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Catalytic steam reforming of methane over $La_{0.8}Sr_{0.2}CrO_3$ based Ru catalysts

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Abstract

$La_{0.8}Sr_{0.2}CrO_3$ based Ru catalysts were studied as potential new anodic materials for Solid Oxide Fuel Cells directly fed with methane and operating at intermediate temperature under water deficient conditions. Two kinds of materials very close in composition were obtained following two different preparation procedures. Catalyst samples were characterized by physicochemical methods (XRD, SEM, BET and Chemical Analysis) and studied in methane steam reforming under water deficient conditions. Carbon formation during catalytic testing was studied by temperature programmed oxidation (TPO). Both types of catalysts were found very active and resistant to carbon formation. The unusual oscillatory behavior of the catalytic activity observed for one type of catalyst was discussed.

Keywords: Steam reforming of methane; Solid oxide fuel cell; Internal reforming; Ruthenium; Strontium-doped lanthanum chromite

1. Introduction

Hydrogen is the preferred feedstock for use in the present generation of fuel cells, such as Solid Oxide Fuel Cell (SOFC). The main reason is its high electrochemical reactivity compared with the more common fossil fuels, such as natural gas, from which it may be derived [1].

Steam reforming is a well-established process for producing hydrogen or synthesis gas from natural gas or other hydrocarbon fuels [2]. For methane, the reforming reaction (Eq. (1)), and associated water–gas shift reaction (Eq. (2)) are carried out over a suitable catalyst, usually nickel cermet (Ni-YSZ):

$$CH_4 + H_2O \leftrightarrows CO + 3H_2, \quad \Delta H^\circ = 206\,\text{kJ mol}^{-1} \tag{1}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2, \quad \Delta H^\circ = -41\,\text{kJ mol}^{-1} \tag{2}$$

Steam reforming of methane is highly endothermic and is normally carried out at temperature above 500 °C, typically around 700–800 °C. In a conventional fuel cell system, hydrogen is usually produced in an external reformer. For high methane conversion and to avoid carbon deposition by methane cracking (Eq. (3)) or by the Boudouard reaction (Eq. (4)), steam is introduced in excess:

$$CH_4 \leftrightarrows C + 2H_2, \quad \Delta H^\circ = 75\,\text{kJ mol}^{-1} \tag{3}$$

$$2CO \leftrightarrows CO_2 + C, \quad \Delta H^\circ = 86.2\,\text{kJ mol}^{-1} \tag{4}$$

The cost and the volume of the reactor limit this process. Fuel cell developers have for many years known that the heat required to sustain the endothermic reforming of natural gas can be provided by the electrochemical reaction in the stack. This has led to internal reforming concept which has been applied to SOFC, on account of their high operating temperature [3]. It has been shown that nickel cermet anode is an excellent catalyst for electrochemical hydrogen oxidation and for steam reforming without the need for additional catalyst. However, the carbon deposition and the endothermicity of the steam reforming reaction which induces local temperature gradient cause anode degradation when steam reforming is carried out for long periods [4].

An alternative concept, called gradual internal steam reforming, has been proposed [5]. The idea is to use the steam

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produced *in situ* by the electrochemical reaction as reactant for methane reforming. Consequently, very low amounts of water are required, allowing important energy savings. Moreover, the endothermicity of the steam reforming reaction is spread out along the anode. However, low water concentrations can induce important carbon deposition which must be definitely avoided. This requires the development of specific anode materials. The material chosen for the SOFC anode must be chemically stable at high temperature (800 °C) under high reducing atmosphere.

It has been shown that strontium doped lanthanum chromites ($La_{1-x}Sr_xCrO_3$) are mechanically and chemically stable under highly reducing atmosphere used in SOFC [6,7]. Moreover, $La_{1-x}Sr_xCrO_3$ (LSC) presents interesting activity for hydrogen electrochemical oxidation [8,9]. Nevertheless, LSC does not catalyse methane reforming. Some metals (Ir, Rh, Ru) are known to exhibit high activity for methane steam reforming [10]. Suzuki et al. have tested Ru/ZrO_2 and Ru/Al_2O_3 cermets under SOFC anode operational conditions [11]. Ru metal has high steam reforming reaction activity, carbon deposition resistance and sintering resistance. Vernoux et al. reached the same conclusion [12].

