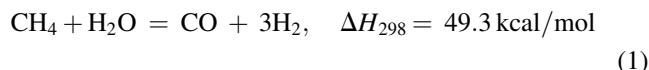© 2005 Elsevier B.V. All rights reserved.

Keywords: Methane reforming; Syngas; Ni perovskites; Auto combustion

1. Introduction

Natural gas stands as a more appropriate broadly available and economic fuel for the protection of the environment [1], locating it as the source of energy of the future. Its world wide considerable proven reserves has stimulated the research related to the development of processes to produce fuels and petrochemicals from sources different from oil, such as coal and natural gas, have been reactivated. There are two main ways for methane conversion: direct conversion to chemicals (mainly hydro-carbons) and indirect conversion to syngas which can be transformed to alcohols, olefins and paraffin's via Fischer–Tropsch or through methanol route to gasoline (MTG) to produce ethane, propane and aromatics.

Obtaining syngas by steam reforming of methane (Eq. (1)), followed by a hydrogenation stage according to the Fischer–Tropsch process is already classic. However, the high temperatures involved favors catalyst deactivation by sintering of the active phase and by formation of coke, through the decomposition of methane and the Boudouard's reaction (Eqs. (2) and (3), respectively).

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H_{298} = 49.3 \, \text{kcal/mol} \tag{1}$$

$$CH_4 = C + 2H_2, \quad \Delta H_{298} = 17.9 \, \text{kcal/mol} \tag{2}$$

$$2CO = CO_2 + C, \quad \Delta H_{298} = -41.2 \, \text{kcal/mol} \tag{3}$$

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The unfavorable energy balance for steam reforming suggests other solutions such as CO_2 reforming of methane (Eq. (4)) to produce syngas with a ratio of $H_2/CO \leq 1$, which is appropriate to Fischer–Tropsch reaction to liquids [2]. It also contributes to minimize the negative environmental effect of these gases.

$$CH_4 + CO_2 = 2CO + 2H_2, \quad \Delta H_{298} = 59.1 \, \text{kcal/mol}$$

$$(4)$$
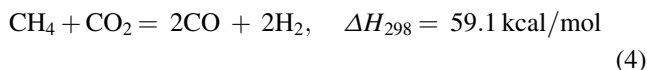
Calculations to predict the thermodynamic potential of graphite carbon deposition as a function of operating conditions for gas mixtures containing CH_4, CO_2, H_2 and H_2O have been previously reported [3–6]. These suggest that carbon formation during CH_4 reforming (with CO_2/CH_4 ratios far above unity) is unfavorable at high temperatures ~1000 K; however, from an industrial standpoint, it may be desirable to operate at lower temperatures with CO_2/CH_4 ratios near unity. This condition makes necessary the use of a reforming catalyst that inhibits carbon formation.

CO_2 reforming of CH_4 has been carried out on metallic catalysts of group VIII supported by a great variety of oxides. Reported order of activity [7] is as follows: Rh, Ru > Ir > Ni, Pt, Pd > Co > Fe, Cu; however, the catalysts are deactivated by deposition of coke on the surface, although novel metals are less prone to deactivation by this cause, they deactivate with time. An alternative is the use of nickel catalysts, a well known catalyst for steam reforming.

Ni catalysts are of special interest since they present a high initial activity for this reaction, interesting redox properties and relatively low cost. However, it is difficult to prevent sintering of nickel and deposition of carbon at high temperatures. In this sense efforts have been carried out to synthesize Ni catalysts resistant to carbon deposition by introducing the metal in perovskite type oxides (ABO_3). These are well defined structures which produce very small particles, in the order of the nanometers, with high metallic dispersion when subjected to reduction processes [8], unfavorable conditions to carbon formation [9], there increasing activity and stability [10]. Also, coke formation can be suppressed by addition of alkaline earth metals with high basicity [11].

