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Article

Synthesis, characterization, and catalytic performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ perovskite catalysts in dry reforming of coke oven gas

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ABSTRACT

The dry reforming of coke oven gas (COG) to produce syngas was performed over $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ catalysts in a fixed-bed reactor at 800 °C. These perovskite-type oxides were synthesized using a sol-gel method and characterized using X-ray diffraction (XRD), N_2 adsorption-desorption, temperature-programmed reduction of H_2 , scanning electron microscopy, transmission electron microscopy, and thermogravimetry-differential scanning calorimetry. XRD results showed that the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ perovskite-type oxides formed quaternary solid solutions. The effects of the degree of Ni substitution (x) and the catalyst calcination temperature on the dry reforming of COG were investigated. XRD analysis of the tested catalysts showed the formation of Ni^0 , Co^0 , and $\text{La}_2\text{O}_2\text{CO}_3$, of which the latter is the main active phase responsible for the high activity and stability, and the suppression of coke formation under severe reaction conditions. COG rich in H_2 can also reduce the formation of carbon deposits by inhibiting CH_4 decomposition.

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1. Introduction

Synthesis gas is an important feedstock for the petrochemical industry, and consists mainly of H_2 and CO. It is widely produced from natural gas (CH_4) and is used in a diverse range of industrial processes [1,2]. The established techniques for producing syngas are effective, and depend on the different characteristics of the CH_4 reforming reactions [3,4] such as steam reforming, dry reforming, and partial oxidation reforming [5]. Among these natural reforming processes, in terms of global warming and growing energy needs, dry reforming or CO_2 reforming of CH_4 ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) has been shown to

have significant environmental and economic advantages, because two harmful greenhouse gases are converted to green H_2 . This process is stimulating increasing interest, because it produces syngas with a low H_2/CO ratio, which is preferable for liquid hydrocarbon production in the Fischer-Tropsch reaction [6–8].

Most current studies in this field concentrate on CO_2 reforming of CH_4 from natural gas, but other CH_4 sources are also appropriate for the reaction [9]. One such alternative is coke oven gas (COG), which is a by-product of coke production from coal in the steel industry [10,11]. The composition of COG is typically H_2 (~58%–60%), CH_4 (~23%–27%), CO (~5%–8%),

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and CO₂ (less than 3%). Only a small fraction of the COG can be used as fuel in the coking plant; the rest is generally burnt off or even discharged into the atmosphere [12]. The environmental impact is large, because of the substantial greenhouse gas emissions [13,14]. Much attention has therefore been given to the CO₂ reforming of COG, which can provide a more sustainable solution for the transformation of this highly energetic gas and minimization of CO₂ concentration [15]. The most significant feature of this alternative is the production of syngas with a H₂/CO ratio close to 2, the ideal proportion for methanol synthesis, without any conditioning stages. Another interesting characteristic of CO₂ reforming of COG is that the energy required for this endothermic reaction can be provided by the blast furnace, which produces a large volume of exhaust gas [16]. Furthermore, CO₂ reforming of COG is a catalysed reaction for which the rapid deactivation of the catalyst caused by carbon deposition is a serious problem [17]. The development of catalysts with high activities and stabilities, and which inhibit carbon formation during the reforming reaction, is therefore important.

In recent decades, noble-metal-based catalysts have been reported to be less sensitive to coking than Ni-based catalysts. However, Ni-based catalysts still warrant investigation, because their low cost and high availability make them more affordable in commercial processes [18,19]. In this respect, one strategy is to introduce Ni and/or Co in a defined structure or solid solution. Perovskite-type oxides (ABO₃) with a well-defined structure have interesting redox properties and are accessible, enabling them to acquire very highly dispersed nanoscale metallic particles under a reducing atmosphere; this promotes the catalytic activity and diminishes coke formation [20,21]. Another advantage of perovskite-type oxides is the wide range of possible substitutions of A and/or B cations, enabling combination of elements with different oxidation states [22].

Valderrama et al. [23] used the B-site-substituted perovskite-type oxide LaNi_{1-x}Co_xO₃ as a catalyst precursor for the dry reforming of CH₄. Ni⁰, Co⁰, and La₂O₂CO₃ were formed in catalytic tests, and gave high activities and stabilities. Sutthiumporn et al. [24] found that a small amount of Sr with a promotional doping element in the A site gave a better catalytic performance, because of the presence of surface oxygen species.

