Potassium effect on the thermal stability and reactivity of NO_x species adsorbed on $Pt,Rh/La_2O_3$ catalysts

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ABSTRACT

In this paper we analyzed the effect of potassium on the thermal stability of NO_x species adsorbed on lanthanum supported catalysts. Catalysts containing only noble metals (Pt and/or Rh) or noble metals and potassium were prepared. The soot combustion process in the presence of NO_x species previously adsorbed on the catalysts has also been studied in order to evaluate the possibility of using these materials for the simultaneous abatement of soot and nitrogen oxides.

It was shown that lanthanum supported catalysts containing Pt and/or Rh exhibited great capacity to decompose previously adsorbed nitrate species in an inert atmosphere. When potassium was added to the formulation this capacity was modified, which proves the existence of a strong interaction between the potassium and noble metals. Such interaction was much stronger in the case of platinum and, therefore, the Pt–K catalyst was able to decompose only a small fraction of the adsorbed compounds in helium stream. However, when decomposition took place in reducing atmosphere (H_2), the NO_x species were reduced at a lower temperature in the presence of platinum.

For all the lanthanum supported catalysts under study, the activity for soot combustion increased in the presence of previously adsorbed nitrate species, even though some of the samples were not very effective for NO_x decomposition. This indicates that NO_x species are capable of reacting with soot in oxidant atmosphere without the need for their previous decomposition, as previously observed in an inert stream.

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1. Introduction

The main pollutants emitted by diesel engines are soot particles and nitrogen oxides. In order to abate nitrogen oxides in diesel exhausts containing oxygen excess, efforts are focused on systems capable of adsorbing and then releasing and reducing NO_x (traps). NO_x storage-reduction catalysts (NSR) work under cyclic conditions alternating a NO_x adsorption step in oxidant atmosphere (normal operation of the diesel engine) with a short reduction step, during which the stored compounds are released and reduced to N_2. This system was first proposed by the Toyota group [1], who developed the first NSR catalyst. Later, this group developed a similar system for the simultaneous abatement of NO_x and soot, which is known as DPNR (diesel particulate NO_x reduction) [2]. The NO_x elimination mechanism in this system corresponds to the one previously proposed for the NSR catalysts.

The possibility of the simultaneous abatement of NO_x and soot according to the DPNR system has only been explored in the last few years. For this reason, and also because the system is very complex, there are still many questions to be solved. Recently, Suzuki and Matsumoto [3] reported that the addition of NO_x storage species to soot combustion catalysts increased their activity for combustion. They attributed this effect to the direct contact between the soot particles and the nitrated material. In agreement, and according to results obtained with $Cs-MnO_x–CeO_2$ catalysts, Ito et al. [4] concluded that soot combustion was promoted by the adsorbed NO_x species. In this vein, Milt et al. [5] reported that when a $Co,Ba,K/CeO_2$ catalyst treated under $NO + O_2$ atmosphere was intimately mixed with the soot and then heated in He, the soot particulates were partially oxidized by the surface nitrate species. Castoldi et al. [6] also attributed soot oxidant properties to the nitrate species stored on $Pt–Ba/Al_2O_3$ catalysts. In a later work [7], they proposed that after exposure of $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ catalysts to NO/O_2 gaseous mixtures, mobile and reactive superficial nitrate species were formed, which promoted soot combustion. However, other authors suggested that the increase in activity was mainly caused by the NO_2 desorption from the NO_x storage sites, as temperature increased [8–11]. NO_2 was subsequently used for $C_{(s)}$ oxidation, or to activate it for the combustion with gaseous O_2.

Our group has previously shown that lanthanum oxide has NO_x adsorption capacity [12]. For this reason, this material was selected

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Table 1
Lanthanum supported catalysts prepared for this work.

