

Nanostructured La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ Perovskite for the Steam Methane Reforming

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Abstract This work describes the synthesis of La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ perovskite using a polymerization chemical route, for application on steam methane reforming reaction, compared to the LaFeO₃ oxide. Results derived from X-ray diffraction (XRD), X-ray photoelectron spectroscopy and transmission electron microscopy (TEM) confirmed the presence of a prevalent orthorhombic structure related with a nanostructured solid (15-33 nm). The methane conversion of La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ oxide is very high compared to the LaFeO₃ oxide at 700 °C. The stability test was performed during 240 h, using the catalyst under similar reaction conditions and the deactivation was low. Post reaction analyses by TEM, XRD and TPO showed growth of crystallite sizes, absence of carbon deposition, but no structural modifications, which suggest that the promoters prevent carbon deposition and resist structure changes during the steam methane reforming reaction.

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1 Introduction

The continuous interest for production of energy from the use of hydrogen as fuel in new devices has emerged, as one of the most highlighted alternatives for energy production in several and critical sectors of an economy based on the consumption of fossil fuels [1, 2]. The advantages of hydrogen as fuel are high efficiency, low emissions, and relatively low cost, but such process depends strongly on the catalytic promoters of the catalyst, enabling higher activity and stability on the steam methane reforming reaction [3, 4]. As known, the methane steam reforming is composed by three reversible reactions, with the formation of syngas and CO_2 ,

besides the exothermic water–gas shift reaction, favoring the H_2 production, as follows [5–7]:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \Rightarrow \Delta H_{298} = +206 \text{ kJ/mol}$$
 (1)

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \Rightarrow \Delta H_{298}^\circ = -41 \text{ kJ/mol}$$
 (2)

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \Rightarrow \Delta H_{298} = +165 \text{ kJ/mol}$$
 (3)

Diverse synthesis of active materials for promoting the steam methane reforming reaction have been suggested, mainly based on the perovskite structure, since these oxides have the possibility to combine different oxidation states and elements in its structure [8]. According to Mihai et al. [9] some of the most interesting perovskite compositions are the substituted systems based on ferrite LaFeO₃ composition, presenting high activity and stability; however, according to Zhao et al. [10], one of the most challenging problem is the carbon deposition on the solid surface and consequently the deactivation of the catalyst. Transition metals based on perovskite-type oxides have variety of properties attributed to the ability of replacing the cations, creating iso-structural solids of $A_{1-x}A_xB_{1-y}B_yO_3$ type [11]. The substitution can have led to the stabilization of unusual oxidation state of the cations, besides the creation of anionic and cationic vacancies. The valence, stoichiometry and presence of vacancies in the oxide structure can interfere on the catalytic activity [12].

Therefore, the partial substitution of A-site cations by Sr and of B-site cations by Cr modifies the properties of ferrite compositions, increasing the dispersion of metallic particles, and thus the catalytic activity and stability. In this regard, Zhang et al. [13] reported that A and B-site metals have proportional effect on the amount of oxygen mobility under reaction conditions. Li et al. [14-16] found that the oxide La_{0.8}Sr_{0.2}FeO₃ is highly effective for the partial oxidation of methane, because it facilitates the ion oxygen mobility. On other hand, similar compositions based in LaBO₃ perovskites, where B = V, Cr, Mn, Fe, Co, Ni were studied and showed that the stability of the LaCoO₃ was lower than of the LaFeO3 oxide [10, 15]. However, structures based on $La_{0.8}Sr_{0.2}Fe_{1-x}M_xO_3$ oxide, modified by transition cations, such as Cr, Rh and Co, depend on synthesis methods to obtain nanoparticles, being one of the most imperative requirements in the field of active materials for catalytic uses. Arai et al. [17], Goldwasser et al. [18] and Zhang et al. [19] studied the effect of the synthesis methods for obtaining perovskites modified with chromium, where the cation provoked surface defects and vacancies, increasing the activity of the catalyst and the selectivity of hydrogen formation. However, the maximum solubility of metal in the lattice of the perovskite-type structure is controversial. Białobok et al. [20] prepared different samples of $La_{1-x}Ce_xCoO_3$ and claimed that the maximum solubility of cerium in the perovskite lattice was $x \le 0.05$, Oliva et al. [21] investigated this structure for different x, and showed that for high content there is segregation of CeO₂. The isostructural substitution favors the formation of vacancies.

