

Catalytic properties of stoichiometric and non-stoichiometric LaFeO₃ perovskite for total oxidation of methane

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Received 10 April 2001; received in revised form 13 June 2001; accepted 28 June 2001

Abstract

Perovskite LaFeO₃ and derived materials La_(1-ε)FeO_(3-1.5ε) with ε = 0.1, 0.2, 0.3 have been prepared as polycrystalline powders by thermal low-temperature decomposition of La and Fe nitrates, a method which ensures a high surface area. They have been used in catalytic methane combustion in the range 300–450 °C, showing a 100% selectivity to carbon dioxide. The reaction is indeed characterised by two ranges with different dependence of the reaction rate on temperature, as shown by the Arrhenius plot, whose slope decreases markedly above about 375 °C. Temperature programmed desorption experiments of oxygen allowed us to ascertain the presence of two surface oxygen species, whose desorption occurs, respectively before and after the above indicated temperature on this basis, we propose here an hypothesis on the way of working of the catalysts. The characterisation of the catalysts has been then completed by means of temperature programmed reduction, whose results contribute to strengthen the hypothesis that the catalyst reduction operated by methane involves a smaller number of lattice planes than reduction of hydrogen. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic properties; Perovskite LaFeO₃; Stoichiometric and non-stoichiometric; Methane

1. Introduction

Perovskite-type oxides with general formula LaMeO₃ with Me = transition metal, display prominent catalytic activities and application in many fields [1–4]. The catalytic properties of perovskites were systematically studied since 1977 and these materials have been used for the total oxidation of methane and of volatile organic compounds. The oxidation of hydrocarbons is supposed to occur on the perovskite surface by means of an intrafacial catalytic mechanism, in which the adsorbed oxygen is partly consumed and regenerated during a continuous cycle [5,6]. On this basis, we can explain why transition-metal perovskites are particularly active in oxidative catalysis if the Me metal on the B-site can fluctuate between two stable oxidation states, like Fe²⁺ and Fe³⁺ in this case. By this way, it is possible to electrically balance the insertion of O⁻ ions in the lattice from environmental O₂ or reversibly to bind O radicals to the hydrocarbon from lattice O⁻.

Moreover, a co-operation of the lattice oxygen and of the oxygen adsorbed onto the catalyst surface has been detected [7,8]. Therefore, the typical perovskite crystal structure as well as a large surface area are required for the catalytic

use of such material. In this communication we refer about the catalytic properties towards methane combustion of non-stoichiometric La_(1-ε)FeO_(3-1.5ε) perovskites with ε = 0, 0.1, 0.2, 0.3, which displays large surface areas and interesting defective structure, and give an explanation of these properties on the basis of the structural features.

2. Experimental

2.1. Catalyst preparation

As elsewhere reported [9], La_(1-ε)FeO_(3-1.5ε) with ε = 0, 0.1, 0.2, 0.3 polycrystalline powders are prepared by thermal low-temperature decomposition of La and Fe nitrates. La(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O are firstly dissolved in a double-weight of distilled water, heated up to the boiling point and then added of pure liquid glycerol, in molar ratio 2.5:1 (moles glycerol : moles La + Fe nitrates).

Heating is continued (under fume board) until the first brown vapours of NO_x evolve, then the liquid is poured in a large plain dish of stainless steel, which has been previously heated up to 200 °C. The dish is kept in oven at 200 °C in air for 30 min, in order to complete the decomposition of metal nitrates assisted by the organic reducing agent (glycerol).

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Table 1
Crystallite size and specific surface area of the catalysts

Composition	Average crystallite size (Å)	Average crystallite size (unit cells)	Specific surface area (m ² g ⁻¹)
LaFeO ₃	376	94	17
La _(0.9) FeO _(2.85)	156	39	42
La _(0.8) FeO _(2.7)	145	36	45
La _(0.7) FeO _(2.55)	141	35	49

The resulting crispy solid is then collected, slightly ground in agate mortar and subsequently heated in porcelain dish at 400 °C for 1 h.

