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Evidence of anti-coking behavior of La_{0.8}Sr_{0.2}Cr_{0.98}Ru_{0.02}O₃ as potential anode material for Solid Oxide Fuel Cells directly fed under methane

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ABSTRACT

La_{0.8}Sr_{0.2}CrO₃ (LSC) based Ru catalysts are very active in methane steam reforming. Nevertheless, they can be easily poisoned under water-deficient conditions. Ru can be deposited as metallic ruthenium particles decorating the LSC grains or be inserted as Ru ions in the perovskite structure. Both Ru-promoted LSC catalysts were studied in methane steam reforming under water-deficient conditions and characterized after testing. Catalytic activity tests showed that ruthenium metal species are deactivated under water-deficient atmosphere, while ruthenium species inserted in LSC presented a remarkable stability and catalytic activity where residual steam plays a key role. Very unreactive carbon species responsible for deactivation were detected by temperature-programmed oxidation and transmission electron microscopy over metallic ruthenium species. Such species were not observed when ruthenium species are inserted and stabilized into the LSC structure. La_{0.8}Sr_{0.2}Cr_{0.98}Ru_{0.02}O₃ appears therefore as a highly promising anti-coking anode material for Solid Oxide Fuel Cells directly fed with methane or natural gas and operating under water-deficient conditions.

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1. Introduction

One great advantage of the Solid Oxide Fuel Cell (SOFC), compared to other fuel cells, is that hydrocarbon fuels like natural gas or its major constituent, i.e., methane, can be converted directly. Due to their high operating temperature of the SOFC (800–1000 °C), several reactions with methane may be considered, such as methane combustion, partial oxidation, or methane reforming. In many respects, internal steam reforming is the most promising concept since the reaction takes place directly in the anode compartment; this improves heat exchange between the endothermic reforming reaction and the exothermic electrochemical hydrogen oxidation within the stack [1]. It can also significantly reduce the requirement for cell cooling which is usually done by flowing excess air through the cathode [2]. However, its development is hindered by the endothermicity of the reaction which produces local cooling in the cell and by carbon deposition due to methane cracking or by the Boudouard reaction [3].

Another model refers to the concept of gradual internal steam reforming [4]. This theory is based on a coupling between the steam reforming reaction and the electrochemical hydrogen oxida-

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tion. This allows the reaction to be delocalized over the entire electrode surface and the steam content to be reduced since water produced by hydrogen oxidation is used to convert methane. Conversion of CO can proceed either via electrochemical oxidation or by the water–gas shift reaction.

However, low water concentrations can produce important carbon deposition. For example, dehydrogenation of hydrocarbons occurs with the most widely used anode, the cermet Ni/YSZ. This leads to the deterioration of anode performance. Some authors have proposed to decrease the conversion rate of nickel in order to avoid carbon deposition. Morimoto et al. have added iron to the Ni/YSZ cermet [5]. Iron addition decreases conversion rate of nickel and adjusts the thermal expansion coefficient toward that of YSZ but important carbon deposition was observed for low water concentrations. Insertion of nickel in strontium-doped lanthanum chromite has also been tested [6]. Nevertheless, the conversion rate decreased and some nickel/chromium agglomerations were observed with nickel content higher than 5 mol%. Nickel addition to Ce–ZrO₂ and/or to Ce–YSZ has also been studied. These supports have been reported as promising but a deterioration of conversion rate was observed at low hydrogen pressure [7–10]. Gadolinium doped ceria catalysts have also been tested but changes in both surface area and redox properties were observed and related to catalytic deactivation [11]. Other metals than nickel can also promote the reforming reaction, such as cobalt and some noble metals such as Pt, Rh, Ir, and especially Ru [12-15].