However, there have been few studies of B-site-substituted perovskite-type oxides with a fixed A-site doping content. The main objective of this study was therefore to investigate the activities and stabilities of quaternary solid solutions, La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃, as catalysts for CO₂ reforming of COG in a fixed-bed reactor. The effect of calcination temperature on the catalytic performance was also studied.

2. Experimental

2.1. Catalyst preparation

La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ quaternary perovskite-type oxides were prepared using a sol-gel method. Stoichiometric quantities of La(NO₃)₃·6H₂O, Sr(NO₃)₂, Ni(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O

were mixed and dissolved in the required amount of deionized water. Ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) were added to the aqueous solution as complexing agents, in appropriate molar ratios (all metal ions/EDTA/CA = 1:1:1.5) [25,26], and the pH was adjusted to 7–8 by ammonia titration. The resulting solution was stirred at near 100 °C with an electromagnetic agitator until evaporation of water had reduced the solution to a hyaloid gel. This gel was dried overnight at 120 °C, and calcined in air for 6 h, after heating to 850 °C at a rate of 5 °C/min.

2.2. Sample characterization

The phase compositions and internal structures of the catalysts before and after reaction were identified by X-ray diffraction (XRD), using a Rigaku D/Max-2200 X-ray diffractometer. The scans (2θ) were conducted over the range 10° to 90° at a rate of 6°/min, using Cu K_α radiation (40 kV, 40 mA).

The surface areas and pore sizes of the solids were measured by N₂ adsorption-desorption at -196 °C, using a Micromeritics ASAP 2010 adsorption meter; the samples (0.1–0.2 g) were degassed for 2 h at 200 °C before measurement.

Temperature-programmed reduction (TPR) studies were performed using a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector (TCD) under a flow of a reducing H₂ mixture. Samples (0.1 g) of fine catalyst were placed in a quartz-tube reactor of radius 5 mm, heated to 200 °C, and purged at constant temperature in an Ar atmosphere. A mixture of 5% H₂ in Ar was then passed through the reaction tube at a flow rate of 30 mL/min; the temperature was increased to 1000 °C at 10 °C/min. The effluent gas was monitored by the TCD to detect variations in the H₂ concentration, which indicate the possible compositions of subproducts.

The morphologies and elemental compositions of the catalysts, and metal dispersion and carbon deposition on the catalysts after the reaction were determined using field-emission scanning electronic microscopy (FE-SEM; JEOL JSM-6700F) and transmission electron microscopy (TEM; JEOL JEM 200CX).

Thermogravimetry-differential scanning calorimetry (TG-DSC) was performed, using a thermal analyser (NETZSCH STA 449 F3), to measure the amount of deposited carbon on the catalyst after reaction. In the TG-DSC process, a sample (20 mg) was exposed to a gas mixture consisting of 10% O₂ in N₂ at a flow rate of 40 mL/min, while the temperature was raised from ambient to 900 °C at a rate of 10 °C/min.

Temperature-programmed hydrogenation (TPH) was also performed using the Micromeritics AutoChem II 2920. A sample (50 mg) of each tested catalyst was placed in a quartz tube and heated to 950 °C at a rate of 10 °C/min under 10% H₂ in Ar. The TPH tail gas was tested using a microreactor-mass spectrometer (Hidden Analytical, Catlab).

2.3. Dry reforming of COG

Catalytic activity tests were performed at atmospheric pressure in a 6-mm internal diameter quartz-tube reactor installed in a fixed-bed continuous flow system, as we have pre-

viously reported [27,28]. The COG (31.5% CH₄, 57.98% H₂, 3.12% CO₂, and 7.4% CO) was mixed with additional CO₂ to obtain a feed reaction gas (24.54% CH₄, 24.54% CO₂, 5.76% CO, and 45.16% H₂), with a 1:1 ratio of CH₄ to CO₂, determined by a mass flow meter. The catalyst (approximately 0.5 g) was placed in the reactor tube and reduced by a mixture of 15% H₂ in N₂ (30 mL/min) for 10 h, after heating from room temperature to 800 °C at a constant rate of 5 °C/min. After reduction, the gas flow was switched to the feed gas, at a rate of 100 mL/min, and the catalyst was tested at 800 °C for 24 h. The gas flow rates were controlled by mass flow controllers. The tail gas from the reactor was first filtered through a dehydrating agent and then analysed using the GC-9160 gas chromatograph with which the instrument was equipped.

