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SCIENTIFIC PAPER

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CO₂ REFORMING OF CH₄ OVER M(Ca,Ba,Sr)_xLa_{1-x}NiO₃ PEROVSKITES USED AS COKE RESISTANT CATALYST PRECURSOR

Article Highlights

- M(Ca,Ba,Sr)_xLa_{1-x}NiO₃ ($x = 0.0, 0.3, 0.5$) perovskites were synthesized as catalyst precursors
- Ca, Sr and Ba doping in the perovskite lattice has evident influence on the reduction behavior
- The higher Ca-, Sr-, Ba-doping content ($x = 0.5$) leads to decreased activity for DRM
- Ca_{0.3}La_{0.7}NiO₃ shows excellent performance for DRM and coke deposition much smaller than LaNiO₃

Abstract

Methane and carbon dioxide are greenhouse gases that have been converted into synthesis gas for the production of oxygenated chemicals and hydrocarbons. In this paper, M(Ca, Ba, Sr)_xLa_{1-x}NiO₃ ($x = 0.0, 0.3$ and 0.5) doped perovskites were successfully synthesized as catalyst precursors aiming at high catalytic activity and stability in the CO₂ reforming of methane. These perovskites were characterized by X-ray diffraction (XRD), temperature programmed reduction by H₂ (H₂-TPR) and O₂-temperature programmed oxidation (TPO). Its activity and carbon suppression were investigated in the CO₂ reforming of methane. Results showed formation of perovskite structure, but La₂NiO₄ spinel and NiO were also detected in doped perovskites. The Ca, Ba and Sr partial substitution had evident influence on the reduction behavior of perovskites. All the doped perovskites used as catalyst precursors had better catalytic performance than LaNiO₃. However, increasing the doping content decreased activity. Among doped perovskites, Ca_{0.3}La_{0.7}NiO₃ showed better catalytic performance for the methane reforming reaction.

Keywords: alkaline-doped LaNiO₃, barium, calcium, strontium, coke, dry reforming of methane.

Natural gas could play a significant role as a carbon source for the world's supply of fuel and fuel-based chemicals in this century [1-3]. Methane is the main component of natural gas and almost all the transformation routes of this hydrocarbon involve its conversion into syngas (mixture of H₂ and CO and some CO₂) [3-4]. As seen in the literature [5], syngas is a key intermediate in the chemical industry and is

produced from methane by steam reforming, dry reforming, autothermal reforming or partial oxidation. According to studies [6-9], dry reforming of methane (DRM) yielded a lower syngas ratio (H₂/CO = 1), which is suitable for the synthesis of oxygenated chemicals and hydrocarbons from Fischer-Tropsch synthesis. In addition, the DRM reaction uses two strong greenhouse gases; CO₂ and CH₄ are converted to syngas and could mitigate the increase of global warming [10-12].

Nickel and noble metals are widely used as active metals for the DRM. Nickel-based catalysts have been most extensively studied for the DRM due to their relative abundance and low cost [13,14]. However, the biggest challenge is deactivating them

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by blocking carbon. For playing down the coke formation, various parameters such as the addition of promoters of alkaline oxides or alkaline-earth metals and highly dispersed nickel species on the support have been investigated [15–17]. According to studies [18–21], an attractive option is the use of perovskite-type precursors which are capable of producing well-dispersed metallic particles upon reduction treatment diminishing coke formation and increasing the activity and stability of the catalyst. Other advantages of perovskite-type oxides (ABO₃) are thermal stability, ease of synthesis, low cost and high composition flexibility due to the partial substitution of A and/or B cations [19]. The cation A is responsible for the thermal resistance of the catalyst whereas the cation B is responsible for the catalytic performance.