Therefore, in this work aims to the synthesis of a $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ pure perovskite structure, using the combustion method to obtain nanoparticles, testing with steam methane reforming reaction and comparing with the pure LaFeO₃ oxide. Characterizations before and post reaction allowed explaining possible deactivation causes and structure modifications.

2 Experimental

2.1 Preparation of Perovskite

The $La_xSr_{1-x}Fe_xCr_{1-x}O_3$ oxide was prepared by the combustion technique, using nitrates of La(NO₃)₃·6H₂O (99.9%), Sr(NO₃)₂ (99.9%), Fe(NO₃)₃·9H₂O (98.9%), Cr(NO₃)₃·9H₂O 99.9% and citric acid monohydrated all from Merck. Stoichiometric quantities of each solid nitrate were dissolved in 20 mL of absolute ethanol until complete dissolution and magnetic stirring, as reported elsewhere [22]. The citric acid was added at 0.5:1 molar ratio with respect to the total concentration of metal salts in dissolution. The solution was kept under reflux at 120 °C for 12 h until formation of a viscous liquid, which was subsequently heated at 150 °C under air flux in an oven, until complete solvent evaporation. The obtained gel was heated at 300 °C for 30 min until the initiation of a combustion process, which consumes most of the organic phase. The carbonaceous remnant was removed by a thermal treatment at 800 °C under oxygen flow for 3 h. The sample was kept in a chamber under controlled humidity (20%), before physicochemical characterization. The stoichiometric composition was calculated based on the total oxidizing and reducing valences (N/C), assuming total combustion of citrate species as shown in Eq. 4 [18].

$$(NO_3)^- + C_6H_{18}O_7 \rightarrow 6CO_2 + N_2 + 9H_2O + oxides$$
 (4)

2.2 Characterization of Catalysts

The chemical composition of the oxide was obtained using X-ray fluorescence (XRF) technique, using a Philips MagiX Pro apparatus. Sample was pressed as pellet and analyzed quantitatively. The specific area BET was evaluated by nitrogen adsorption isotherms at -196 °C, using the ASAP-2020 apparatus (Micromeritics), degassing at 350 °C overnight to remove residual humidity.

The crystalline structure, was determined by X-ray diffraction, in a PANalytical X'Pert PRO MPD equipment, using Cu K_a radiation (λ =1.54186 Å) between 10° and 90°, with steps of 0.05°. Refinement, indexing and the simulation of the diffraction patterns were done with Fullprof software [23], which allowed us to establish the crystallographic structure of the oxides and to perform quantitative phase analysis. The crystallite size was calculated using the highest diffraction peaks, using the Scherrer equation, taking the value of half peak width and using a constant of 0.89, as reference.

X-ray photoelectron spectroscopy (XPS), were done on a Thermo Scientific Escalab 250 XI spectrometer, using Al K_{α} radiation at a pressure of 10^{-9} mbar. First, a survey spectrum was collected using pass energy of 100 eV, in the binding energy interval 0–1300 eV, with energy steps of 1 eV. Then, characteristic photoemission regions for each element present were acquired using energy of 20 eV, with steps of 0.05 eV. Atomic concentrations were calculated from the peak areas, assuming a Shirley-type background of inelastic electrons, using a proper sensitivity factor for each photoemission line measured.

