Cobalt-containing catalysts for the high-temperature combustion of methane

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Cobalt was supported on ZrO_2, La-doped ZrO_2 and La_2O_3 through atomic layer epitaxy (ALE) and wet impregnation. The rate data obtained at 770 K is compared with literature information about cobalt inserted in other matrixes. The ALE technique using ZrO_2 and La-doped ZrO_2 yielded the best cobalt-containing catalysts. Bulk and surface characterization techniques provided key clues to understand the origin of the large difference in catalytic activity reported for cobalt-containing formulations.

Keywords: cobalt, zirconia, atomic layer epitaxy, explosion method, methane combustion

1. Introduction

The catalytic combustion of natural gas, applicable to gas turbines, allows the efficient burning of lean fuel–air mixtures with a minimum pollutant formation as compared to conventional flame combustion [1]. One type of catalytic combustion system is designed to limit the catalyst temperature. In this case the fuel combustion is completed downstream of the catalyst (hybrid systems) [2]. The catalytic system can be divided into two sectors. At the inlet stage, the low-temperature catalyst initiates the combustion (Pd-containing formulations are generally used here). In the following stage, the high-temperature catalyst produces the required outlet gas temperature needed to initiate the homogeneous combustion process [2,3]. Applying a similar concept, in October ’98 Catalytica Inc. started operation of the first commercial gas turbine employing a catalytic burner in an electrical utility [4]. In this publication we refer to catalytic materials that might be used in the high-temperature end of hybrid catalytic burners.

Co_3O_4 is a good catalyst for methane oxidation but it easily sinters at temperatures as low as two thirds the melting temperature (m.p. $= 1170$ K) [5], and at temperatures close to 1270 K it becomes volatile [6]. Therefore, there has been an intense research effort trying to stabilize Co in different matrixes.

The perovskite structure has been thoroughly investigated. $LaCoO_3$ and various partially substituted oxides ($La_{1-x}A_xCo_{1-y}B_yO_3$) were tried for this reaction [7–12]. Other rare earths were used instead of lanthanum [8]. However, none of them yielded high activity per unit mass in part due to the intrinsic low surface area of the massive mixed oxides.

An alternative route is to support Co on high surface area stable solids [5,6]. Few data are available in the literature about such systems being used in high-temperature methane combustion. In our lab, Co/MgO was tried at different cobalt loading without much success [13].

In this work we will present catalytic data concerning Co supported on zirconia and lanthanum-doped zirconia. Their performances will be compared with previous data of our own and rate data reported by others. Through the use of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) the causes underlying the wide difference in performance reported in the literature will be explored.

2. Experimental

2.1. Catalyst preparation

Two different supports were used for the preparation of cobalt-containing catalysts: ZrO_2 (Degussa, 99.99%) and La-doped ZrO_2 (La_2O_3/ZrO_2). The latter was prepared by the wet impregnation of ZrO_2 with a solution of lanthanum acetylacetonate ($La(acac)_3$) in anhydrous THF, evaporating the resulting suspension in an oven at 380 K for 12 h. The dry solid was calcined in air at 770 K for 4 h. The final content of lanthanum was 9.6 wt% La. Commercial La_2O_3 (Anedra, 99.99%) was used as a reference support.

Cobalt was incorporated to these supports using two different techniques: ALE (atomic layer epitaxy) and wet impregnation. For the application of the ALE method, a flow-type reactor operated at low pressure ($P \approx 1330\ \mathrm{N\,m^{-2}}$) was designed and built. Cobalt acetylacetonate ($Co(acac)_3$) was sublimed and chemisorbed at 440 K for 1 h on the surface of the support (preheated at 770 K) using N_2 as carrier, following a purge with N_2 at 440 K. Then, calcination at 770 K for 1 h in air yielded the oxide species on the surface of the support. This reaction cycle was repeated several times in order to increase the amount of

Table 1
Prepared cobalt-containing catalysts.

