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## Applied Catalysis B: Environmental

journal homepage: [www.elsevier.com/locate/apcatb](http://www.elsevier.com/locate/apcatb)Diesel soot and NO<sub>x</sub> abatement: K/La<sub>2</sub>O<sub>3</sub> catalyst stability

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## ABSTRACT

Soot particles and nitrogen oxides are the main pollutants emitted by a diesel engine. In this work, the activity and the stability of the K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst are studied. This catalyst is able to adsorb NO<sub>x</sub>, which is a good property for the catalyst in order to be used as a NO<sub>x</sub> trap. In addition, it is active for soot combustion as determined by temperature-programmed oxidation analyses. FTIR, XRD, CO<sub>2</sub>-TPD, Pulses of CO<sub>2</sub>, and BET techniques are used in order to characterize the catalysts. The catalytic surface composition depends upon the relative partial pressures of H<sub>2</sub>O, CO<sub>2</sub>, NO and O<sub>2</sub>. Despite the different surface compositions, the catalytic activity remains quite stable, under operation conditions similar to those of a real diesel exhaust. High temperature treatments, such as 800 °C, and especially in the presence of water, leads to an irreversible catalyst deactivation due to potassium volatilization. The water condensed on the catalyst, could wash-out a fraction of the potassium from the outer surface, leading to a decrease in activity. However, when the catalyst is treated at 400 °C, potassium diffuses from inside the pores to the external surface, thus recovering activity for soot combustion.

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## 1. Introduction

Soot particles and nitrogen oxides are the main pollutants emitted by a diesel engine. The combination of traps and oxidation catalysts seems to be the most plausible after-treatment technique to eliminate soot particles [1] whereas NO<sub>x</sub> adsorbers (traps) constitute a technology that has been developed for partial lean-burn gasoline engines and for diesel engines [2]. The adsorbers incorporated into the catalyst washcoat, chemically bind nitrogen oxides during the lean engine operation. After the adsorber capacity is saturated, the system is regenerated, and the released NO<sub>x</sub> is catalytically reduced during a period of rich engine operation [3]. In the case of diesel engines, since a constant rich operation is not feasible, periodic fuel injections are necessary. This topic has been the object of several studies, most of them performed with Pt-Ba-supported catalysts [3,4].

K/La<sub>2</sub>O<sub>3</sub> has been previously used as catalyst for NO<sub>x</sub> and soot elimination. It was found that it is able to adsorb NO<sub>x</sub> [5], and consequently it is a good candidate to be used as a NO<sub>x</sub> trap. On the other hand, it was found that K/La<sub>2</sub>O<sub>3</sub> is an active catalyst for diesel soot particles abatement [5,6]. Nevertheless, there are several other characteristics besides being active that a catalyst for diesel exhaust treatment should exhibit. Reaction runaway can occur after the cold engine start, because it is possible that many soot particles accumulate on the catalyst since it is at low temperature. Then,

as the temperature increases, the soot can ignite, leading to the combustion reaction runaway with important local temperature increments. Because of this, the catalyst should be thermally stable. This phenomenon has been recently addressed [7]. It was found that La<sub>2</sub>O<sub>3</sub> has good properties in order to avoid the runaway due to the endothermic dehydroxylation that occurs in the same temperature range in which the soot is burnt. Finally, the catalyst should be stable in the presence of high concentrations of CO<sub>2</sub>, water, NO<sub>x</sub> and the presence of SO<sub>2</sub>. Sulphur dioxide is present among the combustion products since diesel fuels have sulphur in their chemical composition. It is well known that SO<sub>2</sub> is responsible for the catalyst deactivation of many catalytic formulations. A systematic study about the poisoning of the K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst with SO<sub>2</sub> and its regeneration was previously published [17]. Even though all these stability requisites are key issues, not many papers have studied the stability of soot combustion catalysts [9] or catalysts for the simultaneous abatement of NO<sub>x</sub> and soot [10] in the presence of the main components of a diesel exhaust gas. In recent publications [8,11], we have analyzed the effect of temperature, water and sulphur dioxide on the stability of the Ba,K/CeO<sub>2</sub> catalyst during soot combustion.

The effect of the potassium precursor used in the preparation of K/La<sub>2</sub>O<sub>3</sub> catalysts is presented in another work [12].

In the present work, the K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst activity and stability are studied, mainly focusing on the latter. The study includes the analyses of thermal stability, hydrothermal stability, and stability in the presence of CO<sub>2</sub>, NO<sub>x</sub>, and H<sub>2</sub>O. The changes that occur on the catalyst surface composition due to the presence of each of these compounds are addressed.

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## 2. Experimental

### 2.1. Soot and catalyst preparation

The soot was prepared by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. After being collected from the vessel walls, it was dried in a stove for 24 h at 120 °C. The specific surface area of this soot was determined by a multipoint BET analysis, and was found to be 25 m<sup>2</sup>/g. The mean pore diameter is 50 Å and the pore volume is 0.03 mL/g. Temperature-programmed experiments performed using helium as carrier gas provided information regarding the amount of partially oxidized groups of the soot surface, and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, it was determined that the amount of carbon released as CO, CO<sub>2</sub> and hydrocarbons was 9.3 wt% of the soot and the amounts of hydrocarbons was 0.25 wt% of the soot [13].

The K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst was prepared from a La<sub>2</sub>O<sub>3</sub> (Alpha, p.a.) support to which a KOH-containing solution was added in order to obtain a 4.5 wt% load of K. The suspension was evaporated while being vigorously stirred until achieving a paste, which was dried in a stove during 24 h at 120 °C, and calcined at 400 °C during 2 h. Similar procedure was followed when KNO<sub>3</sub> was used to prepare the KNO<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> catalyst.

