Perovskites as catalysts precursors: CO₂ reforming of CH₄ on Ln₁−ₓCaₓRu₀.₈Ni₀.₂O₃ (Ln = La, Sm, Nd)


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Abstract

A series of perovskite-like oxide in which the A-site cation of the precursor perovskite, LaRu₀.₈Ni₀.₂O₃, was partially or totally substituted by calcium, samarium and neodymium have been used to produce in situ nanoparticles of Ru(Ni) well dispersed on a stable support for the carbon dioxide reforming of methane. Perovskites of the type LnₓCa₁−ₓRu₀.₈Ni₀.₂O₃ (Ln = La, Sm, Nd) were synthesized as catalysts precursors. The reduced solids of nominal composition (Ru,Ni)/CaO and/or La₂O₃, Sm₂O₃, Nd₂O₃, were used as catalysts.

The La₁−ₓCaₓRu₀.₈Ni₀.₂O₃ series showed a well-defined perovskite structure with surface areas between 3 and 10 m²/g. However, when lanthanum was replaced by samarium and neodymium, the presence of pyrochlore structures, together with the perovskites, were obtained. After reduction Ru(Ni) crystallites size between 9 and 17 nm were produced. The substitution of La by cations of smaller ionic radii (Ca, Nd, Sm) decrease the stability of the perovskites and lower their reduction temperature. Among the calcium series, La₀.₈Ca₀.₂Ru₀.₈Ni₀.₂O₃ and La₀.₅Ca₀.₅Ru₀.₈Ni₀.₂O₃, proved to be the most active catalysts with the highest selectivity to CO. While samarium-containing perovskite was the best among the lanthanide series.

Correlations between the effect of partial or total substitution of A-site cations of the precursor perovskite and the catalytic activity and stability of in situ formed nickel and ruthenium particles were established.

Keywords: CO₂ reforming of methane; Ru–Ni perovskites; Syngas production; Calcium promotion; Effect of lanthanides

1. Introduction

The need to preserve the environment has prompted the international community to dictate a series of regulations that affect, decrease or increase the price of the activities of the petroleum industry; introducing legal statutes that have to be accomplished by conventional fuels in the short term. In this context, the carbon dioxide reforming of methane emerges as an alternative especially for global environmental protection, since both reactants are thought to contribute to global warming. In addition, this process allows the production of syngas with a H₂/CO ratio more convenient for further applications: while higher H₂/CO ratio favors methane and inhibit chain growth [1–3], a low H₂/CO ratio favors the methanol to gasoline process for ethane, propane and aromatics from methanol.

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ABO₃, in which A-site cation is a rare earth and/or lanthanides, and B-site cation is a transition metal, has been less studied.

Precursors, such as perovskite-like oxides, have been used as catalysts, as shown by Zhang and Verykios [20], and Eldohelyi et al. [21] for Rh and Pd, respectively, in the reforming of methane over different supports. Previous studies on CaRuO₃ [17], LaCoO₃ [18] and LaNiO₃ [19] perovskites indicate that by reduction treatment, the metal (Ru, Co, Ni) is in a highly dispersed state on a matrix composed of the respective metal oxide. Similarly, it has been established that the presence of CaO influenced the morphology and particle size distribution of nickel metal, inhibiting coke formation. This serious problem could be inhibited by using highly dispersed metal species according to the concept of ensemble size control [9–13].

Calcium is a well-known promoter of steam reforming of methane that should further inhibit coke formation. Therefore, it is used as A-site cation due to its basic character, which should further inhibit coke formation. Calcium is a well-known promoter of steam reforming catalysts, its influence on particle size distribution has been previously reported. Gouda et al. [28] and Tang et al. [13] over NiAl₂O₃ catalysts reported that the presence of CaO influenced the morphology and particle size distribution of nickel metal, inhibiting coke deposition. Similarly, Choudary et al. [23] reported the enhancement of activity of Ni catalysts when the support (Al₂O₃ or SiO₂) was precoated with CaO.

However, the drawback of carbon dioxide reforming of methane is deactivation of catalysts caused by carbon deposition. This serious problem could be inhibited by the use of highly dispersed metal species according to the concept of ensemble size control [9–13]. The use of precursors, such as perovskite-like oxides, not only fulfill the stability requirements, but also by further reduction of B-site cations which remain distributed in the structure, they result in the formation of a well-dispersed and stable metal particle catalyst. Thus, we decided to study the effect of such changes. Following these ideas, we used calcium as A-site cation due to its basic character, which should further inhibit coke formation. Calcium is a well-known promoter of steam reforming catalysts, its influence on particle size distribution has been previously reported. Gouda et al. [28] and Tang et al. [13] over NiAl₂O₃ catalysts reported that the presence of CaO influenced the morphology and particle size distribution of nickel metal, inhibiting coke deposition. Similarly, Choudary et al. [23] reported the enhancement of activity of Ni catalysts.