The material is further heated at 600 °C for 24 h. This is the crystallisation temperature of the amorphous mass, as evidenced by differential thermal analyses (DTA); at this temperature sintering and grain growth are strongly suppressed and therefore, the highest surface area is obtained for crystalline material. The X-ray powder diffraction pattern (collected with a Philips PW1710 diffractometer, equipped with graphite monochromator) of the brown powders obtained at 600 °C show marked differences. While for $\epsilon = 0$, the structure is orthorhombic with unit cell dimensions $a_0 = 5.57 \text{ \AA}$, $b_0 = 7.85 \text{ \AA}$ and $c_0 = 5.55 \text{ \AA}$, space group Pnma (no. 62), the patterns for the Fe-rich terms are characterised by a progressive widening of the peaks, whilst contemporarily, the over-structured peaks of the orthorhombic phase decrease in intensity. The X-ray patterns of the non-stoichiometric compositions are surprisingly still monophasic, but the peaks are indexable on the basis of a pseudo-cubic cell with $a_0 = 3.927 \text{ \AA} \pm 0.002$ for all the terms with $\epsilon > 0$. The line broadening, as estimated by the standard Scherrer method [10], however, appears to increase in the samples along with non-stoichiometry, as reported in, thus, indicating a decrease in the crystallite size while the apparent pseudo-cubic symmetry can be accounted for by an enhanced crystalline disorder.

For samples obtained at 600 °C in air, the specific surface areas, as determined by nitrogen absorption at 78 K (BET method) and the average crystallite size as determined by the Scherrer method are reported in Table 1. The crystallite size is also expressed in number of perovskite unit cells.

The catalyst's powders, as prepared, have an apparent grain size of some 10ths of millimetres, high-resolution SEM observation (16,000 ×), obtained on a Philips 515 instrument, as reported in [11], confirm that the particles of the catalyst are composed by a conglomerate of much finer grains of the order of magnitude estimated by the X-ray peaks broadening.

2.2. Catalysts characterisation and catalytic activity determination

Catalytic activity runs have been carried out in a tubular continuous flow reactor on samples of 0.05–0.2 g, in the range 300–450 °C, after a pre-treatment up to 450 °C in a

stream of a mixture consisting in helium (80%) and oxygen (20%).

A flow of methane and oxygen (ratio 1:6) diluted in helium was then allowed on the catalyst samples during reaction. All gases were purified separately with suitable filters and their flows were regulated by Matheson electronic mass flow controllers. The mixture of reactants and products outcoming from the reactor was analysed at predetermined times with C.E. Fractovap gas chromatograph equipped with Poropak Q columns. The tests were performed by increasing the temperature stepwise and analysing the reaction mixture by means of GC analysis, when the steady-state was ensured at every temperature.

Of prominent importance for the catalyst's characterisations is the adsorption onto the catalyst's surface of gaseous oxygen. It is indeed generally believed that the methane activation on surface proceed via a redox mechanism concerning the B-type cation, and involving the abstraction of the surface oxygen species by means of methane (reduction step) and a subsequent uptake of gaseous oxygen by the solid surface (oxidation step of the cation).

Therefore, temperature programmed desorption experiments of adsorbed oxygen and temperature programmed reduction runs were planned and performed. Adsorption of oxygen was allowed, in a tubular reactor, on samples of 0.04–0.08 g of catalysts at room temperature, after a pre-treatment up to 450 °C in a stream of helium (80%) and oxygen (20%) and a subsequent cooling down to room temperature in the same mixture. Subsequently, temperature programmed desorption was realised by heating the sample at 4–16 °C min⁻¹ in a flow of He at 100 ml min⁻¹. All gases have been purified separately with suitable filters and their flows have been regulated by Brooks electronic mass flow controllers. Calibration of the peaks was realised by sampling a known volume of oxygen (20 μl) and measuring the corresponding area. The redox properties of the catalysts were characterised by means of temperature programmed reduction experiments (performed in the same apparatus) on samples of 0.04–0.08 g. The samples were pre-treated up to 450 °C in the same flow of helium plus oxygen and then cooled down to room temperature; before the run a flow of pure helium was flushed on the sample, in order to remove excess oxygen. Subsequently, temperature programmed reduction was realised by heating the sample at 4–16 °C min⁻¹ in a flow of He at 27 ml min⁻¹ and H₂ at 3 ml min⁻¹. Either desorption peaks of oxygen in TPD

or reduction peaks in TPR were monitored by means of a thermal conductivity detector.

3. Results and discussion

Catalytic tests were performed in the range 300–450 °C where preliminary screening experiments showed an interesting activity. The catalytic tests indicate above all, that in the temperature range investigated, either stoichiometric or non-stoichiometric catalysts show

1. 100% selectivity towards CO₂;
2. an activity which increases noticeably from stoichiometric LaFeO₃ to La_{0.9}FeO_{2.85}. The further increase in Fe/La ratio in La_{0.8}FeO_{2.70} and La_{0.7}FeO_{2.55}, slightly decreases the catalytic activity. These activities are reported in Fig. 1, where, it is possible to check also decreasing values when examining La_{0.8}FeO_{2.7} and La_{0.7}FeO_{2.55} samples.

