Production of Hydrogen by Oxidative Reforming of Diesel Fuel over Co and Ru-Co/La$_2$O$_3$ catalysts derived from perovskite precursors

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ABSTRACT:

Oxidative reforming of diesel was studied over Co and Ru-Co/La$_2$O$_3$ catalysts derived from LaCoO$_3$ perovskite precursor. Physicochemical characterization by XPS, TPR and XRD showed that incorporation of Ru to LaCoO$_3$ produces changes in LaCoO$_3$ characterized by a lower particle size of LaCoO$_3$ and cobalt segregation on LaCoO$_3$ surface. The modifications of LaCoO$_3$ due to the addition of Ru directly affect the structure and morphology of Co particles during the reaction. The active phases at the beginning of reaction evolve differently with time on stream, founding that the presence of an extended perovskite phase, whose proportion is greater in Ru/LaCoO$_3$ sample, produces an increase in the catalyst stability. Characterization of used samples reveals that improvements in cobalt surface concentration and Co-La$_2$O$_3$ interactions were the main factors related to the better catalytic stability of Ru/Co/La$_2$O$_3$ derived catalyst.

KEYWORDS : LaCoO$_3$ perovskite, Ru, oxidative reforming, diesel, hydrogen production

1. INTRODUCTION

The reforming of diesel fuel for the production of hydrogen is difficult because of the refractory nature of the compounds present in diesel fractions [1]. The main problems are related to the degradation of catalysts over time due to the harsh operating conditions (high temperatures and high H$_2$O/C ratios) necessary to obtain high system efficiencies. The causes of degradation include the poisoning of the catalysts by sulphur, thermal sintering and extensive coke formation due to the low H:C ratio and the high molecular weight of the molecules. Catalyst formulations typically comprise [2,3] noble (Pt, Rh and Ru) or non-noble metals (Ni and Co) deposited or incorporated into carefully engineered supports (thermal stabilized alumina, doped alumina with promoters to accelerate coke gasification, mixed metal oxides, oxide-ion conducting substrates,.....). In recent years the research on catalysts for CPO, SR and oxidative reforming of hydrocarbons has paid much attention to systems with perovskite structure of general formula ABO$_3$ (where A and B are usually metallic rare earth cations and transition metals, respectively) due to their well-known thermal stability in a broad range of temperature as well as their high OSC and oxygen ion conductivity [4]. Generally speaking, the B-metal site in perovskite oxide forms the primary active sites while the A-site metal has a strong effect on the stability and also provides the possibility to improve catalyst performance by synergetic interactions with metals on B-site. Perovskites not only fulfill the stability requirements for the reforming and oxidation reactions, but also may act as a precursors of active particles by reduction of B-site cations forming a well dispersed and stable metal particles over a stable support (oxide of element A) [5-7]. This fact is very important taking into account the reductive conditions of the reforming reactions for which the use of perovskites may allow to stabilize the small particles of the metal in position B [8] under reaction conditions. Oxidative reforming, a combination of steam reforming (SR) and catalytic partial oxidation (CPO), has been chosen to produce hydrogen because offers advantages respect the individual SR and PO processes such as: less externally energy-intensive, less cost effective and better response to dynamic changes [9]. Moreover, the combination of these reactions can improve the reactor temperature control and reduce the formation of hot spots, avoiding catalysts deactivation by sintering or carbon deposition [10]. Oxidative reforming reaction carries out both CPO and SR of hydrocarbons at the same catalyst, although not necessarily exactly on the same catalytic sites [11]. As indicated in literature, many transition elements, either in metallic or oxide state, possess activity for both oxidation or steam reforming reactions which enables them to become strong candidates for oxidative reforming [12]. For this work we are developing
diesel reforming catalysts based on Co on lanthanum oxide derived from LaCoO₃ perovskites. Lanthanum has been chosen for A-site due to its known promoter effect on both thermal stability and activity [13] whereas cobalt has been chosen as metal in B-site taking into account its probed activity for steam reforming reactions [14]. Moreover, LaCoO₃ has a high tolerance factor (0.883) that allows to form pure perovskite crystals easily. Both A and B sites in perovskite can be partially exchanged resulting in mixed valence states and enhanced mobility of oxygen in the lattice. The exchange at B site can also incorporate noble metals that improve activity stability and sulphur tolerance. Among transition metals anchored into perovskite lattice, ruthenium was particularly effective in catalytic reforming of heavy hydrocarbon fuels [15].