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Previous work clearly established that Ru-promoted $La_{0.8}Sr_{0.2}$ -CrO₃ (LSC) catalysts are promising anode materials for SOFCs directly fed with methane and integrating the concept of gradual internal steam reforming [16]. Depending on catalyst structure, very different catalytic behaviors with time on stream were observed. Ru can be inserted as Ru ions in perovskite structure (LSCRu). In this case, the conversion rate in steam reforming strongly oscillated with time on stream. Ru could alternatively be deposited as metallic Ru particles decorating the LSC grains (Ru/ LSC). In the latter case, the conversion rate in steam reforming was maximized and fairly stable with time on stream. Nevertheless, carbon deposition was more important. However, in both cases, conversion rates were so intense (close to 100% with the 200 mg of catalyst used) that investigations after reaction were limited.

The aim of this paper is to characterize both types of Ru-promoted $La_{0.8}Sr_{0.2}CrO_3$ anode materials in relation with the catalytic activity in methane steam reforming under water-deficient conditions. Samples loaded with 1% Ru were prepared and characterized before and after catalytic testing by XRD, TEM, XPS, and Chemical Analysis. Catalysts quantities used for catalytic tests were optimized and temperature-programmed oxidation was used to measure carbon formation during the reaction and to follow the oxidation state of catalysts.

2. Experimental procedure

2.1. Catalyst preparation

Ru/LSC and LSCRu were synthesized according to methods previously described [16]. Table 1 gives the composition of the two samples. The specific area was measured using the Brunauer– Emmet–Teller (BET) method with nitrogen at 77 K and the composition was determined by ICP chemical analysis at the CNRS Central Analysis Service (Vernaison – France). Both samples were sieved between 40 and 80 µm before characterization and catalytic tests in order to have uniform samples.

2.2. Activity tests

Before activity measurements, catalysts were pre-treated *in situ* in N₂ at 800 °C for 2 h. Catalytic runs were performed at atmospheric pressure in a conventional flow system at 800 °C with a CH_4/H_2O ratio of 10 (50% CH_4 , 5% H_2O , N₂ balance, total flow rate of 6.5 L h⁻¹). Samples (from 10 to 200 mg) were held on quartz wool in a 2 mm inside diameter U-shaped quartz reactor. Steam was added to the feed by flowing the CH_4/N_2 mixture through a saturator maintained at 33 °C. H_2O concentration was measured with an EdgeTech Dew Prime I hygrometer. The reactor effluents (CH₄, CO, H₂, CO₂, and O₂) were periodically (every 5 min) analyzed by a gas microchromatograph (Varian CP 2003 QUAD) equipped with high sensitivity (5 ppm) thermal conductivity detectors (TCD).

2.3. Characterization methods

XRD measurements were performed at room temperature using a Brücker $D8_{ADVANCE}$ diffractometer using Cu-K-L_{2,3} radiation.

Table 1

Results of chemical	analysis and	d BET measurements.	

Transmission Electron Microscopy characterizations were carried out with a JEOL 2000FX microscope before catalytic runs and with a JEOL JEM 2010 microscope after catalytic runs, both operated at 200 kV and equipped with EDX spectrometers. The latter microscope is equipped with a LaB₆ thermoionic gun and an UHR polepiece which has a point-to-point resolution of 0.196 nm; it also allows the analysis by EDX of small individual nanoparticles down to 3 nm [17-21] with probes down to 5 nm providing sufficient current to make EDX analysis within acceptable times (less than 60 s). Temperature-programmed oxidation (TPO) experiments were carried out after 1 and 24 h of steam reforming reaction. After catalytic testing, the catalysts were cooled down to room temperature in reaction mixture and purged 30 min in N₂. The quartz tube reactor was then transferred on TPO apparatus. The samples were then exposed to a 0.98% O_2 in He (1.8 L h⁻¹) with a constant heating rate of 20 °C min⁻¹ from room temperature to 950 °C. The analvsis of gases was carried out continuously with an on-line mass spectrometer (Pfeiffer Vacuum Omnistar Quadrupole). The species followed were O_2 (*m*/*e* = 32), CO_2 (*m*/*e* = 44), H_2O (*m*/*e* = 18), and CO (m/e = 28). Calibration of CO₂ and O₂ allowed quantitative measurements of CO₂ formation and O₂ consumption. XPS experiments were performed in a KRATOS Axis Ultra DLD with a monochromatic Al K α X-ray source, and a spot size aperture of 300 \times 700 µm. The base pressure in the analysis chamber was better than $5\times10^{-8}\,\text{Pa.}$ XPS spectra of Ru3p, Sr3d, La3d, Cr2p, O1s, and C1s were measured at a pass energy of 20 eV. A charge neutralizer is used to control charges effects on powder samples.