The transmission electron microscopy analysis (TEM), were performed on a JEOL 2100 equipment using a LaB_6 thermionic gun operated with an acceleration voltage of 200 kV, equipped with a CCD imaging system. For analysis, the sample was ground to obtain fine powders. Which were sieve to 400 U.S. standard mesh and dispersed in a test tube with 5.0 mL of water, each tube was place in an ultrasonic equipment for a period of 30 min, after which a drop of the top of each tube was take and dried at 45 °C for respective analysis.

Temperature programmed reduction (TPR-H₂) was performed in a Micromeritics AutoChemII instrument equipped with a TCD detector. The sample was heated at 200 °C for 2 h, flowing pure helium and then reduced with a mixture of 5% H₂/He (30 mL min⁻¹), rising up to the maximum temperature reduction at 10 °C min⁻¹. The H₂ consumption was measured using a thermal conductivity detector.

2.3 Catalytic Test

The catalysts were tested in the steam methane reforming. The reaction was performed running for 10 days in an experimental unit consisting of a set of mass flow-meters and a reactor coupled to a resistive furnace. The reaction feed rate mixture ($CH_4/H_2O/Ar$ in gas phase), was 8/24/68 mL min⁻¹, respectively, pre-heated at 200 °C before catalyst contact in a U shape quartz micro-reactor with 12 mm ID and 250 mm long at 700 °C. The sample was supported on quartz wool.

The sample 200 mg was dried at 300 °C for 30 min prior catalytic tests under helium flow (30 mL min⁻¹). After

cleaning and cooling, the gas valve was switched to the gas mixture and adjusted until stabilization, $GSHV = 18000 h^{-1}$ and a contact time of 0.20 s. The reaction was studied under isothermal condition at 700 °C and exhaust gases were analyzed by gas chromatography (HP 5890 series II) equipped with a packed column HAYESEP Q of 5.5 m long, ¹/₄" pore diameter and an inner diameter of 80/100 and a TCD detector. Finally, the flame detector allowed evaluating the formation of minor species.

Main products from methane reaction were hydrogen, methane, carbon dioxide, carbon monoxide, ethylene, ethane, acetaldehyde and diethyl ether. The conversion of methane was calculated from carbon products in molar balance (on dry basis), as shown in Eq. 5, where γ_{Ci} is the ratio of carbon content of product *i* to carbon content of methane molecule, and y_{Ci} is the molar fraction of carbon content products in the effluent flow [24]. The molar selectivity was defined as the ratio of moles of one product and the total moles of products, based on experimental values as follows:

$$X_{Methane}(\%) = \frac{\sum \gamma_{Ci} y_{Ci}}{Y_{Methane} + \sum \gamma_{Ci} y_{Ci}} \times 100$$
(5)

$$S_i(\%) = \frac{\gamma_{Ci} \ y_{Ci}}{\sum \ \gamma_{Ci} \ y_{Ci}} \times 100 \tag{6}$$

2.4 Post Reaction Analyses

After 10 days on stream, under steam methane reforming reaction conditions, the catalyst was removed and analyzed by X-ray diffraction, to evaluate the oxide state. Eventual carbon deposition and other surface modifications were tested with transmission electron microscopy. Finally, the temperature programmed oxidation tests (TPO) were performed to investigate their oxidation behavior. TPO/TPR cycles were carried out in a Micromeritics AutoChemII instrument equipped with a TCD detector. Upstream of the TCD, a CO_2 trap was installed to adsorb water and humidity. In each TPO tests, the sample was exposed to a 20 mL min⁻¹ flow of 2 % O2 in Helium balance. The temperature was first ramped from 25 to 1000 °C, then maintained at 1000 °C for 1 h, and finally ramped down to 30 °C, at constant heating and cooling rate (5 °C min⁻¹). Prior to the admission of the O2 flow, the sample was evacuated at 120 °C in Helium (20 mL min⁻¹) and cooled down to 30 °C. In the TPO/TPR cycles, the TPR tests were performed in 20 mL min⁻¹ of 5% H₂ in Argon balance. The sample was heated from 25 to 1000 °C at 5 °C min⁻¹, maintained at 1000 °C for 1 h, and finally cooled to room temperature under inert atmosphere (20 mL min⁻¹ He). After each TPR, a TPO test was performed and three cycles were repeated to verify the stability of the material.