It appeared interesting to gain a deeper insight in the dependence of the activity on the temperature, for a better correlation of the catalytic activity with the structural behaviour of these materials. By examining in Fig. 2, the Arrhenius plot (natural logarithm of derivative of conversion in respect of time versus reciprocal temperature), it is possible to see that two features emerge immediately

1. at about 375 °C, there is a marked change in the slope of the plot, which evidences two ranges of temperature, characterised by different apparent activation energies;

Table 2

Frequency factor ($\ln A$) and activation energy (E_a) of four catalysts

	$\ln A - E_a$ (kJ mol ⁻¹) $T < 375$ °C	$\ln A - E_a$ (kJ mol ⁻¹) $T > 375$ °C
LaFeO ₃	16.8–106.1	13.7–88.9
La _{0.7} FeO _{2.55}	20.3–112.4	14.4–88.6
La _{0.8} FeO _{2.7}	20.9–115.6	15.7–88.8
La _{0.9} FeO _{2.85}	21.1–117.3	17.0–89.2

2. below 375 °C an activation energy increasing from LaFeO₃ (~105 kJ mol⁻¹) to La_{0.9}FeO_{2.85} (~118 kJ mol⁻¹) characterises the catalytic reaction, with increasing corresponding pre-exponential factors; above 375 °C an activation energy of 84–88 kJ mol⁻¹ characterises the catalytic reaction.

The values of the apparent activation energy and of the apparent pre-exponential factor are reported in Table 2. It must be stressed here that pre-exponential factors include many constant terms, but it seems meaningful that the highest value should be attributed to La_{0.9}FeO_{2.85}.

Temperature seems therefore, to play an important role in this reaction, perhaps, a modification of surface properties of the catalyst reflects the alteration of bulk availability of α - and β -oxygen.

The compensation effect, which seems to be evidenced in the lower temperature range (contemporary increase of temperature dependence and of pre-exponential factor) could be an interesting evidence that at the lowest temperature, when passing from LaFeO₃ to La_{0.9}FeO_{2.85} there could be an

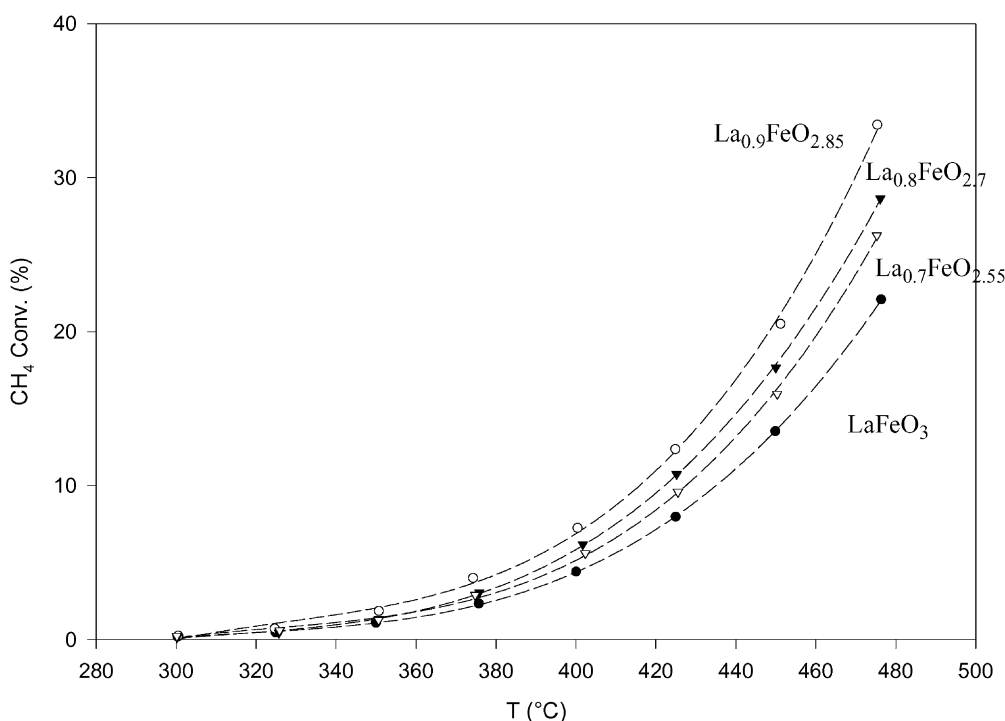


Fig. 1. Methane conversion to CO₂ on 0.1 g of the four types of catalysts.