3. Results

3.1. Catalysts characterization

The results obtained by X-ray diffraction are similar to those obtained previously [16]. The diffractogram for Ru/LSC clearly shows LSC and metallic Ru peaks whereas the diffractogram for LSCRu only shows the peaks corresponding to a trigonal perovskite phase. Fig. 1 presents a typical TEM Ru/LSC image. In this micrograph, small (10-40 nm) ruthenium (identified by EDX analysis) nanoparticles inhomogeneously dispersed on the surface of LSC grains are clearly observed. Such small nanoparticles were never observed on LSCRu where rather large grains (500 nm in average) without specific shape were detected (Fig. 2). EDX analysis reveals the presence of La, Sr, Cr, and Ru within those grains. The surface composition of the two samples obtained by XPS is presented in Table 2. The presence of carbon (respectively 7.8% and 5.7% for Ru/LSC and LSCRu) due to the preparation method (carbonate precipitation) can be noted for both samples. For Ru/LSC, the surface ruthenium content is overestimated due to the presence of metallic Ru nanoparticles. However, for this sample, it can be noted that the surface of LSC particles is La-rich and (Cr and Sr)-poor when compared to the bulk composition. The binding energy measured for Ru-3p3/2 peak (461.9 eV) corresponds to values obtained for metallic Ru [22]. The same difference between surface and bulk compositions is observed for LSCRu and the surface Ru content is higher than the bulk Ru content. The binding energy measured for Ru-3p3/2 (464.2 eV) corresponds to values obtained for Ru(IV) ions [23]. This indicates as it was also indirectly suggested by the EDX results that Ru is well-inserted in the perovskite structure as Ru(IV) ions in substitution of chromium ions as it was intended [16].

Symbols	wt% La	wt% Sr	wt% Cr	wt% Ru	Calculated formula by assuming O ₃ ^a	Specific area (m ² g ⁻¹)
Ru/LSC	47.59	7.3	22.31	0.93	0.92 wt%Ru/La _{0.804} Sr _{0.196} Cr _{1.007} O ₃	1.9
LSCRu	48.72	7.27	22.11	0.91	La _{0.809} Sr _{0.191} Cr _{0.979} Ru _{0.021} O ₃	1.0

^a O was not analyzed.



Fig. 1. TEM micrograph of Ru/LSC powder.



Fig. 2. TEM micrograph of LSCRu powder.

3.2. Catalytic tests

Different tests were performed to determine the catalyst mass to be ultimately used in the catalytic test. For masses of 40 mg and higher, the conversion rate of Ru/LSC is close to 100%. For masses of 10 mg and lower, the catalyst amount is not sufficient to completely cover the quartz wool leading to preferential flow paths and consequent diffusion limitations. The mass applied for catalytic testing was thus an intermediate value of 20 mg. Fig. 3 shows the evolution of the H₂, CO, and CO₂ concentrations obtained in the flowing reaction products during the catalytic steam reforming test at 800 °C using 20 mg of Ru/LSC. The initial behavior of this catalyst confirms that it is both very active (93 ± 2% of water conversion) and very selective (very low CO₂ concentration due to water-gas shift reaction) [24–27]. However, the catalyst slowly and gradually deactivates with reaction time. H₂ and CO concentration are respectively 10% and 3% by the end of the catalytic test. The water conversion decreased to 66 ± 2% after 24 h reaction. Furthermore, a small amount of CO₂ is detected. Therefore, for a ratio methane/water of 10, Ru/LSC deactivates and becomes less selective during methane steam reforming reaction.