In all experiments on the dry reforming of COG, the conversions, *X*, of CH₄ and CO₂ and the selectivities, *S*, of CO and H₂ were separately calculated using the following equations [29,30]:

$$X_{\text{CH}_4} = \frac{F_{\text{in,CH}_4} - F_{\text{out,CH}_4}}{F_{\text{in,CH}_4}} \times 100\%$$

$$X_{\text{CO}_2} = \frac{F_{\text{in,CO}_2} - F_{\text{out,CO}_2}}{F_{\text{in,CO}_2}} \times 100\%$$

$$S_{\text{H}_2} = \frac{F_{\text{out,H}_2}}{F_{\text{in,H}_2} + 2(F_{\text{in,CH}_4} - F_{\text{out,CH}_4})} \times 100\%$$

$$S_{\text{CO}} = \frac{F_{\text{out,CO}}}{F_{\text{in,CO}} + (F_{\text{in,CH}_4} - F_{\text{out,CH}_4}) + (F_{\text{in,CO}_2} - F_{\text{out,CO}_2})} \times 100\%$$

*F*_{in} and *F*_{out} represent the flow rates of the inlet and outlet gases, respectively.

3. Results and discussion

3.1. Catalyst characterization

Figure 1(a) shows the XRD patterns of the synthesized La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ solids calcined at 850 °C. The results show that whatever the degree of Ni substitution (*x*), the samples prepared using the sol-gel method retain good crystallinity in the perovskite structure, without the presence of any impurity phases. The substitution of Ni for Co slowly prompts changes in the diffraction peak intensities; the intensity of the diffraction peak corresponding to the NiO phase increases with increasing Ni content, as reported previously [31]. As can be seen from Table 1, which summarizes the Brunauer-Emmett-Teller (BET) specific surface areas and the main characteristics of the catalysts, the formation of different perovskite phases after calcination is determined by the degree of substitution [32]. For *x* < 0.5, La_{0.6}Sr_{0.4}CoO₃ and LaSrCoO₄ are obtained, and the NiO phase is not apparent; for *x* ≥ 0.5, NiO and La_{1.5}Sr_{0.5}NiO₄ are also observed. The peak structures show a gradual change from LaSrCoO₄ to La_{1.5}Sr_{0.5}NiO₄ as the value of *x* increases.

To investigate the effect of the partial substitution of B cations, the angular area between 31° and 34°, which contains the most intense diffraction peaks of La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃, was magnified, as shown in Fig. 1(b). The diffraction intensity of the peak at around 31.5° increases with increasing Ni content, as a result of lattice distortion, which shows the formation of La_{1.5}Sr_{0.5}NiO₄. However, the peak at about 33.2° does not show any significant shift in symmetry, suggesting the formation of a

Fig. 1. XRD patterns of La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ solids after calcination at 850 °C (a) and more intense peak of La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ (b).

Table 1

BET specific surface areas and XRD results for La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ solids.

Sample	<i>S</i> _{BET} (m ² /g)	XRD phase		
		Synthesized	After redox	After reaction
La _{0.6} Sr _{0.4} NiO ₃	4.66	La _{1.5} Sr _{0.5} NiO ₄ , NiO	Ni, La(OH) ₃ , SrO	Ni, La ₂ O ₂ CO ₃ , SrO
La _{0.6} Sr _{0.4} Ni _{0.7} Co _{0.3} O ₃	3.50	La _{1.5} Sr _{0.5} NiO ₄ , NiO		
La _{0.6} Sr _{0.4} Ni _{0.5} Co _{0.5} O ₃	2.91	La _{0.6} Sr _{0.4} CoO ₃ , LaSrCoO ₄ , NiO	Ni, Co, La(OH) ₃ , SrO	Ni, Co, La ₂ O ₂ CO ₃ , SrO
La _{0.6} Sr _{0.4} Ni _{0.3} Co _{0.7} O ₃	6.42	La _{0.6} Sr _{0.4} CoO ₃ , LaSrCoO ₄		
La _{0.6} Sr _{0.4} CoO ₃	3.02	La _{0.6} Sr _{0.4} CoO ₃	Co, La(OH) ₃ , SrO	Co, La ₂ O ₂ CO ₃ , SrO

Table 2

Lattice parameters for hexagonal and rhombohedral symmetries of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids.