With this background this paper deals with the oxidative reforming of diesel to synthesis gas over Co/La and Ru-Co/La catalysts derived from LaCoO₃ perovskites. Several characterisation techniques such as XRD, XPS, TPR and elemental chemical analysis have been used to characterise fresh, activated and aged catalysts. Surface and structural characteristics in both systems have been related to their different catalytic behaviour.

2. EXPERIMENTAL

2.1 Catalysts preparation

LaCoO₃ perovskite was prepared by the simultaneous precipitation of cobalt and lanthanum ions using a solution of the nitrate salts of cobalt and lanthanum and K₂CO₃ as precipitating agent [16]. The salts La(NO₃)₃·6H₂O (99.9% Johnson Matthey) and Co(NO₃)₂·6H₂O (97.7% min Johnson Matthey) were dissolved in distilled water to obtain 1 M solutions. Both solutions were mixed together under vigorous stirring. Then, a stoichiometric quantity plus 10% of aqueous solution of K₂CO₃ (99.0% min Johnson Matthey) was rapidly added. Under basic (pH>9) conditions, water was partially evaporated by heating the solution around 70º C. Before filtering the precipitate was washed with ice-cooled distilled water, until the pH of the filtrate became neutral. The precursors were then dried at 383 K for 4 hours and calcined at 1023 K for 4 hours. The heating rate used was 3ºC·min⁻¹ from 383 K till 1023 K.

Ru-added catalyst (Ru/LaCoO₃) was prepared by wet impregnation method using the appropriate amount of RuCl₃ (ruthenium chloride, 48,91% de Ru, Premion, Johnson Matthey) to achieve a molar ratio of 0,02 Ru/1 La/1 Co. Impregnation was carried out in a rotary evaporator at 353 K for 2 h. Then, the sample was dried at 383 K for 4 h and calcined at 773 K for 3 h.

2.2 Catalysts characterization

The BET surface area of prepared perovskite precursors was measured by N₂ adsorption/desorption studies using a Micromeritics ASAP 2100 apparatus on samples previously outgassed at 423 K for 12 h. The experiments were performed at liquid nitrogen temperature (77 K) using quasi-gemini method to minimize errors in the measurement of low area samples.

X-ray diffraction patterns were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered CuKα radiation (λ = 0.1538 nm) under constant instrument parameters. For each sample, Bragg angles between 5º and 80º were scanned; a rate of 5 sec per step (step size: 0.04º 2θ) was used during a continuous scan in the above mentioned range. Average LaCoO₃, La₂O₃ and Co₃ particle size was then estimated from X-ray line width broadening using the Scherrer equation. The width (t) is taken as the full width at half maximum intensity of the most intense and least overlapped peak (2·θ = 47.5º, 29.9º and 44.2º, respectively).

XPS measurements were recorded by using a Fisons ESCALAB MkII 200R spectrometer equipped with a hemispherical electron analyser and an Al Kα (hv = 1486.6 eV, 1 eV = 1.6302 ×10⁻¹⁹ J) 120 W X-ray source. Areas of the peaks were estimated by calculating the integral of each peak after smoothing and subtraction of the S-shaped background and fitting of the experimental curve to a mixture of Lorentzian and Gaussian lines of variable proportions. All binding energies (BE) were referenced to the C 1s signal at 284.6 eV from carbon contamination of the samples to correct the charging effects. Quantification of the atomic fractions on samples surface were obtained from integration of the peaks with appropriate corrections for sensitivity factors [17].