In the case of LSCRu, the oscillating behavior of the catalytic activity evidenced previously [16] is observed for masses ranging between 50 and 200 mg. For masses of 40 mg and lower, this behavior disappears. The mass retained for the catalytic test is thus 40 mg; results obtained for 20 mg were similar; however, sensitivity is higher with a larger amount of catalyst namely for the TPO measurements that we will present in Section 3.3.1. Fig. 4 shows the evolution of the H₂, CO, and CO₂ concentrations obtained in the flowing reaction products during the catalytic steam reforming test at 800 °C using 40 mg of LSC Ru. This catalyst is less active $(42 \pm 2\%)$ and less selective (presence of CO₂) than Ru/LSC. After an activation period of 40 minutes, the conversion rate is gradually recovered, stabilizes after 14 h reaction, and then remains constant for the rest of the catalytic test. Between 14 and 24 h reaction, H₂, CO, and CO₂ concentrations measured in the flowing reaction products are 8.3%, 2.4%, and 0.3%, respectively. The water conversion is $53 \pm 2\%$. Several catalytic tests were performed that showed the reproducibility of these results. During one of these catalytic tests, the catalyst did not show any deactivation over the 72 h reaction.

Both samples were characterized after reaction by elemental chemical analysis. The composition of both samples did not change after the catalytic tests within the experimental uncertainty of the technique. In particular, the Ru concentrations are identical before and after reaction indicating that no sublimation of ruthenium oxides RuO_x occurred during the catalytic tests.

3.3. Catalysts characterizations after catalytic testing

3.3.1. TPO

In order to determine the origin of the deactivation of Ru/LSC, we have performed two temperature-programmed oxidations of this sample: one after 1 h reaction (before deactivation) and the other after 24 h reaction.

Fig. 5 shows the profiles of O₂ and CO₂ obtained during the TPO of Ru/LSC (20 mg) after 1 h of catalytic test at 800 °C. The CO₂ profile shows two maxima at 430 and 580 °C. These two types of carbon are generally identified in the literature [28–31] as polymorphic carbon C_{β} and graphitic carbon C_{graph} . The amounts of deposited carbon are presented in Table 3: 54 µmol g⁻¹ for C_{β} and 29 µmol g⁻¹ for C_{graph} . The total amount of carbon is rather low (0.1 wt%) after 1 h reaction.

The profile of the consumed oxygen represents the oxygen consumed by the oxidation of the deposited carbon and consequent

Tab	ole	2

Surface composition and binding energy of ruthenium obtained by XPS.

	wt% Sr	wt% Cr	wt% La	wt% Ru	wt% 0	wt% C	Binding energy Ru 3p _{3/2} (eV)
Ru/LSC	3.3	14.8	45.2	7	21.9	7.8	461.9
LSCRu	5.5	16.2	51.1	2.5	19.0	5.7	464.2
LSCRu after 24 h steam reforming	7.0	15.8	45.1	3	24.2	4.9	462.8



Fig. 3. [H₂] (Δ), [CO] (+), and [CO₂] (×) concentrations obtained upon catalytic reforming of CH₄ over Ru/LSC at 800 °C: sample weight = 20 mg, total flow rate = 6.5 L h⁻¹, feed composition = 50% CH₄, 5% H₂O, N₂ balance.



Fig. 4. [H₂] (Δ), [CO] (+), and [CO₂] (×) concentrations obtained upon catalytic reforming of CH₄ over LSCRu at 800 °C: sample weight = 40 mg, total flow rate = 6.5 L h⁻¹, feed composition = 50% CH₄, 5% H₂O, N₂ balance.