It has been observed [12,13] that the activation of both molecules CH_4 and CO_2 on the surface of the transition metal and of the support depends upon electronic and geometric factors and consequently, the dissociative adsorption of both molecules is structure sensitive. This is due to metal–support interactions and/or the participation of oxygen and OH species present in the catalytic surface [7]. Numerous kinetic models have been proposed [14–16] to describe the reforming reaction CO_2/CH_4; the most consistent pattern at the moment involves: (1) reversible dissociation of CH_4 to form CH_x and H_x species adsorbed on the metal, (2) dissociation of CO_2 on the support, (3) reaction of the CH_x species with adsorbed OH (or O) occurs on the metal–support interfacial region to form CH_xO adsorbed species and (4) finally these species break down to form syngas (CO and H_2).

In this work Ni perovskite type oxides of the general formula $La_{1-x}Sr_xNiO_3$ were synthesized by the auto combustion method and characterized to be used as catalytic precursors in the pulse reaction of dry reforming of methane, with the purpose of avoiding coke formation. The effect of the degree of substitution (x) on the catalytic activity and stability was studied.

2. Experimental

2.1. Synthesis of perovskite type oxides

The solids were prepared by the auto combustion method [17], which consists of adding glycine $H_2NCH_2CO_2H$ to the salts of the metallic nitrates [$La(NO_3)_3 \cdot 6H_2O$ Ventron, $Ni(NO_3)_2 \cdot 6H_2O$ Prolabo and $Sr(NO_3)_2$ Riedel-de Haën] under an equimolar NO_3^-/glycine ratio. These salts are very lightly warmed directly on a metal sheet (~50 °C) with constant agitation until the dissolution of the solids in the minimum quantity of water is achieved, then the water is slowly evaporated (~100 °C) until a gel is obtained. Finally the temperature of the metal sheet increases to the maximum producing an exothermic reaction (auto combustion) that allows the formation of a precursory powder which calcinates on air between 700 and 900 °C for 2 h to eliminate the possible carbon species residues. The supported solid is prepared by the incipient wetness, where the solution of the metal is slowly added to the support La_2O_3, the solvent evaporates and is allowed to dry off for over night, followed by calcinations at 700 °C.

2.2. Characterization

The solids were characterized by means of X-ray diffraction (XRD), BET surface area, temperature-programmed reduction and oxidation (TPR-TPO) and scanning electron microscopy (SEM) techniques.

Specific surface areas were measured using nitrogen–argon adsorption at −196 °C with an N_2/Ar ratio of 30/70 on a Micromeritics Flow Sorb II 2300. X-ray diffraction was performed to obtain information about the crystalline structure of the synthesized solids and in conditions of temperature-programmed reduction to observe the changes of phases before and after each catalytic test, using a Siemens D500 equipment with Cu Kα = 1.5418Å radiation between 10° and 95° (2θ). For the analyses of in situ XRD the solid was placed finely crushed with methanol, on a platinum badge in a Siemens D5005. Heating was conducted increasing the temperature at 4°/min under different atmospheres (Ar, H_2, CO_2).

The TPR analysis was carried out in a quartz reactor with 50 mg of sample, where pulses of H_2 are injected (0.012 mmol diluted in Ar) each 2 min up to 900 °C at 4°/min. With the purpose of studying the reversibility of the redox processes the solid was oxidized (TPO) under the

same previous conditions but in O_2 atmosphere (diluted in He). Prior to the experiments the samples were heated to 600 °C for 2 h under argon.

The elementary analysis of the solids calcined at 800 °C, were carried out through SEM–EDX on the samples covered with carbon. For the study of the morphology the samples were covered with Au. It was used an accelerating voltage of 20 kV and 3×10^{-9} A.

2.3. Reforming of methane with CO_2

The reforming reaction was carried out by pulses to allow the transformation of the catalyst according to the selectivity of the products formed in each pulse. Prior to the reaction, the samples (∼50 mg) were heated at 600 °C for 2 h under argon atmosphere, followed by TPR by H_2 pulses at 700 °C, as previously described [18]. The reduced solid undergoes a temperature-programmed increase of 4°/min up to 700 °C, while every 7 min a mixture of gases of CH_4:CO_2 is injected with a ratio of 1:1 (6 μmol of each component). The analysis of the gases at the exit is carried out by means of a TCD, coupled to a mass spectrometer Pfeiffer-Vacuum.