Alkenes, oxygenates, hydroformylation and acetic acid production are also favored at low H₂/CO ratios [5–8]. Although many previous investigations of the CO₂ reforming of methane have been carried out over transition metals supported on alumina, silica and magnesium oxide [9,13,20,22–26], the use of perovskite-type oxides has been less studied [14–16].

Perovskites of the type LnₓCa₁₋ₓRuₓNiₓO₃ (Ln = La³⁺, Sm³⁺, Nd³⁺) were synthesized as catalyst precursors. The reduced solids of nominal composition (Ru,Ni)/CaO and/or La₂O₃, Sm₂O₃, Nd₂O₃, were used as catalysts to establish correlations between the effect of partial or total substitution of A-site cations of the precursor perovskite and the catalytic activity and stability of in situ formed nickel and ruthenium particles.

## 2. Experimental

### 2.1. Synthesis and characterization of the precursor perovskites

The perovskite-type oxides Laₓ₋₀.₆₋ₓCaₓRuₓ₂NiₓO₃ (La = La, Sm, Nd) were synthesized by a modification of the citrate method [29]. Adequate amounts of the precursor of B-site cations (RuCl₃·xH₂O and Ni(NO₃)₁·₆H₂O), were dissolved in citric acid (99.5 Riedel-de Haen) with an excess of ethylene glycol (99.5 Riedel-de Haen) as the organic polydentate ligand. La(NO₃)₁·₆H₂O, Ca(NO₃)₁·₄H₂O, Sm(NO₃)₁·₆H₂O, Nd(NO₃)₁·₆H₂O were used as A-site cations precursors.

The solids were characterized before and after catalytic tests by means of different techniques. Inductively Coupled Plasma Emission Spectroscopy (ICP) and using a Perkin-Elmer ICP/5500 instrument analyzed the chemical compositions (Ru, Ni, La, Ca, Sm, and Nd) of the perovskite products. The IR spectra of the final product were recorded in a Perkin-Elmer 283 spectrometer between 1200 and 400 cm⁻¹. BET surface areas were determined by nitrogen–argon adsorption at 77 K with an N₂/Ar ratio of 30/70 using a Micromeritics model ASAP 2010. X-ray diffraction (XRD) experiments were conducted using a Siemens D-8 advanced diffractometer with a Cu Ka radiation for crystalline phase detection between 20 and 90° (2θ) and under temperature-programmed reduction (TPR).
in H2. JCPDS-ICDD standard spectra software was used to determine the phases. The ruthenium crystallite size was calculated using Ru(1 1 1) reflection and the Scherrer formula [26,30] with Warren’s correction for instrumental line broadening $d = 0.9/[(\beta^2 - B^2)^{1/2}\cos \theta]$, where $\beta = 1.54056$ Å and the line broadening at 44° 2θ is $B = 0.09^\circ$, by means of TOPAS P Profile Fitting Program from Brucker Analytical X-ray System. TPR was carried out in a Thermo-Quest P Profile Fitting Program from Brucker Analytical System XL) equipped with a TCD and provided with an on-line gas chromatograph (Perkin-Elmer Auto System). TPR was carried out in a Thermo-Quest P TPR/TPR 1100 system using 0.07 g of the sample. Activity tests were performed using 200 mg of catalysts, one in which the lanthanum perovskite LaRuO$_{3}$ (O2) is modified by calcium, named Ca-La series, and the other in which La$_{0.8}$Ni$_{0.2}$O$_{3}$ is modified by samarium and neodymium, named the lanthanide series. 3. Results and discussion 3.1. Perovskites characterization: surface area, chemical analysis, IR and XRD Table 1 lists the synthesized perovskite and the ICP analysis. A close similarity between analytical and nominal values in each case was observed. However, an oxygen deficiency was shown by all synthesized perovskites. In order to assess the presence of the perovskite-like structures, XRD and IR spectra were recorded. The IR spectra for all the solids showed two broad bands characteristics of ABO$_{3}$ perovskites centered around 400 and 600 cm$^{-1}$. Their positions are in good agreement with those reported in the literature [15,16,31]. Surface area, IR bands, cell parameters and corresponding symmetry are shown in Table 2. Most of the synthesized solids showed areas higher than 3 m$^{2}$/g, a decrease in surface area was observed as Ca substituted La, with the lowest value shown by the higher calcium-containing perovskites (3 m$^{2}$/g). It is interesting to note that within the Ca-La series, those precursor perovskites with the higher surface areas showed the best catalytic activity (La$_{0.8}$Ca$_{0.2}$RuO$_{3}$). When calcium was substituted by the lanthanides, an increase in surface area was observed for lanthanum and samarium perovskites (from 3 to 9 m$^{2}$/g) while no change was observed for the neodymium perovskite. For the Ca-La series, the XRD patterns of the as synthesized solids at room temperature revealed that the perovskite structure was the main phase detected, although some deviations from the perfect...
Table 1