Fig. 5. $CO_2 (m/e = 44)$ and $O_2 (m/e = 32)$ profiles obtained during TPO of Ru/LSC after 1 h reaction at 800 °C with $CH_4/H_2O = 10$. TPO conditions: sample weight = 20 mg, 0.98% O_2 in He, flow rate = 1.8 L h⁻¹. "Re-oxidation" corresponds to O_2 consumption for catalyst re-oxidation.

formation of CO_2 and the oxygen consumed during the oxidation of the catalyst. In order to quantify the latter, we added in Fig. 5 the "re-oxidation" profile that corresponds to the difference between the total amount of consumed oxygen and the amount of consumed oxygen for the oxidation of deposited carbon (and CO_2 formation). The profile obtained in this way presents two maxima (290 and 700 °C). The first peak is attributed to the re-oxidation

Table 3

Temperatures of peaks maxima and amounts of O_2 consumed for catalyst reoxidation and CO_2 released during TPO experiments of samples after 1 h and 24 h reaction at 800 °C with CH_4/H_2O = 10.

	T (°C)	CO_2 released (μ mol g ⁻¹)	Т (°С)	O_2 consumed (µmol g ⁻¹)
Ru/LSC after 1 h	430 580	54 ± 3 29 ± 2	290 700	30 ± 5 96 ± 8
Ru/LSC after 24 h	430 570, 650, 700, 800	53 ± 3 54 ± 4	280 690	35 ± 5 93 ± 8
LSCRu after 1 h	430	25 ± 2	260	34 ± 5



Fig. 6. $CO_2 (m/e = 44)$ and $O_2 (m/e = 32)$ profiles obtained during TPO of Ru/LSC after 24 h reaction at 800 °C with $CH_4/H_2O = 10$. TPO conditions: sample weight = 20 mg, 0.98% O_2 in He, flow rate = 1.8 L h⁻¹. "Re-oxidation" corresponds to O_2 consumption for catalyst re-oxidation.

of the support LSC while the second peak is attributed to the reoxidation of ruthenium.

Unlike LaCrO₃, the oxidation state of LSC may vary. This is explained by the partial substitution of La³⁺ ions by Sr²⁺ ions that yields a charge defect which is compensated by the oxidation of a part of the Cr³⁺ ions into Cr⁴⁺ ions and/or by the formation of oxygen defects [32–34]. For 20% substitution, the formula of LSC can evolve from La_{0.8}Sr_{0.2}CrO_{2.9} (reduced form) to La_{0.8}Sr_{0.2}CrO₃ (oxidized form).

The amounts of consumed oxygen are shown in Table 3. For LSC, the consumption of oxygen $(30 \ \mu mol \ g^{-1})$ indicated that, after 1 h of catalytic test, the formula of the support was La_{0.8}Sr_{0.2}CrO_{2.985} which is very close to the oxidized form.

The amount of consumed oxygen for the oxidation of ruthenium $(96 \ \mu mol \ g^{-1})$ corresponds, within the experimental uncertainty, to the amount of dioxygen necessary to oxidize the amount of supported metallic ruthenium, present in the sample, to RuO₂ (92 μ mol g⁻¹). All ruthenium nanoparticles are thus in the metallic form after 1 h of catalytic test.

Fig. 6 shows the profiles of O_2 , CO_2 , and "re-oxidation" obtained during the TPO of Ru/LSC (20 mg) after 24 h of catalytic test at 800 °C.

The profile "re-oxidation" presents exactly the same characteristics after 24 h of catalytic test and after 1 h of catalytic test and the amounts of dioxygen detected are also similar (Table 3). Thus, no change in the oxidation state of both phases was evidenced during the catalytic test.

The CO₂ profile shows five maxima (430, 570, 650, 700, and 800 °C) corresponding to five types of carbon with different reactivity behavior toward oxygen. C_{β} and C_{graph} , already detected after 1 h of catalytic test, are always present. The amount of C_{β} is identical to the one determined after 1 h of catalytic test (53 µmol g⁻¹).



Fig. 7. $CO_2 (m/e = 44)$ and $O_2 (m/e = 32)$ profiles obtained during TPO of LSCRu after 1 h reaction at 800 °C with $CH_4/H_2O = 10$. TPO conditions: sample weight = 40 mg, 0.98% O_2 in He, flow rate = 1.8 L h⁻¹. "Re-oxidation" corresponds to O_2 consumption for catalyst re-oxidation.