A TPO analysis was carried out after the reaction, with the purpose of verifying carbon formation as previously described [18].

The conversions of CH_4 and CO_2 are defined as

$$X_{CH_4} (\%) = \left[\frac{A_{CH_4(in)} - A_{CH_4(out)}}{A_{CH_4(in)}} \right] \times 100 \quad (5)$$

$$X_{CO_2} (\%) = \left[\frac{A_{CO_2(in)} - A_{CO_2(out)}}{A_{CO_2(in)}} \right] \times 100 \quad (6)$$

where $A_{(in)}$ and $A_{(out)}$ are the areas before and after the reaction, respectively.

The selectivities toward CO and H_2 are defined as

$$S_{CO} (\%) = \left[\frac{\eta CO}{\eta CH_4 + \eta CO_{2\,(converted)}} \right] \times 100 \quad (7)$$

$$S_{H_2} (\%) = \left[\frac{\eta H_2}{2\eta CH_{4\,(converted)}} \right] \times 100 \quad (8)$$

η representing the mass of each gas.

Table 1
Specific surface area and elementary analysis of synthesized solids

Precursor solid	$T_{calcinations}$ (°C)	Surface area (m²/g)	EDX metal/Ni
LaNiO₃	700	8.3	La/Ni = 1.0
	800	4.8	
	900	3.4	
La₀.₉Sr₀.₁NiO₃	700	8.5	La/Ni = 1.0
	800	4.8	Sr/Ni = 0.1
	900	2.9	
La₀.₈Sr₀.₂NiO₃	900	3.2	La/Ni = 0.9
			Sr/Ni = 0.2
La₀.₇Sr₀.₃NiO₃	900	3.3	La/Ni = 0.8
			Sr/Ni = 0.3
La₀.₆Sr₀.₄NiO₃	900	3.1	La/Ni = 0.7
			Sr/Ni = 0.3
Ni (5%)/La₂O₃	700	22.0	

3. Results and discussions

The results of specific surface area and elementary analysis are summarized in Table 1. The EDX analyses indicate a narrow similarity between the nominal values and the preparations, with surface areas in the range 3–10 m²/g. The surface area decrease when the temperature of calcination increases due to sintering of the solids when expose to high temperatures [19]. An increase in the Sr content does not produce significant changes in the surface area (Table 1), while the percentage of reduction increases (Table 2) due to the vacancies of oxygen originated by the partial substitution of La^{3+} by Sr^{2+}, facilitating the diffusion of the oxygen from the bulk to the surface where they are easily removed by the reducer gas [20].

In Table 2 the XRD results are indicated before and after a redox cycle. It is observed that the auto combustion method is appropriate for the synthesis of perovskite type oxides at low temperatures of calcination. However, as the temperature of calcination and degree (x) of substitution increase the formation of spinels phases is favored thermodynamically [21].

According to the XRD patterns of the synthesized catalysts, it is observed that $LaNiO_3$ only presents a simple