Catalyst[a]	Support	Preparation method[b]	Surface area ($m^2\,g^{-1}$)	Surface ratio Co/(La + Zr)[c]
Co(0.95)ZrO_2	ZrO_2	ALE[3]	30 ± 3	0.12
Co(1.9)ZrO_2	ZrO_2	ALE[5]	30 ± 3	0.14
Co(1.9)/ZrO_2	ZrO_2	Wet impregnation	30 ± 3	0.13
Co(0.90)La/ZrO_2	La_2O_3/ZrO_2	ALE[3]	30 ± 3	0.12
Co(1.8)La/ZrO_2	La_2O_3/ZrO_2	ALE[5]	30 ± 3	0.15
Co(3.3)/La_2O_3	La_2O_3	Wet impregnation	13 ± 3	0.25
$LaCoO_3$[d]	–	Explosion	6	0.70

[a] For supported catalysts, the numbers between parentheses indicate cobalt percentage by weight. A slash preceding the support indicates wet impregnation while no slash means that the atomic layer epitaxy (ALE) technique was used.

[b] Values in brackets indicate the number of ALE reaction cycles.

[c] Calculated from XPS data (see text).

[d] Bulk oxide [12].

cobalt on the surface of the support. Kytökivi et al. [14] and Jacobs et al. [15] have provided more details about the ALE technique for the preparation of supported catalysts. When cobalt was incorporated by wet impregnation, $Co(acac)_2$ was dissolved in isobutyl alcohol. After impregnation the solid was dried at 380 K for 12 h followed by calcination in air at 770 K for 4 h.

Table 1 shows, in the first column, the prepared catalysts: values in parentheses correspond to the weight percentage of cobalt determined by atomic absorption. For supported systems, a slash preceding the support indicates the use of the impregnation method, and no bar indicates the use of the ALE technique.

Bulk perovskite $LaCoO_3$ was prepared by the explosion method [16], by mixing an equimolar solution of the corresponding metal nitrates (total concentration 0.9 M) with a 1 M citric acid solution. The resulting solution was dried in an oven at 380 K for 10 h in order to obtain a highly porous precursor, which was pressed with benzoic acid to form a pellet containing a filament. The pellet was burned in a calorimetric bomb, loaded with oxygen. After ignition, a porous and expanded solid was obtained. For comparison, $La_2O_2CO_3$ was also prepared by the explosion method but beginning with lanthanum acetate as organic precursor. More details about the explosion method have been given elsewhere [16].

2.2. Characterization

All the catalysts were calcined in air at 970 K for 4 h prior to being characterized and/or evaluated for the combustion of methane. 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 $1^\circ\,min^{-1}$. The BET surface area was determined by N_2 adsorption in a Quantachrome Nova 1000 sorptometer. The amount of carbonate/oxycarbonate retained by the solids was estimated using a TPR system (Okhura TS-2002). The solids were first reduced using 5% of hydrogen in argon and covering the 320–1170 K range. In this first run, H_2 was consumed to reduce both cobalt and the carbonates. Afterwards, this solid was reoxidized *in situ* and reduced again with the same routine. The difference in H_2 consumption between the first and the second TPR experiment gives a fair estimation of the amount of carbonates present in the solid.

The XPS spectra were obtained at room temperature with a Shimadzu ESCA 750 instrument, using Al K_α radiation. The binding energies were corrected considering the value of 284.9 eV for the C 1s signal of the contamination carbon. XPS intensity ratios were calculated using the integrated areas of the Co $2p_{3/2}$ and La $3d_{5/2}$ photoelectron lines (including the satellite peaks), and the sum of the overlapped integrated areas of Zr $3d_{5/2}$ and Zr $3d_{3/2}$ signals. The integrated areas were corrected using the Scofield photoelectron cross-sections.

2.3. Catalytic measurements

The solids were tested in a packed-bed tubular quartz reactor (i.d. 8 mm) with a 2 mm o.d. thermowell. 0.050 g of catalyst were placed on a fritted quartz disk and covered by quartz wool. Mass flow controllers were used to feed the reactants. The gas mixture consisted of 3 vol% methane, 7.2 vol% oxygen and nitrogen balance. The total volumetric gas flow varied between 50 and 800 $cm^3\,min^{-1}$ (STP). The products were analyzed with an on-line gas chromatograph using a Porapak Q column and a thermal conductivity detector (TCD).

