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# Electrochemical promotion of propene combustion in air excess on perovskite catalyst

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The combustion of light hydrocarbons finds an important application in volatile organic compounds (VOCs) abatement. Catalytic combustion is interesting in this domain, because it may be carried out at relatively low temperatures and under large air excess. For this purpose, precious metal-based catalysts are very performing, but the quest for a lower-cost alternative solution is necessary. In this field, conducting mixed oxides such as perovskites are good candidates, especially when they are electrochemically promoted. The present work shows that electrochemical promotion of catalytic activity (NEMCA effect) in propene total combustion can be carried out with $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$, an electron-conducting perovskite-type oxide, deposited on YSZ.

**KEY WORDS:** catalytic combustion; electrochemical promotion; EPOC; NEMCA; propene; VOC; perovskite.

## 1. Introduction

Catalytic combustion of hydrocarbons is a non-polluting means of heat generation and may also be used to destroy volatile organic compounds (VOCs) present at trace level in large oxygen amounts. The most commonly used catalysts for this purpose are supported noble metals such as Pt or Pd [1–3] In spite of their high efficiency, catalysts of this family can not considered in the medium term, due to their excessive cost which makes necessary stages of recovery and recycling. Alternative catalysts based on perovskite-type oxides have been proposed during the last two decades because their lower cost compared to noble metals and their ability to be tailored for various applications. The structure of these materials may be represented by the general formula $ABO_3$ where A is a lanthanide such as La in most cases but sometimes Ce, Pr or Nd. The B sites are occupied by a transition metal such as Co, Mn, Fe, Cr, Cu or V. The sites A can be substituted for by alkaline earth metals such as Sr, Ca or Ba and the sites B by a transition metal. For instance, the replacement of part of $La^{3+}$ ions by $Sr^{2+}$ can highly increase the electronic conductivity of the perovskite and also its combustion activity [4]. The catalytic activity of perovskites is generally lower than that of noble metals [5]. Nevertheless, some studies have shown that perovskites can exhibit quite similar performance especially for methane oxidation [6]. Catalytic activity of perovskites is clearly related to their surface area [7,8]. Unfortunately, obtaining the desired $ABO_3$ structure requires a stage of calcination at high temperature in air, leading to low specific area. In order to overcome this limitation, many different methods of preparation have been tried, such as the so-called citrate, oxalate, acetate or nitrate routes. Some of them, particularly the citrate method, lead to correct specific areas of the order of few tens of square metres per gram of catalyst. Nevertheless, it should be noted that these higher surface often undergo decrease under reaction conditions. In order to overcome the performance limitation of the perovskites due to their low specific areas, we propose to promote the catalytic activity of these oxides using an electrochemical approach. The use of electrochemistry to activate and control the catalytic process is an expanding domain because of the development of new solid electrolytes and the knowledge gained from fuel cell technology. Related materials are ionic (cationic or anionic) conductors. In a solid electrolyte cell, where the working electrode acts both as an electrode and a catalyst, the application of a current or a potential between the catalyst–electrode and an inert counter-electrode (CE) can affect the catalytic activity and the product selectivity, in a reversible and controlled manner. A new concept [9–11], named Electrochemical Promotion of Catalysis (EPOC), has also increased the interest in electrochemical promotion because it is non-Faradaic and then not limited by the migration rate of ionic species in the solid electrolyte. Taking into account that most of perovskites such as lanthanum manganites or lanthanum cobaltites, combine catalytic activity, especially for hydrocarbons total oxidation [12,13] and good electronic conductivity, these materials may be implemented in an electrochemical cell. Moreover, both strontium-doped lanthanum manganite and strontium-doped lanthanum cobaltite are already used as cathode material in solid oxide fuel cells [14]. During the last decade, EPOC appeared as a powerful promotion tool