It is, however, difficult to estimate the amounts corresponding to the other forms of deposited carbon. The total amount of deposited carbon (107 μ mol g⁻¹: 0.13 wt%) has increased by comparison with the one measured after 1 h of catalytic test. The carbon deposition is thus a slow but continuous process during the whole catalytic test.

As for Ru/LSC, we have performed two TPOs of the LSCRu sample after 1 h of catalytic test (when activity reaches its lowest value) and after 24 h of catalytic test. Fig. 7 shows the O₂, CO₂, and "re-oxidation" obtained during the TPO of LSCRu (40 mg) after 1 h of catalytic test at 800 °C. The CO₂ profile presents one maximum at 430 °C. This oxidation temperature corresponds to that obtained for C_{β} with Ru/LSC. The total amount of deposited carbon (25 µmol g⁻¹) corresponds to 0.03 wt% after 1 h of catalytic test; it is much lower than for Ru/LSC and no trace of C_{graph} was evidenced.

The "re-oxidation" profile presents only one broad peak with the maximum at 260 °C similar to the one corresponding to the oxidation of LSC in Ru/LSC (34 µmol g⁻¹ and 30 µmol g⁻¹, respectively). The formula of the catalyst is calculated to be La_{0.809}Sr_{0.191} $Cr_{0.979}Ru_{0.021}O_{2.986}$ after 1 h of catalytic test. The oxidation state corresponds, within the experimental uncertainty, to the obtained for LSC in Ru/LSC. The TPO of LSCRu performed after 24 h of catalytic test neither shows the formation of CO₂ nor the consumption of dioxygen (results not shown). Thus, there is no building-up of carbon on LSCRu after stabilization of the conversion rate during catalytic test. Furthermore, the catalyst is in its oxidized form after 24 h of catalytic test.

3.3.2. Electron microscopy

Fig. 8 shows a high resolution TEM image of Ru/LSC after 24 h of methane steam reforming in water-deficient conditions. The catalyst surface is totally coated with a rather uniform carbon layer (~5 nm). The carbon building-up occurs not only over the ruthenium nanoparticles but also on the LSC support. Conversely, for LSCRu (Fig. 9) no trace of carbon is observed on the surface after 24 h of catalytic test. The surface is perfectly clean and the crystallographic planes are clearly resolved at the surface. The region presented in Fig. 9 is in the [4-41] orientation with resolved (110), (014), and (-104) interplanar distances. Measured distances $(d_{(1\ 1\ 0)} \sim 0.273\ \text{nm};\ d_{(1\ 0\ 4)} = d_{(0\ -1\ 4)} \sim 0.271\ \text{nm})$ and angles (angle between $(1\ 1\ 0)$ and $(0\ 1\ 4) \sim 60.3^{\circ}$; angle between $(0\ 1\ 4)$ and $(-104) \sim 59.2^{\circ}$) are very close to the values expected $(d_{(110)} =$ 0.27464 nm; $d_{(1 \ 0 \ 4)} = d_{(0 \ -1 \ 4)} = 0.27253$ nm and angle between $(1\ 1\ 0)$ and $(1\ 0\ 4) = 60.2553^{\circ}$; angle between $(1\ 0\ 4)$ and $(0\ -1\ 4) \sim$ 59.4895°, respectively) and correspond to the trigonal phase identified by XRD.



Fig. 8. High resolution TEM micrograph of Ru/LSC powder after 24 h reaction at 800 °C with $CH_4/H_2O = 10$. A layer of carbonaceous species is clearly observed covering the Ru nanoparticles (black double-arrow) and the support (white double-arrow) surface.



Fig. 9. High resolution TEM micrograph of LSCRu powder after 24 h reaction at 800 °C with $CH_4/H_2O = 10$. No carbon is observed at the surface. Crystallographic orientation of the presented region as well as the resolved interplanar distances and angles between planes are indicated.