Nomenclature	Pt content (% w/w)	Rh content (% w/w)	K content (% w/w)
NM/La_2O_3	0.9	–	–
	–	0.9	–
	0.9	0.9	–
$NM,K/La_2O_3$	0.9	–	7.5
	–	0.9	7.5
	0.9	0.9	7.5
K/La_2O_3	–	–	7.5

as support for Pt, Rh and K based catalysts. The K/La_2O_3 catalyst proved to be very active for soot combustion, the other main pollutant present in diesel exhausts [13]. However, noble metals are usually incorporated in order to increase the effectivity of the catalytic system, e.g. platinum catalyzes the NO to NO_2 transformation, a necessary previous step in the NO_x storage process. Rhodium is also generally included in the catalytic formulation of diesel engines NO_x traps to promote the reaction between the released NO_x and a reducing compound.

In this work, we prepared La_2O_3 supported catalysts containing only noble metals (Pt and/or Rh), or noble metals and potassium. The main objective was to analyze the effect of potassium, when combined with the noble metals, and assess the capacity of these catalysts to work as NO_x traps. We also evaluated the possibility of using these materials for the simultaneous abatement of soot and nitrogen oxides according to the mechanism proposed in the DPNR system. To do so, we studied the soot combustion process in the presence of NO_x species previously adsorbed on the catalysts.

2. Experimental

2.1. Soot and catalyst preparation

The soot was obtained 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 at 120 °C for 24 h. Its specific surface area was 55 $m^2 g^{-1}$.

Catalysts were prepared by wet impregnation of the precursors over the La_2O_3 support (Strem Chemicals, 99.9%). The solutions used were: H_2Cl_6Pt (8.4 mg Pt mL^{-1}) and $RhCl_3$ (40 mg Rh mL^{-1}) for the noble metals, and KOH 0.1 M for potassium. Solutions were added to the support in order to obtain the required concentration of the corresponding metal. During each impregnation, the suspension obtained was continuously stirred at 100 °C until achieving a paste, which was dried overnight at 120 °C. This powder was calcined in air stream (50 mL min^{-1}) in a fixed-bed reactor at 500 °C for 2 h.

In order to study the influence of potassium addition to lanthanum supported catalysts containing noble metals (Pt, Rh), two different formulations were studied: with and without potassium. The catalysts prepared are listed in Table 1. Catalysts containing noble metals (NM) and potassium were prepared by wet impregnation of the potassium salt over the NM/La_2O_3 solids (successive impregnation).

Prior to some of the experiments, catalysts were treated in a 20 mL min^{-1} flow of NO (4%) + O_2 (18%) (He balance). For this purpose, samples were placed in a fixed-bed reactor, where they were heated to different final temperatures selected for each formulation in order to maximize NO_x adsorption. The final temperature was maintained for 1 h. Finally, catalysts were cooled in the NO + O_2 stream. These samples are referred to as "nitrated catalysts".

2.2. Catalyst characterization

2.2.1. Fourier transformed infrared spectroscopy (FTIR)

Infrared spectra were obtained using an IR Prestige-21 Shimadzu spectrometer. Samples were prepared in the form of pressed wafers (ca. 1% sample in KBr). All spectra involved the accumulation of 40 scans at 8 cm^{-1} resolution.

2.2.2. X-ray diffraction (XRD)

Crystalline phases were identified by powder XRD analysis using a Shimadzu XD-D1 diffractometer, equipped with a Cu Kα radiation source and using a scanning rate of 1 min^{-1}.

2.2.3. Temperature-programmed reduction (TPR) experiments

A Micromeritics Autochem II system, provided with a thermal conductivity detector (TCD) was used. The TPR runs were conducted using a heating rate of 10 °C min^{-1} in a flow of 5% H_2/Ar (50 mL min^{-1}) up to 500 °C. Catalysts were pre-treated in O_2 flow, up to 500 °C, prior to each experiment.