Sample	Hexagonal symmetry			Rhombohedral symmetry	
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	α
$\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$	5.3986	5.3986	13.1643	5.3824	60.20
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_3$	5.4046	5.4046	13.1584	5.3828	60.26
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	5.4020	5.4020	13.2183	5.3982	60.05
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$	5.4212	5.4212	13.1968	5.3988	60.27
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	5.4272	5.4272	13.2214	5.4075	60.24

solid solution containing LaSrCoO_4 and $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$. Table 1 also shows that the specific surface areas of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ catalysts vary from 2.91 to 6.42 m^2/g , depending on the substitutions, although this has no direct relationship with the catalytic activities of the samples.

The cell parameters for the hexagonal and rhombohedral symmetries of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids are shown in Table 2. These were calculated for each *x* value, indexing the most intense diffraction peaks in Fig. 1 in the planes corresponding to (110) and (024) of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (JCPDS 89-5719) to an ideal hexagonal system; the distorted rhombohedral parameters were also calculated using the equations reported by Valderama et al. [33,41]. The rhombohedral parameters decrease with Ni content from 5.4075 to 5.3824 Å, which contributes to the decrease in the B–O distance in the perovskite-type structure [23], confirming solid solution formation among these quaternary systems.

Figure 2 shows the H_2 -TPR profiles of the fresh catalysts, and the corresponding H_2 consumptions for different peaks are shown in Table 3. There are several reduction peaks, arising from the formation of different Ni and Co intermediate phases, and the final reduction temperature and H_2 consumption decrease with increasing Ni content. The two samples with $x < 0.5$ have three H_2 consumption peaks, corresponding to the reduction of Co ions with different valences. The first peak, at 300 °C, corresponds to the reduction of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, the second peak to the reduction of NiO , and the third to the reduction of LaSrCoO_4 . The reduction process is consistent with the results reported by Valderrama et al. [33]:

For $x \geq 0.5$, the transition peak of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ disappears with increasing degree of substitution, and two reduction peaks are observed. The first peak appears at a lower temperature,

Fig. 2. H_2 -TPR profiles of calcined $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids. **Fig. 3.** XRD patterns of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids after reduction with H_2 at 800 °C.

around 350–400 °C, corresponding to free NiO , which is more readily reduced by H_2 . The second peak arises mainly from the reduction of $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$ to La_2O_3 , SrO , and Ni^0 .

The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ XRD profiles after reduction by H_2 at 800 °C are shown in Fig. 3. The results are in keeping with the TPR analysis. The formation of the active species Ni^0 and Co^0 over La_2O_3 and SrO promotes high metal dispersion without formation of a Ni–Co alloy, as shown in Table 1. This is a crucial factor in resistance to the formation of carbon deposits in the CO_2 reforming of COG.

Table 3

Temperatures and H_2 consumptions in TPR analyses of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids.

Sample	1st Peak		2nd Peak		3rd Peak		Total	Particle size (nm)
	<i>T</i> (°C)	Quatity (cm^3/g)	<i>T</i> (°C)	Quatity (cm^3/g)	<i>T</i> (°C)	Quatity (cm^3/g)	Quatity (cm^3/g)	
$\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$	368.0	64.8	474.2	66.2	—	—	131.0	32
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_3$	380.8	55.0	466.6	80.7	—	—	135.7	33
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	384.7	72.4	449.1	75.8	—	—	148.2	28
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$	294.5	39.1	350.8	16.2	445.7	101.7	157.0	34
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	323.8	55.7	485.0	82.6	517.3	24.9	163.2	29

Fig. 4. Catalytic performance in CO_2 reforming of COG over $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids. (a) CH_4 conversion; (b) CO_2 conversion; (c) H_2 selectivity; (d) CO selectivity. Reaction conditions: gas hourly space velocity = 12000 mL/(g·h), CH_4/CO_2 molar ratio = 1.0 (24.54% CH_4 , 24.54% CO_2 , 5.76% CO, 45.16% H_2), $P = 1$ atm, and $T = 800$ °C.

