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The nature of active sites for the oxidation of methane on La-based perovskites

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Highly crystalline, monophasic $LaFeO_3$ and $LaCoO_3$ perovskites, prepared by the explosion method, are shown to be heterogeneous at surface level. The outmost atomic layers of these perovskites contain high concentrations of carbonate-type species. Their specific activities for methane combustion are in fact identical to $La_2O_2CO_3$ and air-exposed La_2O_3. These results compared with pertinent data from the literature hint that surface heterogeneity may be often present in mixed oxides catalysts.

Keywords: perovskites; methane; catalytic combustion; La-carbonate species; surface carbonates; explosion method

1. Introduction

During the past decade, the catalytic combustion of natural gas has received considerable attention as an alternative to conventional thermal combustion. This is mainly due to: (i) more efficient energy utilization, and (ii) the fact that catalytic combustion avoids the formation of hot spots, thus decreasing NO_x formation from the thermal reaction between N_2 and O_2 [1,2]. This application requires materials resistant to high temperatures (> 1070 K) in the presence of steam and oxygen. Among several mixed oxide candidates, perovskite-type oxides (general formula AMO_3) have been frequently used for this purpose [3–5]. $LaCoO_3$ and $LaFeO_3$ have already been tried for methane combustion in the temperature range between 750 and 1150 K.

The variation of the M ion in AMO_3 is more effective to optimize the catalytic activity than the selection of different lanthanides at the A position [3,5,6]. On the other hand, differences in perovskite catalytic behavior may be traced back to surface heterogeneity that might even override changes in bulk composition. The surface composition of perovskites often differs from the bulk and is directly related to the preparation method. It often tends to be poor in M-site cations and could have segregated phases [6,7]. All this complicates the characterization of these solids making it difficult to elucidate the nature of the active sites present on the surface of perovskite-type oxides.

Fierro and Tejuca [8] observed distinct bands of carbonates after adsorption of CO at room temperature on the surfaces of Mn-, Fe- and Co-containing perovskites, while Lombardo et al. [9] reported the formation of a $La_2(CO_3)_3$ layer on the surface of $LaCoO_3$ perovskite. The high reactivity of La_2O_3 towards CO_2 is also well documented. The addition of carbonates to rare earth oxides has been found to improve the selectivity for the oxidative coupling of methane [10,11]. Since hydrocarbon combustion always produces CO_2, could we be facing a similar situation in these systems?

In this study we have tried to develop new insight concerning the nature of sites present on perovskite-type oxides for the high temperature combustion of methane. The mixed oxides were prepared using the explosion method [12] and characterized through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

$LaMO_3$ (where M = Fe, Co) was prepared by the explosion method [12]. Corresponding metal nitrates were mixed to form an equimolar solution (total concentration 0.9 M). A 1 M citric acid solution was added to the mixed nitrate solution. The amount of citric acid was equal to the sum of La + M equivalents. The resulting solution was evaporated in an oven at 380 K for 10 h, yielding a highly porous, amorphous organic precursor. This precursor was pressed with benzoic acid to form a pellet containing a metal filament. Benzoic acid acts as agglomerant and favors ignition due to its high heat of combustion. The solids were mixed in a benzoic acid/precursor ratio of 1 : 4. The pellets were burnt in a calorimetric bomb, loaded with O_2. Ignition occurred instantaneously and the solid, porous and expanded, was recovered from a crucible at the bottom of the bomb.

$La_2O_2CO_3$ was also prepared by the explosion method but starting from lanthanum acetate as organic precursor. La_2O_3 (Anedra, 99.99%) and MgO (Carlo Erba, 99.5%) were used without further purification.

2.2. Characterization

X-ray diffraction analysis was carried out with an XD-D1 Shimadzu instrument with monochromator using Cu K_α radiation at a scan rate of 1° per minute. The BET surface area was determined by N_2 adsorption in a Quantachrome Nova 1000 Sorptometer.

Infrared spectra were obtained using a FTIR Shimadzu 8101M spectrometer. Samples were prepared in the form of pressed wafers (ca. 2 wt% sample in KBr). All spectra involved the accumulation of 80 scans at 4 cm^{-1} resolution.