Table 2
XRD and TPR analyses of the synthesized solids

| x	$T_{calcinations}$ (°C)	DRX initial phases	%Red	DRX phases after redox
0	700	LaNiO₃	80.1	La₂NiO₄, NiO
	800		84.0	
	900		85.4	
0.1	700	La₀.₉Sr₀.₁NiO₃, LaSrNiO₄, NiO	80.7	La₁.₇₁Sr₀.₁₉NiO₃.₉, NiO
	800		86.7	
	900		85.8	
0.2	900	La₁.₅₂Sr₀.₃₈NiO₃.₈₆, NiO	86.3	La₁.₇₁Sr₀.₁₉NiO₃.₉, NiO
0.3	900	La₁.₄Sr₀.₆NiO₄, NiO	89.3	La₁.₅₂Sr₀.₃₈NiO₃.₈₆, NiO
0.4	900	La₁.₅₂Sr₀.₅₈NiO₃.₈₆, NiO	90.7	La₁.₇₁Sr₀.₁₉NiO₃.₉, NiO
Ni/La₂O₃	700	La₃Ni₂O₇, La₂O₃	85.3	La₂NiO₄, La₂O₃
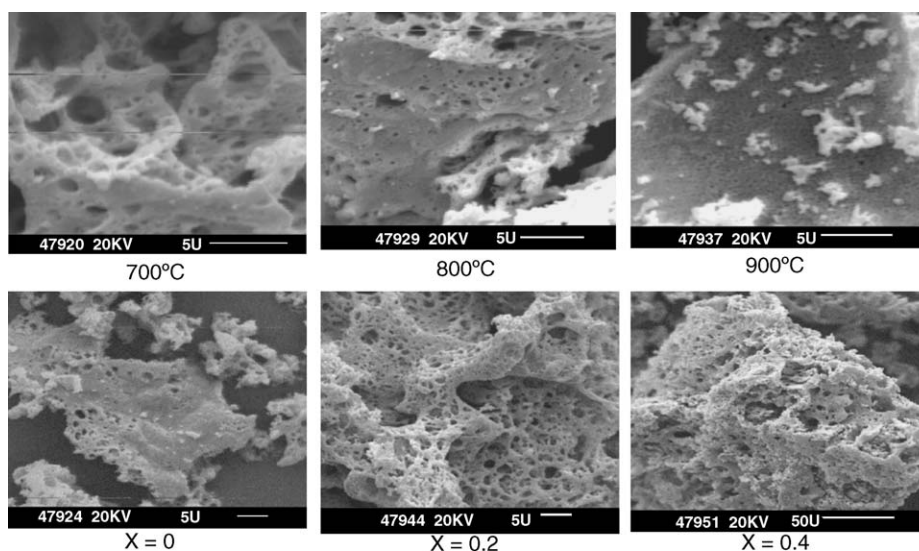
Fig. 1. Effect of the calcinations temperature and substitution degree by Sr (x) on the porosity and morphology of $LaNiO_3$.

phase of perovskite structure where the Ni exists as Ni^{3+}, while for a degree of substitution $x = 0.1$ a mixture of phases is obtained where the perovskite $La_{0.9}Sr_{0.1}NiO_3$ structure prevails, however when increasing the content of Sr ($x \geq 0.2$) the formation of spinels $La_{2-2x}Sr_{2x}NiO_4$ type structures is favored where the number of oxidation of the Ni varies between 2.0 and 2.6, indicating that the Sr facilitates the reduction of the Ni^{3+} with loss of oxygen of the crystalline lattice, in agreement with the observations of Nitadori et al. [22].

The XRD patterns of the solids subjected to redox cycle at 900 °C, show that the obtained phases do not produce again the original perovskite for $x = 0$ and 0.1 but to a spinel type structure, hence these redox processes are not reversible, hence the following reaction of reoxidation of these solids is proposed

$$2Ni + (1-x)La_2O_3 + 2xSrO + (2+x)/2O_2$$
$$\rightarrow La_{2-2x}Sr_{2x}NiO_4 + NiO \qquad (9)$$
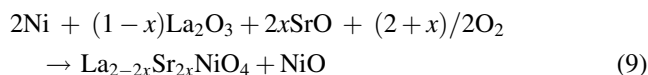
In the case of $x \geq 0.2$ the spinel type structure is preserved since its formation is favored at high temperatures [23].

According to the morphological analysis it is observed that the macro porosity of $LaNiO_3$ diminishes as the temperature of calcinations increases, due to the sintering phenomenon (Fig. 1). As the degree of substitution (x) increases in $La_{1-x}Sr_xNiO_3$ the macro porosity also increases and its morphology changes, due to the formation of solids with more stoichiometric defects which favors the formation of spinels type phases, as observed by XRD (Table 1).