Hydrogen temperature-programmed reductions (H₂-TPR) of catalysts were conducted using a Micromeritics 2900 instrument in a U-shaped quartz reactor. Prior to reduction experiment, the sample (30 mg) was flushed by a helium stream at 110º C for 15 min and then cooled down to room temperature. TPR profiles were obtained by heating the sample under a 10% H₂/Ar flow (50 mL/min) from 303 to 1273 K at a linearly programmed rate of 10 K/min.
Elemental chemical analysis was performed to determine carbon content in used catalysts. It was carried out using a LECO CHNS-932 equipment with an autobalance AD-4 Perkin-Elmer (resolution 0.1 μg).

2.3 Activity tests

Catalytic tests were carried out in a fixed-bed continuous-flow stainless steel reactor. The catalytic bed, 100 mg of catalysts diluted with carborundum (dp=0.5mm SiC/catalyst= 5 volume) to avoid preferential gas flow parts and hot spots, was placed in a tubular reactor (8-mm i.d) with a coaxially centred thermocouple in contact with the catalytic bed. Prior to reaction, perovskite precursors were flushed in helium at 1123 K before admission of feed mixture. The flow rates of diesel and water feeds were controlled by liquid pumps and were preheated in an evaporator before passing through the catalyst bed in the reactor. Nitrogen gas (2 mL/min) was also fed to the evaporator to facilitate the evaporation and passage of both the hydrocarbon and water. For the oxidative reforming of diesel, the reactants were introduced into the reactor in a molar ratio of H2O/O2/C= 3/0.5/1. The total gas flow rate was kept at 75 mL/min (GHSV= 20000 h⁻¹). Activity was measured at atmospheric pressure and 1123 K maintaining the reaction for 80 h at this temperature. The products were analysed periodically by an on-line gas chromatograph (HP 5890 Series II) equipped with a TC detector and programmed to operate under high-sensitivity conditions. A 4A molecular sieve column is used for H2, O2, N2, CO and CH4 separation and a Porapack N (80/100) for CO2, C2H4, C2H6 and H2O. Carbon balances were lower than 100% for each run indicating, as it will be further commented, the possibility of carbon formation. Diesel conversion and hydrogen yield are defined as follows:

\[
\text{Conversion} (\%) = \frac{\text{Total mole amount of carbon components in reformate}}{\text{Total mole amount of C in feed } C_nH_m} \times 100
\]

\[
\text{Yield} (\%)(\text{mol } H_2 / \text{mol } C) = \frac{\text{mole amount of } H_2 \text{ in reformate}}{\text{Total mole amount of C in feed } C_nH_m} \times 100
\]

\[
\text{Yield} (\%)(\text{mol } H_2 + CO / \text{mol } C) = \frac{\text{mole amount of } H_2 + CO \text{ in reformate}}{\text{Total mole amount of C in feed } C_nH_m} \times 100
\]

3. RESULTS

3.1 Characterization of calcined and pretreated perovskites

Surface area and X-ray diffraction (XRD)

Textural data obtained from N2 adsorption-desorption isotherms shows a BET surface area for calcined LaCoO3 and Ru/LaCoO3 samples of 3.3 and 7.2 m²/g, respectively. Taking into account that specific surface areas exposed by perovskite crystals are equal to the geometrical one, as they do not possess internal microporosity, the observed changes in surface area with the incorporation of Ru could be indicative of changes in the particle size of LaCoO3 during the Ru incorporation. Figure 1 shows XRD patterns of calcined and pretreated (after a thermal treatment under He at 1123 K) LaCoO3 and Ru/LaCoO3 samples. The XRD pattern of the calcined LaCoO3 exhibits strong reflections at 32.9° (1 1 0) and 33.3° (1 0 4) that correspond to the stoichiometric perovskite with rhombohedral deformation of the ideal cubic structure of perovskite (JCPDS 48-123). No segregated phases corresponding to La or Co oxides were detected. As observed in Figure 1, the treatment in He at 1123 K provokes a decrease in the height of peaks assigned to LaCoO3 perovskite phase together with the appariation of diffraction lines corresponding to La2O3 (JCPDS 74-2430) and CoO (JCPDS 43-1004). This fact is indicative therefore of the partial decomposition of LaCoO3 perovskite during the pretreatment in inert gas.
The XRD pattern of calcined Ru/LaCoO$_3$ sample only displays the diffraction lines previously observed in calcined LaCoO$_3$ corresponding to rhombohedral perovskite phase. Peaks related to RuO$_2$ are not visible, due possibly to the low concentration of ruthenium added to LaCoO$_3$. Presence of segregated phases associated to La or Co were not observed. Nevertheless, the presence of La/Co phases in very low concentration and/or amorphous state cannot be discarded because of the limitations of XRD technique. As observed in Figure 1, the thermal treatment in He of the Ru/LaCoO$_3$ does not provoke a loss of the perovskite structure as observed previously for the bare LaCoO$_3$.