Photoelectron spectra were acquired with a Fisons Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a Mg K_α 120W X-ray source. A PDP 11/04 computer from DEC was used for collecting and processing the spectra. The powder samples were pressed into small aluminum cylinders and then mounted on a sample rod placed in a pretreatment chamber and outgassed at 10^{-5} Torr prior to being transferred to the analysis chamber. Before obtaining the spectra the samples were maintained in the analysis chamber under a residual pressure ca. 2×10^{-9} Torr for 14 h. This pressure was almost unchanged during data acquisition. The spectra were collected for 20 min at a pass energy of 10 eV (1 eV = 1.602×10^{-19} J) which is typical of high resolution conditions. The intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the "S-shaped" background and fitting the experimental curve to a mix of Lorentzian and Gaussian lines of variable proportion. All binding energies were referenced to the C 1s line at 284.9 eV. This reference gave binding energy values with an accuracy of ±0.2 eV.

2.3. Catalytic measurements

The catalysts were tested in a packed-bed tubular quartz reactor (i.d. 18 mm) with a 4 mm o.d. thermowell. 0.500 g of catalyst were placed on a fritted quartz disk and covered by quartz wool. The gas flows were measured by mass flow controllers. The gas mixture consisted of 3 vol% methane, 7.2 vol% oxygen and 89.8 vol% nitrogen. The total volumetric gas flow was 113 cm^3 min^{-1} (STP). The products were analyzed by an on-line gas chromatograph using a Porapak Q column and a TCD detector.

The temperature range was 720–1020 K. To evaluate the contribution of the homogeneous reaction within this range, the reactant mixture was flowed through the empty reactor (without catalyst). At 1070 K the conversion was lower than 1%. The carbon balance indicates that the methane combustion yields carbon dioxide as the only oxidation product. Thus, the methane conversion was calculated as the ratio between methane concentration and the sum of the carbon compounds concentrations (methane and carbon dioxide) at the reactor outlet.

3. Results

3.1. X-ray diffraction analysis

The XRD patterns of $LaFeO_3$ confirmed the perovskite structure without any segregation of simple oxides, within the limits of detection for this technique. However, $LaCoO_3$ still contained segregated oxide phases and needed to be calcined at 1220 K for 10 h with air to obtain a single phase perovskite. $La_2O_2CO_3$ contained significant amounts of La_2O_3 while the diffraction patterns of La_2O_3 and MgO samples showed no spurious reflections.

3.2. Catalytic activity

Fig. 1 shows the catalytic behavior of all the solids for the combustion of methane. Reaction lights off at ca. 720 K on the lanthanum-based compounds. In this group, the conversion at each temperature increases in

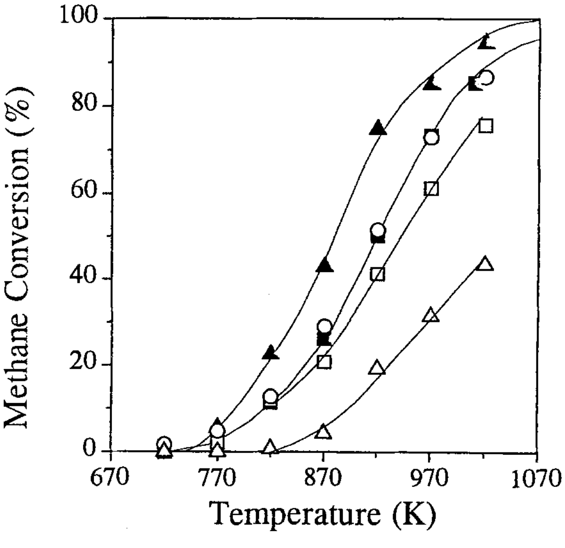

Fig. 1. Catalytic combustion of methane on: (△) MgO; (□) $LaFeO_3$; (○) $LaCoO_3$; (■) $La_2O_2CO_3$ and (▲) La_2O_3. Flow reactor, GHSV = 2700 h^{-1}, reactant composition: 3% CH_4, 7.2% O_2, balance N_2.