3 Results and Discussion

Chemical composition was calculated by X-ray fluorescence, as shown in Table 1. These final composition was close to the proposed nominal values, which allowed evaluate the stoichiometry of proposed composition of La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ oxide. The specific surface area was 60 m² g⁻¹, which can be attributed to the lower autocombustion temperature in the synthesis process, in accordance with Phokha et al. [24]. Such results, confirm that the synthesis method affects significantly obtaining a homogenous material with high surface area when compared to the LaCoO₃ perovskite ($<10 \text{ m}^2 \text{ g}^{-1}$) [25], using Pechini's method of preparation, which can be attributed to the elimination of volatile components in the combustion process. Therefore, an effective way to produce very active materials with higher porous structure [26]. Previously, we observed for perovskite-type oxides $La_{1-x}M_xCoO_3$ (M=Ce, Sr) that the insertion of lower x = 0.2, generated solid solution with a single phase of perovskite, however, higher contents favored phase segregation [25].

The XRD pattern of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ catalyst after polymerization-combustion is shown in Fig. 1. The

quantitative Rietveld phase analysis gives the mass fractions La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ and cell parameters, in accordance with Gabroska et al. [27] and Thirumalairajan et al. [28]. Crystallite sizes for the perovskite phases were estimated using the highest diffraction peak and Scherrer equation, taking the value of half peak width (β), adjusted to a Lorentzian function and using a constant of 0.89 as reference, indicating the presence of nanometric crystallites distributed around 25 nm. It can clearly be seen that the crystallite size depends strongly of time and temperature of the combustion process, enabling sinter of the powder due to the large surface area, and more important, obtaining a single crystalline phase, avoiding the loss of surface properties during the synthesis. These results were compared with the ICDD databases, which permits to identifying the space group, the crystal system and cell parameters, as shown in Table 2.

Transmission electron microscopy analyses (TEM) of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ sample, showed irregular aggregates composed by small crystallites around 25 nm (Fig. 2). In principle, these pictures are related with the texture and the relief formed by elimination of solvent and volatile species during the combustion of organic compounds in the ignition

Table 1 Elemental composition of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide derived from X-ray fluorescence

Oxides	Composition (%)		
	LaFeO ₃	$La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$	
La ₂ O ₃	67.10	59.30	
SrO	_	4.71	
Fe ₂ O ₃	32.89	29.06	
Cr ₂ O ₃	-	6.91	
Total	99.99	99.98	

Table 2 Comparison between crystalline properties of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide obtained by means XRD and TEM analysis

Method	Average crystallite size (nm)	Space group	Crystal system	Cell param- eters (Å)
XRD	41.1	<i>Pbn</i> (62)	Orthorhombic	a = 5.532 b = 5.553 c = 7.835
TEM	41.0	Pbn (62–63)	Orthorhombic	a = 5.425 b = 5.453 c = 7.812







Fig. 2 Transmission electron microscopy images at different magnifications of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide

[29]. With increasing calcination temperature, the spherical morphology and crystallinity of the particles increased, which implies on growth of small particles occurring during the posterior calcination process. In fact, the microstructure and uniformity of the synthesized powder can affect significantly the density of the sintered ceramic and the catalytic properties [30, 31]. The transmission electron microscopy results in Fig. 2 allowed a statistical counting in all micrographs, obtained by reference in a population of 250 particles.