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for hydrocarbons oxidation. This innovative concept is based on the control, by an applied potential, of the work function resulting from electrochemical pumping of ions between a solid electrolyte and the surface of a porous catalyst film. EPOC, also called Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) was observed for a wide range of reactions in the presence of metals such as Pt, Pd, Rh ... or of oxides such as $IrO_2$ and $RuO_2$. The solid electrolytes used were $O^{2-}$-conductors like $Y_2O_3$-stabilised $ZrO_2$ (YSZ) [15–18] or $CeO_2$ [19], $Na^+$-conductors like $\beta''$-$Al_2O_3$ [20,21] or $Na_3Zr_2Si_2PO_{12}$ [22], $H^+$-conductors like $CaZr_{0.9}In_{0.1}O_{3-\delta}$ [23,24] or Nafion [25], $F^-$-conductors like $CaF_2$ [26] and mixed electronic/ionic conductors.

The goal of the present study was to demonstrate that a perovskite material can be promoted using the EPOC concept. The selected chemical reaction was the propene combustion because propene is a very decent representative of common VOCs [27] and also because it was demonstrated that propene combustion on platinum may be drastically enhanced by electrochemical promotion and undergoes an electrophilic NEMCA effect on either an $O^{2-}$-conductor (YSZ [16,18]) or a $Na^+$-conductor (NaSICon [28]). Among the various perovskite materials, the La-based ones doped with manganese or cobalt in B sites are those which received the most interest for VOC deep oxidation [8,29–31]. We selected the compound $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) because it has been intensively studied as an electrode material in SOFC [32]. Furthermore, several studies have shown that lanthanum cobaltite materials were stable under reducing environments. For instance, Xu and Thomson [33] evidenced that the reduction of LSCF in pure methane or ethane did not take place before 750 °C. However, Xu and Thomson have also shown that serious near-surface etching occurs on the LSCF film when it is exposed to 100% $CH_4$ at 850 °C [34]. Wachsman and Clites [35] observed the same chemical instability of LSCF by using this material as a membrane for a direct conversion of methane to syngas. A 900 °C, after 20 h of operation the catalytic activity vanishes to zero and subsequent XRD analysis showed the development of decomposition phases such as $La_{2-x}Sr_xCoO_4$ and $La_2O_4$ across the surface of the membrane. Oxygen deficiency in LSCF is a vital factor for their electrical properties, which may be increased by a partial substitution of $Sr^{2+}$ for $La^{3+}$ in order to increase the concentration of oxygen vacancies in the lattice in order to maintain the neutrality of charges [36]. Tsiakaras *et al.* [37] studied $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ thin films on YSZ as a function of oxygen partial pressure and they demonstrated and ideal Nernst behaviour in the temperature range 400–900 °C and $pO_2$ between 0.5 and 100 kPa. Moreover, the apparent anodic and cathodic transfer coefficients are very close to unity, but they are considerably lowered in the presence of methane. Tsiakaras *et al.* [38] demonstrated that $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ perovskite exhibit interesting properties in methane catalytic and electrocatalytic oxidation. According to the way oxygen is supplied, i.e. cofeeding with methane in the gas phase or electrochemically supplied as $O^{2-}$, methane conversion and product selectivity were considerably changed.

This study reports the EPOC activity of a LSCF film deposited on a dense YSZ substrate for the propene combustion. The "NEMCA" behaviour of LSCF was compared to that of platinum under the same operating conditions.