Quantitative estimation of crystallite sizes of LaCoO$_3$ phase by applying the Scherrer equation (Table 1) has also been calculated from the broadening of the (0 2 4) reflection of LaCoO$_3$ phase (at $2\theta$ angle of 47.5). It can be noted that mean crystallite size of calcined Ru/LaCoO$_3$ was slightly lower than bare LaCoO$_3$ counterpart. After thermal treatment under He it is observed an increase in the LaCoO$_3$ mean crystallite size for bare LaCoO$_3$ while for Ru/LaCoO$_3$ counterpart the thermal treatment does not modify the size of LaCoO$_3$ crystallites obtained after calcination.

**Table 1** Mean crystallite size by Scherrer equation

<table>
<thead>
<tr>
<th></th>
<th>LaCoO$_3$ mean diameter (nm)</th>
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<tbody>
<tr>
<td><strong>Calcined</strong></td>
<td></td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>44</td>
</tr>
<tr>
<td>Ru/LaCoO$_3$</td>
<td>42</td>
</tr>
<tr>
<td><strong>Pretreated</strong></td>
<td></td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>48</td>
</tr>
<tr>
<td>Ru/LaCoO$_3$</td>
<td>43</td>
</tr>
</tbody>
</table>

**X-Ray Photoelectron Spectroscopy (XPS)**

Photoelectron spectroscopy was used to determine the chemical state of the elements and their surface proportions in calcined and thermally treated LaCO$_3$ and Ru/LaCO$_3$ samples. Figure 2 compares the Co2p core level for LaCoO$_3$ and Ru/LaCoO$_3$ calcined and thermally treated under He at 1123 K. LaCoO$_3$ calcined sample exhibited the Co 2p$_{3/2}$ peak at a binding energy close to 780.9 eV. This value is lower than the one typically reported for cobalt oxides [18]. The BE value for Co 2p$_{3/2}$ together with the weakness of shake-up peaks indicate that on calcined LaCoO$_3$ sample surface cobalt atoms forms LaCoO$_3$ phase. Table 2 summarizes the atomic surface Co/La ratios. Measured surface Co/La ratio for calcined LaCoO$_3$ is lower than the nominal ratio. This lower Co/La ratio should be

![Figure 1](image1.png)

*Figure 1 XRD patterns of LaCoO$_3$ and Ru/LaCoO$_3$ (calcined and pretreated under inert gas at 1123 K)*

![Figure 2](image2.png)

*Figure 2 Co2p spectra of calcined and pretreated LaCoO$_3$ and Ru/LaCoO$_3$ samples*
explained through a segregation of La to the surface. This effect is also found in other LaMO₃ perovskites and it is due to the basicity of La³⁺ cations and their tendency to react with atmospheric CO₂ and H₂O [19]. As shown in Figure 2 the Co2p level for LaCoO₃ contains, after thermal treatment under He, a single peak at 780.1 eV and a shake-up peak 790 eV indicative of the presence of surface Co₃O₄ species. This fact points to surface changes in perovskite structure of LaCoO₃ after thermal treatment. The changes in LaCoO₃ developed after thermal treatment also modify Co/La surface concentrations. The treatment in inert flow at high temperature leads to an enrichment of cobalt in surface as indicated by the higher Co/La observed in Table 2.