Throughout the paper, those catalysts whose activities were determined immediately after being prepared are referred to as: “recently prepared catalysts”. If the activities were determined few days after catalyst preparation, the samples are mentioned as “fresh catalysts”.

### 2.2. Activity test

#### 2.2.1. Temperature-programmed oxidation (TPO)

The catalytic activity of K/La<sub>2</sub>O<sub>3</sub> for the combustion of soot was determined by temperature-programmed oxidation (TPO). The soot and the catalysts were mechanically mixed in an agate mortar during 6 min (tight contact) to obtain a soot/catalyst ratio = 1/20 (w/w). The homogeneity of the mixture was verified using an optical microscope. This catalyst is white and the soot is black, and therefore it is easily distinguished if the mixture is not homogeneous. Different mixtures of catalyst and soot were compared, in both loose and tight contact, and different times of mixing for latter. In loose contact or with lower mixing times in tight contact, some white spots were observed. However, with a mixing time of 6 min, no white spots were observed. A gaseous flow rate (40 mL/min) with 5% oxygen in nitrogen was used, the temperature was increased at a rate of 12 °C/min, using 10 mg of the catalyst + soot mixture. A modified TPO technique [14] was employed which consisted in passing the gases coming from the reactor through a methanation reactor, where CO and CO<sub>2</sub> were converted into CH<sub>4</sub>. Afterwards, methane was continuously measured with a FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C. The detailed experimental conditions were carefully adopted in order to: (i) avoid mass and energy transfer limitations, (ii) assure that all soot particles are in good contact with catalyst and (iii) avoid the soot combustion reaction runaway [15].

#### 2.2.2. Temperature-programmed oxidation in presence of water

To determine the effect of water during soot oxidation, the carrier gas was bubbled in water at 25 °C or 50 °C before reaching the reactor, in order to obtain water concentrations in the carrier gas of 3% and 12%, respectively.

#### 2.2.3. Temperature-programmed oxidation in presence of NO<sub>x</sub>

The catalyst activity in the presence of NO + O<sub>2</sub> was measured in a fixed-bed reactor, with a thermocouple placed on the reac-

tor external wall. The operation conditions were the same as those used in the TPO experiments (see Section 2.2.1), except for the presence of NO in the feed stream. The detection was performed by a Mass Spectrometer (MS). The gaseous mixture used as carrier gas contained 5% O<sub>2</sub>, 0.1% NO and He. A 5% O<sub>2</sub> in He was also used for comparison.

### 2.3. Catalyst treatments

#### 2.3.1. Thermal treatment

The catalyst was calcined at 800 °C during 2 h. The catalytic performance of this catalyst was compared with that of the catalyst calcined at 400 °C.

#### 2.3.2. Hydrothermal treatment

A stream of air was saturated with water at room temperature, in order to obtain a water concentration in the air stream of 3%, as compared to a typical 6% in diesel engine exhausts. Afterwards, the wet stream flowed through the catalyst bed which was at 400 °C during 2 h. Then, the system was purged during 2 h with dry air at 400 °C.

A more severe treatment was performed, with a stream of 12% of water in air and the catalyst bed at 800 °C, during 2 h.

#### 2.3.3. “Washing” treatment

An amount of 320 mg of catalyst was placed in a filter paper and was washed with 3 aliquots of 5 mL each of distilled water. The filtered liquid was analyzed by Atomic Absorption Spectroscopy (A.A.), in order to detect the possible K catalytic loss. The washed catalyst was dried and then a TPO was performed with a catalyst–soot tight contact mixture (weight ratio 20:1), as indicated in Section 2.2.1.

#### 2.3.4. CO<sub>2</sub> and (CO<sub>2</sub> + H<sub>2</sub>O) treatment

The catalyst was treated with a carrier gas containing 10% CO<sub>2</sub>, 5% O<sub>2</sub> and N<sub>2</sub>, at 400 °C during 2 h. A similar treatment was also performed, but the gaseous stream was bubbled in a glass container with water at 50 °C in order to obtain a water concentration in the gas carrier of approximately 12%.

#### 2.3.5. NO + O<sub>2</sub> treatment

The NO<sub>x</sub> adsorption studies were performed in a Cahn 2000 Microbalance in order to study the interaction of the catalyst with NO + O<sub>2</sub>. The catalyst was treated with a mixture of NO (4%) + O<sub>2</sub> (18%) (He balance) at 70 °C and under these conditions the formation of NO<sub>2</sub> took place, the NO<sub>2</sub>/NO ratio being equal to 1300, as determined by FTIR downstream the reactor [16]. Then, the catalyst was heated up to 490 °C at 5 °C/min. Afterwards it was maintained at this temperature for 10 min and then cooled down to 70 °C. At this temperature, the feeding mixture was changed to He and then the procedure was repeated with this carrier gas.

The purpose of using this high NO concentration was to study the interaction of NO<sub>x</sub> with the catalyst in short experimentation times.

#### 2.3.6. (CO<sub>2</sub> + NO + O<sub>2</sub> + H<sub>2</sub>O) treatment

The catalyst was treated with a stream with 10% CO<sub>2</sub> and 0.1% NO in air. The gaseous stream was bubbled in a glass container with water at 50 °C, in order to obtain a water concentration of approximately 12%. After the carrier gas was saturated with water, the concentrations were 8.8% CO<sub>2</sub>, 0.09% NO, 22% O<sub>2</sub>, 57% N<sub>2</sub>, and 12% H<sub>2</sub>O. Two treatments were carried out, one at 400 °C and the other at 320 °C, during 2 h. Afterwards, the catalyst was cooled down in dried air.