Sutthiumporn *et al.* [21] studied the effect of the cation B on the performance of La_{0.8}Sr_{0.2}Ni_{0.8}M_{0.2}O₃ perovskite (M = Bi, Co, Cr, Cu, Fe) perovskite-type oxides for DRM. While Fe-substituted Ni catalyst presented a low catalytic activity attributed to its low reducibility, the Cu-substituted Ni catalyst precursor was active. On the other hand, the effect of the partial substitution of the A ion, *i.e.*, the La partial substitution in LaNiO₃, affects the stability, mobility and storage of oxygen, coke resistance, and catalytic activity [22,23]. Lima *et al.* [22] studied a series of La_{1- γ} Ce _{γ} NiO₃ (γ = 0, 0.05, 0.4, 0.7) precursors of catalysts for DRM. The Ni/La₂O₃ reduced from LaNiO₃ is active for DRM but showed a slow deactivation with time on stream. On the other hand, the partial substitution of La by Ce led to an increase of the catalytic activity and stability in DRM due to inhibition of carbon formation. Similarly, La_{1- x} M _{x} NiO₃ precursors also gave better catalytic performance when La was partially substituted by Ce, Ca (for steam reforming), Sr (for oxidation of methane), K (for water–gas shift), Ce and Pr (for DRM) [24]. However, there are some restrictions for the La substitution high levels [25]. Morales *et al.* [26,27] has reported the high activity and very good stability of La_{0.5}Sr_{0.5}CoO_{3- δ} precursors for syngas production by partial oxidation of methane and steam and oxidative reforming. In contrast, there have been few studies of A-site-substituted perovskite-type oxides with only nickel in B-site for DRM, and the amount of carbon deposited on catalysts is rare. In addition, it is expected that the partial substitution of La by Ca, Sr or Ba in the perovskite lattice will improve the suppression of carbon formation and help stabilize the activity of the catalyst in the DRM reaction. In this paper, M(Ca,Ba,Sr) _{x} La_{1- x} NiO₃ (x = 0.0, 0.3, 0.5) family of perovskite-type oxides were synthesized as catalyst pre-

cursors and their activity and formation of carbon were investigated in the DRM reaction.

EXPERIMENTAL

Catalyst preparation

The (Ca,Ba,Sr) _{x} La_{1- x} NiO₃ (x = 0.0, 0.3, 0.5) perovskite-type oxides were prepared by a modification citrate method. Equimolar amounts of citric acid and ethylene glycol and stoichiometric amounts of (La, Ca, Ba, Sr, Ni) nitrates were used. A concentrated solution of citric acid was prepared and added to a solution of nickel nitrate with ethylene glycol, and the mixture was kept at 30 °C for 10 min under constant stirring. Then, solutions of La, Ca, Ba, Sr nitrates were added, the whole solution remaining at 30 °C for 30 min. After, the solution was evaporated and dried at 80 °C for 12 h to obtain spongy amorphous citrate. This material was crushed and calcined in two steps: 550 °C for 3 h and 800 °C for 5 h, both with the heating rate of 4 °C/min.

Catalyst characterization

The (Ca,Ba,Sr) _{x} La_{1- x} NiO₃ (x = 0.0, 0.3, 0.5) perovskites were characterized using X-ray diffraction (XRD), temperature programmed reduction by H₂ (H₂-TPR) and O₂-temperature programmed oxidation (TPO). XRD analyses were performed by the powder method on a Rigaku X-ray diffractometer (MiniFlex 600) operating at 40 KV, 15 mA, CuK α radiation and speed of 2°(2 θ)/min. H₂-TPR analysis was performed on SAMP3 equipment (Termolab Equipment, Brazil) with 100 mg of sample and flow of 30 mL/min (mixture 2% H₂/Ar). The sample was heated up to 1000 °C at 10 °C/min and the hydrogen consumption was monitored by a thermal conductivity detector.

The amount of deposited carbon on the spent catalysts was measured by TPO analyses. The spent catalyst was heated under air flow (30 mL/min) from room temperature up to 800 °C (10 °C/min). The oxygen consumption and CO₂ produced were continuously analyzed by a gas analyzer system (Pfeiffer GSD 320).