For calcined Ru/LaCoO₃ (Figure 2) the binding energy of Co 2p₃/₂ level and the characteristic shake-up satellite line at 791 eV are indicative of the presence of Co₃O₄ in the surface. Measured Co/La ratio for this calcined sample (Table 2) was higher than nominal ratio indicating a degree of segregation of cobalt phase in surface induced by ruthenium deposition step. Chemical changes after treatment in inert gas at 1123 K of Ru/LaCoO₃ sample were also studied by XPS. As shown in Figure 2 after thermal treatment the Co 2p₃/₂ shifted to 780.1 eV and the shake-up peak decreases. Both facts are indicative of the presence of Co₃O₄ phase in the surface changes after treatment in inert gas at high temperature also influences on surface composition. Table 2 shows a decrease in Co/La ratio after thermal treatment achieving a value close to that corresponding to bare calcined LaCoO₃.

### Table 2 Surface Co/La (XPS) for calcined and pretreated LaCoO₃ and Ru/LaCoO₃ samples

<table>
<thead>
<tr>
<th></th>
<th>Co/La</th>
<th>Ru/LaCoO₃</th>
<th>LaCoO₃</th>
<th>Ru/LaCoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined</td>
<td>0.76</td>
<td>1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pretreated</td>
<td>1.63</td>
<td>0.78</td>
<td></td>
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</tr>
</tbody>
</table>

**H₂-Temperature programmed reduction**

TPR profiles of calcined LaCoO₃ and Ru/LaCoO₃ are displayed in Figure 3. The reduction profile of LaCoO₃ indicates clearly that reduction proceeds according to two consecutive steps. The reduction mechanism of LaCoO₃ is controversial. Studies reported in literature [20,21] propose that the reduction of Co³⁺ in LaCoO₃ undergoes the following two steps:

\[
\begin{align*}
2\text{LaCoO}_3 + \text{H}_2 & \rightarrow 2\text{LaCoO}_{2.5} + \text{H}_2\text{O} \\
2\text{LaCoO}_{2.5} + 2\text{H}_2 & \rightarrow \text{La}_2\text{O}_3 + \text{Co}^0 + 2\text{H}_2\text{O}
\end{align*}
\]

Thus, the TPR profile of LaCoO₃ presented two separate peaks at around 693 and 823 K, which were assigned to the consecutive reduction of Co³⁺ to Co²⁺ in the form of LaCoO₂.₅ and to finely dispersed Co⁰ on La₂O₃, respectively. The position of the aforementioned peaks depends on the kinetics of the reduction that is influenced mainly by crystalline size and oxygen defects in perovskite lattice [22,23].

For the Ru-containing LaCoO₃ three H₂-consumption peaks (493, 623 and 803 K) are observed. Peaks at 623 and 803 K are associated to reduction of LaCoO₃ phase while the additional low temperature peak could be associated to the reduction of small proportion of cobalt oxide phases. Looking at reduction temperatures, there is a marked effect of Ru in the reducibility of both cobalt oxides and LaCoO₃ phase. According to literature Ru facilitates the reduction of cobalt oxides by means of the formation of Co-Ru oxides that reduces at lower
temperatures or towards spill-over process with hydrogen species activated and dissociated on ruthenium metallic phases [24]. Peaks corresponding to the two steps reduction of LaCoO\textsubscript{3} phase also shift to lower temperature with addition of Ru. This better reducibility of LaCoO\textsubscript{3} may be associated to the aforementioned spill-over process assisted by ruthenium or more probably to changes in perovskite crystal size/structure during Ru deposition that leads to structures with lower diffusional resistance to hydrogen reduction.