The data were collected and normalized for obtaining regular distributions of crystallite sizes with regular morphology. These results confirm previous X-ray diffraction analysis indicating nanometric crystallites. Figure 3 displays the histogram of particle size distribution, showing unimodal distribution with a marked Gaussian behavior, revealing the presence of nanometric particles varying from 15 to 33 nm. These results can be attributed to the ultrafine structure of the solid and the dispersive effect of the water vapor evolved during the combustion process, in accordance



Fig. 3 Histogram distribution of particle size for a population of 250 particles of La_{0.8}Sr_{0.2}Fe_{0.} 8Cr0.2O3 oxide

with Huang et al. [32]. While the particles sizes are in the desired range of the nanoscale level, the different size distribution can probably affect the sintering of the final product of the solid-state.

From transmission electron microscopy data and X-ray diffraction analysis, it was possible to calculate the unit cell of the $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide, using the ELMIX software. The simulation of crystalline parameters shown in Fig. 4 and Table 2, are consistent with the experimental values obtained from X-ray diffraction and Rietveld calculations [19]. The structural refinements were performed by means of Fullprof software packages in the orthorhombic space group *Pbn*. A polynomial function, and pseudo-Voigt function was employed to model the peak shapes while a sixth order polynomial for the background, zero, LP factor, scale, pseudo-Voigt profile function (U, V, W and X), lattice parameters, atomic coordinates and isothermal temperature factors, in accordance with procedure established by Singh et al. [33].

The TPR-H₂ profile of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide is shown in Fig. 5. The maximum reduction signal occurred at 423 °C and was almost complete at 450 °C, besides a tail



Fig. 4 Unit cell of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide obtained by ELMIX software



Fig. 5 TPR-H₂ profile for $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide (10% H₂-He rate 10 °C min⁻¹)

around 600 °C. According to Jeong et al. [34], the iron-rich solid material can be reduced in four single steps at different temperatures, while the structure collapses, according to Eqs. 6-9.

$$La_2O_3 + 3H_2 \rightarrow 2La^0 + 3H_2O \tag{7}$$

$$SrO + H_2 \rightarrow Sr^0 + H_2O \tag{8}$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2 \rightarrow Fe^0 + H_2O$$
 (9)

$$Cr_2O_3 + H_2 \rightarrow 2CrO + H_2O \tag{10}$$

The profile shows that the reduction of the oxide is facilitated by the reduction of Fe_2O_3 and Cr_2O_3 at lower temperatures. Additionally, the substitution of La provoked vacancies, and thus the formation of Fe and Cr ions in coordination with the O_2^- species.

The XPS analyses and surface composition were determined for the perovskite-type $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide. Figure 6, shows the spectrum referred to the internal levels of La_{3d} , Sr3d, Fe2p, Cr2p and Sr3p for $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide. The sample displays one peak for Fe 2p3/2 centered at 710.4 eV, which is assigned to Fe³⁺ and a peak of Cr 2p3/2 centered at 576.0 eV, for Sr 3d5/2 centered at 131.9 eV and for lanthanum for 3d5/2 is centered at 837.5 eV, which according to Hueso et al. [35] belongs to the lattice of the perovskite structure. Data relative to oxygen was analyzed and found an O 1s signal at 528.9 and 531.2 eV, which is assigned to the oxygen of hydroxide or carbonate species [25, 36].



Fig. 6 X-ray photoelectron spectroscopy images for $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide

Detailed spectrum of lanthanum La 3*d*, as shown in Fig. 7a exhibits binding energies (BE) at 833.7 and a shakeup satellite peak at 837.5 eV, which are assigned to La³⁺ in the lattice [37]. When modified with strontium, the XPS spectrum presents a BE of La 4*d* at 101.15 eV (not shown), corresponding to La³⁺ in the lattice and traces of segregated La₂O₃ at the surface, linked to carbonate ions. Literature showed that the shift to higher binding energies 105.01 and 108.38 eV are assigned to segregated lanthanum, like La₂O₃ (103.0 eV), La(OH)₃ (106.1 eV) and carbonate species [25, 37].