To evaluate the contribution of the homogeneous reaction, the reactant mixture was flowed through the quartz wool packed reactor. At 970 K there was no detectable methane conversion (the detection limit of our system is 0.2% CH_4 conversion). The carbon balance indicates that, under our experimental conditions, the methane combustion only yields carbon dioxide. Thus, the methane conversion was calculated as the ratio between carbon dioxide concentration and the sum of methane and carbon dioxide concentrations (carbon compounds) at the reactor outlet. By operating our reactor in a differential mode, it was possible to obtain the reaction rates for all the catalysts considering at least three data points. In all cases the catalysts were tested at temperatures between 770 and 970 K. No deactivation was observed by repeating the temperature cycle at least once. The rate data is reported at 770 K.

3. Results

3.1. Catalytic activity

The catalytic behavior of our own catalysts is presented in table 2 in terms of the reaction rate values obtained at 770 K and with a composition feed consisting of 3% CH_4, 7.2% O_2 and nitrogen balance. Rates were calculated as

$$v = \frac{aX_{CH_4}F_{CH_4}}{mS},$$

where a is a constant, X_{CH_4} the methane conversion (values $<10\%$ X_{CH_4} were used), F_{CH_4} the CH_4 volumetric flow, m the catalyst mass and S the specific area of the catalyst.

According to the criteria proposed by Carberry et al. [17] and Farrauto et al. [18], it was concluded that inter- and intraphase concentration and temperature gradients were negligible in all cases. The calculated activation energy values (23–29 kcal mol^{-1}) are consistent with the absence of both mass and heat transfer effects.

Table 2 also shows the catalytic behavior of several other cobalt-containing oxides reported in the literature. To make a suitable comparison with our data, the rate data reported by others were corrected by temperature and reactant composition. The activation energies (table 3) and rate laws provided in each work were used to normalize all the rate data to 770 K and our reactant partial pressures. The criteria used in each case including those cases in which the above information was partially missing are explained below.

Spretz et al. [13] proposed the following expression for the reaction rate for cobalt supported on MgO:

$$v = \frac{kK_1Lp_{CH_4}p_{O_2}}{(1 + K_1p_{O_2})},$$

where L is the total surface density of active sites, k is the surface reaction rate constant and K_1 the oxygen adsorption equilibrium constant.

Table 2
Catalytic activities for the combustion of methane at 770 K.[a]

Catalyst	Reaction rate		Ref.
	(μmol s^{-1} m^{-2}) × 10^2	(μmol s^{-1} g^{-1}) × 10^2	
Supported			
Co(0.95)ZrO_2	47	1410	This work
Co(1.9)ZrO_2	66	1980	This work
Co(1.9)/ZrO_2	10	300	This work
Co(0.90)La/ZrO_2	29	870	This work
Co(1.8)La/ZrO_2	32	960	This work
Co(3.3)/La_2O_3	5.4	70	This work
Co(12)/MgO[b]	4.0	–	[13]
Supports			
La_2O_3/ZrO_2	3.4	102	This work
La_2O_3	2.1	27	This work
$La_2O_2CO_3$	3.6	14	[12]
ZrO_2	0	0	This work
MgO	0	0	[13]
Bulk			
$LaCoO_3$	4.3	26	[12]
$LaCoO_3$[b]	–	13	[20]
$LaCoO_3$	48.3	169	[8]
$PrCoO_3$	1.7	9	[8]
$NdCoO_3$	64.4	103	[8]
$GdCoO_3$	68.4	144	[8]
$La_{0.75}Sr_{0.25}CoO_3$[b]	18.6	–	[19]
$La_{0.50}Sr_{0.50}CoO_3$[b]	57.6	–	[19]
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$	19	361	[10]
$La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$	11	89	[10]
$BaMnAl_{11}O_{19-\alpha}$	7.4	202	[21]
$SrMnAl_{11}O_{19-\alpha}$	14.1	227	[21]
$LaMnAl_{11}O_{19-\alpha}$	19.7	377	[21]
Single oxide			
Co_3O_4	486.5	3308	[19]

[a] In our data reactant composition is: 3 vol% CH_4 and 7.2 vol% O_2. Data from literature was extrapolated to these conditions (see text).

[b] Rate data reported by the authors (no surface area data were provided).

Table 3
Activation energies of the solids for the catalytic combustion of methane.

