ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 404 (2003) 177–186

thermochimica acta

www.elsevier.com/locate/tca

Thermal analysis of K(x)/La_2O_3, active catalysts for the abatement of diesel exhaust contaminants

V.G. Milt, C.A. Querini, E.E. Miró*

Instituto de Investigaciones en Catálisis y Petroquímica-INCAPE (FIQ, UNL-CONICET) Santiago del Estero 2829,
3000 Santa Fe, Argentina

Received 18 October 2002; received in revised form 14 February 2003; accepted 15 February 2003

Abstract

Potassium loaded lanthana is a promising catalyst to be used for the abatement of diesel exhaust pollutants. In this paper we have combined several thermal techniques to study relevant processes that take place during the soot combustion reaction. Temperature programmed oxidation (TPO) experiments show that with potassium loadings between 4.5 and 10 wt.% and calcination temperatures between 400 and 700 °C, these catalysts mixed with soot give maximum combustion rates between 350 and 400 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicate that the reaction coexists with the thermal decomposition of bulk hydroxide species. For the La_2O_3 solid, the $La(OH)_3 \rightarrow LaO(OH)$ and $LaO(OH) \rightarrow La_2O_3$ processes occur at ca. 360 and 500 °C, respectively, whereas the presence of K in the K(x)/La_2O_3 catalysts provokes a shift of these endothermic peaks to higher temperatures. In all the studied solids, oxycarbonates decompose in the 550–800 °C temperature range. On the other hand, *microbalance* results show that the bulk carbonate formation depends on both the potassium content and the calcination temperature. The High Frequency CO_2 Pulses technique is useful to study the dynamics of the CO_2 adsorption–desorption process and to characterize the surface basicity of the solids. When both La_2O_3 and K/La_2O_3 solids are calcined at 700 °C, a strong decrease on the CO_2–surface interaction takes place, which correlates with a small decrease in catalytic activity and with an increase in the K/La surface ratio. These effects may be originated, at least in part, by a decrease in oxygen vacancies concentration and a thermal dehydroxylation of the catalysts.

Keywords: Potassium-lanthana catalysts; Thermal analyses; Diesel exhausts; Soot combustion

1. Introduction

An active search has been under way in the last several years to find active catalysts for the abatement of diesel exhaust contaminants. The main pollutants emitted by this type of engine are soot particles and nitrogen oxides. The combination of traps and oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [1].

Studies with a large number of formulations have been reported during the last few years [2–7]. However, the reaction mechanism and therefore a rational catalyst design for this system have been scarcely addressed. In previous works [8–12] we reported results on Co and K catalysts supported on MgO, CeO_2, and La_2O_3. We found that K/La_2O_3 is a promising catalyst to be used for the abatement of diesel soot particles. These catalysts mixed with soot gave maximum combustion rates between 350 and 400 °C in

---

* Corresponding author. Tel.: +54-432-4536861;
fax: +54-432-4536861.
E-mail address: emiro@fiqus.unl.edu.ar (E.E. Miró).

0040-6031/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00155-2

the TPO experiments, showing a good hydrothermal stability.

Both the bulk and the surface of the K(x)/La_2O_3 solids display many changes depending upon pretreatments and reaction conditions. Temperature and exposure to water and carbon dioxide affect the degree of hydroxylation and carbonation of the solids under study. This study analyzes the impact of such changes on the activity for soot combustion.

In a previous work [10] we suggested that the soot combustion reaction occurs via a carbonate-type intermediate. Soot particles are oxidized to form carbonate species (most probably oxycarbonate) and afterwards these species are decomposed to form adsorbed CO_2 which is in turn released to the gas phase. The overall reaction is thus a combination of surface reaction, adsorption steps, and solid-phase transformations.

The aim of this work was to study these steps by combining different thermal techniques. K/La_2O_3 catalysts with different K loadings and pre-treatment temperatures were prepared and the soot combustion activity was determined by TPO experiments. The capacity of the catalysts to form oxycarbonate species was analyzed by adsorbing CO_2 in a Cahn microbalance. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods were applied to characterize the phase transformations of the catalyst against thermal treatments and reaction conditions. Finally, the dynamics of the CO_2 adsorption–desorption process was studied by the High Frequency CO_2 Pulses technique. This technique, which was first presented in a previous work [10], proved to be very sensitive to minor changes occurring at the surface of basic catalysts.

2. Experimental

2.1. Soot and catalysts preparation

The soot was obtained by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. More details about soot obtention and characterization are reported elsewhere [8]. After being collected from the vessel walls, it was dried in a stove at 120 °C for 24 h.

The K(x)/La_2O_3 catalysts were prepared by addition of a KOH solution (0.1N) to La_2O_3 (Alpha, 99.95%), in order to obtain $x = 4.5$, 7.5 or 10, where x represents the K weight percentage. The suspension was evaporated while being vigorously stirred until achieving a paste, which was dried in a stove at 120 °C for 24 h and then calcined either at 400 or at 700 °C for 2 h. After that, the solids were stored in containers under room conditions. The soot and the K(x)/La_2O_3 catalysts (1:20) were mixed during 3 min in an agate mortar.