Table 1
Reaction rates for lanthanum-based oxide compounds at 770 K

Catalyst	Surface area ($m^2\ g^{-1}$)	Reaction rate ($\mu mol\ s^{-1}\ m^{-2}$) × 10^2
$LaFeO_3$	3.0	4.0
$LaCoO_3$	5.7	4.3
La_2O_3	7.1	3.9
$La_2O_2CO_3$ (La_2O_3) [c]	3.9	3.6
$LaFeO_3$ [a]	5.1	6.2
$LaCoO_3$(Co_3O_4) [a,c]	11.2	9.1
Co_3O_4 [a,b]	6.8	260
Fe_2O_3 [a,b]	5.2	36

[a] Ref. [16].
[b] Reaction temperature 800 K.
[c] Compounds between parentheses are segregated phases shown in the XRD patterns.

the following order: $LaFeO_3 < La_2O_2CO_3$, $LaCoO_3 < La_2O_3$, thus correlating with the increase in specific surface area (table 1). This indicates in turn that interphase diffusion is not a limiting factor. The nature of the surface involved does play a role in this system. To illustrate this point the MgO (16.6 m^2/g was included in fig. 1.

At 770 K, where the conversion is lower than 6% in all cases, the reactor can be considered as a differential one thus allowing the calculation of the reaction rate. When the latter is expressed per unit area, the values of La-containing catalysts are close to ca. 4×10^{-2} μmol-CH_4 s^{-1} m^{-2} (table 1).

3.3. Fourier transform infrared spectroscopy

The IR spectra of the solids may yield clues to understand the similar kinetic behavior of the La-containing compounds. Fig. 2 shows the spectrum of La_2O_3 after exposure to air at 300 K. The sharp band at 3624 (ν) cm^{-1} and the broad one at 654 (δ) cm^{-1} are characteristic of stretching and bending OH vibrations of lanthanum hydroxide, respectively [10]. On the other hand, broad and intense bands at 1500 (ν_3) and 1398 (ν_3) cm^{-1} as well as smaller ones at 1070 (ν_1) and 863 (ν_2) cm^{-1} are observed. These bands correspond to the principal vibrations of CO_3^{2-} groups and are similar to those observed in the crystallized lanthanum carbonate ($La_2(CO_3)_3 \cdot xH_2O$) [10,11,13]. As expected, the La_2O_3 exposed to atmospheric air reacts with CO_2 to form surface carbonates.

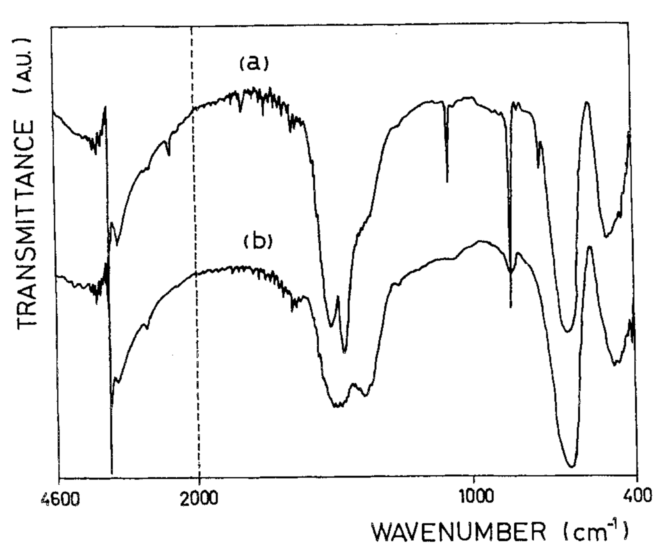

Fig. 2. FTIR spectra of (a) $La_2O_2CO_3$, and (b) La_2O_3.

The IR spectrum of $La_2O_2CO_3$ is also shown in fig. 2. The characteristic bands of hexagonal (type II) structure of this compound (1520 (ν_3), 1470 (ν_3), 1093 (ν_1), 863 (ν_2), 752 (ν_4) cm^{-1}) and $La(OH)_3$ (3624 (ν), 654 (δ) cm^{-1}) are observed. However, contributions of the monoclinic (type Ia) structure can be assigned due to the splitting of ν_1 and ν_2 nondegenerate modes. It is well known that for the monoclinic polymorph, the ν_1 and ν_2 nondegenerate modes are respectively split into three frequencies [10,11]. The presence of lanthanum carbonate is evidenced by the shoulder at 1398 (ν_3) cm^{-1}.