Catalyst	Activation energy (kcal mol^{-1})	Temperature range (K)	Ref.
Supported			
Co(1.9)ZrO_2	23	750–800	This work
Co(1.9)/ZrO_2	26	750–800	This work
Co(0.90)La/ZrO_2	29	770–820	This work
Co(12)/MgO	Not given		[13]
Bulk			
$LaCoO_3$	Not given		[12]
$LaCoO_3$	Not given		[20]
$LaCoO_3$	24.8 ± 0.2^a	770–870	[8]
$PrCoO_3$	26.3 ± 2.4^a	1025–1075	[8]
$NdCoO_3$	24.6 ± 0.5^a	770–825	[8]
$GdCoO_3$	23.6 ± 0.5^a	770–870	[8]
$La_{0.75}Sr_{0.25}CoO_3$	19.3^b	∼900	[19]
$La_{0.50}Sr_{0.50}CoO_3$	16.7^b	∼900	[19]
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$	22	670–870	[10]
$La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$	25.1^c	650–920	[10]
$BaMnAl_{11}O_{19-\alpha}$	17.4^d	720–770	[21]
$SrMnAl_{11}O_{19-\alpha}$	20.2	620–720	[21]
$LaMnAl_{11}O_{19-\alpha}$	19.6	620–720	[21]
Single oxide			
Co_3O_4	15 ± 0.5^b	650–800	[19]

[a] Apparent activation energies calculated by the authors at conversions below 10%.
[b] Effective activation energies calculated by the authors from the temperature-programmed reaction curves in the low (<15%) conversion regions.
[c] Overall apparent activation energy.
[d] We have estimated this value from given conversion data at 723 and 773 K.

Baiker et al. [8] studied the influence of the A-site cation in the activity of the cobalt-containing perovskite ($ACoO_3$, A = La, Pr, Nd and Gd), employing a reactant feed consisting of 1% CH_4 and 4% O_2. The authors did not report the rate law for their systems; thus, we decided to use the pressure dependencies given by McCarty and Wise [19] for $La_{1-y}Sr_yCoO_3$, i.e., $p_{O_2}^{0.5}$ and p_{CH_4}.

Klavana et al. [10] studied $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ and $La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$. They found that the rate of combustion over the first catalyst was well described by a first-order kinetic model for temperatures lower than 950 K in methane lean mixtures. In contrast, they found that for the second catalyst, the rates of combustion were fitted by the following equation:

$$v = \frac{k_1 p_{CH_4} k_2 p_{O_2}^n}{(2k_1 p_{CH_4} + k_2 p_{O_2}^n)},$$

where $n = 1.6$ and k_1 and k_2 are the specific rate constants.

O'Connell et al. [20] studied the perovskite $LaCoO_3$, while Marcelin and coworkers [21] worked with Mn-substituted hexaaluminates. In no case were data reported on the pressure dependence of the reaction rate; accordingly, we corrected their rate values as we did for the $ACoO_3$ perovskites of Baiker et al. [8].

There are also a few other references whose catalytic data cannot be used because no information is given to calculate rates under our reaction conditions.

For cobalt supported systems there is a clear division of the catalysts into two groups, one being about ten times more active than the other (table 2). The one being more active includes cobalt supported on ZrO_2 and La-doped ZrO_2 while the less active group includes cobalt supported on lanthana and MgO. Note that our own $LaCoO_3$, La_2O_3, $La_2O_2CO_3$ and La_2O_3/ZrO_2 also belong to the second group.

Other features observed in table 2 are: (i) the discrepancy in the rate data obtained from three different sources for $LaCoO_3$, (ii) the enhanced activities of Sr-containing cobaltates, and (iii) the rate data belonging to three substituted β-aluminates shown for comparison with our best supported catalysts. The reaction rates per gram are also given to better ascertain the potentiality of the catalysts compared in this work.

Table 3 collects the activation energies obtained by us and reported by the authors whose rate data are included in table 2. Note the wide variation in activation energies in going from Co_3O_4 (15 kcal mol^{-1}) to Co(0.90)La/ZrO_2 (29 kcal mol^{-1}). However, the activation energies of the best catalysts (rows 1, 3 and 17) indicate that no major changes in rate order will be observed at temperatures higher than 770 K.

Let us now see if the characterization data obtained by us and/or provided by others can help understand the causes underlying this widely distinct behavior of cobalt in different matrixes.