## 2. Experimental

Perovskite $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$ (LSCF) was prepared by the ceramic route, from the corresponding oxides, crushed and fired at 1200 °C in air. Specific surface area, determined by $N_2$ adsorption at 77 K according to the BET method, was $5.3\ m^2 \cdot g^{-1}$ The LSCF powder was deposited on YSZ (formula: $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$) pellet, 17 mm in diameter, by spray-painting from a slurry based on ethanol, ethyl acetate, polyvinylpyrrolydone and polyvinylbutyral. After calcination at 1050 °C for one hour, we obtained a thin perovskite layer, about 10 $\mu$m in thickness, adhering to the YSZ substrate. The catalyst/working electrode LSCF film exhibited a good electronic conduction at room temperature, evidenced by a measure test with ohmmeter. On the opposite side of the YSZ disc, gold reference and CEs were deposited from paste Engelhard-Clal no. A1644 and annealed at 800 °C for 1 h in air. The coated YSZ disc was sealed at the end of a Pyrex tube with a temperature-resisting ceramic epoxy (Thermeez Hi-Seal from Cotronics) cured at 120 °C overnight. A schematic drawing of the electrochemical cell is shown in figure 1. It is a two atmosphere cell, where only the working electrode was exposed to reactive gas mixture. Counter and reference electrodes were exposed to the air. The reference electrode was deposited close to the CE, but at a distance (3 mm) sufficient to avoid any electrical perturbation.

Catalytic activity measurement was performed as reported earlier [39]. The reaction medium was made from a hydrocarbon, $C_3H_6$ (Air Liquide, 7710 ppm ± 231 ppm $C_3H_6$ in He), $O_2$ (Air Liquide, 99.995% purity), and helium (Air Liquide, 99.995% purity). This last one was used as a carrier gas. The stream composition was controlled by mass flowmeters (Brooks, with an accuracy better than 1%) in order to obtain 2000 ppm $C_3H_6$ and an $O_2$ concentration ranging from 1 to 4 vol% in He. The overall gas flow rate was kept constant at $1.8\ L \cdot h^{-1}$ The reactant and product gases were analysed by two chromatographs. The first one (Intersmat, IGC 120 MB) was equipped with a thermal conductivity detector and a CTR1 column from Alltech (Porapak and molecular sieve), heated at 45 °C, which

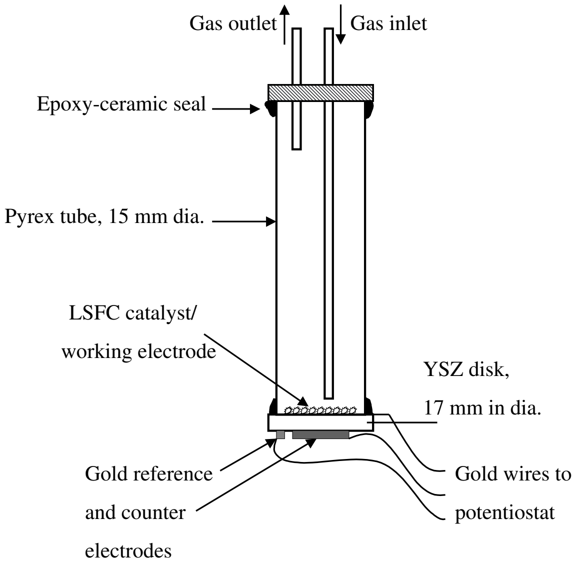

Figure 1. Schematic drawing of the electrochemical cell for catalytic tests.

enabled the separation of $O_2$, $CO_2$ and CO. The second chromatograph (Intersmat, IGC 120 FL) used a PORAPAQ column, heated at 170 °C, and analysed $C_3H_6$ with a flame ionisation detector. A PC with dedicated programme controlled the valve injection system, data acquisition, the integration of chromatographic data and potentiostat control. A part of the flow exiting the reactor (about $0.6\ L \cdot h^{-1}$) was sampled by a heated capillary and analysed by a VG Gasslab 300 quadrupole mass spectrometer. Signals at $m/e = 16$, 18, 28, 32, 44 amu corresponding to $O_2^+$, $H_2O^+$, $N_2^+$ or $CO^+$, $O_2^+$ and $CO_2^+$ ions, respectively, were recorded. Propene concentration in the flow was determined from signals at $m/e = 41$ and 42 amu. Carbon monoxide was never detected, according to our 50 ppm lower detection limit. The three electrodes, Working electrode/catalyst (W), Reference (R) and CE were connected to a potentiostat–galvanostat Voltalab 80 (Radiometer Analytical). The catalyst potential $V_{WR}$ was measured between the working electrode (LSCF) and the Au electrode exposed to the constant oxygen partial pressure in air. The overpotential $\Delta V_{WR}$ was defined as the difference between $V_{WR}$ and the open-circuit voltage (OCV), then $\Delta V_{WR} = V_{WR} - \text{OCV}$. The effect of the overpotential on the catalytic activity is characterized by the enhancement ratio ($\rho$) of $CO_2$ production rate, defined by