This work concerns the catalytic study of $Ru/La_{0.8}Sr_{0.2}CrO_3$ catalysts in methane steam reforming under water deficient conditions. Two samples Ru/LSC loaded with 1 wt.% Ru have been prepared. These catalysts were characterized by physicochemical methods (XRD, SEM, BET and Chemical Analysis). The carbon formation during the reaction was measured by temperature programmed oxidation.

2. Experimental procedure

2.1. Catalyst preparation

Two samples of LSC loaded with 1 wt.% Ru have been prepared. The first one, referenced as Ru/LSC, was synthesized in a two steps way, which are (i) preparation of the $La_{0.8}Sr_{0.2}CrO_3$ matrix by co-precipitation of La, Sr and Cr cations in a buffered carbonate medium followed by an adequate high temperature thermal treatment, (ii) impregnation of the LSC matrix with $Ru(NO)(NO_3)_3$ aqueous solution, followed by a second calcination step. In details, the LSC support powder was obtained from the following starting materials: La_2O_3 (Rhodia—99.99%), $SrCO_3$ (Aldrich—99.98%) that were both first calcinated at 1000 and 600 °C, respectively; $Cr(NO_3)_3.9H_2O$ (Prolabo—99%), nitric acid (Prolabo, ANALYPUR®—70%w) and ammonium carbonate (R.P. Normapur™ Analytical reagent, Merck Eurolab-Prolabo) were used as dissolving and precipitating agents, respectively. The ammonium carbonate is actually an equimolar mixture of ammonium hydrogeno-carbonate and ammonium carbamate which is itself in equilibrium in water with di-ammonium carbonate; the solution is buffered around pH 9.

All the cation sources were weighed in stoichiometric ratio of the targeted LSC composition and the quantity of nitric acid was calculated to exactly dissolve both La_2O_3 and $SrCO_3$. Chromium nitrate was then added in the resulting argon desaerated aqueous solution that was then slowly poured under stirring into the desaerated ammonium carbonate aqueous solution (ammonium carbonate was used in a large excess to buffer the pH to about 9). The precipitate was washed with distilled and desaerated water then dried in a oven for a night; the blue-violet cake was crushed into a very homogeneous powder that was (i) calcinated at 1300 °C under air for 2 h to obtain a dark brown powder, (ii) washed with water to dissolve the unavoidable residual amount of strontium chromates that generally forms during the synthesis of LSC compounds. The as-obtained powder is called the LSC matrix. The Ru/LSC sample was prepared by impregnation of this catalytic support with $Ru(NO)(NO_3)_3$ dissolved in water, evaporation of the solvent (rotavapor), drying in an oven for a night at 70 °C and heat-treatment at 900 °C under 2% hydrogenated argon for 5 h. For the second sample, referenced as LSCRu, the idea was to prepare a LSC sample with 1 wt.% Ru in solid solution, which corresponds to the exact composition $La_{0.8}Sr_{0.2}Cr_{0.9773}Ru_{0.0227}O_3$ [13,14]. This sample was prepared by nitrate co-precipitation too but after washing the precipitate with water, it was re-dispersed in a $Ru(NO)(NO_3)_3$ aqueous solution. The solution was evaporated to half of its volume in a rotating evaporator and finally vacuum-filtrated over a Büchner funnel (the filtrate was completely colorless indicating that Ru was quantitatively trapped into the powder). After drying in an oven at 70 °C overnight, the product was treated at 1300 °C in air for 2 h.

2.2. Characterization methods

Crystallographic and micro structural analysis were examined by XRD (Brücker $D8_{ADVANCE}$, θ–2θ, Cu K $L_{2,3}$) and Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) (LEO 1530 with SPIRIT EDS analysis from PGT) micrographs, respectively. The specific surface areas were determined by the Brunauer–Emmet–Teller (BET) method with nitrogen at 77 K. Samples were analyzed before and after catalytic tests by ICP chemical analysis at the CNRS Central Analysis Service, Vernaison.