As shown in Fig. 6 the BE positions of O1s spectra yield two peaks. The stronger peak is associated with O^{2-} ions at 528.87 (529.6) eV, which is related to oxygen in the perovskite structure, indicating that the oxygen ions remain coordinated in structure [38]. The peak at 531.16 eV is due to an intermediate oxidation state for oxygen [O^{-x}] and may be related to carbonate compounds as well as to defects, such as oxygen vacancies [39].

Separated spectrum of Sr $3d_{5/2}$ in Fig. 7b showed BE of Sr²⁺ at 131.92 and 133.77 eV. The BE at 131.92 (0.61) eV evidences the presence of Sr²⁺ at the surface and in the SrO_{2-x} sub-layer of the perovskite structure, while the band at 133.77 eV suggests the presence of carbonates, as

reported by Li et al. [40]. The migration and segregation of SrO in the perovskite structure from the bulk to the surface and probably reaction of SrO with Cr species may be occur [41].

$$Cr - Sr - O + CrO_3 + SrO \rightarrow SrCrO_4$$
 (11)

Besides, the segregated species may also exist with the SrCrO₃, as shown in the spectrum of Sr $3d_{5/2}$ in Fig. 7b for BE of Sr²⁺ at 132.2 eV, in agreement with Chen et al. [41]. The excess of segregation is probably attributed to the decomposition of the perovskite structure.

The XPS spectra Fe 2p3/2 and Fe 2p1/2 of the Fe₂O₃ sample are shown in Fig. 7c. The Fe 2p spectrum shows that 29% of Fe³⁺ ions are related to the doublet of BE at 710.46–723.81 eV. These Fe³⁺ species are located at the surface suggesting that part of Fe³⁺ ions were inserted in the lattice. The Fe 2p3/2 peak is narrower and stronger than Fe 2p1/2 and the area of the Fe 2p3/2 peak is greater than of the Fe 2p1/2, because its spin–orbit coupling, according to Yamashita et al. [42]. According the literature, the peak position of Fe 2p3/2 peak has associated a satellite peak that is shifted approximately by 8 eV relative to the main Fe 2p3/2



Fig. 7 Slow scan X-ray photoelectron spectroscopy images for a La 3*d*, b Sr $3d_{5/2}$ c Fe 2p3/2 and Fe 2p1/2 and d Cr 2p3/2 oxide components, with corresponding binding energies

peak. Yamashita et al. [42] obtained binding energies of Fe 2p3/2 and Fe 2p1/2 of 711.0 (standard deviation SD=0.01) and 724.6 eV (SD=0.17), respectively, in good agreement with our work. The satellite peak at 717.92 eV is close to that reported in the literature [718.8 (SD=0.13) eV] and does not overlap either the Fe 2p3/2 or Fe 2p1/2 peaks. In addition, another satellite peak appears at 731.5 eV, which may be associated to a satellite peak of Fe 2p1/2. According to the literature, the Fe 2p3/2 spectrum of Fe₃O₄ does not exhibit a satellite [43]. The absence of the satellite peak was confirmed in present study.

Figure 7d shows the XPS spectra of Cr 2p3/2. It displays three distinct BE of Cr 2p3/2 at 576.06, 577.7 and 579.34 eV, which are assigned to Cr₂O₃, Cr₂O₅ and SrCrO₄ respectively, in good agreement with that reported by Chen et al. [41]. These results agreed with XRD diffraction pattern after Rietveld refinement, as presented in Table 3.

Zhang et al. [43] investigated by XPS the electronic structure of Fe^{4+} ions in the SrFeO₃ perovskite oxide and concluded that there is a large increase of charge on Fe sites that led to a chemical shift to a higher BE.

Indeed, XPS results showed the presence of an intermediate oxidation state for oxygen $[O^{-x}]$ and may be related to carbonate compounds as well as to defect, such as oxygen vacancies. Results showed also the presence of iron at the surface with the formation of Fe³⁺/O²⁻ species at the interface, besides, the presence of Sr²⁺ at the surface, which resulted in the formation of vacancies.