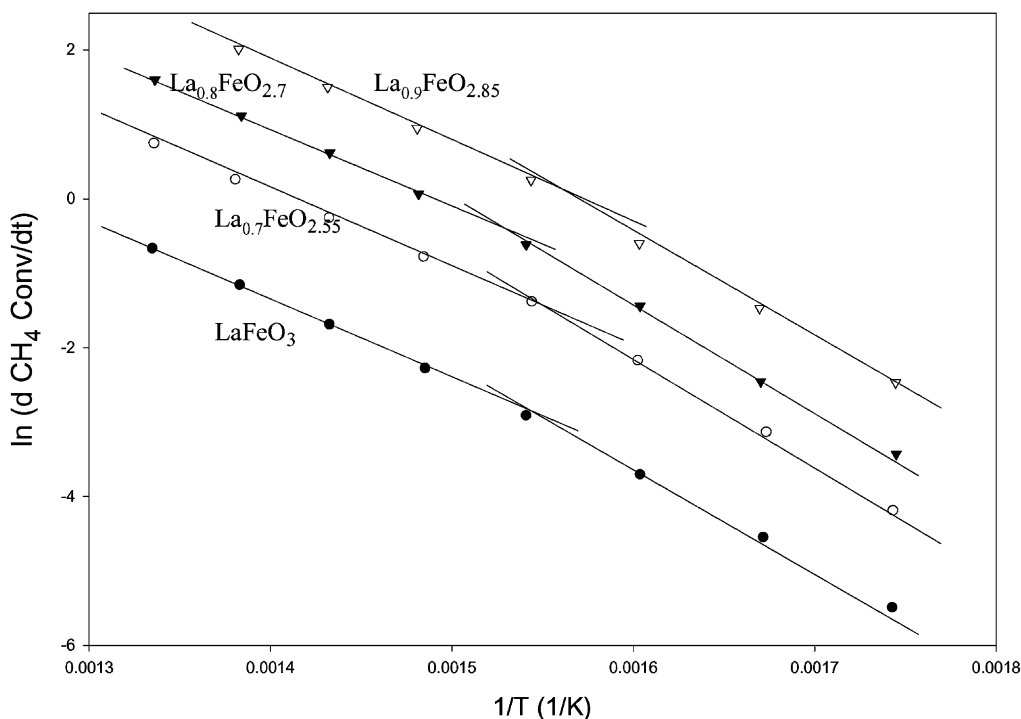


Fig. 2. Plots of $\ln(d \text{ CH}_4 \text{ Conv./dt})$ vs. $1/T$ corresponding to values of Fig. 1.

increase of the active sites density and of their interactions with adsorbed molecules (especially with oxygen). The subsequent increase in iron content could decrease the active site density and their interactive capabilities with reactants.

On the contrary, above 375 °C, the activation energies are rather similar, indicating that above this temperature the order of activity of the catalyst can find explanation in the constitution of the active sites and not in their density on the surface of the catalyst.

The reliability of the above tests was confirmed by experiments, as reported in [11], which showed that the catalyst show no deactivation at the low-temperatures and a slow and small deactivation at the highest temperatures of the range investigated.

In order to give an explanation of these results in terms of surface adsorptive features of the catalysts investigated, and above all in terms of participation of oxygen surface species, a series of temperature programmed desorption experiments was performed.

As it is possible to see in Fig. 3, it must be stressed above all that all samples show a first peak, which, when detected with mass analyser, correspond to the evolution of water and therefore, could be due to surface hydroxyls; moreover they show a larger peak at very high temperatures at about 800–900 °C but the oxygen species related to this peak, surely do not participate in the methane activation at the temperatures investigated.

The most important part of every spectrum is surely placed in the central range of temperature as it is possible to see in Fig. 3, the samples show in this range two small and

broadened peaks; the first centred at about 300 °C and the second centred at about 400 °C. These peaks are nearly absent on $\text{La}_{0.7}\text{FeO}_3$ but however, Table 3 shows the amounts of oxygen adsorbed on the different types of samples.

The existence of two types of oxygen species on all the catalysts corresponding to these two peaks, could explain the presence of two apparent activation energies in the Arrhenius plots, and this hypothesis could be reinforced by the experimental evidence that the two peaks are centred before and respectively, after the temperature, where it is found, the variation of the slope of the Arrhenius plot.