$$\rho_{CO_2} = r/r_0, \tag{1}$$

where $r_0$, in mol/s is the combustion catalytic rate at OCV and $r$ the catalytic rate under polarisation. The magnitude of the electrochemical promotion effect is described by the Faradaic efficiency, $\Lambda$, defined by

$$\Lambda = \Delta r/(I/nF), \tag{2}$$

where $\Delta r = r - r_0$ is the electrochemically induced change in catalytic reaction rate, $I$ the current, $n$ the number of charge carried by conducting ion, and $F$ the Faraday's constant.

Oxygen TPD spectra were obtained by heating the catalyst at $5\ °C \cdot min^{-1}$ in $1.47\ L \cdot h^{-1}$ He flow. Evolved species were analysed by an on-line micro gas-chromatograph (Varian CP2003). A molecular sieve heated at 90 °C (10 m length and 0.32 mm in internal diameter) preceded by a back flush column analysed $O_2$ with a detection limit of 1 ppm. The overall duration of one analysis was only 35 s.

## 3. Results and discussion

The catalytic performances for propene combustion of the LSCF film were found to be very low compared to those of platinum [18]. The maximum conversion obtained in this study was 30% under oxygen excess, at 480 °C which is the upper working limit of our Pyrex cell. The catalytic activity of the LSCF powder itself, which was used to elaborate the film, is also extremely higher under similar operating conditions (total flow rate and gas composition) since the propene conversion is full from 300 °C. This difference of activity may be due to the specific electrochemical cell in which the reactants just licked the catalyst while in a classical U-fixed bed reactor the mixture passed trough the catalyst powder. Then, the contact time between the catalyst and the reactants is significantly lower for the film. Taking into account that the objective of this study is to demonstrate the influence of an electrical polarisation on the catalytic properties of a perovskite material, the level of propene conversion is not critical. However, in a further stage, the electrochemical cell as well as the microstructure of the LSCF film should be improved in order to get reasonable catalytic performances.

Previous studies [18,28] showed that propene combustion on platinum is mainly governed by a competitive adsorption between hydrocarbon and oxygen onto the precious metal. We have shown in previous studies on Pt/YSZ and Pt/NaSICon systems by temperature-programmed desorption (TPD) measurements and solid electrolyte potentiometry that, at OCV and near the $O_2$/$C_3H_6$ stoichiometric ratio, the Pt surface is predominantly covered by propene or by propene-derived carbonaceous species. Then electrochemical promotion proceeds by establishing more balanced oxygen and propene coverage. To determine if a similar behaviour is observed on LSCF, propene conversion variation with respect to oxygen partial pressure was determined, at a constant $C_3H_6$ concentration (2000 ppm) and at constant temperature (460 °C). The results plotted in figure 2 clearly indicate a linear increase of propene conversion when the $O_2$ concentration varies from 1% to 4%. In all cases, $O_2$ concentration is larger than the stoichiometric one (0.9%). A similar variation of the propene conversion versus the partial pressure of oxygen