**Table 1**  
FTIR and XRD phases present on  $K_{OH}/La_2O_3$  catalysts.

Catalyst treatments	FTIR	XRD
Fresh (calcined at 400 °C)	$La_2O_2CO_3$ , $La_2(CO_3)_3/CO_3^{-2}$ , $La(OH)_3$ (*), $K_2CO_3$	$La_2O_2CO_3$ , $La(OH)_3^a$
Calcined at 800 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3/CO_3^{-2}$ , $La(OH)_3^a$ , $K_2CO_3$	$La_2O_2CO_3$ , $La(OH)_3^a$
$CO_2$ at 400 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3/CO_3^{-2}$ , $La(OH)_3^a$ , $K_2CO_3$	$La_2O_2CO_3$ , $La(OH)_3^a$
Wet air at 400 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3/CO_3^{-2}$ , $La(OH)_3^a$ , $K_2CO_3$	$La_2O_2CO_3$ , $La(OH)_3^a$
$CO_2 + H_2O$ at 400 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3/CO_3^{-2}$ , $La(OH)_3^a$ , $K_2CO_3$	$La_2O_2CO_3$ , $La(OH)_3^a$
$NO + O_2$ (microbalance)	$La_2O_2CO_3$ , $La(NO_3)_3$ (traces), $KNO_3$	Not done
$H_2O + CO_2 + NO + O_2$ at 320 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3$ , $La(OH)_3$ , Free $NO_3^-$	Not done
$H_2O + CO_2 + NO + O_2$ at 400 °C	$La_2O_2CO_3$ , $La_2(CO_3)_3$ , Free $NO_3^-$	Not done

<sup>a</sup> Not present immediately after preparation or immediately after thermal treatment.

## 2.4. Catalysts characterization

**X-ray diffraction (XRD).** The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu  $K\alpha$  radiation at a scan rate of  $4^\circ \text{ min}^{-1}$ , from  $2\theta = 10$  to  $80^\circ$ .

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

**High frequency  $CO_2$  pulses.** The high frequency  $CO_2$  pulses technique was carried out at different temperatures, by sending pulses of  $0.135 \mu\text{mol}$  of  $CO_2$  in 6%  $O_2$  in  $N_2$  carrier every 10 s [3]. The  $CO_2$  was detected with a FID after methanation, as described in Section 2.2.1. The  $CO_2$  peak comes out of the cell with a distortion, depending on the interaction with the catalyst. The absence of a  $CO_2$  peak at the cell outlet means that there is a strong interaction and, on the other hand, 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 constant amplitude of oscillation, as long as the adsorption–desorption process is fast enough. If the amplitude is lower than the reference (reference or blank: cell without catalyst) the dynamics of the process allows the surface to adsorb–desorb the  $CO_2$  at the same rate as it is injected.

**Surface area and pore volume.** Nitrogen adsorption was employed to determine BET surface area, and pore volumes were estimated by means of  $t$ -plots. The determinations were carried out on a fresh catalyst, pre-treated under vacuum at  $250^\circ\text{C}$  during 3 h, using a Micromeritics Accusorb 2100 sorptometer.

## 2.5. Determination of the K content by Atomic Absorption Spectroscopy (A.A.)

This method was used to determine the K content, since K can be lost either by dissolution (after wet treatments) or by volatilization (after thermal treatments). In order to determine the K content, the catalysts were dissolved with acids.

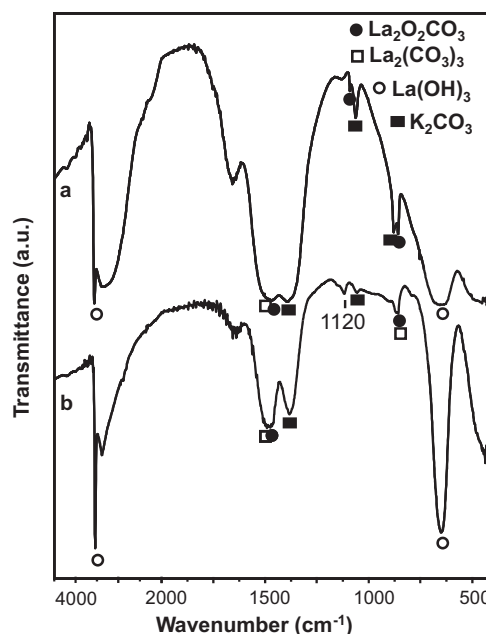
## 3. Results and discussion

### 3.1. Fresh catalyst characterization

The main phases found on the  $K_{OH}/La_2O_3$  catalyst are  $La(OH)_3$ ,  $La_2O_2CO_3$ ,  $La_2(CO_3)_3$  and  $K_2CO_3$ , as shown in Fig. 1, curve a. The same lanthanum phases were found on the catalyst prepared using  $KNO_3$  ( $KNO_3/La_2O_3$ ). In addition, in this catalyst  $KNO_3$  was observed, as shown in Fig. 2, curve a.

Tables 1 and 2 summarize the phases found by FTIR and XRD analyses.

The BET areas of  $La_2O_3$  and recently prepared  $K_{OH}/La_2O_3$  catalysts are 10 and  $3.5 \text{ m}^2/\text{g}$  respectively, while the fresh  $K_{OH}/La_2O_3$  has a BET area of  $4 \text{ m}^2/\text{g}$ . Since the reaction under study involves soot particles with diameter in the order of the micron, which is much bigger than the pore diameter, mainly the external surface



**Fig. 1.** FTIR spectra for  $K_{OH}/La_2O_3$  catalysts. (a) Fresh; (b) used in the TPO experiment up to  $700^\circ\text{C}$ .

of the catalyst is involved in the reaction, and consequently the BET area is generally not related to the catalyst activity for soot combustion.