Catalytic activity

The dry reforming of CH₄ (DRM) was carried out in a fixed bed quartz U-tube microreactor with an inner diameter of 8 mm. The reactor was placed in an electrical furnace equipped with PID control of temperature. Prior to the reaction, the catalyst was activated by reducing *in situ* with H₂ (30 mL/min) from room temperature to 700 °C and was kept at this temperature for 1 h. The performance of the catalysts in the DRM was carried out at 700 °C and atmospheric

pressure. For all the experiments, a stoichiometric mixture of CH₄ (25 mL/min) and CO₂ (25 mL/min) was flowed into the reactor and 50 mg of catalyst was used for each run. The gaseous mixture flows were adjusted by electronic controllers (Brooks Instrument 0254). The conversions of methane and carbon dioxide were calculated according to Eqs. (1) and (2), respectively:

$$\chi_{\text{CH}_4} (\%) = 100 \left(\frac{F_{\text{input}} - F_{\text{output}}}{F_{\text{input}}} \right) \quad (1)$$

$$\chi_{\text{CO}_2} (\%) = 100 \left(\frac{F_{\text{input}} - F_{\text{output}}}{F_{\text{input}}} \right) \quad (2)$$

where χ is the conversion of reactants, F_{input} is the molar flow of the introduced reactant, and F_{output} is the molar flow of the corresponding composition in the effluent. The reactor was coupled in line to a mass spectrometer (Pfeiffer Thermo-Star GSD 320T) for continuous gas analysis. The data on the mass spectrometer were collected at an interval of 0.5 s. The feed and the effluent gases were analyzed using the following: CH₄ ($m/z = 16$ and 15), CO₂ ($m/z = 44$), H₂ ($m/z = 2$), and CO ($m/z = 28$).

RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of calcined (Ca,Ba,Sr)_xLa_{1-x}NiO₃ ($x = 0.0, 0.3, 0.5$) samples. All the peaks of LaNiO₃ ($x = 0.0$) match a cubic perovskite phase (JCPDS PDF No. 33-0710), indicating high phase purity of the synthesized sample. However, the peaks intensity of the perovskite structure

was reduced when La was partially replaced by alkaline-earth metal. Additionally, (Ca,Ba,Sr)_xLa_{1-x}NiO₃ ($x = 0.3$ and 0.5) doped perovskites show also reflection lines for La₂NiO₄ spinel (JCPDS PDF No. 11-0557) and NiO (JCPDS PDF No. 04-0835). No evidence of CaO, SrO and BaO peaks (JCPDS PDF No. 01-1160, 01-0886 and 01-0746, respectively) was observed. This behavior is in good agreement with literature data [23] that reports the formation of segregated oxides at $x \geq 0.7$, besides the perovskite phase. However, the existence of tiny Ca-, Sr- and Ba oxides cannot be totally excluded as considering their amounts are possibly below the XRD detection limit. According to Scherrer's equation, the average crystal size of the perovskite phase was in the range of 20-30 nm. It indicated that perovskites could promote the dispersion or inhibit the agglomeration of the Ni particles.

Since metallic nickel crystallites are deemed as the active sites for the DRM reaction, the perovskite-type precursors must be activated by reduction prior to reaction. Figure 2 shows all H₂-TPR profiles of (Ca,Ba,Sr)_xLa_{1-x}NiO₃ perovskites. The LaNiO₃ perovskite ($x = 0.0$) shows the reduction of Ni³⁺ to Ni²⁺ (460 °C), *i.e.*, LaNiO₃ to La₂NiO₄ [23] or La₂Ni₂O₅ [28], and then reduction of Ni²⁺ to Ni⁰ (640 °C), which remains supported on lanthanum oxide [23,28]. In addition, the ratio of areas under the peaks (second/first), near 2, corresponds to the expected hydrogen consumption for both processes and proves the coherence with the XRD results.