In order to obtain the spectra of the colored perovskite solids they were diluted in KBr. Their spectra did not show, however, any carbonate-type absorption bands. This is not surprising in view of the results reported by Zhong et al. [14], who prepared $LaFeO_3$ by a sol–gel technique using citric acid. They reported that the carbonate bands were clearly visible up to calcination temperatures of 820 K but they disappeared after treatment at higher temperatures. Maybe the concentration of carbonates becomes too low to be seen by this bulk technique but carbonates might still be revealed using a surface sensitive technique (vide infra).

3.4. XPS data

To further investigate the origin of the almost identical specific activity of La-containing compounds (table 1) it was deemed necessary to use a surface sensitive technique such as XPS.

Both $LaFeO_3$ and $LaCoO_3$ presented two well-differentiated C 1s signals as shown in fig. 3 and table 2.The lower binding energy (BE) peak corresponds to the reference (284.9 eV) and the higher one can be assigned to carbonated species [9], whereas three C 1s peaks were observed for $La_2O_2CO_3$ (see table 2). The signals that appear at 288.4 and 289.6 eV are due to different carbonated species. Samples of La_2O_3 show the same characteristic C 1s spectrum as that observed for $La_2O_2CO_3$.

Fig. 4 shows the O 1s spectra of $LaCoO_3$, and $LaFeO_3$ in which two different oxygen species are evident. The lower BE peak is generally assigned to the lattice oxygen [9,15] and the other one corresponds to carbonated species on the surface. When $LaFeO_3$ was analyzed after evacuation for only 1 h in the analysis chamber at 2×10^{-9} Torr, a third oxygen peak was

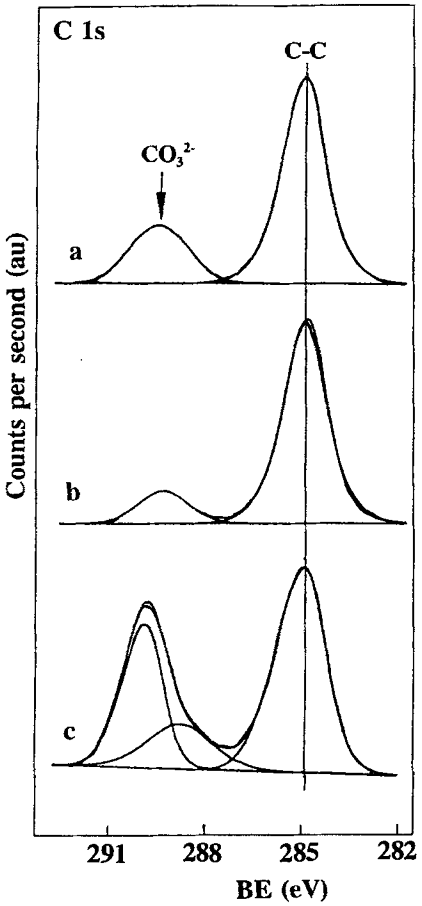

Fig. 3. C 1s core level spectra of different samples: (a) $LaFeO_3$; (b) $LaCoO_3$; and (c) $La_2O_2CO_3$. The arrow in the high BE side corresponds to carbonate species. Note that these carbonate structures are more complex on carbonated lanthana.

observed corresponding to chemisorbed oxygen (533.1 eV). La_2O_3 and $La_2O_2CO_3$ catalysts present two O 1s signals at ~ 531 and 532 eV.

The La $3d_{5/2}$ spectra of perovskites (fig. 5, table 2) may be convoluted with two overlapping doublets. The one at the lowest BE is assigned to the perovskite lattice, while the other would correspond to a La-carbonated species. Similar spectra were reported by Lombardo et al. [9] for $LaCoO_3$ prepared by precipitation with a base from nitrate solutions. However, Gunasekaran et al. [15] reported just a single doublet for La $3d_{5/2}$. In the case of La_2O_3 and $La_2O_2CO_3$ (fig. 6) it is interesting to note the broad La signal appearing at 835.4 eV. This could be due to the overlapping of La signals corresponding to La_2O_3 and to La-carbonated species.

The surface composition of the solids is given in tables 2 and 3. The data in the C 1s column of table 2 may explain why the IR carbonate bands are seen both in the lanthanum oxide and oxycarbonate but they are not visible in the perovskite spectra. Note that the relative surface concentration of carbonates is much higher in the former than in the latter.