The reduction of the perovskite type oxides occur through the following reaction [20]

$$La_{1-x}Sr_xMO_3 + (3+x)/2H_2$$
$$\rightarrow M + (1-x)/2La_2O_3 + xSrO + (3+x)/2H_2O$$
$$(10)$$
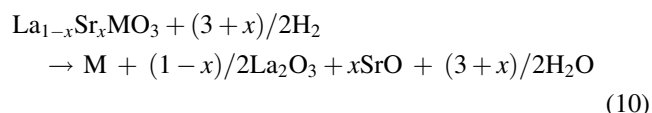
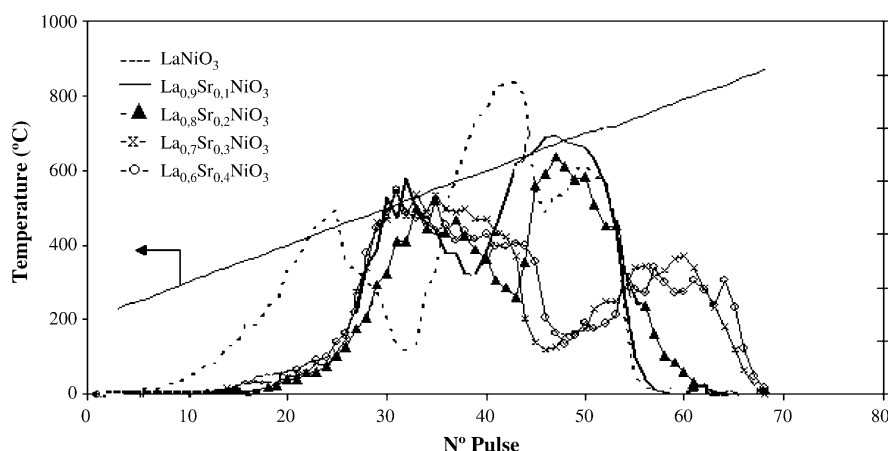The behavior observed during the reduction of these solids (Fig. 2) shows the formation of several peaks which

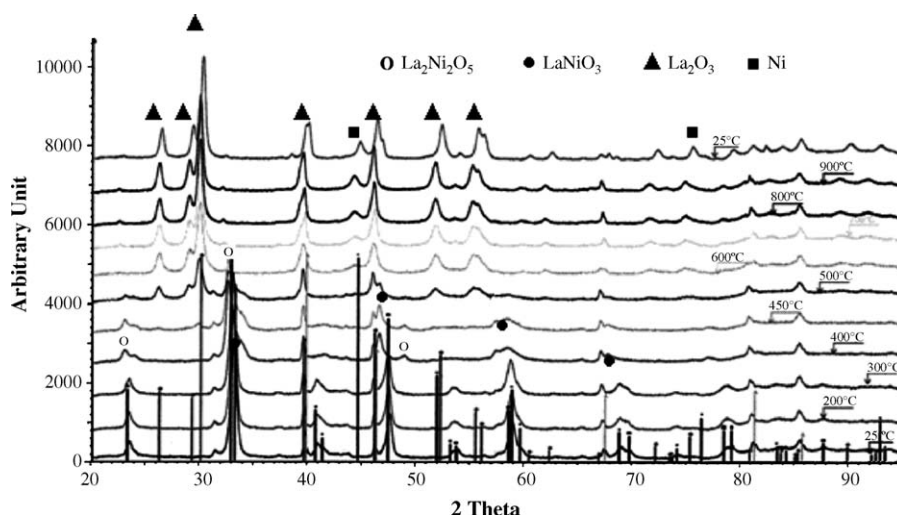Fig. 2. TPR analysis of $La_{1-x}Sr_xNiO_3$. Effect of substitution (x) degree.