2.2. Activity test

The catalytic activity of K(x)/La_2O_3 for the combustion of soot was determined by the temperature programmed oxidation (TPO) of the mixtures of soot and catalysts. A gaseous flow with 6% oxygen in nitrogen was used and the temperature was increased at a rate of 12 °C/min, using 10 mg of the catalyst + soot mixture. A modified TPO technique [13] was employed which consisted in passing the gases coming from the reactor through a methanation reactor, where CO and CO_2 were converted into CH_4. Afterwards, methane was continuously measured with an FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C.

2.3. Catalysts characterization

2.3.1. Calorimetric measurements

DSC experiments were performed in order to detect energy changes during the heating treatment of the catalysts or the catalyst + soot with synthetic air, from 25 to 600 °C, in a DSC821^{e} Mettler Toledo differential scanning calorimeter. Typically, 10 mg of each solid were placed in the sample holder inside an aluminum crucible, using an empty crucible in the reference holder. The heating rate was 10 °C/min and the airflow was 90 ml/min. The main objective of these experiments was to study the thermal decomposition processes that take place in these solids during the catalytic combustion of soot.

2.3.2. Thermogravimetric analyses (TGA)

The phase transformations of the catalysts during the heating treatments in air were further studied in Mettler Toledo TGA/SDTA 851 equipment. Usually, 10 mg of catalysts were heated from 25 to 900 °C at 10 °C/min in an air flow of 90 ml/min.

2.3.3. CO_2 adsorption: microbalance experiments

They were performed in Cahn 2000 equipment to study the capacity of CO_2 adsorption and carbonate formation for the solids studied. The sample was dried during 2 h at 400 °C in He stream and then cooled down to 70 °C, stabilizing the weight at this temperature (w). After this, CO_2 was fed and the temperature was maintained at 70 °C until no changes in weight were detected. Then, the catalyst was heated up to 490 °C at 5 °C/min, maintained at 490 °C for 10 min and then slowly cooled down to 70 °C. At this temperature, the feeding stream was changed to He, repeating the process above described with the He stream.

2.3.4. High Frequency CO_2 Pulses technique

It was carried out at different temperatures, by sending pulses of 0.135 μmol of CO_2 in He carrier every 10 s. Thermal treatments between pulse cycles were also carried out. Typically, the procedure was as follows: the catalyst was heated up to 500 °C at which a series of 20 pulses was sent. Then the temperature was decreased to 400 °C, at which a new series of pulses was performed, and then the temperature was decreased to 25 °C, for the final set of pulses in the first cycle. Following this first cycle of pulses a thermal treatment was performed, heating up to 700 °C. Afterwards, a new set of pulses was carried out at 500, 400, and 25 °C to complete the second cycle. In some cases, there were three or four cycles. The CO_2 was detected with an FID after methanation, as described above.

The CO_2 peak comes out of the cell with a distortion, depending on the interaction with the catalyst surface. The absence of a CO_2 peak at the cell outlet means that the interaction is too high, and on the opposite site, when the peak is sharp, there is no interaction at all. When several pulses are consecutively sent to the cell, the system might reach a pseudo steady state, with a constant amplitude of oscillation, as long as the adsorption–desorption process is fast enough.

2.3.5. X-ray photoelectron spectroscopy (XPS)

The XPS data were obtained at room temperature with a Shimadzu ESCA 750 instrument, using Mg Kα radiation. The anode was operated at 8 kV and 30 mA and the pressure in the analysis chamber was about 2×10^{-6} Pa during the spectrum collection. The binding energies were referred to the C 1s signal (284.6 eV). More experimental details are given elsewhere [14].

3. Results and discussion

3.1. Catalytic soot combustion with oxygen

The catalytic activity of the solids was studied using the TPO technique. It should be noted that the non-catalytic combustion occurs at ca. 600 °C. Fig. 1 shows the TPO profiles of $K(x)/La_2O_3$ catalysts ($x =$ 4.5, 7.5 and 10) calcined at 400 °C and mixed with soot. These catalysts display good activity for soot combustion, with a first maximum in the TPO profiles between 350 and 400 °C. Higher temperature peaks could be due to either the CO_2 retained on the catalyst (CO_2 is the product of the combustion of soot) or to the combustion of a fraction of soot.

As can be seen from this figure, there is no linear relationship between the K content and the catalytic activity. In the case of $x = 4.5$ and 7.5 the activity increases as the K content increases, as indicated by the first peak. Nevertheless, for $K(10)/La_2O_3$, the maximum is shifted to higher temperatures. These results show that not only is the K content important but also the ratio of La_2O_3 to K, since as we have previously proposed, both components play a role in the soot oxidation [10]. When the K content is too high (10 wt.% K), the role of La is masked.

In order to study the effect of the calcination temperature on the activity of the $K(x)/La_2O_3$ catalysts for the soot combustion, another aliquot of $K(4.5)/La_2O_3$ was calcined at a different temperature: 700 °C. The TPO curve (also shown in Fig. 1) indicates two differences in these profiles: the main peak is wider for the catalyst calcined at 700 °C and the second peak is shifted to higher temperatures. Nevertheless, the catalytic activity is essentially the same, thus meaning that the thermal treatment at 700 °C for 2 h does not significantly affect the catalytic performance of this solid.