3.2. X-ray diffraction patterns

La_2O_3 contains $La_2O_2CO_3$ and $La_2O_2CO_3$ has La_2O_3 as a segregated phase. Both the monoclinic and the tetragonal phases are shown in the XRD patterns of ZrO_2. In the case of La-doped zirconia, there appear those phases detected for zirconium and lanthanum oxides but no mixed oxide phase, such as $La_2Zr_2O_7$, was detected.

In the case of cobalt supported by the impregnation method on La_2O_3 (Co(3.3)/La_2O_3), both the $LaCoO_3$ perovskite and Co_3O_4 reflections appear together with those of the support. But for cobalt supported on ZrO_2 or La-doped ZrO_2, the XRD patterns do not show any cobalt compound.

The XRD patterns of $LaCoO_3$ calcined in air at 1220 K for 10 h show the perovskite structure and small amounts of La_2O_3, but no cobalt oxides reflections were detected.

Table 1 presents the BET surface areas of the prepared catalysts. La_2O_3 and $La_2O_2CO_3$ have 13 and 4 m^2 g^{-1}, respectively. For both ZrO_2 and La-doped ZrO_2, the surface area is 30 m^2 g^{-1}. These values did not change after cobalt impregnation and calcination at 970 K. In the case of $LaCoO_3$ perovskite, the surface area is 6 m^2 g^{-1}.

3.3. XPS results

The fourth column of table 1 gives an idea of the exposure of cobalt on the solid surface. For cobalt supported on

Table 4
XPS binding energy values (eV).[a]

Catalyst	Signal			
	Co $2p_{3/2}$	La $3d_{5/2}$	Zr $3d_{5/2}$	C 1s[b]
Co(0.95)ZrO_2	782.1	–	182.6	286.2[c]
Co(1.9)ZrO_2	782.7	–	183.5	286.5[c]
Co(1.9)/ZrO_2	782.7	–	183.5	286.1[c]
Co(0.90)La/ZrO_2	782.1	835.2	182.7	285.9–287.5[d]
Co(1.8)La/ZrO_2	782.0	835.2	182.8	285.9–287.5[d]
Co(3.3)/La_2O_3	780.6	835.1	–	286.2–290.0[e]
$LaCoO_3$	779.7	833.6–835.6	–	289.3[e]
La_2O_3/ZrO_2	–	835.2	182.5	285.9[d]
La_2O_3[f]	–	835.4	–	288.4–289.6
$La_2O_2CO_3$[f]	–	835.4	–	288.4–289.6
ZrO_2	–	–	182.4	–
Co_3O_4[g]	782.0	–	–	–

[a] BE values were referred to the carbon contamination C 1s signal at 284.9 eV.

[b] The reference signal is not included in this column.

[c] No carbonates are detected by TPR.

[d] Bulk carbonates are present in La_2O_3/ZrO_2-supported oxides (estimated amount is 0.3 wt% ($La_2O_2CO_3 + La_2(CO_3)_3$)).

[e] For La_2O_3-supported oxides the estimated amount of bulk carbonates is 4 wt% ($La_2O_2CO_3 + La_2(CO_3)_3$).

[f] [12].

[g] [22].

ZrO_2 and La-doped ZrO_2, the Co/(La + Zr) ratio is almost constant (0.12–0.15). Note that cobalt supported on La_2O_3 by wet impregnation exhibits the highest ratio (0.25) of the supported catalysts whereas for the perovskite, the Co/La ratio is smaller than the stoichiometric one (0.7 vs. 1).

Considering cobalt supported on ZrO_2 and La-doped ZrO_2, table 4 shows a shift in the binding energy values of Co and Zr in two cases (Co(1.9)ZrO_2 and Co(1.9)/ZrO_2). This indicates an interaction between these two elements on their surfaces. Co $2p_{3/2}$ in $LaCoO_3$ exhibits a lower BE as expected from previous results [12]. Co(3.3)/La_2O_3, which contains the perovskite (XRD results), shows an intermediate Co $2p_{3/2}$ BE value. XPS is undoubtedly useful to confirm the presence of $LaCoO_3$ in the upper layers of supported cobalt catalysts. However, the detection limit of this technique is not known.