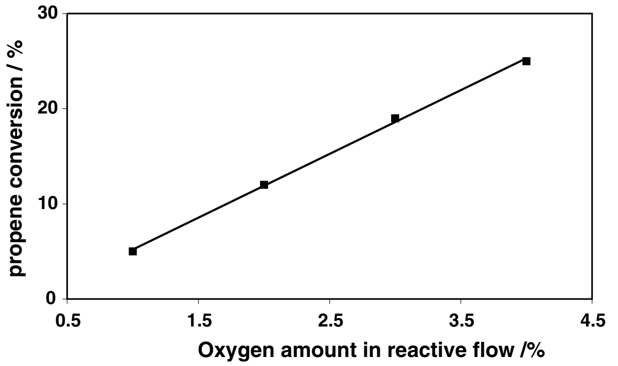

Figure 2. Propene conversion versus oxygen amount in the reactive flow (0.2% $C_3H_6$, 450 °C).

has been observed with platinum [18], except that with platinum the conversion reached 100% from 2.5% of oxygen. Let us note that the higher partial pressure of oxygen used in these experiments, i.e. 4%, corresponded to the regulation limit of the mass flowmeters. These observations seem to indicate that the catalytic behaviour for propene combustion on LSCF is similar to that observed on platinum. A competitive adsorption of the two reactants takes place on the same active site (L-H model) and the more strongly propene is adsorbed, the lower oxygen coverage on LSCF is. Then, we may conclude that electrochemically increasing the oxygen coverage should increase propene conversion, as observed on Pt/YSZ [18] and on Pt/NaSICon [28]. According to the classification of Vayenas [40], propene is considered as an electron-donor, as predictable from the presence of $\pi$-electrons in its structure, while oxygen is defined as an electron acceptor. Applying a negative polarisation ($\Delta V_{\mathrm{WR}} < 0$) produces a decrease of platinum work function ($\Phi$) [41] and then, when negative overpotentials are applied, Pt-propene bonds are made weaker and Pt–O bonds stronger, leading to an increase of the ratio $\theta_{\mathrm{O}}/\theta_{\mathrm{propene}}$. Such a negative polarisation was applied to the LSCF/YSZ system, exposed to 2000 ppm $C_3H_6$/2% $O_2$ at 460 °C and results are reported in figure 3 where MS signals of propene and $CO_2$ are plotted with respect to time. During the first 4 minutes, the catalyst is at OCV and conversion is stable around 13%. Then, the catalyst is polarized at $\Delta V_{\mathrm{WR}} = -4$ V leading to an immediate decrease of propene concentration and a concomitant increase of $CO_2$ concentration. This last curve exhibits the shape classically described in the literature [10,42] reaching a plateau after 12 min for a conversion of 23% which remains stable along the time. The enhancement ratio ($\rho$) of $CO_2$ production rate is 1.8 and the Faradaic efficiency ($\Lambda$) is about −12. This value is not high when compared to those observed on precious metals, that may reach $10^2$ or $10^3$ for some reactions [10]. The catalyst was also polarized at $\Delta V_{\mathrm{WR}} = +4$ V and we observed any effect of the potential. Therefore, electrochemical promotion of propene oxidation on LSCF/YSZ is clearly non-Faradaic (NEMCA effect) and electrophilic (with $\partial r/\partial\Phi < 0$) similarly to what one may observe on platinum.

Figure 4 shows the effect of applying a negative current (−100 $\mu$A) to the LSC catalyst/electrode. Signals corresponding to reaction products, $CO_2$ and $H_2O$ are plotted versus time. At OCV, the catalyst undergoes a slight but continuous deactivation. When applying −100 $\mu$A an electrophilic NEMCA promotion is observed and propene conversion is increased by a factor of about 2. The Faradaic efficiency of the same order of magnitude to that observed previously under a negative voltage, i.e. −28. Steady state is obtained after 30 min and then polarisation is stopped. The $CO_2$ and $H_2O$ signals recover their original values observed at OCV before deactivation, and we observe a fully reversible promotion with no permanent effect.