3.2. Calorimetric experiments

The simple manipulation of La_2O_3 in air induces both its carbonation in bulk and its hydration [15,16]

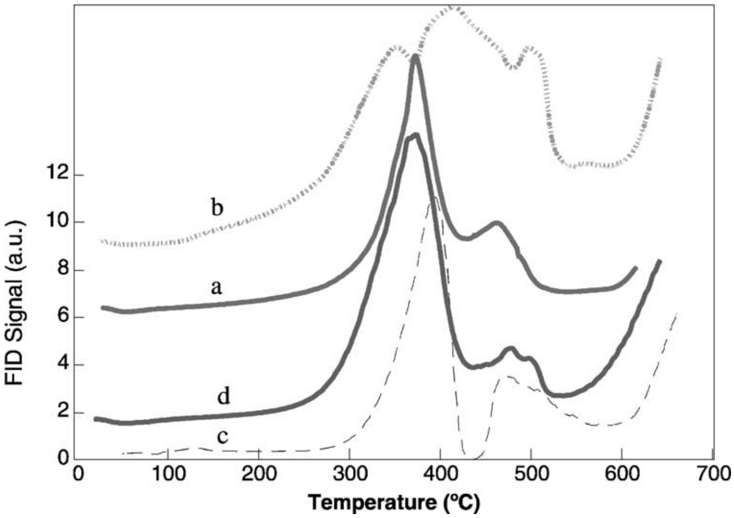

Fig. 1. TPO experiments of K(x)/La_2O_3 catalysts calcined at 400 °C. Gaseous feed: O_2 (6%) and He (balance). (a) $x = 4.5$ wt.% K, (b) $x = 7.5$ wt.% K and (c) $x = 10$ wt.% K. Effect of the calcination temperature: (d) $x = 4.5$ wt.% K, calcined at 700 °C.

so that in order to gain insight into this type of interaction and their role in the soot combustion reaction, DSC experiments were performed.

For comparison, before showing the DSC runs with K(x)/La_2O_3 catalysts mixed with soot in air, and in order to assign the observed signals, the profiles obtained with K/SiO_2, La_2O_3 and $La(OH)_3$ are shown in Fig. 2, including the one obtained for K(4.5)/La_2O_3. While the K(x)/SiO_2 sample shows almost a flat DSC pattern, several endothermic peaks are observed for La_2O_3 and $La(OH)_3$ samples. XRD results (not shown) revealed that the La_2O_3 support calcined at 400 °C and exposed to air is mainly composed of $La(OH)_3$ and $La_2O_2CO_3$ crystalline phases. Comparing the curves for both La_2O_3 and $La(OH)_3$ solids in Fig. 2, the peak at around 350 °C can be assigned to the dehydration of $La(OH)_3$ to LaO(OH) bulk species [17]. The smaller, higher-temperature peaks can be assigned to the $La_2(CO_3)_3$ decomposition to form $La_2O_2(CO_3)$, which typically starts at around 460 °C [18], in addition to the $LaO(OH) \rightarrow La_2O_3$ dehydration. All these assignments are in agreement with results obtained by Taylor et al. [17] concerning lanthanum phases detected for different starting materials (i.e. La_2O_3, $La(OH)_3$, $La_2O_2CO_3$ and $La_2(CO_3)_3$) as a function of temperature. For $La(OH)_3$ as starting solid, Taylor and Schrader [17] found the following phases: $La(OH)_3$ and [$CO_3{}^{2-}$] after heating at 200 °C; LaO(OH), [$La_2O_2CO_3$] and [La_2O_3] after heating at 400 °C; La_2O_3 and [$La_2O_2CO_3$] after heating at 600 °C. Minor phases are indicated between brackets. In the case of $La_2O_2CO_3$, no phase transformation occurred until 700 °C.

It should be pointed out that the absence of signals from the K species is not surprising, since KOH and K_2CO_3 are very stable compounds. KOH retains hydrogen without loss of water well past its melting point (360.4 °C) and K_2CO_3 does not begin to decompose appreciably until 1000 °C [19]. Moreover, we did not detect any change in mass until 900 °C when heating K(9)/SiO_2 in air during a TGA experiment.

Fig. 2 also shows the DSC experiment carried out on K(4.5)/La_2O_3 calcined at 400 °C. The main signal observed for the K(4.5)/La_2O_3 sample is an endothermic peak at ca. 380 °C, which can be safely assigned to the dehydration of hydroxy-type species like $La(OH)_3$ and LaO(OH). This peak is shifted to higher temperatures if compared with La_2O_3, probably due to the increase in surface basicity originated by the presence of potassium.