3.2 Activity tests

Activity of LaCoO\textsubscript{3} and Ru-LaCoO\textsubscript{3} samples treated in He at 1123 K were evaluated in the oxidative reforming of diesel performed, as indicated in the experimental section, at atmospheric pressure and 1123 K. Figure 4 presents the evolution of the hydrogen yield (primary produced during oxidative reforming (graph at the top) and also the potential that will be produced from CO during WGS reaction (graph at the bottom) as a function of reaction time. For both catalysts diesel conversion was 100 % and maintains with reaction time. In spite that total diesel conversion maintains with reaction time on LaCoO\textsubscript{3} derived catalyst, the product distribution changes with time-on-stream, as Figure 4 shows. The reaction over LaCoO\textsubscript{3} starts with high selectivity to H\textsubscript{2} and CO but the product distribution changes in the first hours on stream. As it is observed in Figure 4, hydrogen and CO concentrations decrease a 40% throughout the 80 h of reaction. In contrast with bare perovskite, the activity of Ru/LaCoO\textsubscript{3}-derived catalyst remained high and stable during the entire 80 h of reaction. An excellent hydrogen yield (90%, in relation to the maximum theoretical value, including the produced from CO by WGS) during the 80 h of the oxidative reforming of commercial diesel was obtained over this catalyst formulation. The activity and stability results achieved over this catalyst were similar to the best results in diesel reforming published in open literature [15].

Figure 5 shows gaseous product compositions corresponding to the 50 hour on stream as representative values of “stabilized” catalysts. Comparison of the molar fractions towards the diverse reaction products (Figure 5) also reveals differences for the Ru-containing and bare LaCoO\textsubscript{3} derived catalysts. A lower degree of hydrogen extraction as well as a higher proportion of hydrogen-containing molecules such as methane, ethane and ethylene, were observed for bare LaCoO\textsubscript{3} based catalysts with respect to those obtained on the Ru-containing counterpart.
3.3 Characterization of used catalysts

**X ray diffraction (XRD)**

Diffraction patterns of used catalysts are displayed in Figure 6. None of the used samples show diffraction peaks corresponding to crystalline forms of graphitic carbon at \(2\theta = 26.2^\circ\) (JCPDS-75-1621). Both used samples exhibited reflections corresponding to La\(_2\)O\(_3\) (JCPDS 74-2430) and metallic Co (JCPDS 15-806). As observed in Figure 6, diffraction lines corresponding to metallic Co and La\(_2\)O\(_3\) phases show higher degree of definition and intensity on used LaCoO\(_3\)-derived catalyst than on Ru-containing counterpart. Quantitative estimation of crystalline domains of Co\(_0\) and La\(_2\)O\(_3\) in used samples, by applying the Scherrer equation (Table 3), indicates the larger Co\(_0\) and La\(_2\)O\(_3\) crystal size after reaction for LaCoO\(_3\)-derived catalyst than that of Ru/LaCoO\(_3\) counterpart.

**X- Ray Photoelectron Spectroscopy (XPS)**

XPS analyses of LaCoO\(_3\) and Ru/LaCoO\(_3\)-derived catalyst used in the oxidative reforming of diesel were also performed in order to know the evolution of active phases after reaction. Binding energy for Co 2p\(_{3/2}\) core level of used catalysts appears at 778 eV (Figure 7). This binding energy corresponds to metallic Co surface species. Calculated XPS Co/La ratio for the used samples (Table 3) revealed differences in Co surface exposition after reaction. Higher Co exposition was observed for used Ru-containing catalyst respect to that calculated for bare perovskite derived catalyst.