<table>
<thead>
<tr>
<th>Perovskites</th>
<th>La (%)</th>
<th>Ca (%)</th>
<th>Ru (%)</th>
<th>Ni (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>Analytical</td>
<td>Nominal</td>
<td>Analytical</td>
<td>Nominal</td>
<td>Analytical</td>
</tr>
<tr>
<td>LaRu$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>49.70</td>
<td>45.30</td>
<td>–</td>
<td>–</td>
<td>28.93</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ca$</em>{0.2}$Ru$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>42.78</td>
<td>42.91</td>
<td>3.09</td>
<td>3.16</td>
<td>31.13</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$Ru$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>30.19</td>
<td>29.62</td>
<td>8.71</td>
<td>8.46</td>
<td>35.14</td>
</tr>
<tr>
<td>La$<em>{0.2}$Ca$</em>{0.8}$Ru$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>13.86</td>
<td>13.57</td>
<td>16.00</td>
<td>14.69</td>
<td>40.35</td>
</tr>
<tr>
<td>CaRu$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>–</td>
<td>–</td>
<td>22.18</td>
<td>17.83</td>
<td>44.75</td>
</tr>
<tr>
<td>Sm$<em>{1}$Ca$</em>{0.8}$Ru$<em>{0.2}$Ni$</em>{0.2}$O$_3$</td>
<td>44.74</td>
<td>41.98</td>
<td>2.98</td>
<td>1.96</td>
<td>30.07</td>
</tr>
<tr>
<td>Sm$<em>{2}$Ru$</em>{2}$O$_7$</td>
<td>30.19</td>
<td>29.62</td>
<td>8.71</td>
<td>8.46</td>
<td>35.14</td>
</tr>
<tr>
<td>Nd$<em>{1}$Ca$</em>{0.8}$Ru$<em>{0.2}$Ni$</em>{0.2}$O$_3$</td>
<td>13.86</td>
<td>13.57</td>
<td>16.00</td>
<td>14.69</td>
<td>40.35</td>
</tr>
<tr>
<td>Nd$<em>{2}$Ru$</em>{2}$O$_7$</td>
<td>44.74</td>
<td>41.98</td>
<td>2.98</td>
<td>1.96</td>
<td>30.07</td>
</tr>
</tbody>
</table>

All perovskites could be indexed with an orthorhombic or cubic symmetry of the $A$BO$_3$ type with the exception of Sm$_{1}$Ca$_{0.8}$Ru$_{0.2}$Ni$_{0.2}$O$_3$ and Nd$_{1}$Ca$_{0.8}$Ru$_{0.2}$Ni$_{0.2}$O$_3$ that showed a perovskite structure mixed with a pyrochlore. On these solids, the perovskite-type structures correspond to double perovskites, such as Ln$_2$RuNiO$_6$ (JCPDS-ICDD file 45-0658), in which part of the lanthanide cation has been replaced by calcium. The pyrochlore structure formed between samarium and ruthenium (JCPDS-ICDD file 28-0997) and between neodymium and ruthenium (JCPDS-ICDD file 28-0673) could be due to the difference of ionic radii between samarium and neodymium with respect to that of calcium, since both lanthanides have ionic radii smaller than calcium. The variation of the lattice parameters with composition is shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Perovskites</th>
<th>Area (m$^2$/g)</th>
<th>IR bands</th>
<th>Symmetry</th>
<th>Cell parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>LaRu$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>9</td>
<td>592</td>
<td>4</td>
<td>417</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ca$</em>{0.2}$Ru$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>8</td>
<td>600</td>
<td>4</td>
<td>418</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ca$</em>{0.8}$Ru$<em>{0.2}$Ni$</em>{0.2}$O$_3$</td>
<td>10</td>
<td>568</td>
<td>4</td>
<td>465</td>
</tr>
<tr>
<td>La$<em>{0.2}$Ca$</em>{0.8}$Ru$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>6</td>
<td>–</td>
<td>–</td>
<td>O</td>
</tr>
<tr>
<td>CaRu$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>O</td>
</tr>
<tr>
<td>Sm$<em>{1}$Ca$</em>{0.8}$RuNiO$_{3.3}$</td>
<td>9</td>
<td>576</td>
<td>4</td>
<td>431</td>
</tr>
<tr>
<td>Sm$<em>{2}$Ru$</em>{2}$O$_7$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>C</td>
</tr>
<tr>
<td>Nd$<em>{1}$Ca$</em>{0.8}$RuNiO$_{3.3}$</td>
<td>2</td>
<td>578</td>
<td>4</td>
<td>413</td>
</tr>
<tr>
<td>Nd$<em>{2}$Ru$</em>{2}$O$_7$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>C</td>
</tr>
</tbody>
</table>