In Figure 2, the Ca, Ba and Sr partial substitution has evident influence on the reduction behavior of (Ca, Ba, Sr)_xLa_{1-x}NiO₃ perovskites ($x = 0.3$ and 0.5). The partial substitution promoted by the (Ca,Ba,Sr)-

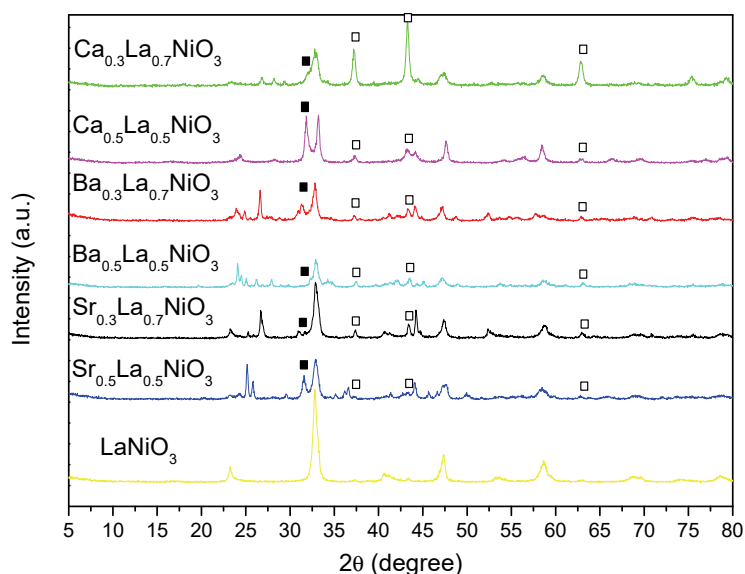


Figure 1. XRD patterns of $M(\text{Ca, Ba, Sr})_x\text{La}_{1-x}\text{NiO}_3$ ($x = 0.0, 0.3, 0.5$) perovskites. Peaks relating to NiO (■) and La₂NiO₄ spinel phase (□).

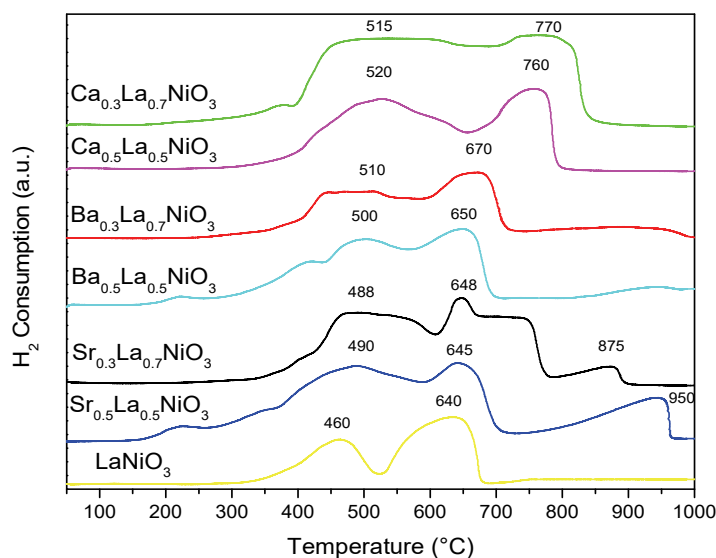


Figure 2. H₂-TPR profiles of M(Ca,Ba,Sr)_xLa_{1-x}NiO₃ (x = 0.0, 0.3, 0.5) perovskites.

-doping, modifies the LaNiO₃ perovskite to produce a more stable structure, which showed broad peaks of H₂ consumption at higher temperature. For doped perovskite samples, the first peak to near 500 °C corresponds to reduction of segregated NiO and (Ca,Ba,Sr)LaNiO₃, which happen almost simultaneously. Then, a peak at 600–800 °C was attributed to the reduction of La₂NiO₄ spinel. This also proves the existence of NiO and La₂NiO₄ in these samples, as observed by XRD. Thus, the high temperature peaks above 850 °C of TPR profiles of Sr- and Ba-doped samples were assigned to the NiO_x species, which are part of bulk perovskite lattice (Sr- or Ba-O-Ni⁺²) [29]. It is also possible to note an increase in intensity of this peak with increasing Sr and Ba content. Ca-doped samples show no peaks above 850 °C, but it is possible to note an increase in intensity of the peaks at low temperature [30]. Nevertheless, it could be noted that the intensity ratio between the first and second peaks is not 1:2 as expected in the perovskite reduction. This increase in intensity of the first peak was attributed to NiO reduction, which was detected by XRD patterns as segregated phase in (Ca,Ba,Sr)_xLa_{1-x}NiO₃ samples together with the perovskite structure (Figure 1). After the reduction, the Ni metal could be in a disperse state onto a matrix of La₂O₃ and alkaline oxides (CaO, SrO, BaO) particles [25]. In addition, (Ca,Ba,Sr)_xLa_{1-x}NiO₃ perovskites could be catalytically reduced and activated for the DRM.