The DSC experiments performed on K(x)/La_2O_3 mixed with soot are shown in Fig. 3. The catalysts calcined at 400 and 700 °C exhibit exothermic and endothermic peaks. The former ones correspond to

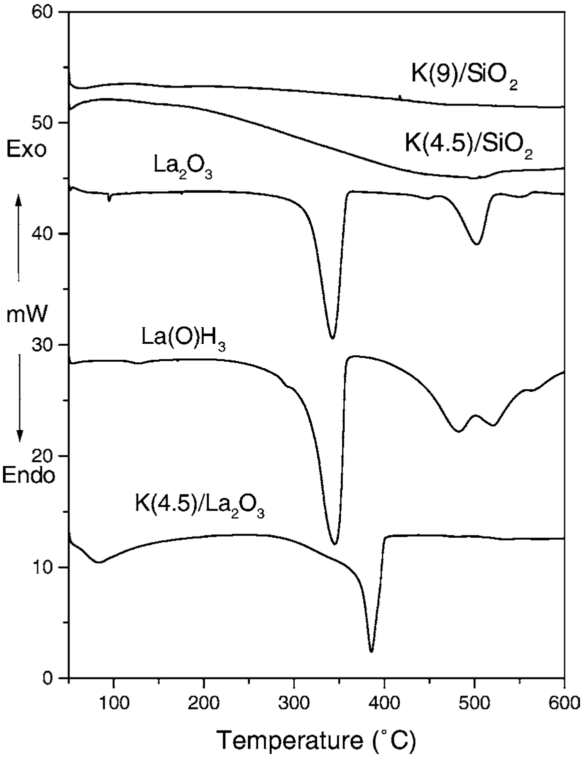

Fig. 2. DSC experiments with K/SiO$_2$, La$_2$O$_3$, La(OH)$_3$ and K(4.5)/La$_2$O$_3$ (calcined at 400 °C). Conditions: sample mass: 10 mg, atmosphere: air and heating rate: 10 °C/min.

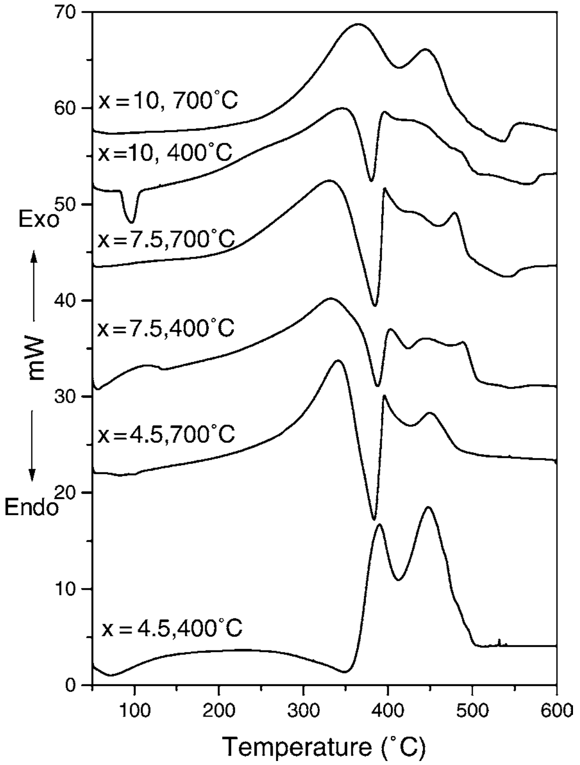

Fig. 3. DSC experiments with the different K(x)/La$_2$O$_3$ solids (calcined at 400 and 700 °C) + soot (20:1). Conditions: sample mass: 10 mg, atmosphere: air and heating rate: 10 °C/min.

the combustion of different fractions of soot and the latter to dehydrations and bulk carbonate decomposition. The strong endothermic signal observed at around 380–400 °C corresponds to the dehydration of La hydroxide species. The behavior observed for the K(7.5)/La$_2$O$_3$ and K(10)/La$_2$O$_3$ is similar to that of K(4.5)/La$_2$O$_3$, the only difference being the wider exothermic peaks in the case of the higher K loading when they are mixed with soot.

An important finding from DSC experiments is that the strong endothermic peak at about 380–400 °C overlaps with the soot combustion exothermic signal (see Figs. 2 and 3). The same endothermic peak is observed in the DSC experiments with K(4.5)/La$_2$O$_3$, La$_2$O$_3$ and La(OH)$_3$ not mixed with soot (Fig. 2). Also, carbonate species are decomposed at around 500 °C. This indicates that a very complex process occurs during the soot combustion reaction, since the catalytic phenomenon coexists with phase transformations by which bulk and surface hydroxide and carbonate species are thermally decomposed.

3.3. *Thermogravimetric analyses (TGA)*

As shown in the previous section, the system under study is very sensitive to CO$_2$ exposure. To further study the phase transformations detected by the energy changes in the DSC experiments, TGA runs were performed. Moreover, the TGA equipment employed allowed higher temperatures than the DSC (900 °C versus 600 °C, respectively).

The corresponding thermograms for the K(x)/La$_2$O$_3$ solids calcined at 400 °C are shown in Fig. 4 (for the solids calcined at 700 °C similar thermograms, not shown, were obtained). A small decrease in weight from room temperature to ca. 200 °C was observed due to physically-adsorbed water on the La$_2$O$_3$ surface. The weight loss observed between 300 and