3.1 Activity and Selectivity

The steam methane reaction was performed at 700 °C, at space velocity (GSHV) 18.000 h^{-1} , with a contact time of 0.20 s. Catalytic tests were carried out on the

Table 3 Binding energy, bulk (XRF) and surface (XPS) atomic concentrations of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ sample

Element	Photo- emis- sion line	Binding energy (eV)		Bulk atomic concentration by XRF (%)	Surface atomic con- centration by XPS (%)
La	3 <i>d</i>	$3d_{5/2}$	837.5	16.67	6.2
Sr	3 <i>d</i>	3d _{5/2} 3d _{3/2}	131.9 133.8	4.16	5.7
Fe	2 <i>p</i>	$2p_{3/2} \ 2p_{1/2}$	710.5 723.8	16.67	5.6
Cr	2 <i>p</i>	$2p_{3/2} \ 2p_{1/2}$	576.1 585.5	4.16	2.8
0	1 <i>s</i>	1s 1s*	528.9 531.2	58.33	54.2
С	1 <i>s</i>	1 <i>s</i> 1 <i>s</i> *	284.6 288.3	_	25.6

 $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide and compared to sample (LaFeO₃) in powder form. Blank results did not show activity. The reaction was performed after elimination of diffusion or mass transport effects. The conversion, H₂/CO ratio and selectivity for H₂ and CO, for three experiments showed good reproducibility.

The initial methane conversion for the $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide was $97 \pm 2\%$, while the H₂/CO ratio was close to 3.0 at 700 °C, as expected for a methane steam reforming reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H_{298 \text{ K}}^\circ = 206 \text{ kJ/mol})(12)$$

The average methane conversion, using the reference sample (LaFeO₃) was 66.3 ± 1.08 %. The H₂/CO ratio was of the order of 3.0, suggesting high formation of H₂. Tests during 240 h on stream under isothermal conditions at 700 °C, showed a methane conversion of 95% and excellent selectivity to carbon monoxide and hydrogen of 93 and 94%, respectively.

In fact, XPS results showed the presence of chromium and iron at the surface with the formation of ion species at the interface, which are active centers for CH_4 reforming. In fact, Ghaffari et al. [44] observed that for LaFeO₃, the iron in the perovskite structure contains Fe³⁺ and Fe⁴⁺ ions, and that with increasing Fe content it promotes a significant growth Fe³⁺ ions and besides, the presence of Sr²⁺ at the surface resulted in the formation of vacancies, in accordance with our results.

700°C The methane conversion at for the La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ oxide is very high, compared to the reference sample, which can be attributed to the strong dependence vacancies, in accordance with the literature [45–48]. The steam reforming reaction on multicomponent oxides suggests a redox mechanism, where CH₄ may also combine with oxygen of the lattice. The reduced oxide may be oxidized by water, increasing hydrogen concentration and allowing the formation of intermediate species by an associative mechanism. The main reaction occurs between the bidentate intermediate and the terminal hydroxyl groups on the oxide, which is then decomposed to form H₂ and carbonate species according to Sun et al. [49].

The stability test was performed during 240 h under similar reaction conditions. Results are displayed in Fig. 8. The deactivation of the $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide was low compared to the reference sample (LaFeO₃). In fact, XPS results evidenced clearly the presence of segregated lanthanum, like La_2O_3 , $La(OH)_3$ and carbonate species. Besides, Sr showed also the formation of SrO_{2-x} sub-layer and carbonates, such as $SrCrO_4$ [50]. Therefore, the post reaction analyses are important to provide a clue on the main factors that may affect the stability of the promoted catalyst.



Fig. 8 Stability test during 240 h for steam methane reaction on $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ and $LaFeO_3$ as reference catalysts

3.2 Post-reaction Analysis

The $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide was analyzed by TEM, XRD and TPO after the stability test. TEM analyses of the sample does not evidence carbon deposition, as shown in Fig. 9, suggesting that the catalyst presents resistance to carbon deposition.