3.2. Catalytic performance

Figure 4 shows the catalytic activities and stabilities of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ catalysts obtained from CO_2 reforming of COG at 800 °C; the averages of all catalytic parameters in the process are summarized in Table 4. As expected, the conversions of CH_4 and CO_2 and the selectivities for CO and H_2 are improved greatly by increasing the degree of Ni substitution to 1, suggesting that the reforming reaction is favoured by the presence of Ni. This behaviour arises because metallic Ni^0 has better activity than Co^0 for the suppression of carbon deposition during the reforming reaction, and the reduction of polyvalent Co ions requires higher temperatures, according to the TPR profiles [34]. An increase of x from 0 to 0.3 significantly improves the catalytic activity, with the CH_4 conversion increasing from 50.5% to 87.2%. This indicates that Ni doped in the samples has a synergetic effect, which accelerates Co acti-

Table 4

Average values of conversion, selectivity, and carbon deposition in CO_2 reforming of COG over $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids.

Sample	Conversion (%)		Selectivity (%)		Carbon deposition (wt%)
	CH_4	CO_2	H_2	CO	
$\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$	93.3	96.3	88.8	98.8	16.1
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_3$	91.2	95.0	85.6	96.4	25.4
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	87.4	94.5	85.6	95.6	28.4
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$	87.2	94.3	86.9	97.4	19.2
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	50.5	85.0	80.8	98.6	0.6

vation and eliminates the initial induction period. Furthermore, the CH_4 conversions shown in Table 4 are a little smaller than the CO_2 conversions. Valderrama et al. [23] reported that the presence of Sr slightly promoted the side reactions of CO_2 reforming of COG, including the reverse water-gas shift reaction; this not only increases the CO_2 conversion but also gives rise to higher selectivity for CO by the participation of H_2 and CO_2 [29]. Furthermore, there are no changes in the activities over other catalysts during 20 h runs, indicating excellent stability.

The effect of calcination temperature on the catalytic activities of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$ catalysts was investigated. The results are shown in Fig. 5, and the average values are listed in Table 5. It is evident that the CH_4 and CO_2 conversions of all the catalysts do not have large temperature gradients, with the values ranging from 89.9% to 92.8%. However, the results still show different catalytic activities. When the temperature is increased from 600 to 800 °C, the conversions of CH_4 and CO_2 increase from 91.6% and 98.6%, respectively, to 92.8% and 99.8%. The higher calcination temperature leads to the formation of a more strongly interacting perovskite structure, which requires a higher temperature for reduction. This decreases the content of free NiO and causes the metal Ni particles from the perovskite structure to be highly dispersed on the support, leading to better catalytic activity. However, when the temperature rises to 900 °C, the conversions of CH_4 and CO_2 fall to 90.7% and 98.7%, respectively, suggesting that the catalytic activity is related not only to the degree of metal dispersion but also to the amount of carbon deposited, which is determined by the interactions. When the calcination temperature is over 800 °C,

Fig. 5. Catalytic activity in CO₂ reforming of COG over La_{0.6}Sr_{0.4}NiO₃ solids with different calcination temperatures. (a) CH₄ conversion; (b) CO₂ conversion; (c) H₂ selectivity; (d) CO selectivity. Reaction conditions: GHSV = 12 000 g⁻¹ h⁻¹, CH₄/CO₂ molar ratio = 1.0 (24.54% CH₄, 24.54% CO₂, 5.76% CO, 45.16% H₂), P = 1 atm, and T = 800 °C.

the phase structure of the catalyst changes with the disappearance of La₂O₃, which leads to a decrease in metallic Ni in the crystalline phase, and therefore a decrease in the catalytic activity, as reported by Zhang et al. [35,36].

3.3. Coke deposition on tested La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃

Figure 6 shows the XRD patterns of the La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ catalysts after reaction; Ni⁰, Co⁰, SrO, La₂O₃, SrCO₃, and La₂O₂CO₃ phases are observed. Previous research has shown that an important CO₂ adsorption produces SrCO₃ and La₂O₂CO₃ in the CO₂ reforming of COG [37]. The observation of the La₂O₂CO₃ phase here provides corroborating evidence that it is an important reaction intermediate and has a significant impact on the reforming process. It is evident that La₂O₃ doped with Sr provides oxygen vacancies, which promote the oxidation of CH₄, enabling La₂O₂CO₃ to be formed more readily, as reported by Fierro et al. [38]. The La₂O₂CO₃ phase and CH₄ interact to regenerate La₂O₃, which inhibits coke deposition and

contributes to the high catalytic activity. Furthermore, the XRD analyses show that the presence of Ni⁰ and Co⁰ can be attributed to the reducible atmosphere (CO–H₂). These phases are highly dispersed in the lattice of the perovskite crystal, also preventing the formation of deposits [39].