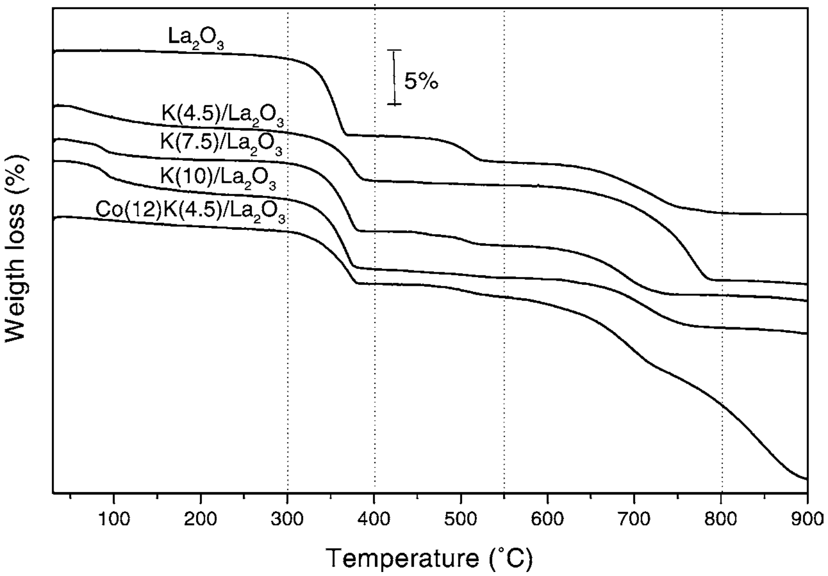

Fig. 4. Thermogravimetric analyses for the K(*x*)/La_2O_3 catalysts. Conditions: sample mass: 10 mg, atmosphere: air and heating rate: 10 °C/min.

400 °C (first step) corresponds to the $La(OH)_3 \rightarrow LaO(OH)$ dehydration, in accordance with the DSC results. The oxyhydroxide decomposes to form La_2O_3 in the 400–550 °C temperature range (second step), in agreement with results reported by González-Cortés et al. [20], who observed this transformation between 460 and 570 °C. This second step can be clearly observed in the La_2O_3 catalyst, whereas K/La_2O_3 catalysts show a negligible phase transformation in this temperature range, as has also been observed in the DSC experiments (see Fig. 2). Finally, the last weight loss step observed for the K(*x*)/La_2O_3 catalysts (third step) appears between 550 and 800 °C, and is associated with the thermal decomposition of carbonate species. XRD results revealed that $La(OH)_3$ and $La_2O_2CO_3$ were the main crystalline phases present in our samples, so that the last step in the TGA profiles would correspond to the $La_2O_2CO_3 \rightarrow La_2O_3$ transformation.

Table 1 shows the weight loss percentages for the K(*x*)/La_2O_3 catalysts calcined at either 400 or 700 °C for different temperature ranges, according to the different steps observed in the thermograms. Note that if the first (300–400 °C) and the second (400–550 °C) steps corresponded to the proposed dehydrations, the ratio between them would be 2.00. Nevertheless, the

Table 1
Quantitative results from TGA experiments: weight loss percentages

$x = 0$	$x = 4.5$	$x = 7.5$	$x = 10$	Temperature range (°C) with the main phase transformations
K(*x*)/La_2O_3 (400 °C)[a]				
6.97	4.46	6.27	6.39	300–400 $La(OH)_3 \rightarrow LaO(OH)$
2.33	0.38	1.21	0.79	400–550 $LaO(OH) \rightarrow La_2O_3$
4.55	8.61	4.55	4.47	550–800 $La_2O_2CO_3 \rightarrow La_2O_3$, $2KNO_3 \rightarrow K_2O + 2NO_2$
K(*x*)/La_2O_3 (700 °C)[a]				
8.49	7.89	7.08	6.17	300–400 $La(OH)_3 \rightarrow LaO(OH)$
3.29	1.01	1.52	0.31	400–550 $LaO(OH) \rightarrow La_2O_3$
2.95	6.07	2.94	2.62	550–800 $La_2O_2CO_3 \rightarrow La_2O_3$

[a] Values between parentheses indicate the calcination temperature and "*x*" indicates the weight percentage of potassium.

values found (Table 1) were higher than 2.00, this effect being more noticeable when K is present. This is probably due to adsorbed CO_2 on lanthanum oxide structural defects, in agreement with results obtained by González-Cortés et al. [20]. This surface carbonation would reduce the amount of hydroxide ions in the lanthanum hydroxide lattice, leading to the second step in the thermograms being lower than those expected from the dehydration process. Additionally, as shown below, these catalysts interact with CO_2, forming a surface carbonate-type intermediate which decomposes in the same temperature range. Therefore, the higher-than-2 ratio could be partially due to surface CO_2 desorption at temperatures below 400 °C. In this way, the surface of the $K(x)/La_2O_3$ catalysts would be partially covered by a hydroxycarbonate phase. Thus, in order to compare the different catalysts, the higher the value corresponding to the second step in the TGA runs, the higher the amount of $La(OH)_3$.

When potassium is incorporated in to La_2O_3, the basicity of the surface increases so that the $K(4.5)/La_2O_3$ solid adsorbs more CO_2 than La_2O_3. The adsorbed CO_2 diffuses inside the solid producing bulk La-carbonates (compare the files corresponding to the 550–800 °C temperature range of Table 1 for the solids calcined at 400 and 700 °C). When the potassium loading increases ($x \geq 7.5$), it tends to cover the catalyst surface (see Table 2, XPS results), so that the stable K_2CO_3 formed inhibits diffusion of the CO_2 in to the bulk of the solid.