The BE of La $3d_{5/2}$ is the same for all the prepared samples (within the experimental error), except in the case of the $LaCoO_3$ perovskite. In this case there are two overlapping doublets that contribute to this signal. The lower BE signal corresponds to the perovskite and the other, to La carbonated species [12]. This is consistent with the presence of surface carbonates, which also appear in all the oxides listed in table 4, except for ZrO_2 and Co_3O_4. Note, however, that the TPR technique is not able to detect the presence of carbonated species on the solids not containing lanthanum. On the other hand, the amount of carbonated species increases in going from La-doped zirconia to both La_2O_3 and $LaCoO_3$. This observation is entirely consistent with the XRD patterns described above.

The XPS data also reveal a sharp distinction between the two groups of catalysts we prepared. Co^{2+} is detected on all the Co(x)ZrO_2 and Co(x)La/ZrO_2 solids while this species is not seen on Co(3.3)/La_2O_3 and $LaCoO_3$.

4. Discussion

Table 2 shows that the best catalysts on a mass basis are those supported on ZrO_2 or La-doped ZrO_2. When the rate is expressed per unit area there are massive perovskites and hexaaluminates that yield activities similar to the supported catalysts. All this is strictly true at 770 K, but the activation energies reported in table 3 indicate that this trend is maintained at higher temperatures.

There are roughly two orders of magnitude of difference in reaction rates in the data gathered in table 2. What is the origin of this wide difference in catalytic behavior? There is of course no single answer to this question. By comparing several subsets of rate data and with the help of the characterization data we can find some clues to better understand these systems.

Let us first take a look at the rate data of our bulk $LaCoO_3$, La_2O_3, $La_2O_2CO_3$ and Co(3.3)/La_2O_3. All of them exhibit strong C 1s carbonate and/or oxycarbonate signals (table 4). Furthermore, their activities are practically all the same (table 2), although $LaCoO_3$ and Co(3.3)/La_2O_3 present the perovskite structure by XRD. These two solids have surface Co^{3+} and show Co $2p_{3/2}$ BE around 780 eV (Co^{2+} being absent from their surfaces). Besides, for these two solids, the La $3d_{5/2}$ spectra have the contributions of both La belonging to the perovskite lattice (833.6 eV) and La associated to La carbonated species (835.6 eV). For La_2O_3 and $La_2O_2CO_3$, the broad La $3d_{5/2}$ signal appearing at 835.4 eV would probably have the contributions of both La_2O_3 and La carbonated species. All these indicate that $LaCoO_3$ perovskite is present in the upper layers of both $LaCoO_3$ and Co(3.3)/La_2O_3.

Considering that differences between bulk and surface composition are often encountered in perovskites [12], and the great affinity of CO_2 towards La_2O_3, this leads us to envisage all these solids covered by a thin layer of lanthanum carbonate that is "seen" by the reacting molecules. As a matter of fact lanthanum oxycarbonate is stable up to 1050 K [23]. The presence of surface carbonates on $LaCoO_3$ of a similar nature as those observed for lanthana is further documented elsewhere [12]. In brief, although the $LaCoO_3$ perovskite is present on the surfaces of both Co(3.3)/La_2O_3 and $LaCoO_3$, the outmost atomic surface layers of these solids would be probably covered by lanthanum carbonated species responsible for their catalytic behavior.

Looking at table 2, one wonders why Co(12)/MgO with 12 wt% of Co is a poor catalyst. The reason is probably related to the preparation method [13], which leads to the formation of the (MgCo)O solid solution (detected by XRD [24]). This strong interaction between Co and MgO seems to impair the redox ability of cobalt thus decreasing its oxidation performance.