TPR experiments were also carried out using nitrated catalysts. Catalysts treated as described in Section 2.1 were exposed to a reducing atmosphere (H_2) with the aim of studying the NO_x reduction temperatures, as well as the products generated. 100 mg of the nitrated catalyst were placed in a stainless steel, ¼ in. diameter reactor. The sample was then heated in 50 mL min^{-1} H_2 flow, from room temperature to 500 °C, at 5 °C min^{-1} rate. During such thermal treatment, the released species were followed by mass spectroscopy using a GC–MS Shimadzu equipment (GC-14A QP2000A).

2.3. NO_x adsorption–desorption experiments

NO_x adsorption–desorption experiments were performed in a Cahn 2000 microbalance in order to study the interaction of the catalysts with NO + O_2. The samples were dried by heating them at 450 °C in He for 30 min, followed by a second heating step up to 490 °C during 10 min, after which the samples were stabilized at 70 °C, where the weight was determined. After this, a mixture of NO (4%) + O_2 (18%) (He balance) was fed, and the samples were stabilized at 70 °C in this stream. When a constant weight value was obtained, the samples were heated up to 490 °C at 5 °C/min, 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 the procedure was repeated in this stream.

2.4. Soot combustion activity

To study the activity for soot combustion, catalysts were mixed with soot in 20:1 weight ratio in a mortar for 6 min (tight contact). The catalytic activity was determined by heating these mixtures at 12 °C min^{-1}, using 10 mg of the catalyst + soot mixture. A modified TPO (temperature-programmed oxidation) technique was employed which consisted in passing the gases coming from the reactor trough a methanation reactor, where CO and CO_2 were converted to CH_4. Afterwards, methane was continuously measured with a FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C.

In order to evaluate the individual contribution to the soot combustion process of the adsorbed NO_x species and the gaseous oxygen, combustion reactions were carried out using different experimental conditions. In the first case, nitrated catalysts were used, and combustion took place in an inert atmosphere (N_2). In the second case, fresh (non-nitrated) catalysts were employed for conventional TPO experiments (5% O_2/N_2 stream). Finally, both processes were studied simultaneously, in which case TPO experiments were performed using nitrated catalysts.
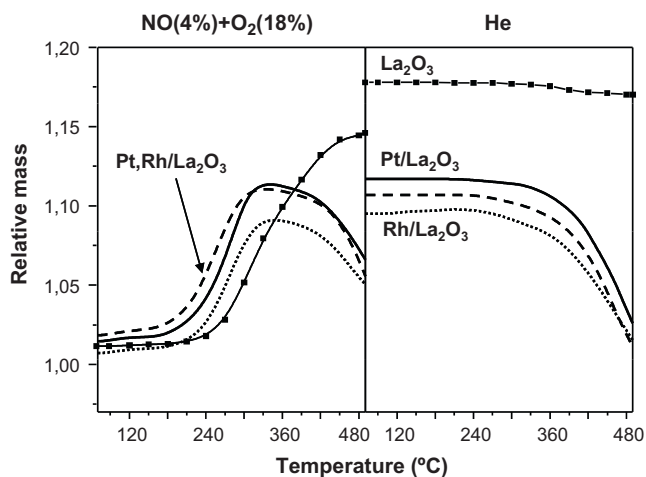
Fig. 1. $NO(4\%)+O_2(18\%)$ adsorption (left) and decomposition in He (right) in microbalance. NM/La_2O_3 catalysts and lanthanum oxide support (calcined at 500 °C).

Table 2
Mass loss during the helium desorption step with lanthanum supported catalysts.

General formulation	Metals	$\Delta m\,(\%)^{a}$
NM/La_2O_3	Pt	9.07
	Rh	7.97
	Pt,Rh	9.57
$NM,K/La_2O_3$	Pt,K	1.41
	Rh,K	7.73
	Pt,Rh,K	5.91

[a] $\Delta m\,(\%)=(m_1-m_2)/w_0\times 100$.
m_1: mass value at the beginning of the desorption step (70 °C); m_2: mass value at the end of the desorption step (heating in He until 490 °C followed by cooling in the same stream); w_0: initial mass value (measured at the end of the helium pre-treatment).