Table 3 shows the concentration of surface species calculated from the XP spectra. The first five ratios were directly measured while the latter five were calculated making some necessary assumptions. The La_C/La_L ratio (fourth row) was obtained from the La $3d_{5/2}$ peak, where subscript C means carbonated species and L perovskite lattice. This is the least accurate measured value due to the inherent uncertainty of this convolution.

4. Discussion

The surface composition of perovskite type oxides is significantly different from the bulk and is affected by the gases in contact with the solid during synthesis. These factors play a decisive role in defining the catalytic behavior of these oxides. As a matter of fact, they may even blur the distinct behavior arising from different bulk compositions. A similar surface composition of all the solids studied seems in fact to be the explanation of their almost identical specific activities.

Let us now analyze the results reported here and the pertaining literature data that supports the above statements. The infrared spectrum of La_2O_3 which was

Table 2
XPS binding energy values (eV) of C 1s, O 1s, La 3d and transition metal 2p over La-based oxide compounds

Catalyst	C 1s [a]	O 1s [a]	La $3d_{5/2}$ [a]	M $2p_{3/2}$
$LaFeO_3$	284.9(87) 289.4(13)	529.3(35) 531.6(65)	834.1(39) 835.5(61)	710.4
$LaCoO_3$	284.9(85) 289.3(15)	528.9(30) 531.8(70)	833.6(43) 835.6(57)	779.7
La_2O_3	284.9(27) 288.4(18) 289.6(55)	531.0(62) 532.0(38)	835.4	–
$La_2O_2CO_3$ (La_2O_3)	284.9(27) 288.4(18) 289.6(55)	531.7(86) 532.8(14)	835.4	–

[a] Values between parentheses correspond to the surface molar %.

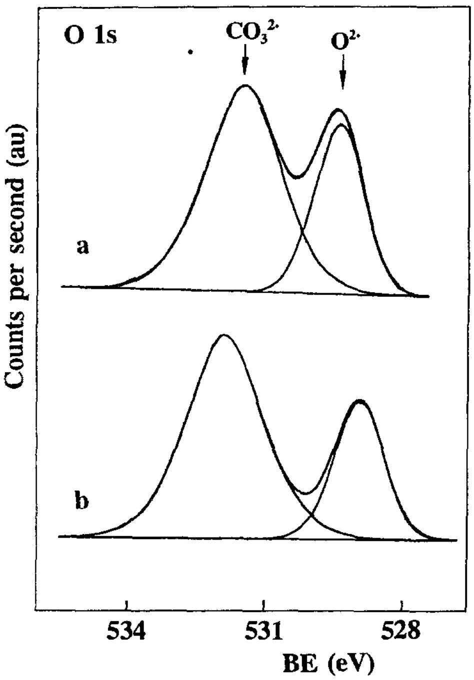

Fig. 4. O 1s core level spectra of perovskite samples: (a) LaFeO$_3$, and (b) LaCoO$_3$. Arrows indicate the position of lattice oxygen and carbonate species.

exposed to wet air at 300 K (fig. 2) clearly shows that CO$_2$ is adsorbed on the surface as a carbonate-type species. The asymmetry it introduces into the CO$_3^{2-}$ (XY$_3$) simple structure when the mono- or bidentate ligands are formed, causes the ν_1 ($\sim$ 1080 cm^{-1}) vibration to be infrared active [13] and the ν_3 (double degenerate) vibration to be separated into two components. The degree of separation between them depends on the type of ligand formed and on the covalent character of the metal–oxygen bond. The separation is smaller for monodentates ($\sim$ 100 cm^{-1}) than for bidentates ($\sim$ 300 cm^{-1}) [13]. Since this separation in the La$_2$O$_3$ spectrum is $\sim$ 100 cm^{-1} we concluded that CO$_2$ adsorbed on its surface at room temperature would be forming a monodentate ligand.