*a Symmetry: O = orthorhombic, C = cubic.

3.2. Temperature-programmed reduction and in situ XRD

The relative stability of the perovskites in reducing atmosphere was determined, for all solids, by in situ XRD and by TPR. The XRD patterns for La$_{0.8}$Ca$_{0.2}$Ru$_{0.8}$Ni$_{0.2}$O$_3$ and La$_{0.8}$Ca$_{0.8}$Ru$_{0.2}$Ni$_{0.2}$O$_3$, as synthesized and reduced at different temperatures, are shown in Figs. 1 and 2, respectively. The room temperature patterns for both perovskites show peaks at 2θ = 23, 33, 47, 58 for La$_{0.8}$Ca$_{0.2}$Ru$_{0.8}$Ni$_{0.2}$O$_3$ and at 32, 46, 56, 66 for La$_{0.8}$Ca$_{0.8}$Ru$_{0.2}$Ni$_{0.2}$O$_3$ which correspond almost exactly to CaRu$_{0.8}$O$_3$ perovskite (JCPDS file 82-1476) and LaRu$_{0.8}$O$_3$ perovskite (JCPDS file 82-1477). It is observed that when the temperature is raised, cations in position B are reduced to metals while those in position A are transformed to the respective oxides. For the Ca-La series, the most drastic...
changes are seen between 300 and 400°C for the higher calcium content perovskites (Fig. 1, Table 3), while for the more lanthanum-containing samples, degradation of the perovskite start at 400–500°C (Fig. 2, Table 3). The perovskite is progressively degraded until approximately 700°C. Perovskites with a higher lanthanum content being more stable.

For all solids, the observed phases after reduction at changes are seen between 300 and 400°C for the higher calcium content perovskites (Fig. 1, Table 3), while for the more lanthanum-containing samples, degradation of the perovskite start at 400–500°C (Fig. 2, Table 3). The perovskite is progressively degraded until approximately 700°C. Perovskites with a higher lanthanum content being more stable. For all solids, the observed phases after reduction at

Table 3
In situ XRD results: phases and average size of Ru(Ni) after reduction

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degree (2θ)</th>
<th>T of degradation (°C)</th>
<th>Phases after reduction</th>
<th>Mean size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaRu0.8Ni0.2O3</td>
<td>32.100</td>
<td>400–500</td>
<td>Ru0, Ni0, La2O3</td>
<td>9.9</td>
</tr>
<tr>
<td>La2Ca0.8Ru0.8Ni0.2O3</td>
<td>32.230</td>
<td>400–500</td>
<td>Ru0, Ni0, CaO, La2O3</td>
<td>10.3</td>
</tr>
<tr>
<td>La2Ca0.8Ru0.8Ni0.2O3</td>
<td>32.486</td>
<td>300–500</td>
<td>Ru0, Ni0, CaO, La2O3</td>
<td>15.1</td>
</tr>
<tr>
<td>La2Ca0.8Ru0.8Ni0.2O3</td>
<td>32.887</td>
<td>300–400</td>
<td>Ru0, Ni0, CaO, La2O3</td>
<td>17.4</td>
</tr>
<tr>
<td>CaRu0.8Ni0.2O3</td>
<td>32.912</td>
<td>300–400</td>
<td>Ru0, Ni0, CaO</td>
<td>14.9</td>
</tr>
<tr>
<td>Ca2Sm0.8Ru0.8Ni0.2O3</td>
<td>32.700</td>
<td>400–600</td>
<td>Ru0, Ni0, CaO, Sm2O3</td>
<td>10.7</td>
</tr>
<tr>
<td>Ca2Nd0.8Ru0.8Ni0.2O3</td>
<td>32.480</td>
<td>400–600</td>
<td>Ru0, Ni0, CaO, Nd2O3</td>
<td>9.2</td>
</tr>
</tbody>
</table>

*Evolution of the most intense peak at 2θ °C.
Fig. 2. In situ XRD of La$_{0.8}$Ca$_{0.2}$Ru$_{0.8}$Ni$_{0.2}$O$_3$ as synthesized and reduced at different temperatures. (#) Time in hours at a given temperature; (□) Ni; (●) La$_2$O$_3$; (▲) Ru; (■) CaO; (▲) perovskite.