The CO₂ reforming reaction of CH₄ was carried out at 700 °C. Figures 3 and 4 show the methane and carbon dioxide conversions on the (Ca,Ba,Sr)_xLa_{1-x}NiO₃ samples, respectively. For all samples, the CH₄ and CO₂ conversions began to rise during the reaction

time, tending to reach a steady state. Only LaNiO₃ shows decrease in CH₄ and CO₂ conversions after few hours on-stream. This catalytic deactivation occurs due to higher deposition of coke on the nickel active sites (Eq. (3)). On the other hand, all the doped perovskites (Ca,Ba,Sr)_xLa_{1-x}NiO₃ (x = 0.3 and 0.5) were more active and stable than LaNiO₃ in the DRM. The fact could be explained in the hypothesis that some other factors as nonstoichiometric, crystalline defects, oxygen vacancies and particle size may contribute to the best performance of the doped perovskites [31–33].



The addition of Ca, Sr and Ba should increase the oxygen transfer rate, consequently increasing the coke removal and thus contributing to the stability of the catalysts.

Note that Ca_{0.3}La_{0.7}NiO₃ presented better performance than Sr_{0.3}La_{0.7}NiO₃ and Ba_{0.3}La_{0.7}NiO₃. However, a higher Ca-doping content (x = 0.5) leads to decreased activity. The same fact also occurs for Sr- and Ba-doped samples. According to literature [34], La substitution low levels altered the geometric nature of the catalyst surface, *i.e.*, dividing the nickel particles into smaller ensembles less prone to coking. Another advantageous influence of (Ca,Ba,Sr)-doped perovskites may be considered due the increasing basicity of the catalysts surface, which in turn increases the ability of the catalyst to chemisorb CO₂. The increase in the concentration of adsorbed CO₂ is believed to reduce carbon formation in the CO disproportionation reaction. According to Lima *et al.* [30], the maximum values of methane and CO₂ conversion

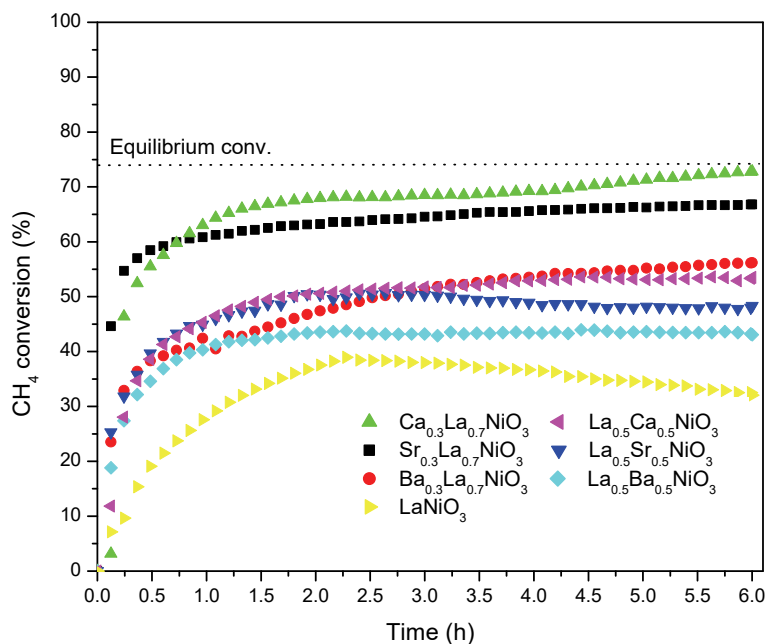


Figure 3. Conversion of methane on $M(\text{Ca,Ba,Sr})_x\text{La}_{1-x}\text{NiO}_3$ ($x = 0.0, 0.3, 0.5$) samples in the DRM at 700 °C.