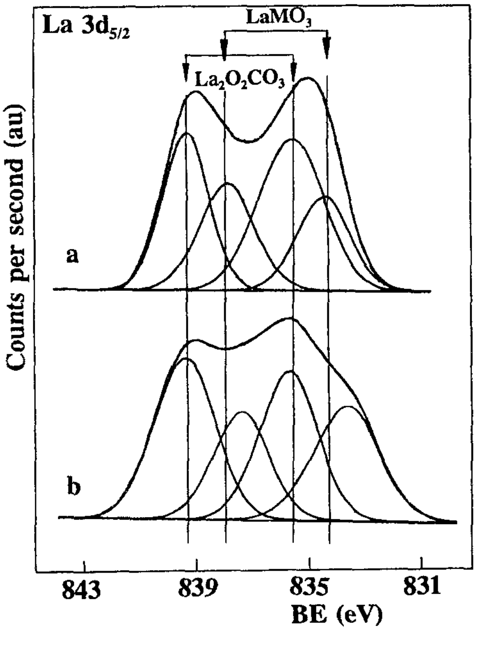

Fig. 5. La 3d$_{5/2}$ core level spectra of: (a) LaFeO$_3$; and (b) LaCoO$_3$. The two arrow sets correspond to LaMO$_3$ (M = Fe, Co) and La$_2$O$_2$CO$_3$ species.

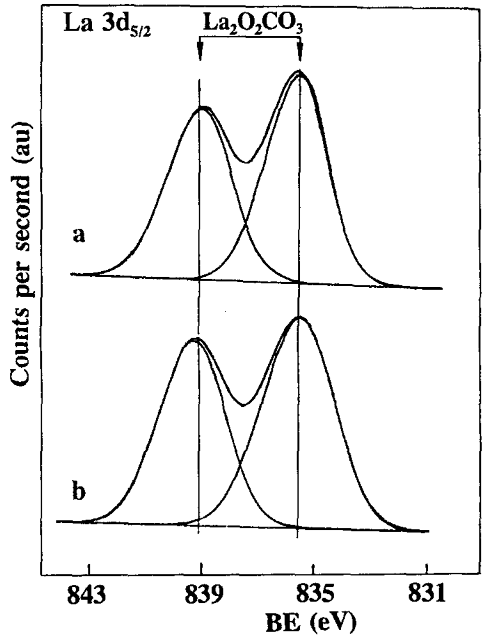

Fig. 6. La 3d$_{5/2}$ core level spectra of lanthanum oxide samples: (a) La$_2$O$_3$; and (b) La$_2$O$_2$CO$_3$.

All the signals observed by IR for the La$_2$O$_2$CO$_3$ sample (fig. 2) correspond to the hexagonal (type II) and monoclinic (type Ia) structures of this compound, except for the shoulder clearly visible at 1398 cm^{-1}. This band hints the presence of carbonate-type surface species (monodentate form) of the kind present on La$_2$O$_3$ (compare the IR spectra, fig. 2).

This monodentate carbonate species on the surface of both solids, La$_2$O$_3$ and La$_2$O$_2$CO$_3$, would be responsible for the predominant C 1s signal located at 289.6 eV (fig. 3 and table 2). The same C 1s binding energy value was determined for both LaFeO$_3$ and LaCoO$_3$, indicating that this La-carbonate species would be present on the surface of the four samples under study. This is further confirmed by the O 1s spectrum (fig. 4) that clearly shows the presence of two peaks, one assigned to the perovskite lattice and the other to carbonate oxygen. Accordingly, the La 3d$_{5/2}$ signals are made up from contributions of carbonate-type surface compounds and the perovskite bulk oxide (fig. 5). This has already been observed by Lombardo et al. [9] who detected the presence of very stable La$_2$(CO$_3$)$_3$ over LaCoO$_3$. Tejuca and coworkers [7,8] also reported the presence of carbonate bands on the LaMO$_3$ oxides (M = Mn, Fe or Co) after

Table 3
The concentration of surface species on lanthanum single and mixed oxides

Atomic ratio [a]	$LaFeO_3$	$LaCoO_3$	La_2O_3	$La_2O_2CO_3$
measured				
C_C/La_T	1.1	0.7	0.4	1.1
O_T/La_T	3.7	2.2	2.9	4.2
O_C/La_T	2.4	1.5	1.1	[b]
La_C/La_L	1.6	1.3	–	–
M_T/La_T	1.1	0.7	–	–
calculated				
O_L/La_L	3.3	1.5	–	–
O_L/M_T	1.2	0.9	–	–
M_T/La_L	2.8	1.6	–	–
O_C/C_C	2.2	2.1	2.8	[b]
C_C/La_C	1.8	1.2	–	–

[a] Subscripts: C: carbonate, T: total, L: perovskite lattice. M = Fe or Co.
[b] These ratios cannot be calculated in the oxycarbonate (see text).

the adsorption of either CO or CO_2 at room temperature, although they did not specify which are the metals associated to the carbonate.