Moreover, the above Tables 1–3 shows, by considering the amount of oxygen desorbed per unit surface area, that the amounts of both types of oxygen adsorbed tend to decrease, going from LaFeO_3 to $\text{La}_{0.7}\text{FeO}_{2.55}$, except for $\text{La}_{0.9}\text{FeO}_{2.85}$ first peak, which shows a maximum.

This could be a reasonable hint to consider the activity of $\text{La}_{0.9}\text{FeO}_{2.85}$ as related to a greater density of sites characterised by a great mobility of surface oxygen species, able to activate methane and to be replaced by gaseous oxygen.

Since, the capacity of the catalysts of allowing a surface oxidation of methane is based on a redox process on the catalysts itself, temperature programmed reduction runs have been carried out, in order to elucidate this aspect also of the reactivity.

In Fig. 4, TPR spectra obtained from the catalysts, are reported; apart from a peak at very high temperatures, they evidence two peaks, at 300–350 °C and respectively, at 500–550 °C, their progressive extension when going from LaFeO_3 to $\text{La}_{0.7}\text{FeO}_{2.55}$ seems indicating that the amount

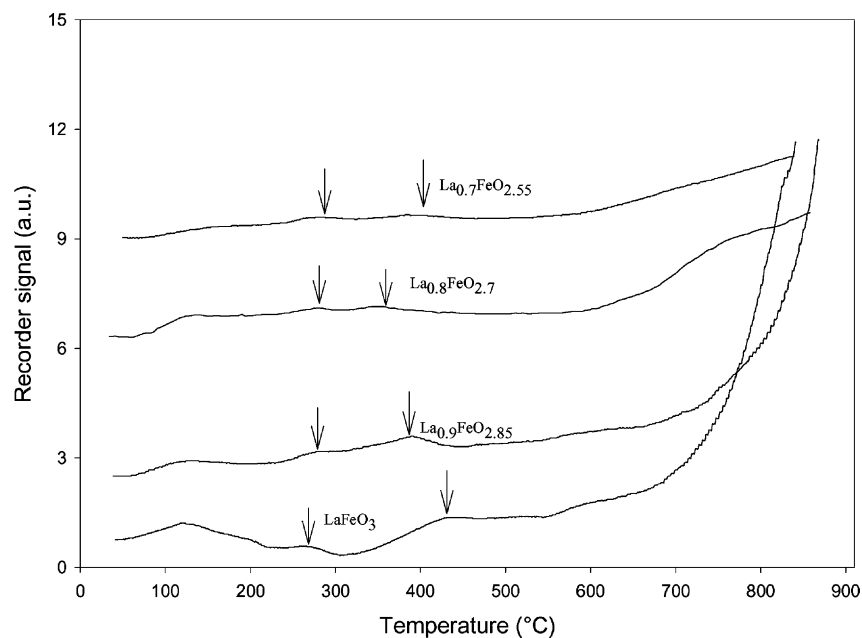


Fig. 3. TPD spectra with adsorbed oxygen of the four catalysts (the arrows show the location of the peak maxima).

Table 3

Amounts of oxygen adsorbed as determined from the first and from the second low-temperature peaks

	LaFeO ₃	La _{0.9} FeO _{2.85}	La _{0.8} FeO _{2.7}	La _{0.7} FeO _{2.55}
First peak (mol m ⁻² catalyst)	2.7×10^{-6}	5.4×10^{-6}	1.4×10^{-6}	6.2×10^{-7}
Second peak (mol m ⁻² catalyst)	1.6×10^{-7}	1.3×10^{-7}	3×10^{-8}	1.3×10^{-8}