It is now convenient to remember the effect of the calcination temperature on the catalytic activity of $K(4.5)/La_2O_3$: as the calcination temperature increased, the main peak in the TPO profile was wider and the second one was shifted to higher temperatures. Considering the results shown in Table 1, the higher the calcination temperature, the lower the carbonate content of the catalysts (compare the rows corresponding to the third step for both catalysts calcined at 400 and at 700 °C). Since carbonates are considered as intermediates in the reaction mechanism of the soot combustion [10] it can be suggested that this higher carbonate formation capacity would favor the activity of the catalysts, which is in line with our results.

Table 2
Effect of the calcination temperature on the potassium surface content

Catalyst	Calcination temperature (°C)	K/La[a]
$K(4.5)/La_2O_3$	400	0.75
	700	0.90
$K(7.5)/La_2O_3$	400	1.3
	700	2.70

[a] Determined by XPS analysis at room temperature with a Shimadzu ESCA 750 instrument, using Mg Kα radiation.

3.4. Microbalance studies: CO_2 adsorption

Microbalance experiments, where changes in weight were recorded versus temperature, allowed us to further study the interaction of the catalysts with CO_2. Fig. 5 represents the relative mass, i.e. the actual mass divided by w, where w is the weight value achieved after the treatment in helium up to 400 °C. The figure is divided into two parts by a dotted line: the left part corresponds to the CO_2 stream, and the right one to the He stream. The slow cooling in CO_2 produces the discontinuity observed for each curve before and after the dotted line. Neither the cooling in the CO_2 stream nor the cooling in the He stream is represented.

For the $K(4.5)/La_2O_3$ catalyst calcined at 400 °C, there is an increase in weight as the heating in the CO_2 stream progresses, and moreover, after the cooling in CO_2, the achieved weight is still higher than that obtained at 490 °C (note the discontinuity of the graph at both sides of the dotted line). This indicates that equilibrium is not reached and CO_2 continues diffusing and forming carbonates during the cooling-down step. It should be remarked here that both La and K are able to react with CO_2 to form the corresponding carbonate species. As the calcination temperature increased, the interaction of $K(4.5)/La_2O_3$ with the carbon dioxide followed the same trend. Note that for the $K(4.5)/La_2O_3$ catalyst, the higher the amount of $La(OH)_3$ present in the catalyst (i.e. the higher the value of the second step in the thermograms, Table 1), the higher the interaction with CO_2. It can also be observed that the weight loss begins at or below 400 °C in He which means that carbonate decomposition is effectively taking place at this temperature.

In the case of $K(7.5)/La_2O_3$, for the lower calcination temperature (400 °C), the tendency of the curve shows a higher interaction with CO_2 when the K loading is higher. Nevertheless, a completely different behavior is observed when this catalyst was calcined at

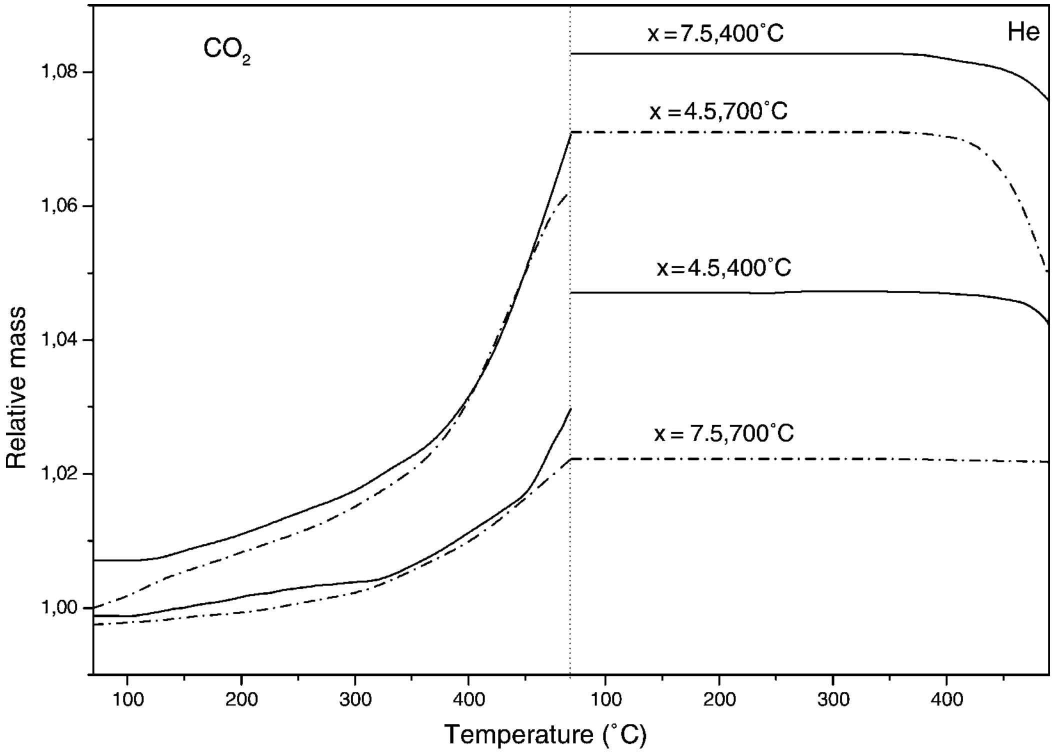

Fig. 5. Microbalance experiments for K(4.5)/La_2O_3 and K(7.5)/La_2O_3 (calcined both at 400 and 700 °C), treated with flowing CO_2 and He.