Microstructural analyses of the La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ solids after reaction were performed using SEM; the images are shown in Fig. 7. The surface structures of the tested catalysts with different degrees of Ni substitution differ significantly. Some agglomeration of metallic particles and whisker carbon species is evident, suggesting the formation of deposits of dif-

Table 5

Average values for conversion, selectivity, and carbon deposition in CO₂ reforming of COG over La_{0.6}Sr_{0.4}NiO₃ solids with different calcination temperatures.

Calcination temperature (°C)	Conversion (%)		Selectivity (%)		Carbon deposition (wt%)
	CH ₄	CO ₂	H ₂	CO	
600	91.6	98.6	85.1	97.0	23.4
700	92.8	99.8	87.4	97.8	17.3
800	92.3	99.3	85.6	99.4	16.4
900	90.7	98.7	85.5	97.0	24.6
1000	89.9	98.0	86.4	98.1	22.6

Fig. 6. XRD patterns of La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O₃ solids after reaction at 800 °C.

Fig. 7. SEM images of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids after reaction at 800 °C. (a) $x = 0$; (b) $x = 0.5$; (c) $x = 1$.

ferent qualities after the reforming reaction. TEM was used to further observe the dispersion of the metallic particles and coke formation over the catalysts; the images are shown in Fig. 8. It can be seen that the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ catalyst, which has the lowest activity, has few carbon nanotubes. When $x = 0.5$, a large number of carbon nanotubes are observed. However, for $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$, the number of carbon nanotubes is smaller, indicating that the increase in their formation with increasing degree of Ni substitution occurs only within a certain range of x . The metallic particles are uniformly dispersed on the matrix solid and are not covered by the whisker carbon, which indicates that the perovskite-type catalyst precursors have stable structures and good catalytic activities under severe reaction conditions [40,41].

The specific amount of carbon deposited was determined using TG-DSC. Figure 9(a) and (c) show an obvious weight gain for the samples, caused by Ni oxidation, from 300 to 500 °C. Varying degrees of weight loss then occur, because of oxidation of carbon species on the used catalysts, from 500 to 700 °C. The amount of carbon deposited ranges from 0.7% to 28.4%, depending on the degree of substitution. $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ has the least amount of deposited carbon, because of its low catalytic activity, although the amount of carbon is not maximum on $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$, confirming the SEM and TEM results. The effects of calcination temperature on the carbon deposits are shown in Fig. 9(c) and (d). When the temperature is increased from 600 to 800 °C, the amount of deposited carbon decreases from

23.4% to 16.5%, but then rises again to 24.7% at 900 °C. These results indicate that a low calcination temperature leads to instabilities in the crystal structure, and a high temperature leads to sintering of metallic Ni particles, promoting the formation of carbon deposits.

TPH analysis was performed to further study the type of carbon deposited; the results are shown in Fig. 10(a) and the mass spectrum is shown in Fig. 10(b). These results indicate the formation of different carbon species, as we have previously reported [42]. The first peaks (230 and 270 °C) are related to removal of active carbon species such as CH_x ($x = 1, 2, 3$) [43]. The negative peak at 330–350 °C is assigned to the reaction of deposited carbon species with H_2 at the Ni/ $\text{La}_2\text{O}_2\text{CO}_3$ interface to produce CH_4 , as shown in Fig. 10(b). Slagtern et al. [44] found that CH_x can react with H_2 to form CH_4 . The second peaks observed in the TPH profiles (500 and 610 °C) are related to whisker-type carbon and graphitic carbon, largely originating from CH_4 decomposition [45], as observed in the SEM and TEM images. The second negative peak, at 750–800 °C, arises from formation of C_2H_4 , as the mass spectrum shows. The carbon corresponding to the peak at 793 °C probably originates from CH_4 decomposition and CO disproportionation [46]. The TPH analysis also indicates that CH_4 decomposition is a reversible process, and that high concentrations of H_2 in the COG can efficiently inhibit carbon deposition in the reforming reaction.

Figure 11 shows a schematic diagram of the surface reaction over the reduced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ perovskite catalysts. Both

Fig. 8. TEM images of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ solids after reaction at 800 °C. (a) $x = 0$; (b) $x = 0.5$; (c) $x = 1$.