Fig. 3. LaNiO$_3$ crystalline phases as a function of the reduction temperature.

correspond to different intermediary species of Ni [23] and can be deduced starting from an in situ XRD analysis under hydrogen atmosphere (Fig. 3).
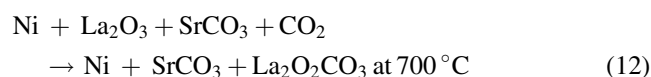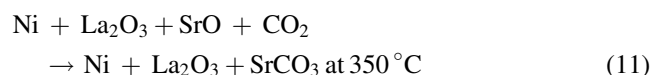
According to TPR results, the total reduction of the solids to Ni, La$_2$O$_3$ and SrO occurs near 780 °C, the percentage of reduction being always less than 100% (Table 1) since they stoichiometry can be reduced to La$_{1-x}$Sr$_x$NiO$_{3-\lambda}$ [24]. On the other hand, it is observed that the reduction of the solids is favored as the degree of substitution (x) increases, property that can be related to the catalytic activity that these precursors may present in the reforming reaction.

In general, the reduction of these solids is favored due to the mobility of the oxygen of the lattice [25] toward deficient oxygen areas or "holes" that are generated as the species of surface oxygen react with hydrogen.

According to the in situ XRD (Fig. 3) of LaNiO$_3$ calcined at 800 °C, the formation of the phase La$_2$Ni$_2$O$_5$ is observed at 420 °C [26], Ni, NiO and La$_2$O$_3$ at 610 °C [27], while the

total reduction to metallic Ni and La$_2$O$_3$ take place at 690 °C. These results are in agreement with previously reported values [25,28]. The in situ XRD analyses (Fig. 4) carried out during the TPO under CO$_2$ atmosphere on previously reduced La$_{0.6}$Sr$_{0.4}$NiO$_3$, showed an important CO$_2$ adsorption prior to the CO$_2$ methane reaction, producing the active species SrCO$_3$ and La$_2$O$_2$CO$_3$ active for the reforming reaction, as pointed out by Inui et al. [29].

According to the previous results the following reactions are established

$$Ni + La_2O_3 + SrO + CO_2$$
$$\rightarrow Ni + La_2O_3 + SrCO_3 \text{ at } 350\,^\circ C \tag{11}$$

$$Ni + La_2O_3 + SrCO_3 + CO_2$$
$$\rightarrow Ni + SrCO_3 + La_2O_2CO_3 \text{ at } 700\,^\circ C \tag{12}$$

With regard to the CO$_2$ methane reforming reaction by pulses, it is observed that the previously reduced at 700 °C
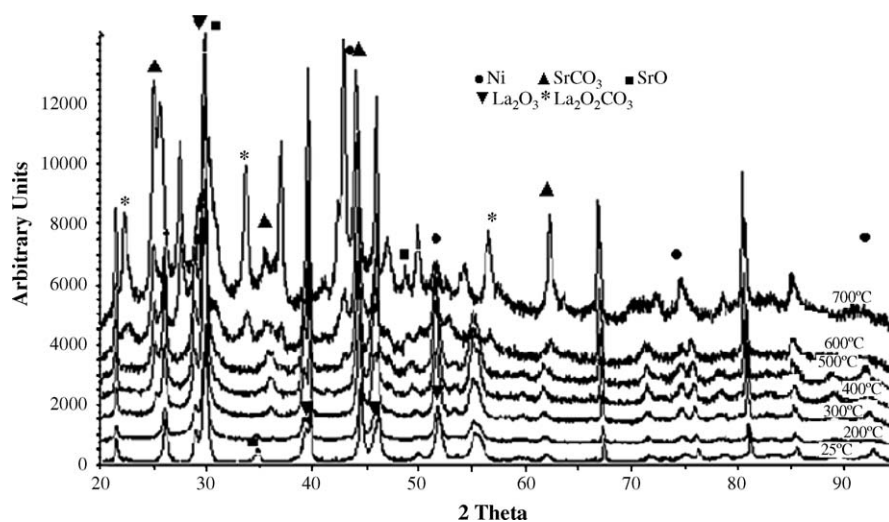