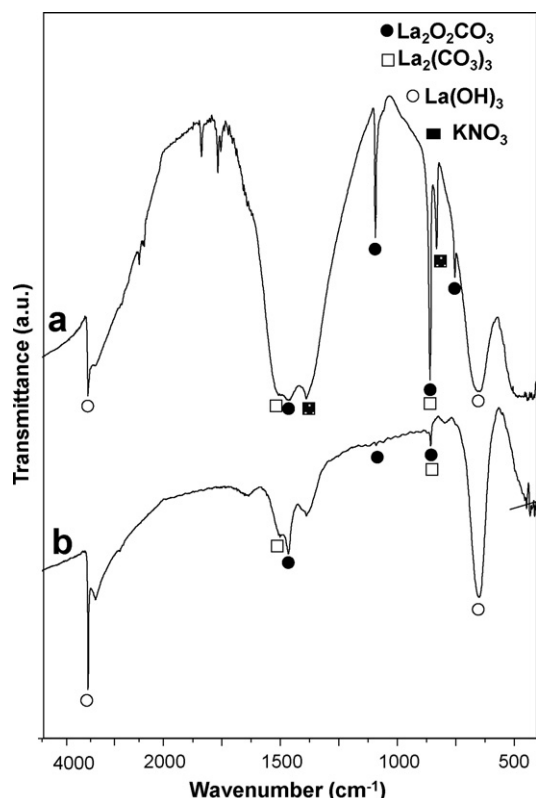
### 3.2. Catalyst activity

The TPO profile obtained with a fresh  $K_{OH}/La_2O_3$  catalyst mixed with soot is shown in Fig. 3. A complex profile can be observed. We have previously shown that the first two TPO maxima correspond to soot combustion, and the other two TPO maxima correspond to carbonate decompositions [12]. The chemical state of potassium influences the basicity of the catalyst surface [12]. This basicity should not be too high since the  $CO_2$  liberated during soot oxidation could form stable carbonates on the surface, thus changing the catalyst activity. When  $KNO_3$  was used as precursor, the TPO profile displayed a single peak. On the other hand, when the pre-

**Table 2**  
FTIR bands corresponding to the main compounds.

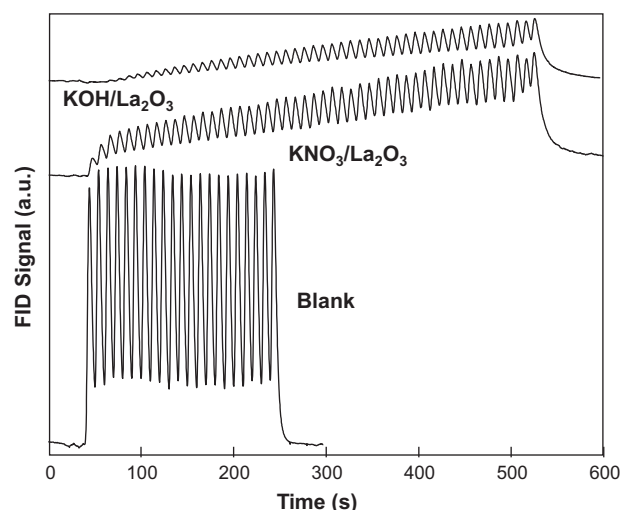
Compound	FTIR band ( $\text{cm}^{-1}$ )
$La_2O_2CO_3$	1520, 1470, 1093, 863, 752
$La_2(CO_3)_3$	1500, 1388, 1070, 863 <sup>a</sup>
$La(OH)_3$	3620, 644
$K_2CO_3$	1490, 1370, 1060, 880, 830, 740
$KNO_3$	1385, 825
Free $NO_3^-$	1385

<sup>a</sup> These bands could also correspond to  $CO_2$  ads. on  $La_2O_3$ .



**Fig. 2.** FTIR spectra for  $\text{KNO}_3/\text{La}_2\text{O}_3$  catalysts. (a) Fresh; (b) used in the TPO experiment up to  $700^\circ\text{C}$ .

cursor was KOH or  $\text{K}_2\text{CO}_3$ , a second combustion peak was observed in the TPO profiles due to a higher basicity of these catalysts [12]. In these cases, the  $\text{CO}_2$  generated during the soot combustion is irreversibly adsorbed on the catalyst changing its activity. Consequently, a second TPO peak is observed in the profile due to the combustion of a fraction of the soot; and another peak at higher temperature that corresponds to the desorption/decomposition of the adsorbed carbonates. The difference in basicity is reflected by the level of interaction of the catalyst with  $\text{CO}_2$ , as seen in Fig. 4. This figure shows results obtained in the high frequency pulses of  $\text{CO}_2$  experiments with the catalysts prepared with  $\text{KNO}_3$  and with KOH. The blank (empty cell) is included as reference. The signal obtained with the  $\text{KNO}_3/\text{La}_2\text{O}_3$  catalyst has higher amplitude than that obtained with  $\text{KOH}/\text{La}_2\text{O}_3$ . This indicates that the former gen-



**Fig. 4.**  $\text{CO}_2$  pulses at  $350^\circ\text{C}$  on recently prepared  $\text{KOH}/\text{La}_2\text{O}_3$  c.  $400^\circ\text{C}$  and  $\text{KNO}_3/\text{La}_2\text{O}_3$  c.  $400^\circ\text{C}$  catalysts.

erates a less basic surface, and consequently the level of interaction of the catalyst with  $\text{CO}_2$  is lower.