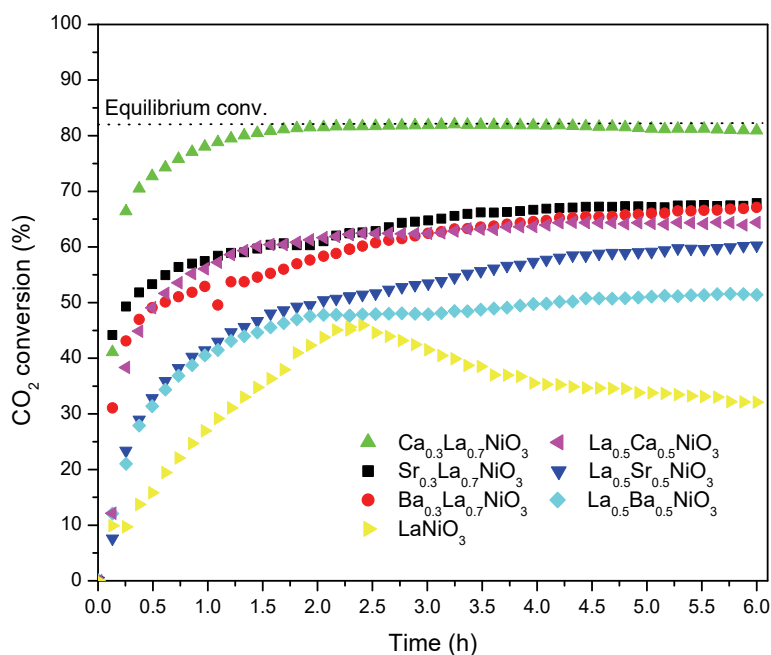


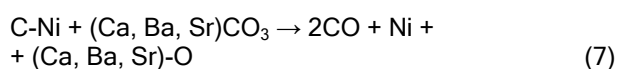
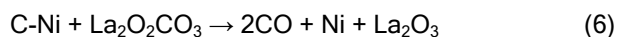
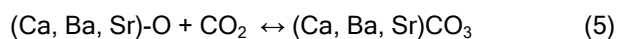
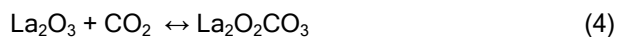
Figure 4. Conversion of carbon dioxide on $M(\text{Ca,Ba,Sr})_x\text{La}_{1-x}\text{NiO}_3$ ($x = 0.0, 0.3, 0.5$) samples in the DRM at 700 °C.

are reached for $x = 0.3$ and 0.5 . The composition is optimized for $x = 0.3$ and 0.5 , with the presence of the doping Ca but a reduced surface segregation. On the other hand, in high doping content can form a layer of Ca, Sr and Ba carbonate on the active site, decreasing the activity. However, $(\text{Ca,Ba,Sr})_x\text{La}_{1-x}\text{NiO}_3$ ($x = 0.3$ and 0.5) doped perovskites showed stability after 24 h time on stream, while LaNiO_3 showed full deactivation.

Table 1 shows the quantification of the carbon deposited measured by TPO for each sample after the DRM reaction. LaNiO_3 shows deactivation for DRM that can be associated with high amounts of surface carbon. On the other hand, all the doped perovskites $(\text{Ca,Ba,Sr})_x\text{La}_{1-x}\text{NiO}_3$ ($x = 0.3$ and 0.5) showed good stability and low amount of surface carbon.

According to results, the presence of lanthanum oxycarbonate (Eq. (4)) [21,25], combined with

(Ca,Ba,Sr) carbonate (Eq. (5)), suggests that the deposited carbon on the catalyst surface could be removed by reaction (Eqs. (6) and (7)), and the La₂O₃ and (Ca,Ba,Sr) oxides regenerated, enhancing the stability of the catalyst:



The results suggest that the presence of (Ca, Ba, Sr)-carbonates provides an alternate pathway to oxidize the carbon species on Ni surface, consequently increasing the coke removal during DRM. Furthermore, the results indicated that the increase in the alkaline strength of the Ca<Sr<Ba-doped perovskite decreases the catalytic activity and minimizes the formation of carbon. Therefore, Ca_{0.3}La_{0.7}NiO₃ presented better performance for DRM and amount of surface carbon much smaller than LaNiO₃ perovskite. Additionally, the amount of carbon deposited over Ca_{0.3}La_{0.7}NiO₃ was very low in comparison to values presented in the literature [30,35].