Fig. 4. In situ XRD patterns of La$_{0.6}$Sr$_{0.4}$NiO$_3$ reduced at low CO$_2$ atmosphere.
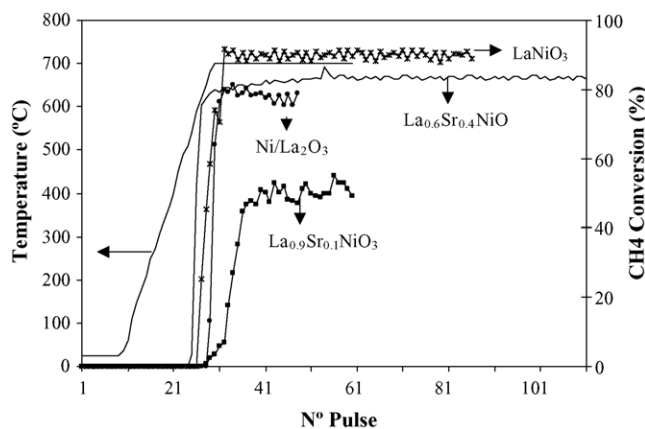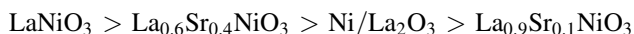
Fig. 5. $CH_4 + CO_2$ reforming over previously reduced $La_{1-x}Sr_xNiO_3$.

Fig. 7. S_{CO}/S_{H2} ratio during dry reforming of methane.

$LaNiO_3$ perovskite presents higher activity with conversions of CH_4 and CO_2 of 95 and 75%, respectively, maintain constant up to ~10 h (Fig. 5). The order of activity depends on the content of Sr

$$LaNiO_3 > La_{0.6}Sr_{0.4}NiO_3 > Ni/La_2O_3 > La_{0.9}Sr_{0.1}NiO_3$$

Oxidation analysis after reaction followed by mass spectrometry does not reveal carbon deposition on the solids. The reforming on $La_{0.6}Sr_{0.4}NiO_3$ presents a conversion of CH_4 and CO_2 of 85 and 71%, respectively; which remain constant for 20 h.

On the other hand, CH_4 and CO_2 conversions (75 and 70%, respectively) are smaller on the supported Ni (5%)/La_2O_3. This result could be due to a smaller quantity of Ni on the solid and to the lack of homogeneity of the metallic phase due to the preparation method. In this sense, the perovskite type oxides are used as precursors because they present high metallic dispersion when they undergo reduction.

According to the XRD results, after the reforming reaction on $La_{0.6}Sr_{0.4}NiO_3$ (Fig. 6) the phases $SrCO_3$, La_2O_3 and Ni are observed, indicating that the phase $La_2O_2CO_3$ is an intermediate [30] of great importance in the reforming reaction allowing the oxidation of methane and the
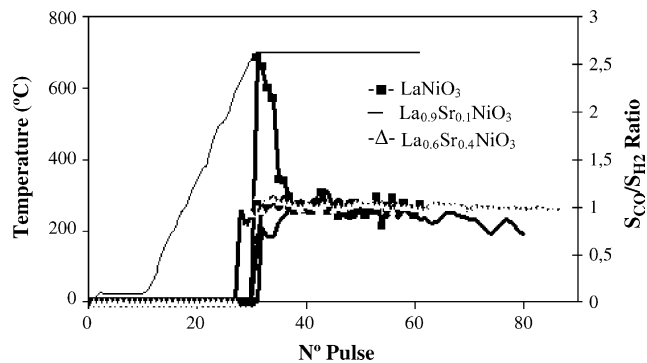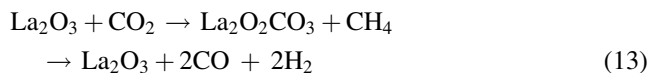
regeneration of La_2O_3, according to

$$La_2O_3 + CO_2 \rightarrow La_2O_2CO_3 + CH_4$$
$$\rightarrow La_2O_3 + 2CO + 2H_2 \qquad (13)$$

Other authors [31,32] have reported that the incorporation of Sr in La_2O_3 provides vacancies of surface oxygen making the oxidation of methane more favorable on the surface than in the bulk of the solid, hence $La_2O_2CO_3$ is formed so easily. The catalytic activity can also be related to the capacity to regenerate the vacancies of oxygen reagents on the surface when reforming reactions occur.