800 °C were: Ru metal (alone or alloyed with Ni), CaO and La$_2$O$_3$ in different proportions depending on the composition of the starting perovskite.

A similar behavior was shown by TPR (Fig. 3). The temperature, at which an increase in hydrogen consumption is observed, coincided with that where changes were seen by XRD for these solids. The TPR indicate that, in general, the perovskite reduction proceeds in two steps. A first peak, with a maximum at around 200–400 °C depending on the perovskite, and a second peak appearing above 400 °C. Hurst et al. [33] suggest for ruthenium and nickel on different supports that the first peak is due to the reduction of the Ru$^{3+}$ to Ru$^{2+}$ and/or Ni$^{3+}$ to Ni$^{2+}$, while the second peak at higher temperature is due to the reduction of the Ru$^{2+}$ and/or Ni$^{2+}$ to Ru$^0$ and Ni$^0$. In our case, the XRD in situ reduction results seems to indicate that the first peak of reduction could be attributed to weakly bound Ru-Ni cations and to residues of the precursors. This could be inferred from the fact that for all studied perovskites the diffraction peaks remain essentially in the same position up to 350 °C (Figs. 1 and 2, Table 2) changing only in intensity. The second peak could be attributed to a simultaneously Ru and Ni reduction to produce Ru$^0$ and Ni$^0$ probably with an alloy formation. Even that formation of an alloy could not be verified, the position of the peaks at 2θ 44.2, intermediate to that of 44.00 for hexagonal Ru (JCPDS file 06-0663) and 44.505 for cubic Ni (JCPDS file 04-0850) are in favor of this possibility.

When lanthanum is partially substituted by calcium, a shift to lower temperatures is clearly observed (Fig. 3). The substitution of an A-site cation by another of lower valence could significantly influence
the reducibility of the perovskite [32,34–37]. This effect is attributed to the fact that a cation of lower ionic radius (Ca2+) is replacing one of higher radius (La3+), which decreases the stability of the perovskite structure, increasing the mobility of the oxygen in the structure and facilitating its elimination as water during reduction. In order for the structure to remain stable after the substitution of La3+ by Ca2+, charge compensation is needed. This could be achieved through the existence of some Ru and/or Ni ions with valence states higher than 3+, or by formation of an oxygen-deficient perovskite of the type ABO3−δ. The ICP and XPS results indicate that the second statement is taking place since a deficiency of oxygen was observed for these solids. These changes in the precursor perovskites favor their reducibility as seen by the reduction pattern of the perovskites: the higher the calcium contents the easier the reduction of the perovskites. The observed ease of reduction was: CaRu0.8Ni0.2O3 > La0.2Ca0.8Ru0.8Ni0.2O3 > La0.5Ca0.5Ru0.8Ni0.2O3 > La0.8Ca0.2Ru0.8Ni0.2O3 > LaRu0.8Ni0.2O3. As expected, lanthanum the largest ion in the series forms the most stable perovskite structure [14,37].

For the lanthanide series, an additional effect was observed (Fig. 4). Samarium- and neodymium-containing perovskites showed two very intense peaks, while for lanthanum perovskite a sharp peak was observed at high temperature, with a small peak at low temperature. This is in agreement with the XRD results for the neodymium and samarium solids, where a mixture of perovskites and pyrochlore phases was observed. The presence of these mixed phases, make structures less stable, which reflects in a higher reduction facility compared to lanthanum perovskite.