Table 1. Amount of carbon deposited on the M(Ca,Ba,Sr)_xLa_{1-x}NiO₃ (x = 0.0, 0.3, 0.5) samples after dry reforming of methane at 700 °C

Sample	Coke (mg/g _{cat.} h)
Ca _{0.3} La _{0.7} NiO ₃	0.37
Ca _{0.5} La _{0.5} NiO ₃	0.14
Ba _{0.3} La _{0.7} NiO ₃	0.06
Ba _{0.5} La _{0.5} NiO ₃	0.08
Sr _{0.3} La _{0.7} NiO ₃	0.24
Sr _{0.5} La _{0.5} NiO ₃	0.07
LaNiO ₃	4.50

CONCLUSION

(Ca,Ba,Sr)_xLa_{1-x}NiO₃ (x = 0.0, 0.3, 0.5) family of perovskite-type oxides were successfully synthesized by citrate method. After calcination, LaNiO₃ (x = 0.0) exhibited a single cubic perovskite phase and additionally La₂NiO₄ spinel and NiO were detected in doped perovskites (Ca,Ba,Sr)_xLa_{1-x}NiO₃ (x = 0.3 and 0.5). The Ca, Ba and Sr partial substitution has evident influence on the reduction behavior of doped perovskites, but only Ca-doped samples showed no peaks above 850 °C. All the doped perovskites used as catalyst precursors had better catalytic performance, higher stability and lower coke deposition than

LaNiO₃ in the DRM reaction. However, increasing the doping content decreased activity and Ca_{0.3}La_{0.7}NiO₃ presented the better performance for the DRM.

Acknowledgments

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NAUČNI RAD

REFORMING METANA UGLJEN-DIOKSIDOM KORISTEĆI PEROVSKITE $M(\text{Ca}, \text{Ba}, \text{Sr})_x \text{La}_{1-x} \text{NiO}_3$ KAO PREKURSORE KATALIZATORA OTPORNIH NA KOKS

Metan i ugljen-dioksid su gasovi sa efektom staklene bašte koji su konvertovani u sintezni gas za proizvodnju oksigenovanih hemikalija i ugljovodonika. U ovom radu, uspešno su sintetizovani perovskiti dopirani $M(\text{Ca}, \text{Ba}, \text{Sr})_x \text{La}_{1-x} \text{NiO}_3$ ($x = 0, 0,3$ i $0,5$) kao prekursor katalizatora sa ciljem postizanja visoke katalitičke aktivnosti i stabilnosti u reformingu metana sa CO_2 . Ovi perovskiti se okarakterisani difrakcijom XRD metodom, temperaturno programiranom redukcijom vodonikom (H_2 -TPR) i oksidacijom kiseonikom (TPO). Njihova aktivnost i supresija ugljenika istraženi su u reformingu metana sa CO_2 . Rezultati su pokazali formiranje strukture perovskita, ali su u dopiranim perovskitima nađeni i La_2NiO_4 spinel i NiO . Delimična supstitucija Ca, Ba i Sr ima evidentan uticaj na redukciono ponašanje perovskita. Svi dopirani perovskiti koji se koriste kao prekursori katalizatora imali su bolje katalitičke performanse od LaNiO_3 . Međutim, povećanje sadržaja dopinga smanjilo je aktivnost. Među dopiranim perovskitima, $\text{Ca}_{0,3}\text{La}_{0,7}\text{NiO}_3$ pokazao je najbolje katalitičke performanse za reakciju reformiranja metana.

Ključne reči: alkalno dopirani LaNiO_3 , barijum, kalcijum, stroncijum, koks, suvi reforming metana.