Some perovskites are known to be easily reducible at moderate temperatures in oxygen-free reactive stream or in inert media [43]. To check for its stability, the system LSCF/YSF was submitted to an overnight treatment in

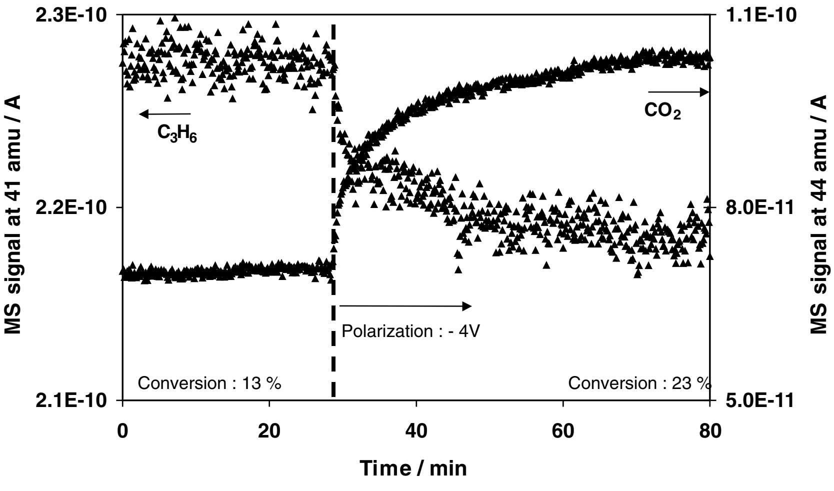

Figure 3. Propene conversion changes upon negative polarisation (2% $O_2$, 0.2% $C_3H_6$, 450 °C).

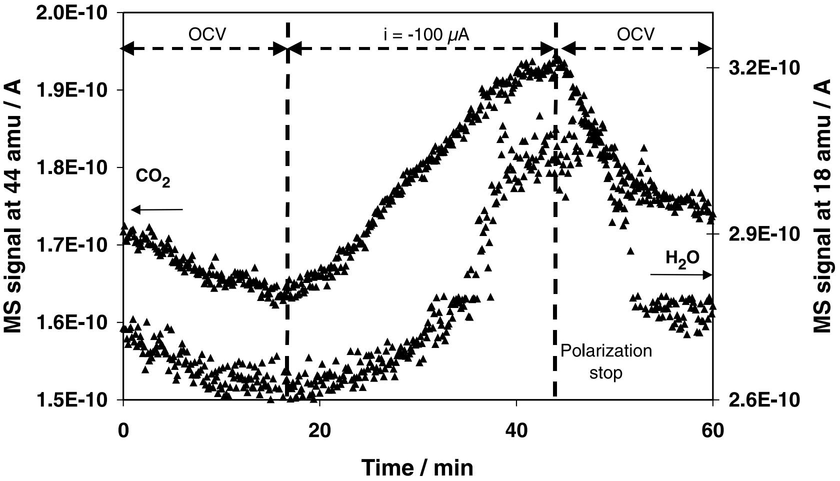

Figure 4. $CO_2$ and $H_2O$ production changes upon negative current and recovery after polarisation stop (2% $O_2$, 0.2% $C_3H_6$, 450 °C).

helium flow at 450 °C. After that, catalytic test was carried out again and results are plotted in figure 5. The same conclusions that on "fresh" catalyst may be drawn, i.e. we observe a non-Faradaic electrophilic promotion and no effect of positive overvoltage. The promotional effect is fully reversible and general shape of conversion versus time curves under polarisation and at OCV is similar to that reported previously. The main difference is the overall propene conversion level, decreased from 13% to 5% at OCV and from 23% to 8% for negative overvoltage. When the applied voltage is −4 V, we measure a negative current $i = -600$ µA, instead of −800 µA under the same operating conditions with a "fresh" LSCF catalyst not exposed to He (see figure 3). The Faradaic efficiency is only −5. Another difference is that the time necessary to stabilise the conversion is larger than on the fresh catalyst and now reaches 44 min. These results suggest a deterioration of the LSCF/YSZ interface. Moreover, the decrease of the catalytic activity seems to indicate that a large part of active sites were destroyed during the overnight treatment under helium at 450 °C responsible for a chemical modification of the perovskite surface. Unfortunately, this deactivation seems irreversible as oxidising treatments (pure oxygen at 480 °C for 12 h) do not allow for catalytic activity recovery. XRD spectra (figure 6) demonstrate that no bulk structural change occurred during deactivation, the main peaks observed are from LSCF perovskite and YSZ. Quartz contamination is also observed with the deactivated catalyst. This is attributed to contamination by particles of sealant remaining at the catalyst surface after dismounting the cell. The modification surely concerns a partial reduction of the catalyst top surface. Additional experiments are necessary to clarify this point.