700 °C: the interaction of this catalyst with the carbon dioxide is the lowest observed for the studied solids. Now it is convenient to remember the potassium surface concentrations observed by XPS (Table 2): note that for the three upper curves which appear in Fig. 5, the interaction with CO_2 is higher when the surface K concentration is increased. However, in the case of the K(7.5)/La_2O_3 solid calcined at 700 °C, the surface K/La ratio is 2.7, a very high value compared with the others appearing in Table 2. It means that when the potassium surface concentration is too high, the potassium tends to cover all the catalyst surface and the surface K_2CO_3 inhibits the migration of CO_2 inside the lanthanum lattice to form bulk carbonates. A similar conclusion was obtained in TGA experiments. Also, the activity results indicate that when the potassium loading was too high (10 wt.% K) the activity of the K(x)/La_2O_3 catalyst decreased. This result is in agreement with the synergetic effect between La_2O_3 and K, having an optimal composition regarding catalyst activity.

3.5. CO_2 pulses experiments

The dynamics of the CO_2 adsorption–desorption process was studied with this technique. On pure La_2O_3, a strong interaction between CO_2 and the support is observed at 500 °C. However, when the solid is calcined at 700 °C prior to the pulses, the interaction decreases.

Fig. 6 shows the profiles obtained for K(4.5)/La_2O_3 in four consecutive series of CO_2 pulses at 400 and 500 °C, with heating up sequences to 700 °C between them. The promotion of lanthana with potassium increases the interaction with CO_2. The same was found in MgO [10] and CeO_2 [11] using a single pulse technique. The pulses at 500 °C show the very strong interaction between the catalyst and CO_2, a larger number of pulses than in the case of pure La_2O_3 being necessary to approximate the pseudo steady state. After heating up to 700 °C (sequence 2), the interaction strongly decreases as in the case of pure La_2O_3. This effect correlates with a small decrease in catalytic

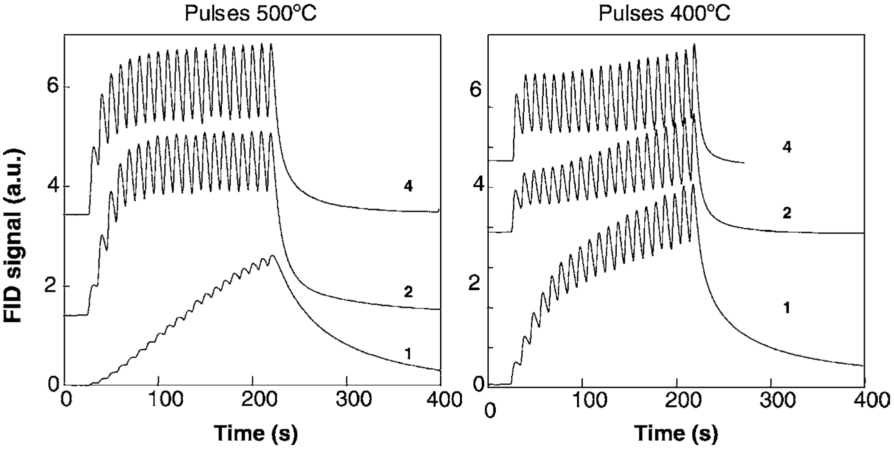

Fig. 6. High Frequency CO_2 Pulses with K(4.5)/La_2O_3 catalyst. Numbers 1, 2 and 4 indicate the first, second and fourth cycles, respectively.

activity for soot combustion (see Fig. 1) and with an increase in the K/La surface ratio (see Table 2) and it is probably originated in the decomposition of hydroxyl groups [21] which results in a lower basicity of the catalyst. It must also be considered that the formation of a solution between an alkaline metal and La_2O_3 is endothermic [22]. Therefore, upon high temperature treatments, a limited solubility might occur. Since the oxygen vacancies increase with the increase in solubility, the effect of a high temperature treatment could result in changing the oxygen vacancy concentration [22] and, therefore, the interaction with CO_2.

Since both potassium and lanthanum strongly interact with CO_2 (at temperatures as high as 500 °C) to form carbonate-type species, the CO_2 adsorption–desorption process must play an important role in the soot combustion mechanism. In a previous work [10] we suggested that the soot combustion reaction probably occurs via a carbonate-type intermediate, formed by the consumption of carbon from the soot, which decomposes releasing CO_2. This suggests the role that La_2O_3 plays in the reaction rate, associated to the formation of a carbonate-type intermediate. Since the activity of the active component (potassium) is modified by the support, it is important that the carbonate-type intermediate formed due to the interaction between CO_2 and the support decompose at the reaction temperature. Otherwise, the surface of the support would be irreversibly deactivated due to the formation of such carbonate.

4. Conclusions

Potassium loaded La_2O_3 catalysts calcined at 400 and 700 °C and mixed with soot are active and thermally stable, burning the soot at TPO maximum rates between 350 and 400 °C.