A more detailed look at the C 1s spectra of La_2O_3 and $La_2O_2CO_3$ hints the presence of at least two types of carbonated compounds. The larger peak at 289.6 eV is the one associated with the monodentate carbonate. The other cannot be assigned with these data. The La $3d_{5/2}$ signal hints the presence of two compounds because it is about 25% wider at half height than in the mixed oxides (fig. 6). However, on this sole basis it is not possible to ascertain the presence of different La compounds. This should be expected since the difference in the La binding energy corresponding to the oxide and the carbonates is small [9].

Let us see now if the surface concentration data shown in table 3 allow a further refinement of the surface model. The first row shows a higher concentration of carbonate carbon on the surface of the oxides produced by the explosion method without further treatment. This is consistent with the higher partial pressure of CO_2 in the bomb atmosphere than in air. Both the total oxygen and the carbonate oxygen per lanthanum (second and third rows) follow the same trend. The O_C/La_T ratio for the oxycarbonate could not be calculated because the signal at 532.8 eV may be assigned to terminal OH groups while the wide signal at 531.7 eV (table 2) is likely to include the contributions of both carbonates and lanthanum oxide. The increased concentration of lanthanum from carbonate in the Fe perovskite is also consistent with this overall picture (fourth row). The higher partial pressure of CO_2 in the bomb favors the segregation of lanthanum due to its high affinity to form the stable carbonate.

The excess metal over lattice La (eigth row) and to a certain extent the data in the sixth and seventh rows seem to indicate that the composition of the surface layers is quite different from the bulk. Two possible candidates are the transition metal carbonates and/or oxides. The former decompose at temperatures below 470 K while the presence of segregated transition metal oxides is neither supported by the catalytic results nor by the XRD data. Further studies with other techniques are needed to elucidate in greater detail the surface phase composition. The O_C/C_C ratios (ninth row) are consistent with the presence of monodentate species as suggested by the FTIR spectra (fig. 2).

Therefore, the first surface layers of both perovskites would have similar compositions with abundance of carbonated species. These species also present in the single La compounds may be responsible for the similar catalytic activity of all the solids studied. At this point it is interesting to look back at table 1, which includes data from the literature for related systems [16]. Note that the rate data for the single phase mixed oxides are similar to ours and very different from Co_3O_4. This might indicate that surface carbonated species are quite common in these mixed oxides. Baiker et al. [5] reported that the presence of Co_3O_4 impurity in the $ACoO_3$ samples (A = La, Pr, Nd, Gd) strongly influences their catalytic activity. $LaCoO_3$ with amorphous Co_3O_4 (7 wt%) can enhance its activity making it comparable with the activity of bulk Co_3O_4. Consequently, if there were segregation of simple oxides, these would not be exposed on the most external surface layers.

According to the studies performed, the La on the surface of these solids would be as a La-carbonate type species at room temperature. However, taking into account both that CO_2 is a product of methane combustion and that lanthanum oxide is highly reactive towards CO_2 even at temperatures higher than 1050 K [17], it could be expected that under the reaction conditions employed, the La-carbonate species be present on the surface. Note that, despite the 10 h treatment at 1220 K, the Co perovskite still contains significant amounts of carbonates. As a matter of fact, Lombardo et al. [9] showed that the only way to remove the carbonates from $LaCoO_3$ was to heat the solid in hydrogen at 570 K. Besides, if at the upper end of the temperature range explored the transition metal oxides would become exposed a sharp increase in catalytic activity should be observed (see last two rows of table 1). This was not seen with either the Fe or the Co perovskite. In any case the small amounts of carbonates present on these low surface mixed oxides could not be quantified in our laboratory. This remains a challenging matter to be addressed in future investigations.

5. Conclusions

The first few surface layers of La-based mixed oxides bear little resemblance to their bulk structure and composition. They are affected by the composition of the gases in contact with the solid during synthesis.

Carbonated species are abundant on the surface of $LaCoO_3$ and $LaFeO_3$ defining their catalytic behavior. The carbonate concentration is higher in solids prepared by the explosion method than by traditional procedures. However, the similar catalytic results reported by other laboratories and our own experience indicate that surface carbonates are almost always present on La-based mixed oxides.

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