Figure 7 shows a TPD spectrum of fresh LSCF powder after a treatment in oxygen stream (at 500 °C) and cooling down under oxygen atmosphere. We observe two clearly distinguishable types of oxygen, as already reported in the literature [43,44]. TPD spectrum exhibits a peak around 250 °C, noted as α. This corresponds to weakly adsorbed oxygen species which

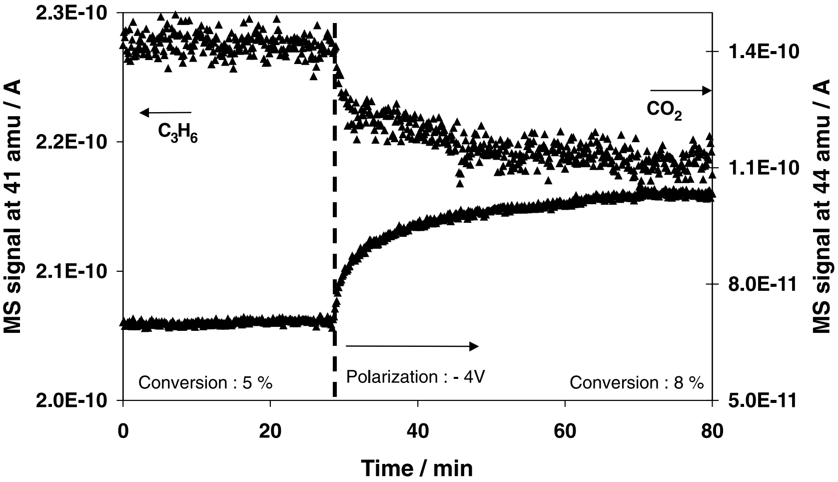

Figure 5. Propene conversion changes upon negative polarisation (2% $O_2$, 0.2% $C_3H_6$, 450 °C) on LSCF/YSZ after one night in He flow at 450 °C.

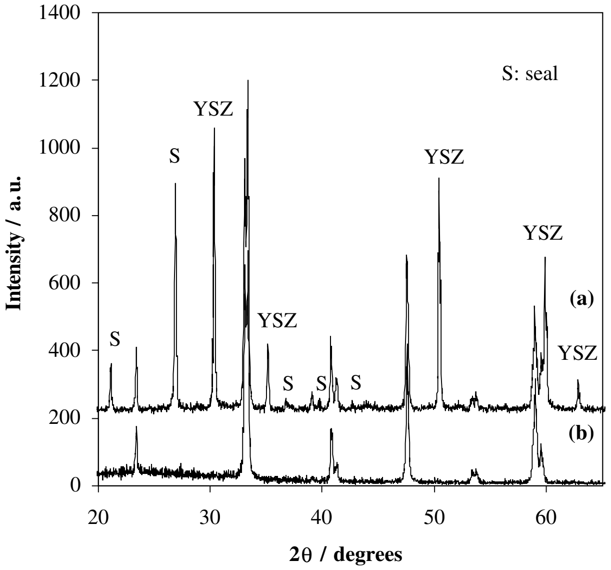

Figure 6. XRD spectra of (a) fresh LSCF powder and (b) LSCF film after one night in He flow at 450 °C.