2.3. Activity tests

Measurements of catalytic activity in steam reforming of methane were carried out during 24 h at 800 °C in a conventional flow system at atmospheric pressure. Two hundred milligrams of catalyst were introduced in a U-shaped quartz reactor equipped with a 20 mm inner diameter porous disk. The reaction mixture consisted of 50% CH_4, 5% H_2O ($CH_4/H_2O = 10$) and N_2 as carrier gas. Water vapour was added to the feed by flowing the CH_4/N_2 mixture through a saturator maintained at 33.1 °C. The total flow rate was 6.5 L h^{-1}. Before activity measurements, catalysts were pre-treated *in situ* in N_2 at 800 °C during 4 h.

H_2O concentration was measured with an EdgeTech Dew Prime I hygrometer. The concentrations of the other effluent gases (CH_4, CO, H_2, CO_2 and O_2) were obtained at regular time intervals (5 min) using a gas chromatograph (Varian CP 2003 QUAD) equipped with a Thermal Conductivity Detector (TCD).

2.4. Temperature Programmed Oxidation (TPO) experiments

After catalytic tests, the catalysts were cooled down to room temperature in reaction mixture, purged 30 min in N_2 and recovered for performing subsequent TPO experiment to characterize eventual carbon deposits formed by methane cracking during reaction. Fifty milligrams of catalyst were introduced in a U-shaped quartz reactor equipped with a 10 mm inner diameter porous disk. A 0.98% O_2/He gas mixture ($1.8\ L\ h^{-1}$) was passed through the sample heated from room temperature to 800 °C at a constant rate of $5\ °C\ min^{-1}$. The analysis 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 ($m/e = 44$) and H_2O ($m/e = 18$). CO was never formed during these experiments. Calibration of CO_2 allowed quantitative measurements of CO_2 formation.

3. Results and discussion

3.1. Catalysts characterization

The XRD pattern (result not shown) of the Ru/LSC sample showed the presence of LSC as major phase and metallic Ru particles (peaks at 42 and 44° 2θ). This observation was confirmed by FEG-SEM analysis. Particles (few tens of nanometers) which were not homogeneously dispersed at the surface of large grains of the LSC matrix could be observed and identified as Ru particles by EDXS analysis (Fig. 1). In large grains without any Ru particles at their surface, no Ru could be detected by EDXS analysis. The concentration of 0.92 wt.% of ruthenium was measured by chemical analysis. BET measurements of the LSCRu powder sample revealed a specific surface area of $2.0\ m^2\ g^{-1}$.

XRD analysis of the LSCRu sample revealed the presence of a pure LSC orthorhombic perovskite phase, which strongly suggested the desired solid solution was obtained. Nevertheless, it is well known that the XRD detection threshold is too low to allow detecting very small amount of minor phases which could contain ruthenium. This prompted us to examine the powder by FEG-SEM. Fig. 2 shows a photograph representative of these observations. Regular grains are observed. EDX analysis of the grains reveals the presence of La, Sr, Cr and Ru. In this case too, elemental chemical analysis of the powder indicated a final concentration of 0.92 wt.% of ruthenium. It could be suggested that Ru in LSCRu sample has been inserted into the crystal structure of LSC. Sauvet et al. have shown that Ru^{4+} can be inserted up to 20% in LSC structure in substitution of chromium ions [14]. This insertion is made possible due to the very weakly differing size of Ru^{4+} ($r = 0.62$ Å), Cr^{3+} ($r = 0.61$ Å) and Cr^{4+} ($r = 0.55$ Å) [16]. The BET specific surface area of the powder ($1.1\ m^2\ g^{-1}$) was lower than for LSCRu.

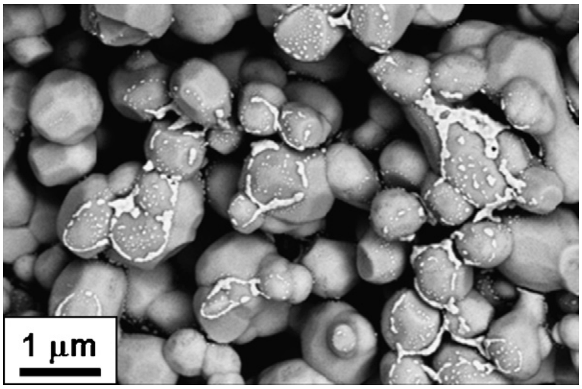

Fig. 1. FEG-SEM micrograph of Ru/LSC powder.