The catalysts were analyzed by FTIR before and after the TPO test. The  $\text{KOH}/\text{La}_2\text{O}_3$  catalyst shows a band at  $1120\text{ cm}^{-1}$  (Fig. 1, curve a), which increases after the TPO was performed (Fig. 1, curve b). This band corresponds to carbonates. This band was not observed in the spectra obtained with the  $\text{KNO}_3/\text{La}_2\text{O}_3$  catalyst (Fig. 2). These results indicate that the interaction strength between the  $\text{CO}_2$  and the catalyst changes depending upon the basicity generated by the potassium, which depends on the chemical state of this compound. i.e., if it is as nitrate, hydroxide, or carbonate.

### 3.3. Thermal stability

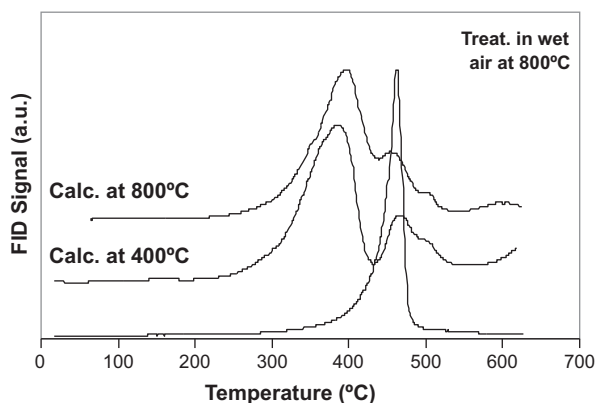
The  $\text{KOH}/\text{La}_2\text{O}_3$  catalyst was calcined at  $800^\circ\text{C}$  during 2 h, and the activity determined after this treatment. The catalytic activities were determined immediately after the calcination. Fig. 3 shows the TPO profiles of this catalyst. The TPO obtained with the catalyst calcined at  $400^\circ\text{C}$  is included as reference. In the case of the catalyst calcined at  $800^\circ\text{C}$ , the first TPO maximum is slightly shifted to higher temperature, which indicates that it is a little less active than the catalyst calcined at  $400^\circ\text{C}$ . The difference in activity upon high temperature treatment can be attributed to a loss of K by volatilization. The Atomic Absorption Spectroscopy analysis revealed that 60% of K was lost.

### 3.4. Hydrothermal stability

The catalyst stability in a wet atmosphere was studied, pretreating the catalyst during 2 h at  $400^\circ\text{C}$  with a stream of air saturated in water. Fig. 5A shows the TPO profiles obtained with the fresh and with the treated catalysts. It can be observed that after 2 h of treatment the catalyst still keeps its activity, thus showing a good hydrothermal stability at  $400^\circ\text{C}$ . However, the hydrotreatment at  $800^\circ\text{C}$  considerably deactivates the catalyst as seen in the TPO profile shown in Fig. 3. The K content decreases significantly during this treatment, with a loss of 74%.

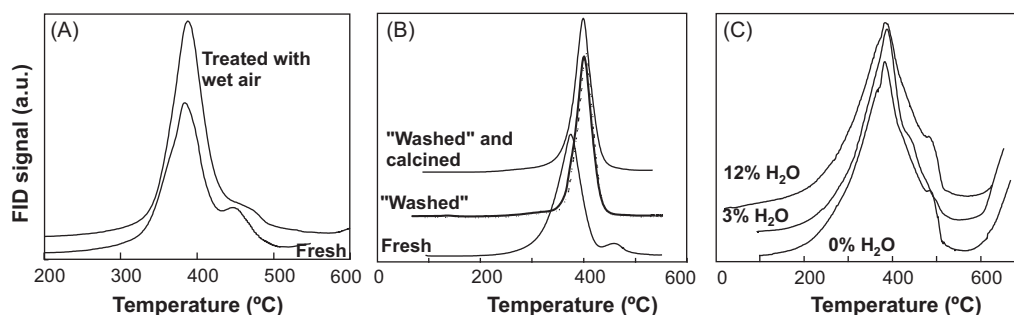
### 3.5. Stability in water at room temperature

The catalyst was treated with liquid water as explained in Section 2.3.3 (catalyst 'washing'). Afterward, the washing liquid was analyzed by Atomic Absorption Spectroscopy. The catalyst presented a loss of 37% of K. Fig. 5B shows the TPO profiles of the fresh



**Fig. 3.** TPO profiles for mixtures of soot and  $\text{KOH}/\text{La}_2\text{O}_3$  catalysts calcined at  $400^\circ\text{C}$  (fresh) and treated at  $800^\circ\text{C}$  in dry air and in wet air.





**Fig. 5.** TPO profiles for mixtures of  $\text{KOH/La}_2\text{O}_3$  c.400 °C + soot. (A) Fresh and treated in wet air during 2 h at 400 °C catalysts. (B) Fresh, "washed" and washed and calcined catalysts. (C) Dry carrier and wet carrier.