3.3.3. XPS

Only LSCRu was analyzed by XPS after the catalytic tests since the carbon layer on Ru/LSC hinders its analysis. The surface of LSCRu contains more strontium after testing than before test; there is thus segregation of strontium in preference to lanthanum during the catalytic test. It is also worth noting that the amount of carbon detected on the surface of this catalyst after reaction is lower than the amount detected before reaction. This catalyst not only resists to carbon deposition during methane steam reforming in waterdeficient conditions but it is also capable of self cleaning (at least partially) the carbon already present on its surface.

4. Discussion

Our results show that the steam reforming reaction is the main reaction in the reactor together with a small contribution from water-gas shift reaction for both catalysts. The contribution of methane cracking reaction yields only several tens of micrograms over 24 h for Ru/LSC (from TPO). Although this is significant on the surface of the catalyst (TEM), it is almost impossible to detect it on each measure point of the catalytic test.

4.1. Ru/LSC

The amount of oxygen consumed for the oxidation of ruthenium shows that the ruthenium is in metallic form during the catalytic test. Matsui et al. studied the mechanisms of dry reforming of methane over supported Ru catalysts on different supports. During reaction, ruthenium reacts with CH₄ to form Ru-CH_x and with CO_2 to form Ru– O_x and CO. Oxygen is then transferred from Ru– O_x toward Ru-CH_x yielding CO and metallic ruthenium. The XRD analysis of the phases after the catalytic test shows the presence of both RuO₂ and metallic ruthenium [35]. Ferreira-Aparício et al. obtained similar results with Ru/SiO₂ [36]. The authors proposed a Langmuir-Hinshelwood type mechanism in which the two reactants dissociate on the metallic phase. In our case, ruthenium only exists in the metallic form after testing which suggests that only methane dissociates on the metal. The mechanism is thus certainly different and the LSC support, used in the present work, must play an important role in the dissociation of steam as it has already been shown for other supports in the case of methane steam reforming [37,38] as well as in the case of the dry reforming of methane [39,40].

The "re-oxidation" profiles, obtained by TPO, after 1 h and 24 h of catalytic test show two peaks (Figs. 5 and 6) attributed to each of the two phases (support and catalyst). The second peak, corresponding to the oxidation of ruthenium, is very broad (from 450 to 950 °C). This very slow ruthenium oxidation can be explained by the formation of a surface RuO_2 layer on the Ru nanoparticles that acts as a barrier for the diffusion of oxygen as it has been observed by Balek et al. for the oxidation of metallic ruthenium (30–50 nm) to RuO_2 [41]. It is important to note that the two profiles obtained after 1 h and 24 h of catalytic test are similar. These results show clearly that the observed deactivation is neither due to a change in the oxidation state of the phases present nor to a phase modification during the catalytic test.

Ru/LSC is composed by two phases: metallic ruthenium and the LSC support. The catalytic test of this sample shows a slow and continuous deactivation of the catalyst during the whole test (Fig. 3). The catalytic test conditions (water-deficient reaction mixture) lead thus to a deterioration of the catalyst. This deactivation could be explained by the partial sublimation of ruthenium in the form of RuO_x oxides during the catalytic test [42]. However, the amount of ruthenium in the sample, measured by chemical analysis, is the same before and after reaction. Furthermore, no deposit was observed on the walls of the reactor. Thus, the decrease in conversion rate cannot be explained by the sublimation of ruthenium in the form of RuO_x oxides.

The TPO performed after 24 h of catalytic test (after deactivation) reveals the presence of five forms of carbon. By comparison with the TPO performed after 1 h of catalytic test (before deactivation), three other (very stable) carbon forms were detected. These rather unreactive carbonaceous species are certainly responsible for the observed deactivation of Ru/LSC. In other words, the experimental conditions that were used in this work (water-deficient reaction mixture) significantly modify the capability of metallic ruthenium to resist to the deposition of carbon and this study clearly establishes that the sample Ru/LSC does not meet the criteria required for its application as an anode material in SOFCs operating with natural gas and using the gradual internal methane reforming concept.