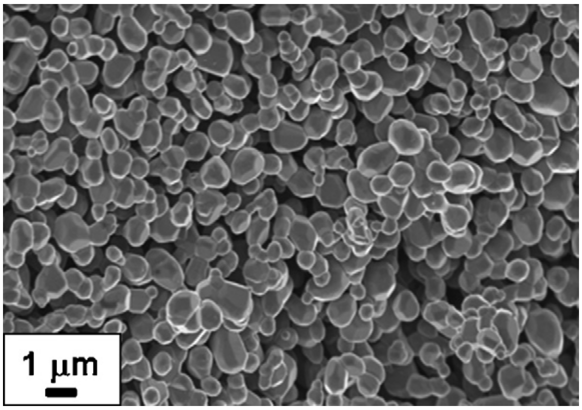

Fig. 2. FEG-SEM micrograph of LSCRu powder.

In conclusion, structural analysis tended to prove that ruthenium was present as metal particles at the LSC surface in the Ru/LSC sample while, for the LSCRu sample, it would be mostly inserted into the LSC structure as Ru^{4+} ions in substitution of Cr^{3+}/Cr^{4+} ions, *i.e.* in the B site of the perovskite cell, as well described in [14].

3.2. Catalytic activity

LSC sample (results not shown for the sake of clarity) exhibited very low catalytic activity: 0.8% H_2 was produced at 800 °C. This concentration was very low compared to the maximum amount of H_2 which could be produced with 5% H_2O in the feed, *i.e.* 14% H_2. On the contrary, Ru/LSC sample was very active (Fig. 3). Fourteen percent H_2 and 4.8% CO were produced over the Ru/LSC sample, *i.e.* the maximum amount which can be produced with 5% H_2O. This result together with the absence of CO_2 in the products indicated the absence of any contribution from water–gas shift reaction (Eq. (2)). These results confirm that Ru metal exhibit high activity for methane steam reforming as reported previously [10–12]. Interestingly, the Ru content after catalytic testing was found to be the same as that before testing, indicating no loss of ruthenium even after 24-h reaction at 800 °C.

H_2, CO and CO_2 concentrations were measured in effluent gases upon catalytic test of LSCRu at 800 °C (Fig. 4). LSCRu was also found very active. Nevertheless, after 30 min of test, the activity of LSCRu strongly oscillated with time on stream. Oscillations period increases with time on stream reaching 30 min after 700 min reaction.

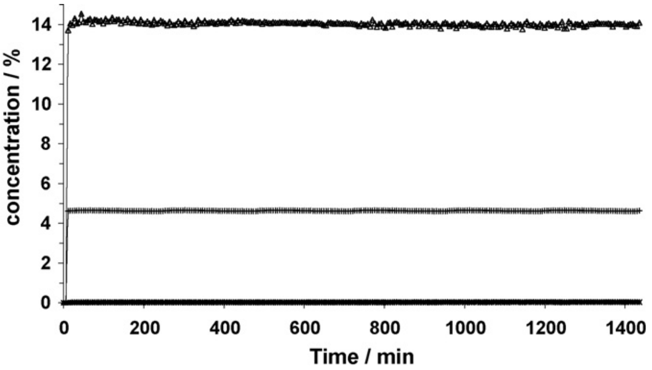

Fig. 3. $[H_2]$ (Δ), [CO] (+) and $[CO_2]$ (×) concentrations obtained upon catalytic reforming of CH_4 over Ru/LSC at 800 °C: sample weight = 200 mg, total flow rate = 6.5 L h^{-1}, feed composition = 50% CH_4, 5% H_2O, N_2 balance.

It could be noticed that the H_2 and CO concentrations exceeded sometimes 14% and 4.8%, respectively, *i.e.* the values corresponding to 100% conversion of H_2O. The formation of CO in excess had therefore to be related to the participation of oxygen species from the catalyst itself. In other words, these data clearly indicated that the catalyst could be reduced during the catalytic testing. This would also suggest that the low activity experimental points could be attributed to the catalytic behavior of the reduced form of the catalyst. The oscillating behavior should be then explained by a switch between oxidized and reduced forms of the catalyst, the reduced form being much less active than the oxidized one. When the reduced form was present, CO_2 was detected, which indicated the contribution of the water–gas shift reaction. This behavior was not observed in previous studies on the same type of catalysts [13,14].