XRD analysis was also used to determine the metal particles size of the crystallites by means of the Scherrer equation [26,30]. Sizes were calculated at around 44° (2θ), which correspond to the most intense band for Ru metal (44.37°), very close to that of Ni (44.50°). With the exception of the catalyst from LaRu0.8Ni0.2O3, on the perovskites reduced at 800°C, peaks correspond mainly to Ru, slightly shifted in comparison to Ru alone, due to the presence of Ni. For LaRu0.8Ni0.2O3 the intensity of the Ru-Ni peak is wider indicating that the crystallites does not change with temperature, while for the more calcium-containing perovskites the destruction starts
when the temperature start raising (300° C) and the metal peaks become sharper indicating the presence of larger particles. Lanthanum seems to stabilize the Ru(Ni) metal crystallites. In addition, an inverse relationship seems to exist between the size of the metallic crystallites and the temperature at which the second reduction peak appears in the TPR. The higher the temperature of the second peak, the smaller the particle size. It appears as if during the destruction of the perovskite by reduction, the metallic ions are being released in a controlled way avoiding formation of large metallic clusters by sinterization. For all structures, the mean particle size values are between 9 and 17 nm (Table 3), indicating a high dispersion and/or uniform distribution of Ru(Ni) in the CaO–Ln₂O₃ matrix after reduction. These values are smaller than those reported by Choudary et al. [19] for Ni/ Ln₂O₃ obtained from LaNiO₃ (31.3 nm) and much smaller than that (125 nm) for NiO–La₂O₃ [38]. These results corroborate the advantage of the sol–gel method to obtain metallic supported nanoparticles [13,15,16,25].

After reaction, the identified phases were Ru₀, Ni₀, CaO, CaCO₃ and Ln₂O₃. The carbonate observed on these solids is formed from reaction of the oxides by decomposition of the precursor perovskite and CO₂ from the reaction mixture. Those perovskites with a high lanthanum content (LaRu₀.8Ni₀.2O₃ and La₀.8Ca₀.2Ru₀.8Ni₀.2O₃) also show peaks corresponding to lanthanum dioxomonocarbonate, La₂O₂CO₃. This phase, which is in fast equilibrium with the carbon dioxide in the gas phase during reaction, has been claimed as responsible for the no-deactivation of the catalyst by carbon [15,16,20,22,32].

3.3. X-ray Photoelectron Spectroscopy

The XPS results of both Ca–La and lanthanide series showed that under the experimental conditions used only B cations (Ru and Ni) are reduced to the zero oxidation state, while those cations in position A do not show any reduction.

For Ca-La series it was observed that the presence of calcium leaves the La 3d doublets very much unaffected, except for a very small displacement (0.2 eV) towards lower binding energies. For the lanthanide series, the presence of lanthanum, samarium or neodymium did not affect the binding energy of the Ca 2p signals. Again, as for the Ca-La series only metals in position B were completely reduced.

To evaluate the chemical state and evolution of the metals at the surface, a semi-quantitative analysis was performed. Only RuO and Ru(A + A') ratios are
Table 4: Bulk and surface stoichiometry of the reduced perovskites

<table>
<thead>
<tr>
<th>Samples</th>
<th>LaRu0.8Ni0.2O3</th>
<th>CaRu0.8Ni0.2O3</th>
<th>Ca0.2Sm0.8Ru0.8Ni0.2O3</th>
<th>Ca0.2Nd0.8Ru0.8Ni0.2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>1.0 – 0.15 0.08</td>
<td>1.0 – 0.60 0.20</td>
<td>0.5 – 0.35 0.02</td>
<td>0.5 – 0.35 0.02</td>
</tr>
<tr>
<td>Bulk</td>
<td>1.0 – 0.20 0.32</td>
<td>1.0 – 0.30 0.17</td>
<td>1.0 – 0.30 0.13</td>
<td>1.0 – 0.30 0.13</td>
</tr>
</tbody>
</table>

*Sm or Nd.

Presented since attempts to extract reliable quantification of Ni was extremely difficult due to the severe covering of the Ni 2p signals by the complex La 3d region. This situation was worsened by the low nickel content of the perovskites. Similarly, quantification of neodymium in the presence of lanthanum is difficult: Nd 4d is perturbed by La 4d, and the most intense signal Nd 3d interfere with the Auger peaks of oxygen (Al source). Table 4 shows a comparison of the stoichiometry of the bulk and surface of reduced perovskites.

If it is assumed that for the Ca-La series Ru⁶⁺, CaO and La₂O₃ are the main phases present after reduction, as observed by XRD, the Ru/O ratio should be around three times smaller than that of Ru/La [39,40]. However, it is observed that the substitution of lanthanum by calcium lead to a Ru/O ratio approximately equal to that of Ru/La indicating a great deficiency in oxygen. These results are in good agreement with ICP and TPR observations, where the formation of an oxygen-deficient perovskite of the type Laₓ₋ₓCaₓRu₀.₈Ni₀.₂O₃₋₋ was invoked to compensate for the difference in charge produced when Ca²⁺ substitutes La³⁺. In agreement with TPR and XRD results, the observed oxygen deficiency was lower for the most stable perovskite LaRu₀.₈Ni₀.₂O₃.