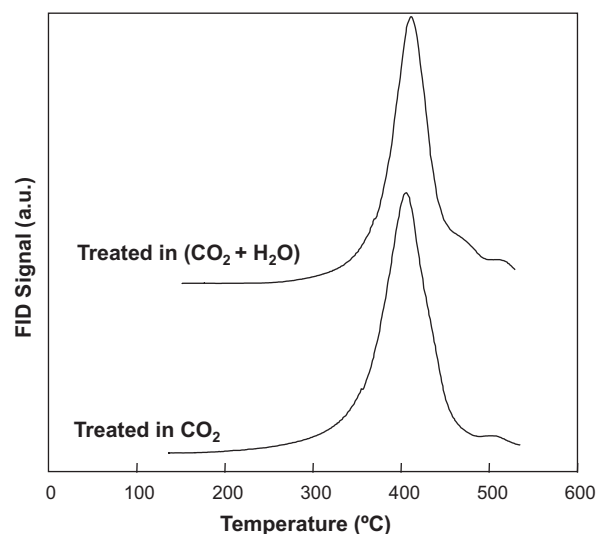
and the washed catalysts. It can be observed that the washing procedure leads to catalyst deactivation. Most probably, the K from the external particle surface is dissolved, while the K inside the pores remains in the water contained within the pores, and redeposited after drying. The washed catalyst was calcined 2 h at 400 °C. This treatment led to an improvement in activity, as can be observed in Fig. 5B. These results suggest that during the calcination at 400 °C the K migrates from inside the pores to the external surface where the soot interacts with the catalyst and the reaction takes place. It is important to note that the catalyst will be in contact with liquid water after the engine is stopped and cooled down. In any case, the water amount used for the "washing" process in these experiments was very high as compared with a real situation.

### 3.6. Soot combustion activity in presence of water

The effect of the presence of water in the reaction media, was analyzed by carrying out TPO experiments in which the gas carrier was saturated with water at 25 °C and at 50 °C, obtaining a water concentration of approximately 3% and 12%, respectively. Fig. 5C shows the TPO profiles for dry carrier (standard TPO) and wet carrier. It can be observed that there is no difference in activity between dry and wet reaction media.

### 3.7. Stability in the presence of $\text{CO}_2$ and $(\text{CO}_2 + \text{H}_2\text{O})$

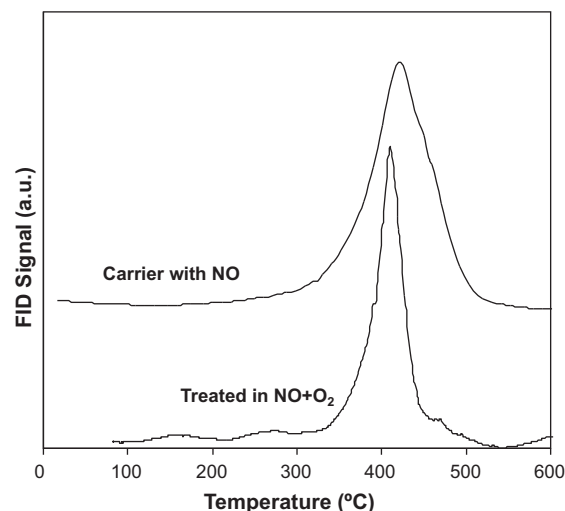
Diesel exhausts contain high  $\text{CO}_2$  and water concentrations. To simulate these conditions, a  $\text{K/La}_2\text{O}_3$  catalyst was treated with a mixture containing 10%  $\text{CO}_2$ , 5%  $\text{O}_2$  ( $\text{N}_2$  balance) for 2 h at 400 °C. A similar treatment was also performed, but with this mixture saturated with water at 50 °C, in order to obtain approximately a water concentration of 12 vol%. After these treatments, the catalysts were mixed with soot, and the activity determined by TPO. Fig. 6 shows the results. After both treatments, the temperature of the TPO maximum slightly increased. In addition, all the soot was burnt giving a single TPO maximum. The fresh, the  $\text{CO}_2$ -treated and the  $(\text{CO}_2 + \text{H}_2\text{O})$ -treated catalysts were characterized by XRD (not shown). The crystalline phases found on the three catalysts were  $\text{La}(\text{OH})_3$  and  $\text{La}_2\text{O}_2\text{CO}_3$ . In the fresh catalyst, the main crystalline phase was  $\text{La}(\text{OH})_3$  (JCPDS #36-1481), and in both treated catalysts the main crystalline phase found was  $\text{La}_2\text{O}_2\text{CO}_3$  (JCPDS #37-804). These results demonstrate that at high temperature, the catalyst interaction with  $\text{CO}_2$  predominates over the interaction with  $\text{H}_2\text{O}$ , and consequently the main type of compound formed on the catalyst is carbonate. The consequence of this is that during the soot combustion, the interaction between the surface and  $\text{CO}_2$  is lower than when OH groups are present on the surface (fresh catalyst), as explained in Section 3.2, and the soot is completely burnt giving a single TPO combustion maximum.  $\text{CO}_2$  adsorption does not occur during the reaction since the surface is already saturated with carbonates.



**Fig. 6.** TPO profiles for mixtures of  $\text{KOH/La}_2\text{O}_3$  c.400 °C + soot. Catalysts: fresh, treated in  $\text{CO}_2$  for 2 h and treated in  $(\text{CO}_2 + \text{H}_2\text{O})$  for 2 h.

### 3.8. Stability in presence of $\text{NO}_x$

Fig. 7 shows the TPO profile obtained with the catalyst pre-treated with a mixture of  $\text{NO} + \text{O}_2$  as described in Section 2.3.5. It can be observed that after the  $\text{NO}_x$  treatment, the profile presents only



**Fig. 7.** TPO profiles for mixtures of  $\text{KOH/La}_2\text{O}_3$  calcined at 400 °C + soot. Catalysts: treated with 4%  $\text{NO} + 18\% \text{O}_2$ , carrier: 5%  $\text{O}_2/\text{N}_2$  and fresh catalyst, carrier 5%  $\text{O}_2$ , 0.1%  $\text{NO}$ , He.