The oscillatory behavior in methane reforming could be related to Ru insertion into LSC structure. When inserted, Ru would be stabilized in the structure. This would change the redox properties of the solid, which can be, depending on the reaction mixture, either reduced or oxidized. This would lead to a switch between very active and less active phases. Depending on the catalytic activity, the composition of the reaction mixture would change between conditions where H_2O is absent or present. LSCRu can be easily reduced by CH_4 when conversion is total and oxidized by steam when conversion is partial. Such oscillatory behavior can be compared to previous data observed in partial oxidation of methane over palladium catalysts [16–18] and Ni catalysts [19,20]. Further work is required to better understand the process.

3.3. Temperature Programmed Oxidation after catalytic test

Eventual carbon deposits formed by methane cracking during steam reforming reaction were investigated by TPO-MS measurements. Fig. 5 shows the CO_2 and O_2 profiles obtained during TPO of Ru/LSC after 24 h of reaction at 800 °C. No H_2O was formed during the experiment. It can be derived that carbonaceous deposits are mainly in the form of carbon deposits. CO_2 formation curve exhibits 2 maximums at 430 and 550 °C and O_2 consumption curve exhibits 3 maximums at 430, 550 and 340 °C (Table 1). The maximum at 340 °C can be attributed to LSC re-oxidation. The amount of O_2 consumed for catalyst re-oxidation is found equal to 140 μmol g^{-1}. Both others maximums of O_2 curve coincide with the two maximums of CO_2 curve. This indicates the presence of two carbon species with different reactivity towards O_2, usually attributed to structural differences. It is generally assumed that the low temperature peak of the profile corresponds to less ordered (more reactive) carbon while the high temperature peak is assigned to more ordered (less reactive) carbon [21,22]. For the more reactive carbon (430 °C), the amount of consumed O_2 and released CO_2 are found both equal to 110 μmol g^{-1}. For the less reactive carbon (550 °C), the amount of consumed O_2 is found equal to 150 μmol g^{-1} and the amount of released CO_2 is found equal to 120 μmol g^{-1}. The total amount of carbon (230 μmol g^{-1}) corresponds to 0.3%, which is very small compared to carbon deposition observed on Ni/YSZ [23].

Fig. 6 shows the CO_2 and O_2 profiles obtained during TPO of LSCRu after 24 h of reaction at 800 °C. No H_2O was formed during this experiment too. As for Ru/LSC, O_2 profile presents a maximum at 320 °C where no CO_2 is produced (Table 1). This

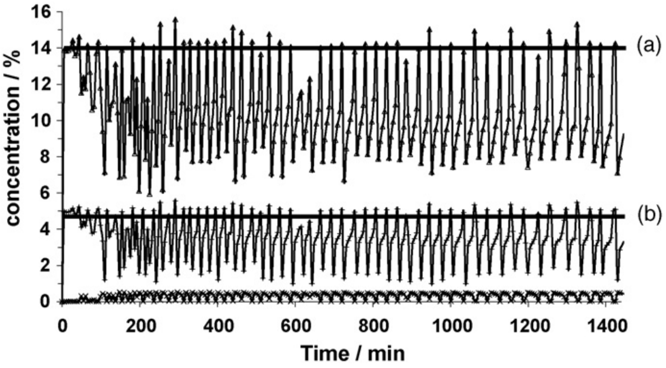

Fig. 4. $[H_2]$ (Δ), [CO] (+) and $[CO_2]$ (×) concentrations obtained upon catalytic reforming of CH_4 over LSCRu at 800 °C: sample weight = 200 mg, total flow rate = 6.5 L h^{-1}, feed composition = 50% CH_4, 5% H_2O, N_2 balance. Lines (a) and (b) correspond to the maximum amount of H_2 and CO, respectively, which can be produced with 5% H_2O through the steam reforming reaction.