DSC results indicate that on K(x)/La_2O_3 catalysts the soot combustion reaction coexists with the thermal decomposition of hydroxide and carbonate species, occurring in the same temperature range (350–460 °C). The presence of potassium increases surface basicity shifting the endothermic decomposition signal to higher temperatures.

TGA experiments show that for the K(x)/La_2O_3 solids the $La(OH)_3 \rightarrow LaO(OH)$ dehydration occurred between 300 and 400 °C. The oxyhydroxide decomposes to form La_2O_3 in the 400–550 °C temperature range. Finally, the last weight loss step observed for the K(x)/La_2O_3 catalysts appeared between 550 and 800 °C and corresponded to the thermal decomposition of carbonate species ($La_2O_2CO_3 \rightarrow La_2O_3$ transformation).

Microbalance results show that the bulk carbonate formation depends on both the potassium content and the calcination temperature. The loading of La_2O_3

with 4.5 wt.% of K results in a partial coverage of the surface increasing the surface bacisity and the capacity of the solid to form bulk oxycarbonates. However, higher surface coverage (obtained by higher potassium loadings or high calcination temperature) results in an inhibition of this capacity.

Interactions of the catalytic surface with CO_2 were investigated using a new surface characterization technique, namely High Frequency CO_2 Pulses. This technique proved to be very useful to verify the stability of the surface to thermal treatments. A strong decrease of the CO_2–surface interaction was observed when the solids were treated at 700 °C. This interaction decreased together with a small decrease in the catalytic activity (as observed by TPO experiments) and with an increase in the K/La surface ratio (as observed by XPS characterization), may have originated, at least in part, in both a change in oxygen vacancy concentration and a thermal dehydroxylation of the catalyst surface. The dynamics of the CO_2 adsorption–desorption process at the reaction temperature is fast enough to allow the carbonate-type intermediate to be formed and decomposed, providing a reaction path for soot combustion.

Acknowledgements

The financial support received from ANPCyT (PICT 14-6971) and from Universidad Nacional del Litoral (CAI + D Program) is acknowledged. Prof. Elsa I. Grimaldi assisted with the edition of the English manuscript.

References

[1] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control, Van Nostrad Reinhold, New York, 1995.
[2] V. Serra, G. Saracco, C. Badini, V. Specchia, Appl. Catal. B: Environ. 11 (1997) 329.
[3] B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 28 (2000) 253.
[4] Y. Watanabe, K. Yrako, T. Miyajima, T. Yoshimoto, Y. Murakami, SAE paper 830082, 1983.
[5] G. Mul, J.P.A. Neeft, F. Kapteijn, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 6 (1995) 339.
[6] B.A.A.L. van Setten, R. van Dijk, S.J. Jelles, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 21 (1999) 51.
[7] J.P.A. Neeft, O.P. van Pruissen, M. Makkee, J.A. Moulijn, Stud. Surf. Sci. Catal. 96 (1995) 549.
[8] C.A. Querini, M.A. Ulla, F. Requejo, J. Soria, U. Sedrán, E.E. Miró, Appl. Catal. B: Environ. 11 (1997) 237.
[9] E.E. Miró, F. Ravelli, M.A. Ulla, L.M. Cornaglia, C.A. Querini, Stud. Surf. Sci. Catal. 130 (2000) 731.
[10] C.A. Querini, L.M. Cornaglia, M.A. Ulla, E.E. Miró, Appl. Catal. B: Environ. 20 (1999) 165.
[11] E.E. Miró, F. Ravelli, M.A. Ulla, L.M. Cornaglia, C.A. Querini, Catal. Today 53 (4) (1999) 631.
[12] V.G. Milt, M.L. Pisarello, E.E. Miró, C.A. Querini, Appl. Catal. B: Environ. 41 (2003) 397.
[13] S.C. Fung, C.A. Querini, J. Catal. 138 (1992) 240.
[14] J.M. Moggia, V.G. Milt, M.A. Ulla, L.M. Cornaglia, Surf. Interface Anal. 35 (2003) 216.
[15] R. Alvero, J.A. Odriozola, J.M. Trillo, S. Bernal, J. Chem. Soc., Dalton Trans. (1984) 87.
[16] S. Bernal, J.A. Diaz, R. García, J.M. Rodríguez-Izquierdo, J. Mater. Sci. 20 (1985) 537.
[17] R.P. Taylor, G.L. Schrader, Ind. Eng. Chem. Res. 30 (5) (1991) 1016.
[18] K.C. Patil, G.V. Chandrashekhar, M.V. George, C.N.R. Rao, Can. J. Chem. 46 (1968) 257.
[19] T.P. Whaley, in: The Chemistry of Lithium, Sodium, Potassium, Rubidium, Cesium and Francium. Pergamon Texts in Inorganic Chemistry, vol. 13, Pergamon Press, Oxford, 1973.
[20] S.L. González-Cortés, J. Orozco, B. Fontal, Appl. Catal. A: Gen. 213 (2001) 259.
[21] S. Bernal, F.J. Botana, R. García, F. Ramírez, J.M. Rodríguez-Izquierdo, Appl. Catal. 31 (1987) 267.
[22] D.J. Ilett, M. Saiful Islam, J. Chem. Soc., Faraday Trans. 89 (20) (1993) 3833.