3.4. Catalytic studies

In previous work [15,16], the effect of parameters, such as reaction temperature, space velocity, reactant partial pressure and time on stream, was investigated and optimized to higher yields of syngas. It was found that the best Ru-Ni combination was obtained for LaRu₀.₈Ni₀.₂O₃. In the present work, partial or total substitution of lanthanum by calcium was carried out, to increase the basicity of the catalysts in order to inhibit coke formation.

The study was started with La₀.₅Ca₀.₅Ru₀.₈Ni₀.₂O₃ perovskite under previous optimized conditions. For this solid, it was observed that the previously used reduction conditions were not sufficient to reach total transformation of B-site cations. Under these conditions (Tₖ = 700 °C, T_R reduction = 700 °C/3 h), the obtained catalyst showed a lower activity compared to that of the reference perovskite LaRu₀.₈Ni₀.₂O₃. Consequently, both reaction temperature and reduction time were increased to 800 °C and 8 h, respectively. Under these conditions, the catalyst from La₀.₅Ca₀.₅Ru₀.₈Ni₀.₂O₃ showed a higher activity. Methane and CO₂ conversions were 98 and 77%, respectively, with a CO selectivity of 86% (Table 5). The next step was to study the effect of calcium content on the precursor perovskite. The following
perovskites were prepared: $\text{La}_{0.8}\text{Ca}_{0.2}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$, $\text{La}_{0.2}\text{Ca}_{0.8}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and $\text{CaRu}_0.8\text{Ni}_0.2\text{O}_3$. It was observed that as the content of calcium increases in the perovskite (Fig. 5), a decrease in the induction period (time needed for the precursor perovskite to start showing activity) was decreased as compared to the reference perovskite $\text{LaRu}_0.8\text{Ni}_0.2\text{O}_3$, in agreement with the TPR and in situ XRD experiments where reduction was easier for those perovskites. Their catalytic activity is shown in Table 5. As observed, at 800 °C most catalysts showed CH$_4$ conversions near 100%, with the best selectivity to CO (90%) achieved by $\text{La}_{0.8}\text{Ca}_{0.2}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$.

To maintain conversions away from thermodynamic equilibrium, the temperature was adjusted to 700 °C. Fig. 6 shows the influence of calcium content on these perovskites. A decrease in conversion as lanthanum is substituted by calcium was observed, being higher for CH$_4$ than for CO$_2$. However, the selectivity to CO remains almost constant. Among this series, the best activity was obtained for $\text{La}_{0.8}\text{Ca}_{0.2}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$. The fact that CO$_2$ conversion was always lower than that of methane and that H$_2$/CO ratios lower than 1, indicates the occurrence of other reactions. Partial combustion of methane by oxygen present in the nitrogen (∼2%) used as diluent could not be discarded.

![Fig. 5. Methane conversion vs. time on stream for Ca-La series.](image)

Table 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>800 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XCH$_4$ (%)</td>
<td>XCO$_2$ (%)</td>
</tr>
<tr>
<td>$\text{LaRu}_0.8\text{Ni}_0.2\text{O}_3$</td>
<td>78.6</td>
<td>83.9</td>
</tr>
<tr>
<td>$\text{La}<em>{0.8}\text{Ca}</em>{0.2}\text{Ru}<em>{0.8}\text{Ni}</em>{0.2}\text{O}_3$</td>
<td>96.35</td>
<td>95.47</td>
</tr>
<tr>
<td>$\text{La}<em>0.2\text{Ca}</em>{0.8}\text{Ru}<em>{0.8}\text{Ni}</em>{0.2}\text{O}_3$</td>
<td>99.77</td>
<td>99.30</td>
</tr>
<tr>
<td>$\text{CaRu}_0.8\text{Ni}_0.2\text{O}_3$</td>
<td>99.77</td>
<td>99.30</td>
</tr>
<tr>
<td>$\text{Nd}<em>0.8\text{Ca}</em>{0.2}\text{Ru}_{0.8}\text{Ni}_0.2\text{O}_3$</td>
<td>95.47</td>
<td>95.47</td>
</tr>
<tr>
<td>$\text{Nd}_2\text{Ru}_2\text{O}_7$</td>
<td>95.47</td>
<td>95.47</td>
</tr>
<tr>
<td>$\text{Sm}<em>0.8\text{Ca}</em>{0.2}\text{Ru}_{0.8}\text{Ni}_0.2\text{O}_3$</td>
<td>99.77</td>
<td>99.77</td>
</tr>
<tr>
<td>$\text{Sm}_2\text{Ru}_2\text{O}_7$</td>
<td>99.77</td>
<td>99.77</td>
</tr>
<tr>
<td>Commercial catalyst</td>
<td>99.77</td>
<td>99.77</td>
</tr>
</tbody>
</table>