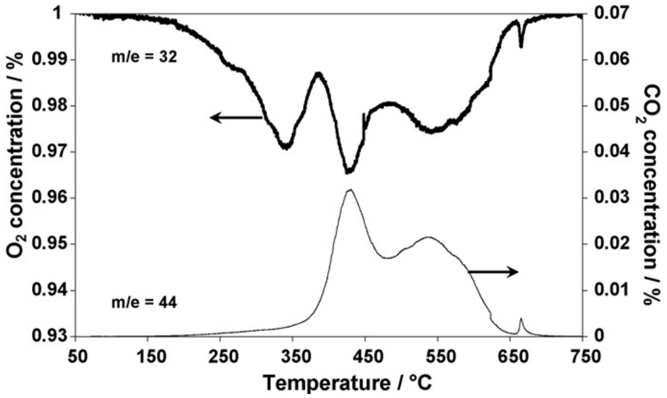

Fig. 5. CO_2 (*m*/*e* = 44) and O_2 (*m*/*e* = 32) profiles obtained during TPO of Ru/LSC after 24 h reaction at 800 °C with CH_4/H_2O = 10. TPO conditions: sample weight = 50 mg, 0.98% O_2 in He, flow rate = 1.8 L h^{-1}.

Table 1
Temperatures of peaks maximums and amounts of O_2 consumed and CO_2 released during TPO experiments of samples after 24 h reaction at 800 °C with $CH_4/H_2O = 10$

Ru/LSC			LSCRu		
T (°C)	O_2 consumed (μmol g^{-1})	CO_2 released (μmol g^{-1})	*T* (°C)	O_2 consumed (μmol g^{-1})	CO_2 released (μmol g^{-1})
340	140		320	140	
430	110	110	430	80	80
550	150	120			

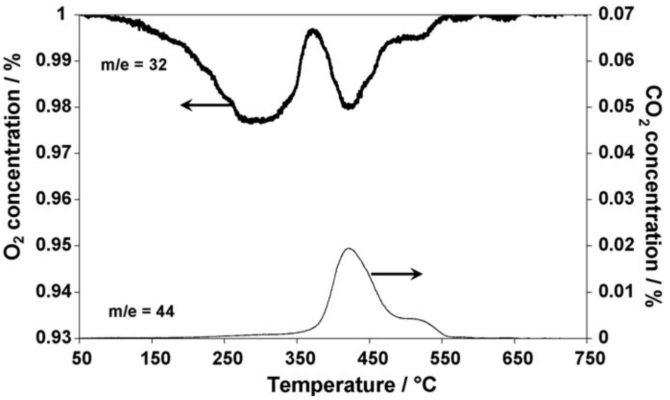

Fig. 6. CO_2 (*m*/*e* = 44) and O_2 (*m*/*e* = 32) profiles obtained during TPO of LSCRu after 24 h reaction at 800 °C with $CH_4/H_2O = 10$. TPO conditions: sample weight = 50 mg, 0.98% O_2 in He, flow rate = 1.8 L h^{-1}.

maximum is attributed to LSCRu re-oxidation and the amount of O_2 consumed is found equal at 140 μmol g^{-1}. This value is in agreement with the value found for Ru/LSC sample. The CO_2 evolution exhibits a maximum at 430 °C coincidently with the other maximum in O_2 consumption profile. The amount of consumed O_2 and released CO_2 are found both equal to 80 μmol g^{-1}. The total amount of carbon corresponds to 0.1% which is much less than for Ru/LSC. It is important to note that the more ordered and less reactive carbon (550 °C) obtained with Ru/LSC sample is not detected on LSCRu sample.

4. Conclusion

LSC based Ru catalysts are very active in methane steam reforming under water deficient conditions and very low amounts of carbon are formed on catalysts during catalytic reaction. They appear thus as promising anode materials for SOFCs directly fed with methane or natural gas and integrating the concept of gradual internal steam reforming. Ru can be inserted as Ru ions in perovskite structure. In this case, carbon deposition is very low and Ru is stabilized in the structure. Nevertheless, the catalytic activity in steam reforming strongly oscillates with time on stream. The oscillating behavior is explained by a switch between oxidized and reduced forms of the catalyst, the reduced form being much less active than the oxidized one. Ru can be alternatively deposited as Ru particles decorating the LSC grains. In this case, the catalytic activity in steam reforming is maximum and stable with time on stream. However, carbon deposition is more important although being still weak and RuO_x evaporation is possible.

Acknowledgments

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