XRD analysis does not present any secondary structure or composition alteration, discarding the presence of contaminant phases or phase change during the reaction, as shown in Fig. 10. Calculations, showed that the of space group, crystal and cell parameters of material, using ICDD databases, retain the same structural characteristics. The crystallite size, calculated using the highest diffraction signals $D_{(0 \ 1)}$, $D_{(0 \ 0 \ 2)}$ and $D_{(2 \ 1)}$ by means Debye– Scherrer equation, exhibited growth of the crystallite sizes, about 220–310 nm, using the principal diffraction signals of La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ sample after catalytic test, ratifying that crystallite size was almost 81% larger than before the test. This fact justifies the deactivation process. The



Fig. 10 X-ray diffraction pattern of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide after catalytic test during 240 h

deactivation of the catalyst is usually attributed to sintering, which depends largely on the temperature, time exposure and the nature of the reducing environment, among other factors. However, the oxide resists structural changes during the steam methane reforming reaction.

Temperature programmed oxidation (TPO) of the spent sample, using $2 \% O_2 (v/v)$ to simulate a condition of stability at high oxygen conversion is displayed in Fig. 11. The TPO profile shows the re-oxidation peak centered around $350 \degree$ C and no carbon. The peak around $210 \degree$ C may be attributed to the reduction of binary phases of Sr-Cr, in agreement with Zheng et al. [51]. Repeated TPR/TPO cycles confirm the results.

Noteworthy are the XPS results, showing the reduction of the redox couples Fe^{3+}/Fe^{2+} and Cr^{4+}/Cr^{3+} . In analogy with the mechanism proposed by Tanaka et al. [52] for the LaFeO₃ structure, we propose for this catalyst LaFeCrO₃ (Cr^{6+}) structure the following reaction mechanism:

$$CH_{4(g)} + CrO_3 + Vacancy \rightarrow CrO_2 + CO$$

+ $2H_2 + 2Vacancy$ (13)

$$CrO_2 + H_2O_v - 2 Vacancy \rightarrow CrO_3 + H_2 + Vacancy$$
 (14)



Fig. 9 TEM micrographs at different amplifications for $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide after 240 h on stream



Fig. 11 Temperature programmed oxidation profiles of $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ oxide using 2% O_2 in He at 20 mL min⁻¹ as function of temperature



Fig. 12 Reaction model of methane reforming on $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ perovskite

Figure 12 shows the scheme of the structure, according equations 13 and 14. The vacancies of FeCrO₃ (Cr⁶⁺) are occupied by methane and with the oxygen of the structure release CO and H₂O, as product in the first step, leaving then two vacancies (Cr⁴⁺). Then, H₂O (reactant) is dissociated in OH and H, occupying two vacancies and releases H₂ (product), recovering again the initial structure of the FeCrO₃ (Cr⁶⁺) with one free vacancy, completing the reaction cycle, without affecting the structure, confirming the XRD results of post-reaction analyses.

4 Conclusions

A multi-component perovskite oxide was prepared via citric acid polymerization in aqueous medium. XRD results of the calcined oxide showed a pure orthorhombic La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃ phase. The physicochemical characterization showed the presence of an active nanometric catalyst of homogeneous appearance and an excellent stoichiometric composition. XPS results showed the presence Fe^{3+}/Fe^{2+} and Cr^{4+}/Cr^{3+} , besides, the presence of Sr^{2+} at the surface, which resulted in the formation of vacancies. Tests during 240 h on stream under isothermal conditions at 700 °C showed high methane conversion of 95% and excellent selectivity to hydrogen and lower deactivation when compared to the LaFeO₃ as reference.

Post reaction analyses by TEM, XRD and TPO showed absence of carbon deposition, growth of crystallite sizes. However, the structure of the $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ was not affected and no phase changes were observed during the reaction, which suggest that the structure resists structure modification during the steam methane reforming reaction and that the promoters prevent carbon deposition.

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