$\mathrm{T}_R = 800, 700$ °C, $t_{\text{inc}} = 24$ h, WHSV = 24 l/h g, CH$_4$/CO$_2 = 1$, $(P_{\text{CH}_4} + P_{\text{CO}_2})/P_T = 0.2$, $W = 200$ mg, $T_{\text{Red}} = 700$ °C/8 h.
Fig. 6. Effect of substitution of La by Ca vs. time on stream. $T_0 = 700 ^\circ C$, WHSV = 24l/h g, $\text{CH}_4/\text{CO}_2 = 1$, $(P_{\text{CH}_4} + P_{\text{CO}_2})/P_T = 0.2$, $W = 200 \text{mg}, \text{Red.} = 700 ^\circ C/8 \text{h}$.

Since $\text{La}_{0.8}\text{Ca}_{0.2}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$ showed the best catalytic activity for both sets of experimental conditions, as observed from Table 5, the next step was to study the influence of the substitution of lanthanum by other lanthanides, such as samarium and neodymium. The initial tests were carried out at $800 ^\circ C$ maintaining other variables constant. As observed in Table 5, the methane and $\text{CO}_2$ conversion and the selectivity to CO were very high. Even at $700 ^\circ C$ an increase in CO selectivity for samarium- and neodymium-containing perovskite and a small increase in methane and $\text{CO}_2$ conversion was observed compared to that shown by lanthanum perovskite (Fig. 7).

Under the optimized experimental conditions, catalysts did not show significant coke deposition even after 120h on stream (1.38% carbon/g of catalyst), maintaining their activity and selectivity to CO (Fig. 8), which corroborate the low coke formed in these solids. When working with supported nickel catalyst for steam reforming, Trimm [10] suggested that the presence of rare earth oxides added to the support should diminish coke formation by favoring coke gasification. This could be the case since on $\text{La}_{0.8}\text{Sm}_{0.2}\text{Ru}_{0.8}\text{Ni}_{0.2}\text{O}_3$ only 0.51% of carbon/g of catalyst was observed [41].

Comparison with an industrial catalyst containing 12% Ni, used for steam reforming of methane, was
carried out. The conversions of methane, CO$_2$, and the selectivity to CO and the stability of the commercial catalyst were similar to that shown by catalysts obtained from the perovskites precursors (Fig. 8, Table 5), which evidence that further improvement of catalysts prepared by using the perovskites looks promising.

4. Conclusions

Preparation of the precursor perovskites by the sol–gel method produces solids with a high homogeneity and crystallinity as confirmed by the different characterization techniques. The Ca–La series La$_{1-x}$Ca$_x$Ru$_{0.8}$Ni$_{0.2}$O$_3$ showed a well-defined perovskite structure. However, when lanthanum is replaced by samarium and neodymium, the presence of pyrochlore structures, together with the perovskites, were observed as evidenced by the XRD analysis.

The TPR curves of the precursor perovskites showed that the substitution of lanthanum by cations of smaller ionic radii (Ca, Nd, and Sm) favored the reactivity of the lattice oxygen, which gives rise to lower stability of the perovskite and lower temperature of reduction.

Reduction before reaction of the precursor perovskites produced small Ru–Ni nanoparticles that avoid coke formation and give rise to active and stable catalysts.

When the best reaction conditions were determined ($T_R = 800^\circ$ C, $\text{WHSV} = 24$ h$^{-1}$, $\text{CH}_4/\text{CO}_2 = 1$, $(\text{P}_{\text{CH}_4} + \text{P}_{\text{CO}_2})/\text{P_T} = 0.2$, $\text{W} = 200$ mg, $\text{Red.} = 700^\circ$ C/8 h), all catalysts showed high conversion and good selectivity to CO. Among the Ca–La series, the solids with the best catalytic performance were: La$_0.8$Ca$_0.2$Ru$_{0.8}$Ni$_{0.2}$O$_3$ and La$_0.5$Ca$_0.5$Ru$_{0.8}$Ni$_{0.2}$O$_3$, with the highest selectivity to CO.

It was observed that the unchanged composition of B-site cations of the precursor perovskites keeps approximately constant the methane and CO$_2$ conversions, while the change of the nature and composition in A-site cations of the precursor perovskite strongly modifies the stability and selectivity of the catalysts.

Acknowledgements

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References