4.2. LSCRu

The different characterizations performed on this catalyst clearly showed that LSCRu is composed by a single perovskite phase where ruthenium is inserted in the structure as Ru(IV) ions in substitution of chromium ions in perovskite B sites [43].

At the beginning of the catalytic test (Fig. 4), a quick deactivation followed by a slower reactivation is observed prior to the stabilization of the activity. This apparent induction effect can be explained in following way: at the beginning of the catalytic test, the methane-rich mixture reduces the catalyst which provokes a deactivation since the reduced form of the catalyst is less active than the oxidized form; the decrease in conversion rate modifies the reaction mixture composition leading to a re-oxidation of the catalyst and a stabilization of the conversion rate.

The TPO performed after 1 h of catalytic test (when activity is at its lowest value) shows only the presence of a very reactive carbon form C_{β} (Table 2). Moreover, no carbon deposit was detected up to the end of the catalytic test. The other stable forms of carbon observed for Ru/LSC do not appear for LSCRu. Thus, unlike metallic ruthenium, Ru(IV) ions do not lead to the formation of stable carbon species during the catalytic test.

Furthermore, the catalytic activity behavior of LSCRu in methane steam reforming is very different from the one observed for Ru/LSC which confirms that Ru configuration within the material catalyst is different between the two samples. In particular, LSCRu is both less active and less selective than Ru/LSC. This can be explained by the fact that ruthenium ions do not present the same activity as metallic ruthenium and also by the fact that those ions are less accessible since they are inserted in the perovskite structure. However, unlike Ru/LSC, LSCRu does not deactivate with reaction time; it is thus much more stable than Ru/LSC even under a water-deficient reaction mixture at 800 °C. This study confirms LSCRu thermal stability [44] as well as its catalytic stability during methane steam reforming in water-deficient conditions [25].

The "re-oxidation" profile after 1 h of catalytic test shows very low dioxygen consumption all over the TPO temperature range. However, the amount of consumed oxygen is similar to the one detected for the oxidation of LSC for Ru/LSC. This result shows that the insertion of ruthenium in the perovskite structure modifies its oxidation properties.

The XPS study after reaction showed a segregation of strontium to the surface of the catalyst during methane steam reforming. This segregation of strontium decreases the number of oxygen surface defects and modifies the redox properties of the catalyst; numerous studies show a modification of redox properties of perovskite-containing ruthenium under reducing conditions [25] or under inert gas after oxidation [45].

After stabilization of the activity. LSCRu is in the oxidized form despite a reaction mixture very deficient in water. Unlike our previous study, with a higher catalyst mass (200 mg), in the same conditions [16], no oscillation was observed even during the 72 h catalytic test. It is worth noting that the catalytic conversion never attains 100% with 40 mg of catalyst whereas total conversion was achieved with 200 mg of catalyst. Residual steam is thus in contact with the catalyst during the whole test (water conversion lower than 100%). These results indicate that this residual steam certainly plays a very important role in methane steam reforming reaction mechanism over LSCRu. The presence of steam is directly connected to the extinction of the oscillating behavior of the catalyst. Thus, the conversion rate of the catalyst depends on the reaction mixture and, in particular, on the presence or absence of residual steam. In other words, for LSCRu, the catalytic activity behavior clearly depends on the conversion rate.

The present study clearly establishes that, unlike Ru/LSC, LSCRu meets the criteria required for its application as an anode material in SOFCs operating with natural gas and using the gradual internal methane reforming concept.

5. Conclusion

The results obtained in this study show that ruthenium in metallic form deactivates during methane steam reforming in water-deficient conditions ($CH_4/H_2O = 10$). This deactivation is explained by the formation of very stable carbonaceous species at the surface of the catalysts during reaction. Conversely, when ruthenium is inserted in the perovskite structure as Ru(IV) ions, no car-

bon build-up and no deterioration of the catalyst were evidenced. Furthermore, the conversion rate of the latter catalyst remains constant over 72 h after an activation period. The LSCRu catalyst appears as a promising anode material for SOFCs operating with natural gas and using the gradual internal methane reforming concept.

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