Table 2 shows widely different reaction rates for $LaCoO_3$ of different origin. The explanation of this discrepancy comes, however, from the presence of segregated Co_3O_4 detected for the most active $LaCoO_3$ perovskites. Baiker et al. [8] reported that their lanthanum cobaltates contained Co_3O_4 as segregated phase (about 7 wt%) detected by TPD of oxygen. These proportions are more than enough to explain the high activity of their solids if we consider the high activity of Co_3O_4 (right bottom part of table 2). O'Connell et al. [20] found in the corresponding XRD patterns the presence of 0.4 mol% Co_3O_4 impurity ($\sim$0.4 wt% Co_3O_4). Note that the smaller the amount of Co_3O_4 segregation, the lower the activity of $LaCoO_3$ perovskite. In our sample we could not see any traces of Co_3O_4 in the XRD patterns. On the other hand, O'Connell et al. [20] considered that lanthana exposed on the surface of $LaCoO_3$ perovskite is explicitly related to their activity. However, they did not present any XPS data of their "single phase $LaCoO_3$". Thus the possibility of surface lanthana enrichment cannot be discarded. We think that this perovskite could present lanthana and probably carbonates on its surface, in a similar manner to our own $LaCoO_3$, which defines its catalytic behavior.

It is a well-known fact that the partial substitution of La by alkaline earth cations makes the lattice oxygen of the perovskite structure more labile and therefore more active for oxidation reactions [25]. Therefore, it is not surprising that the Sr-containing cobaltates exhibit such a high activity (table 2). But the stability of the Sr-containing catalysts is lower, due to a high loss in surface area [19]. Besides, the presence of Co_3O_4 cannot be discarded in the Sr-containing perovskites prepared by McCarty and Wise [19], or in the $ACoO_3$ perovskites prepared by Baiker [8] (A being Pr, Nd or Gd).

A closer look to the cobalt-supported catalysts (left-hand side of table 2) discloses some relevant features. The use of ALE led us to prepare the best Co-containing ZrO_2 and La-doped ZrO_2 formulations. Note the large difference in rates between Co(1.9)ZrO_2 and Co(1.9)/ZrO_2. The former prepared through ALE and the latter by wet impregnation. Neither of them shows Co_3O_4 crystallites. XPS did not show any difference between the two solids. The only reason for the difference in performance can be ascribed to the nature of the ALE process. The sublimed cobalt acetylacetonate reacts with surface hydroxyls leaving a layer of anchored Co-containing moieties that after calcination yield highly dispersed active species. In this manner, the ALE technique allows a uniform distribution of the active species on the surface of Zr-containing supports, as was expected from previous publications [14,15].

Since catalysts of cobalt supported on ZrO_2 by the ALE method appear to be more active than the analogous samples supported on La-doped ZrO_2, one could wonder about the role of doping ZrO_2 with lanthanum. The answer might be an enhanced stability of the systems containing lanthanum. Stability runs have to be made in order to elucidate the role of this rare earth in the performance of these active catalysts.

Marcelin and coworkers [21] stated that $LaMnAl_{11}O_{19-\alpha}$ may be a candidate for catalytic gas turbine combustors. In the same vein, Arai et al. [1], as well as Trimm [26] and Sadamori [27], also noted the good performance of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$. The comparison of the rate data for $LaMnAl_{11}O_{19-\alpha}$ and those reported for our Co(x)ZrO_2 and Co(x)La/ZrO_2 (table 2) clearly favor the latter formulations. All these systems are less active than Co_3O_4 but this oxide easily sinters above 800 K.

Although the rate comparisons have been made at 770 K (table 2), the activation energy data (table 3) confirm the previous statement. On the other hand, the large spread in activation energies may mask in some cases the presence of other phenomena. As the reaction temperature increases above ca. 770 K, thermal effects and catalytically initiated homogeneous gas-phase combustion [28] may become increasingly important. A more precise definition of the threshold temperature cannot be given because this is a function of reactant concentration, catalyst amount and activity, and reactor design. In our own measurements (table 3), we found that above 800–825 K the apparent activation energies increased sharply due to either or both of these phenomena. Thus, great care should be taken when reporting activation energies for methane combustion; the same applies to exothermic radical reactions.

5. Conclusions

The best Co-containing catalysts for methane combustion are obtained using the atomic layer epitaxy method starting from cobalt acetylacetonate and either ZrO_2 or La-doped ZrO_2.

Our best catalysts possess similar or higher activity than $LaMnAl_{11}O_{19-\alpha}$, which is pointed out as a good candidate for the catalytic combustion of methane.

The formation of very stable carbonates and oxycarbonates on the surface of lanthanum containing bulk mixed oxides has a negative impact in their catalytic activity. However, when ZrO_2 is doped with lanthanum this adverse effect is not observed.

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