O 1s XPS signal of used LaCoO\(_3\) and Ru/LaCoO\(_3\)-derived catalysts shows two main photolines at 529 eV and 530.8 eV. According to literature [25], the low binding energy peak must be assigned to lattice oxygen and the high binding energy to adsorbed oxygen species (such as carbonates associated to La\(_2\)O\(_3\)). The relative concentration of both oxygen species was calculated and also summarized in Table 3. As it is shown in Table 3, the calculated adsorbed/lattice oxygen ratio was higher for Ru/LaCoO\(_3\) derived catalysts indicating the greater proportion of surface carbonates in the form La\(_2\)O\(_2\)CO\(_3\) in the surface of this sample respect to the used bare perovskite counterpart [25].
Table 3 Different properties of used catalysts

<table>
<thead>
<tr>
<th>Used catalysts</th>
<th>Surface Co/La (XPS)</th>
<th>Adsorbed oxygen/ lattice oxygen (XPS)</th>
<th>Average diameter La$_2$O$_3$ (XRD)</th>
<th>Average diameter Co$^0$ (XRD)</th>
<th>% C (E.C.A.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>0.68</td>
<td>1.12</td>
<td>51</td>
<td>43</td>
<td>0.84</td>
</tr>
<tr>
<td>Ru/LaCoO$_3$</td>
<td>1.18</td>
<td>1.77</td>
<td>37</td>
<td>36</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Elemental chemical analysis

Elemental chemical analysis of the used LaCoO$_3$ and Ru/LaCoO$_3$-derived catalysts were carried out to calculate the amount of carbonaceous residues retained in the catalysts after reaction by measuring the CO$_2$ emitted during its temperature programmed oxidation under oxygen gas flow. The coke contents in used catalysts presented in Table 3 were calculated from the CO$_2$ emissions between 573 K and 1100 K. For both samples the coke content after reaction was low. Nevertheless differences on surface coke formation were observed depending on the nature of catalyst. In this sense a lower carbon deposition was observed (Table 3) for Ru-added catalyst (0.56 wt %) respect to the bare-perovskite counterpart (0.84 wt%).

4. DISCUSSION

Physicochemical characterization of calcined perovskite precursors revealed that deposition of Ru on LaCoO$_3$ modifies its properties at different level. Changes in particle size after Ru deposition was observed from BET and XRD results. The higher BET area together with the lower intensity of XRD peaks observed for Ru/LaCoO$_3$ (Figure 1) are indicative of the decrease in the particle size of the LaCoO$_3$ crystallites after Ru incorporation. The shift in the second step of LaCoO$_3$ reduction observed in TPR experiments on calcined Ru/LaCoO$_3$ corroborates the reorganization of LaCoO$_3$ during Ru deposition leading to a lower particle size of LaCoO$_3$ crystallites. Partial dissolution of LaCoO$_3$ during Ru deposition may be in the origin of the observed changes in particle size as the partial segregation of cobalt phase toward the surface detected by XPS (Table 2). The modifications of LaCoO$_3$ due to the addition of Ru directly affect the structure and morphology of Co particles after the thermal treatment in inert atmosphere prior to reaction. For bare LaCoO$_3$ thermal treatment provokes its partial decomposition in lanthanum and cobalt oxide as XRD (Figure 1) and XPS (Figure 2) indicates. By the contrary this partial decomposition after thermal treatment was not observed in the case of Ru/LaCoO$_3$, maintaining this sample the perovskite structure of LaCoO$_3$. The better stability of Ru/LaCoO$_3$ is probably related not only to the morphological properties of the LaCoO$_3$ crystallites (TPR experiment showed lower Co-O-La strength) but also to the presence of cobalt and lanthanum oxides in the surface of LaCoO$_3$ after Ru incorporation that may difficult the oxygen diffusion from LaCoO$_3$ lattice, thus modifying perovskite decomposition process under reaction.