could be the effective ones for propene combustion at low temperature. This α peak has be attributed to oxygen adsorption onto the oxygen vacancies formed by the partial substitution of $La^{3+}$ cations by $Sr^{2+}$ [44]. Then, oxygen vacancies could be the catalytic active sites. Moreover, strong relation between the catalytic activity and oxygen vacancies cationic defects was underlined in the literature [45] and shows the great importance of such weakly bound oxygen species. The overall quantity of oxygen vacancies, calculated from the amount of Sr integrated to the perovskite structure [43,46], corresponds to 212 $\mu$mol $O_2$ $g^{-1}$. The amount of desorbed oxygen relative to the α peak is only 2.43 $\mu$mol $O_2/g^{-1}$. This value is very consistent with weakly bound oxygen species desorbing to leave a surface monolayer of $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta=0.11}$. Considering this relation between the α peak and the surface active sites, one can estimate that the fraction of oxygen vacancies accessible to the reactants is only 1%. This observation could explain the low catalytic activity of LSCF by comparison to a well-dispersed Pt catalysts. When peak α is terminated, a continuous increase of oxygen desorption is observed (figure 7), starting from a quite low temperature, i.e. 400 °C and stretching toward higher temperatures of the TPD run, i.e. 850 °C. According to previous studies [44,47] this type of oxygen is coming from the bulk of the perovskite and may be attributed to the reduction of $Co^{4+}$ cations to $Co^{3+}$. These observations indicate that during the treatment at 450 °C under He for one night, oxygen species coming from the bulk of the perovskite are desorbing and could be at the origin of the irreversible lost of catalytic activity.

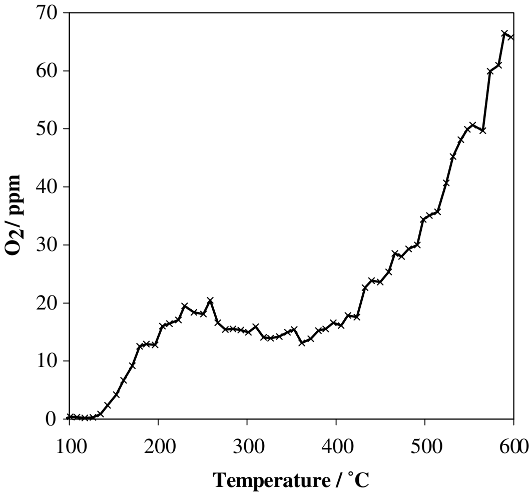

Figure 7. $O_2$-TPD spectra of LSCF after oxygen adsorption at 500 °C.

## 4. Conclusions

The results presented in this study show the interest of applying the electrochemical promotion to mixed oxides, in the goal to substitute them to precious metals used in the complete catalytic combustion of hydrocarbons. We may conclude that

- LSCF thin films may be used as catalyst/working electrode due to their electronic conduction.
- Electrochemical promotion of propene catalytic combustion is possible on LSCF, even in oxygen excess and this promotion is non-Faradaic (NEMCA effect).
- NEMCA effect on propene catalytic combustion on LSCF follows the same basic rules than on platinum/YSZ or Pt/NaSICon, i.e. the reaction is promoted when the catalyst is submitted to a negative potential or current, which favours the adsorption of electron-accepting molecules such as oxygen.
- LSCF good electronic conductivity at low temperatures, associated to its catalytic properties, make this compound a good and low-cost candidate as a substitute to precious metals such as platinum.
- As perovskites of this type may be prepared by the sol gel route [48,49] and dip-coated onto various supports such as membranes, knits or monoliths, they could be very useful to produce low-cost and very adaptable NEMCA electrocatalytic reactors.
- However, the main drawback of such LSCF is that they undergo irreversible damages when exposed to (even slightly) reductive atmospheres and then their use is restricted to oxidising atmosphere.

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