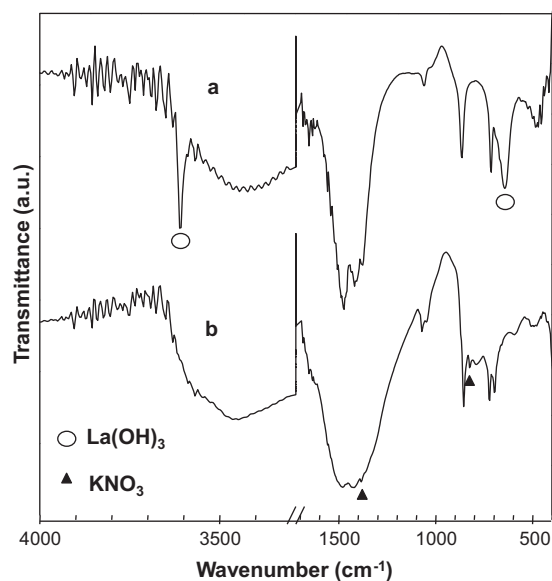


Fig. 8. FTIR spectra for K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> fresh (a) and treated with NO + O<sub>2</sub> (b).

one soot combustion maximum, shifted 20 °C to higher temperatures as compared to the first peak of the fresh catalyst. In the case of the latter, the appearance of a second maximum was explained in terms of the CO<sub>2</sub> adsorption during the reaction forming carbonates. CO<sub>2</sub> pulses experiments previously reported showed that the catalyst treated with NO + O<sub>2</sub> presents a much lower interaction level with CO<sub>2</sub> than the fresh catalyst [12]. In addition, the IR spectrum of the catalyst treated with NO + O<sub>2</sub> showed the bands of KNO<sub>3</sub>, the absence of La(OH)<sub>3</sub> signals and the presence of a signal at 1050 cm<sup>-1</sup>, which was ascribed to La(NO<sub>3</sub>)<sub>3</sub> (Fig. 8). Therefore, the CO<sub>2</sub> formed during soot combustion is not retained by the catalytic surface due to the weaker interaction of CO<sub>2</sub> with the surface and, consequently, a single TPO peak is observed.

### 3.9. Soot combustion activity in the presence of NO + O<sub>2</sub>

The soot combustion catalytic activity in the presence of NO<sub>x</sub> was studied carrying out TPO experiments using a carrier gas containing 5 vol% of O<sub>2</sub> and 0% or 0.1% of NO. Fig. 7 shows the TPO profile obtained with the carrier containing 0.1% of NO and a freshly prepared K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst. It can be observed that the temperature of the TPO maximum (*T<sub>M</sub>*) slightly increases when adding NO to the feed. These results are consistent with the results also shown in the same figure, obtained with the nitrated catalyst, where the *T<sub>M</sub>* for this catalyst is slightly higher (about 20 °C) than that for the fresh catalyst. These results also agree with results obtained in the study of the effect of the potassium precursors on the catalyst activity [12], where *T<sub>M</sub>* for KNO<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> is slightly higher than in the case of K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub>. In all cases in which nitrates are present on the surface, the TPO profiles display a single peak, indicating that the mechanism of reaction and CO<sub>2</sub> release strongly depends on the chemical state of the surface.

### 3.10. Stability in presence of H<sub>2</sub>O + CO<sub>2</sub> + NO + O<sub>2</sub>

The catalyst was treated with H<sub>2</sub>O + CO<sub>2</sub> + NO + O<sub>2</sub> in concentrations similar to those found in a typical exhaust stream, at 400 °C and at 320 °C. The TPO profiles are shown in Fig. 9 and the corresponding FTIR spectra are shown in Fig. 10. For both treatments, the activity was practically the same, and all the soot was burnt giving a single TPO maximum. After both treatment, the phases found on the catalysts were La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and free NO<sub>3</sub><sup>-</sup>, and only the cata-

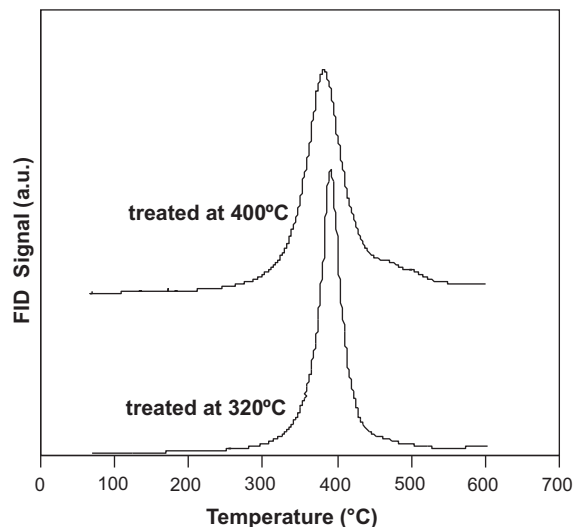


Fig. 9. TPO profiles for mixtures of soot and K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalysts treated with H<sub>2</sub>O + CO<sub>2</sub> + NO + O<sub>2</sub> at 320 °C and at 400 °C.

lyst treated at 320 °C presents La(OH)<sub>3</sub>. The hydroxide/carbonate signals intensity ratio in the FTIR spectrum corresponding to the catalyst pretreated at 320 °C is very low compared to the ratio found with the fresh catalyst. In agreement with this, the fresh catalyst displays two combustion maxima in the TPO profile due to the higher amount of CO<sub>2</sub> adsorbed during the reaction, forming carbonate that then decomposes at higher temperature. Therefore, taking into account all these results, it can be concluded that the surface of the K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalyst is extremely dynamic, changing its composition very easily, depending upon the gas phase composition and the temperature. An important observation is that when the gas contains H<sub>2</sub>O, CO<sub>2</sub>, NO, and O<sub>2</sub> in concentrations similar to those found in the exhaust gases, the K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> activity is good, burning the soot with a single maximum in the TPO profile below 400 °C.