The XRD analyses indicate that the appreciable activity shown by these solids is attributed to the fact that the active phase for adsorption CH_4 stays as Ni^0 even after reaction, due to the reducible atmosphere ($CO–H_2$) formed during the reforming. The activity could also be attributed to the inhibition of coke deposits, considering that the Ni ions are highly dispersed in the lattice of the crystal of the perovskite and when reduced a good metallic dispersion is obtained on the La_2O_3–SrO matrix, which disfavors the deposition of coke on the active sites. Previous work [23] with time-on stream experiments has shown evidences of the good dispersions obtained. However, it has been reported [33] that the coke formation increases with the Sr content. These
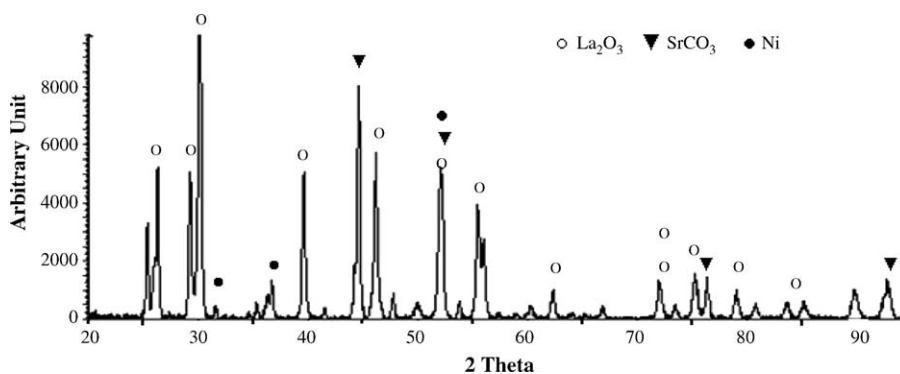

Fig. 6. XRD pattern of $La_{0.6}Sr_{0.4}NiO_3$ after $CH_4 + CO_2$ reaction.

results do not coincide with those observed in this work because the reaction was carried out by pulses and probably the time of reaction is too short to observe deposits of coke.

The ratio S_{CO}/S_{H_2} obtained for the different solids during the reaction was close to one (Fig. 7) indicating that the dry reforming is the main reaction taking place.

4. Conclusions

The partial substitution of La^{3+} for Sr^{2+} in $La_{1-x}Sr_xNiO_3$ structure decreases the oxidation state of Ni favoring its reduction and producing solids with the spinel type structure, due to the increase on vacancies that facilitate the mobility of the oxygen toward the surface of the solid.

The redox processes on the perovskite structure occur through intermediary species and they are not reversible, since changes of phases occur forming first $La_2Ni_2O_5$ at 420 °C, NiO at 610 °C and Ni, La_2O_3 at 690 °C, while $La_{0.6}Sr_{0.4}NiO_3$ becomes NiO at 500 °C and when the temperature increases to 700 °C it is reduced completely to Ni, La_2O_3 and SrO.

Before the reaction an important adsorption of CO_2 occurs, contributing to the formation of $La_2O_2CO_3$.

The high activity that these precursory solids present in the dry reforming of methane is due to the presence of Ni^0 during the course of the reaction and to the formation of $La_2O_2CO_3$ that allows the oxidation of methane and the regeneration of La_2O_3, besides suppressing carbon deposits.

Acknowledgements

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