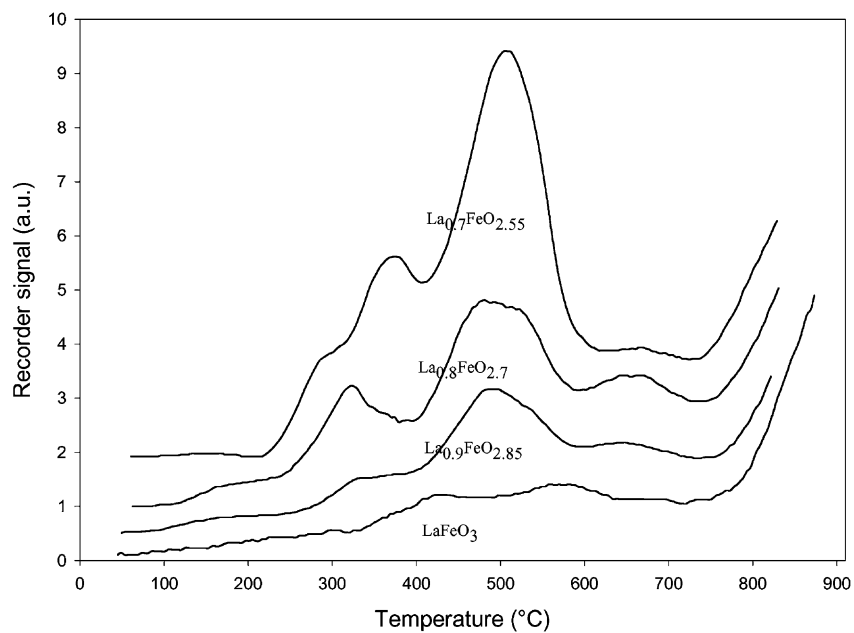


Fig. 4. TPR spectra obtained with a flow of He + H₂ obtained from the four catalysts.

of oxygen species involved in this reduction processes increases in the direction above mentioned.

In the TPR spectrum of $\text{La}_{0.7}\text{FeO}_{2.55}$, a third peak between the two already described appears, strengthening the hypothesis that on this type of catalyst there is a large availability of oxygen species for hydrogen.

The reduction processes evidenced by these experiments seem to induce hypothesis in contrast with the results obtained by activity and desorption experiments; $\text{La}_{0.7}\text{FeO}_3$ is indeed the most reducible among the catalyst investigated and should be the most active.

But, we must consider that lanthanum defectivity introduces increasing distortions on the surface and in the bulk, characterised also by means of X-ray diffraction measurements [11].

The increased distortion stimulates the formation and the presence of defective layers inactive for combustion. But, since hydrogen is a small molecule and can penetrate inside the bulk, an increasing amount of reducible species is accessible to reduction with increasing defectivity, either on the surface or in the bulk.

On the contrary, methane is a much larger molecule and can activate reduction processes only on the surface, where, because of the presence of well-definite crystal planes, the active site do not increase as much as defectivity increases.

Therefore, only the mobility of oxygen species revealed in temperature programmed desorption experiments can be really meaningful for the catalytic activity.

4. Conclusions

A trend in the catalytic activity, increasing from stoichiometric LaFeO_3 to non-stoichiometric $\text{La}_{1-\epsilon}\text{FeO}_{3-1.5\epsilon}$ has been evidenced. It can be explained by means of a decrease of crystal size and an increase of the specific area. Increased surface area induces a higher number of exposed active sites, probably constituted by Fe octahedral sheets, perhaps with uncoordinated Fe. However, the decreasing of the lanthanum content under $\text{La}_{0.9}$: (a) does not cause a marked increase of the surface area and therefore, the density of the surface active sites does not increase; (b) causes a progressively increasing excess Fe, which for the $\text{La}_{0.7}\text{FeO}_{2.55}$ composition can be no longer accommodated on the surface sheets, forming Fe_2O_3 nanoparticles, which can be recognised only by Mössbauer spectroscopy, as previously reported [11].

These latter Fe_2O_3 layers are inactive, as they do not possess the regular perovskite structure and evidently, the oxygen adsorption is less favoured, as demonstrated by temperature programmed desorption experiments. The first factor results prevailing for $\epsilon = 0$ and 0.1 samples, whilst the second is prevailing for $\epsilon = 0.2$ and markedly for 0.3. The highest catalytic activity is therefore encountered for the $\epsilon = 0.1$ sample. As shown by means of rough calculations from oxygen conversion values up to about 375°C , the amounts of oxygen converted in methane combustion (average $5.10^{-6} \text{ mol m}^{-2}$) are of the same order of the amounts of the oxygen present on the surface and revealed by the evolution of the first peak. This could give an indication that oxygen consumption during reaction is about in equilibrium with its uptake from the gaseous phase and therefore, the most activated step should be the activation of C–H bond, on surface sites where weakly bond oxygen species are involved. Above about 375°C , the amounts of oxygen consumed in the reaction are much larger than those of oxygen (strongly) anchored on the surface and revealed by the development of second TPD peak. An hypothesis can therefore be made, concerning the possibility of abstraction of oxygen (not revealed by TPD) by means a redox mechanism induced by methane and acting as a rate limiting step.

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