Scheme 1 shows the changes of phases observed in this system, and summarizes the findings of this and previous works [12,17], regarding the change in the phases present on the catalytic surface during storage and operation.

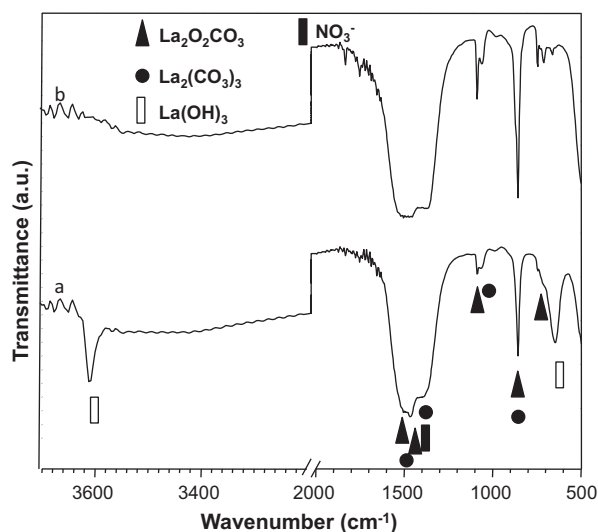
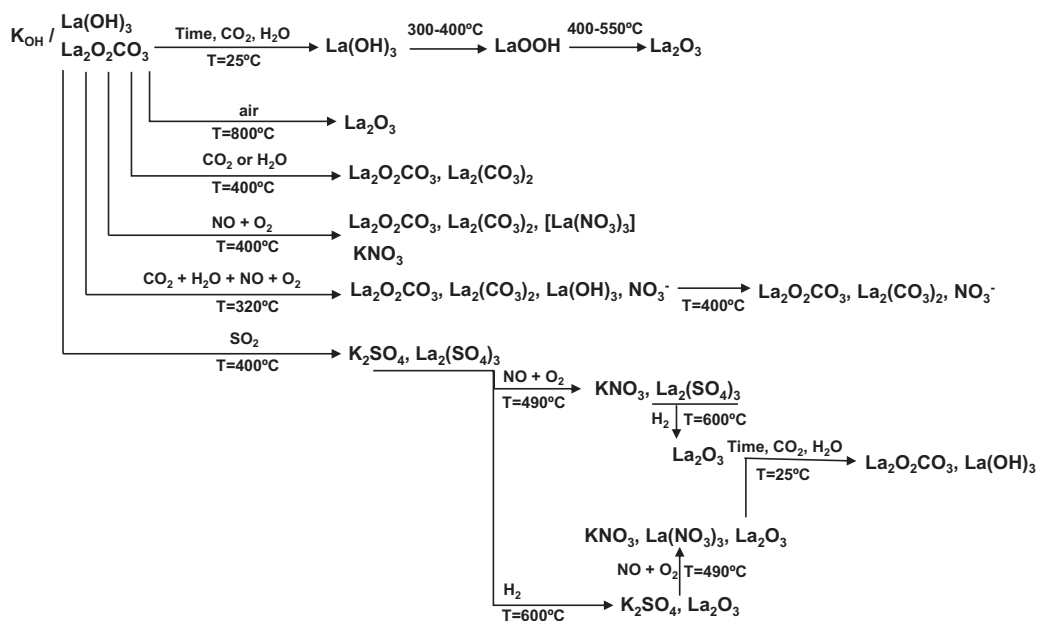


Fig. 10. FTIR spectra for K<sub>OH</sub>/La<sub>2</sub>O<sub>3</sub> catalysts treated with H<sub>2</sub>O + CO<sub>2</sub> + NO + O<sub>2</sub> at 320 °C (a) and at 400 °C (b).



Scheme 1.

#### 4. Conclusions

The surface composition of  $K_{OH}/La_2O_3$  catalyst is strongly affected by the environment composition, readily changing from the lanthanum hydroxide to the lanthanum carbonate and oxycarbonate.

The  $NO_x$  treatment of the  $K_{OH}/La_2O_3$  catalyst leads to the formation of superficial nitrates. These changes of phases present on the catalyst lead to a lower interaction between the catalyst and the  $CO_2$ , and because of this, the soot is burnt giving a single TPO maximum since no  $CO_2$  irreversible adsorption occurs during the soot combustion reaction. The same conclusion can be drawn for the fresh catalyst when  $NO + O_2$  is present in the reaction media.

The  $K_{OH}/La_2O_3$  catalyst presents a slight deactivation after being treated at 800 °C during 2 h, even with a high K loss.

The treatment in wet air at 400 °C does not provoke any activity change. Similarly, the presence of water in the reaction medium does not modify the activity. Only the presence of high amounts of liquid water wetting the catalyst at room temperature lead to catalyst deactivation, due to K elimination from the external catalytic surface. A treatment at moderate temperature of this catalyst, leads to a redispersion of K from the internal surface to the external surface, partially recovering the activity loss caused by the K wash-out.

However, the treatment in wet air at 800 °C during 2 h strongly deactivates the catalyst, with a considerable loss of K.

In a gas stream similar to that of normal operation conditions in a diesel engine exhaust, depending upon the partial pressure of  $CO_2$ ,  $H_2O$ ,  $NO$ , and  $O_2$ , the surface composition will be different, and despite of this, the catalytic activity is still the same. This is a very important result, because with these experiments it is demonstrated that this complex atmosphere favours

the formation of surface compounds with good activity for soot combustion.

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