Activity measurements coupled with the physicochemical characterization of used catalysts point out that metallic-dispersed transition metal on the surface of the lanthanum oxide plays an essential role in the catalytic behavior of perovskite derived catalysts. In spite of the intrinsic reforming capacity of ruthenium, the comparison of the initial activity (LaCoO$_3$>Ru/LaCoO$_3$, Figure 4) with surface cobalt concentration (LaCoO$_3$>Ru/LaCoO$_3$, Table 3) indicates that the higher initial activity observed for bare LaCoO$_3$-derived catalysts may be related to the higher cobalt concentration achieved after thermal decomposition on this sample respect to that corresponding to Ru/LaCoO$_3$. The active phases at the beginning of reaction evolve differently with time on stream, founding that the presence of an extended perovskite phase, whose proportion increases in Ru/LaCoO$_3$, produces an increase in the catalyst stability (Figure 4). Changes in cobalt surface concentration is a factor to be considered in the evolution of LaCoO$_3$ and Ru/LaCoO$_3$-derived catalysts under reaction. For used catalysts, XRD and XPS analyses showed the greater cobalt exposition and cobalt-lanthanum contact achieved in catalyst with Ru (Table 3). This fact may be related with the lower size of perovskite crystallites detected on Ru/LaCoO$_3$ sample or to a promotion effect of ruthenium
preventing the sintering of cobalt atoms from perovskite reduction [23]. Besides cobalt surface concentration, catalyst deactivation due to the formation of carbon is another factor to be considered in order to describe the evolution of catalysts under reaction. As seen in Table 3, lower quantities of carbonaceous deposits were observed for Ru-catalyst respect to bare LaCoO₃. It is known [26] that higher carbonaceous deposits appear on metal particles of larger size and the nature of the support play a major role in assisting coke removal. In agreement with this, the higher cobalt dispersion observed for the Ru/LaCoO₃ used sample (Table 3) may contribute to the lower carbon concentration in this catalyst. Additionally to this reason, the lower carbon deposition may also be related to the presence of La in the formulation. In literature, positive effect of lanthanum as support of noble metals applied to steam reforming of hydrocarbons are explained by the ability of lanthanum to adsorb CO₂ forming lanthanum oxycarbonates which participate in coke gasification [27-29]. Some differences have found by XPS in the carbonate surface concentration on used catalysts (Table 3). Concentration of these surface oxygen species is lower in the less stable LaCoO₃ derived catalyst than in the Ru/LaCoO₃ one. The greater proportion of surface carbonates in Ru containing sample is in accordance with the smaller La₂O₃ particle size found by XRD for this sample (Table 3). Therefore, it can be inferred some participation of lanthanum, probably through an enhanced adsorption of CO₂ increasing the lanthanum carbonates concentration, in the improvement in catalytic stability observed for the Ru/LaCoO₃-derived catalyst. From results presented here both effects, higher cobalt dispersion and lower carbon deposition, contribute to the observed enhancement in the reforming capacity and stability of the LaCoO₃-derived catalysts with the incorporation of Ru.

CONCLUSIONS

Ruthenium added to LaCoO₃ increases activity and stability of LaCoO₃ derived catalyst for hydrogen production by oxidative reforming of diesel. Reorganization of LaCoO₃ during Ru deposition leads to a lower particle size of LaCoO₃ crystallites and surface cobalt segregation. The modifications of LaCoO₃ due to the addition of Ru directly affect the structure and morphology of Co particles after the thermal treatment in inert atmosphere prior to reaction. In Ru containing sample, the partial decomposition of perovskite in cobalt and lanthanum oxides during activation is inhibited, resulting in a well defined perovskite structure at the beginning of reaction. The active phases at the beginning of reaction evolve differently with time on stream, founding that the presence of an extended perovskite phase, whose proportion increase in Ru/LaCoO₃, produces an increase in the catalyst stability. Changes in cobalt surface concentration are a factor to be considered in the evolution of LaCoO₃ and Ru/LaCoO₃-derived catalysts under reaction. Better cobalt exposition and cobalt-lanthanum contact achieved in catalyst with Ru after reaction, related with the lower size of perovskite crystallites detected on Ru/LaCoO₃ sample, or a promotion effect of ruthenium preventing the sintering of cobalt atoms, contribute to the observed better catalytic stability on catalyst with Ru. Additionally it is inferred some participation of lanthanum in the better stability of Ru-containing catalyst through an enhanced adsorption of CO₂ increasing the formation of lanthanum carbonates which participate in coke gasification.

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