Fig. 9. TG-DSC profiles of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{1-x}\text{Co}_x\text{O}_3$ catalysts and $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$ with different calcination temperatures. (a), (c) TG weight analysis; (b), (d) DSC analysis.

Fig. 10. TPH analysis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{1-x}\text{Co}_x\text{O}_3$ solids after reaction at 800 °C. (a) TPH profiles; (b) Mass spectrum of TPH tail gas.

CH_4 and CO_2 activation are assumed to occur directly on the metallic surface to form adsorbed hydrogen and carbon atoms, and an important CO_2 adsorption occurs on the La_2O_3 – SrO matrix, producing SrCO_3 and $\text{La}_2\text{O}_2\text{CO}_3$, the active species for CO_2 reforming of COG. The reaction of carbonate species with surface carbon species occurs at the metal sites, converting the carbon species to CO [6]. In this way, the elimination and production of CH_x and graphitic carbon on the surface of the catalysts reach equilibrium. The following scheme summarizes the related elementary steps:

The catalytic activity and stability are therefore not affected by the formation of carbon deposits, mainly for the following reasons: (1) the presence of $\text{La}_2\text{O}_2\text{CO}_3$ inhibits carbon formation by reacting with CH_4 to reform CO; (2) the strong interactions between the highly dispersed metallic particles and the support enable the catalyst to maintain high activity; and (3) COG containing abundant H_2 can also reduce the formation of carbon deposits by inhibiting decomposition of CH_4 .

Fig. 11. Schematic diagram of proposed mechanism of surface reactions over reduced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.4}\text{Co}_{1-x}\text{O}_3$ perovskite catalysts.

4. Conclusions

A series of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ catalysts were prepared using a sol-gel method, and tested in CO_2 reforming of COG. The results indicate that partial substitution of Ni for Co improves the catalytic activity and stability, because metallic Ni^0 has better activity than Co^0 in the reforming reaction. The active Ni^0 and Co^0 species, which are nanoscale particles stabilized by the Sr doping, are highly dispersed on the matrix of the solid $\text{La}_2\text{O}_3\text{--SrO}$ and suppress coke formation. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3$ calcined at 800 °C displays the best catalytic activity and anti-coking ability. The XRD results indicate that $\text{La}_2\text{O}_2\text{CO}_3$ is a reaction intermediate that plays a very important role in the reforming reaction by inhibiting the formation of carbon deposits, accelerating the oxidation of CH_4 and regeneration of La_2O_3 under the severe reaction conditions used.

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Graphical Abstract

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Synthesis, characterization, and catalytic performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ perovskite catalysts in dry reforming of coke oven gas

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CO_2 is adsorbed on a $\text{La}_2\text{O}_3\text{--SrO}$ matrix producing SrCO_3 and $\text{La}_2\text{O}_2\text{CO}_3$, the active species for CO_2 reforming of COG; these species inhibit carbon formation by reacting with CH_4 to reform CO and H_2 . The reaction of carbonate species with surface carbon species occurs at the metal sites, converting the carbon species to CO. COG containing abundant H_2 can also reduce the formation of carbon deposits by inhibiting decomposition of CH_4 .

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焦炉煤气二氧化碳重整制合成气中 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ 钙钛矿催化剂的合成、表征和催化性能研究

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摘要: 采用溶胶凝胶法制备了 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ 钙钛矿催化剂, 并测试了该催化剂在焦炉煤气 CO_2 重整反应中的性能。通过X射线衍射、 N_2 吸附脱附、程序升温还原、扫描电镜、透射电镜和热重-微分扫描量热等方法对催化剂进行了表征。结果表明, 溶胶凝胶法合成的 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ 催化剂形成了钙钛矿结构的固溶体。着重考察了钙钛矿催化剂焙烧温度和A位Ni的掺杂含量对其催化性能和反应后积碳的影响。结果表明: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Co}_{1-x}\text{O}_3$ 钙钛矿催化剂在反应中生成了活性金属Ni, Co颗粒和 $\text{La}_2\text{O}_2\text{CO}_3$, 这些组分对催化剂的活性和稳定性起关键性的作用, 并且能够抑制积碳的形成; 焦炉煤气中的富氢气体具有抑制甲烷裂解反应发生的作用, 从而减少催化剂的积碳。

关键词: 合成气; 催化活性; 钙钛矿; 干重整; 焦炉煤气; 积碳

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