3. Results and discussion

3.1. Interaction of NO_x with the catalyst surface: effect of potassium

Fig. 1 displays microbalance experiments, in which the weight increase due to $NO+O_2$ adsorption is measured. The first point of each curve (at 70 °C) represents the NO_x adsorbed at this temperature. The graph is divided into two sections: the left one corresponding to the NO_x stream and the right one, to the He stream. The discontinuity observed for each curve is due to re-adsorption during the cooling in the NO_x stream. Note that neither the cooling in the NO_x stream nor the cooling in the helium stream are represented.

It has been previously established that La_2O_3 has a great capacity to interact with nitrogen oxides, forming superficial nitrates that can eventually migrate to the interior of the solid forming volumetric species [12]. For this reason, in the catalysts studied in this work, the lanthanum oxide support plays an essential role in relation to their performance as NO_x traps. Both potassium and noble metals introduce major modifications in La_2O_3 behavior during adsorption–desorption experiments.

The NO_x adsorption–desorption profiles corresponding to the lanthanum oxide support and to the mono and bimetallic lanthanum supported catalysts (NM/La_2O_3) are shown in Fig. 1. La_2O_3 has low adsorption capacity below 200 °C, but above this temperature it starts increasing fast, and at the end of the thermal treatment, at 490 °C, saturation has not been reached yet. As a result, during the cooling step in $NO+O_2$ flow (not shown), the solid continues adsorbing NO_x, which is evidenced in the higher relative mass value measured at the beginning of the helium treatment. The species formed on the lanthanum surface are very stable, and do not decompose in inert flow until 490 °C. These results are in agreement with those previously reported by our group [12].

During the adsorption step, at low temperatures, the three noble metal containing catalysts showed a behavior similar to the one observed for the lanthanum oxide support. Nevertheless, above 300 °C approximately, the noble metals (Pt and Rh) catalyze the decomposition of the adsorbed NO_x species, causing a significant decrease of the relative mass as the temperature increases. This decomposition allows the readsorption of NO_x species during the cooling step, which are again decomposed at high temperature during the thermal treatment in inert stream.

Only small differences can be observed among the Pt, Rh and $Pt,Rh/La_2O_3$ catalysts. As regards the adsorption capacity, according to the left side of Fig. 1, the rhodium catalyst shows a slightly lower capacity than the other two solids, in the temperature range under study. However, the adsorption profiles are very similar. For all catalysts, the amount of NO_x adsorbed is very small at low temperatures, below 200 °C approximately. Above this temperature, the three samples display a sharp increase in the relative mass value, i.e., the adsorption rate is very fast in the 200–330 °C temperature range, due to the formation of bulk nitrate species. Finally, once the maximum adsorption capacity has been achieved, the adsorbed nitrates start decomposing in $NO+O_2$ atmosphere. Table 2 shows the mass losses during the desorption step calculated for the different catalytic formulations studied. According to these values, and to the right side of Fig. 1, all metal-loaded La_2O_3 catalysts exhibit a high ability to decompose the nitrate species in inert stream, and the platinum catalyst shows higher capacity than rhodium. In relation to this, many authors have reported a beneficial effect of Pt regarding NO_x decomposition. Fridell et al. [14] studied NO_x adsorption on BaO/Al_2O_3 catalysts, with and without Pt. They found that when the sample contained Pt, the trapped NO_x desorption temperature was about 100 °C lower than the value corresponding to the BaO/Al_2O_3 catalyst. Similar results were obtained by Olsson et al. [15] with the same catalytic formulations. They observed an increase in the trapped NO_x decomposition rate, along with a decrease in the desorption temperature in the presence of platinum. Based on these results, the authors proposed a mechanism of superficial NO_2 spillover between the Pt and BaO sites. Fanson et al. [16] also reported that Pt was capable of taking part in a spillover mechanism, even though the compound adsorbed and dissociated over Pt was O_2, and in the case of the reducing step, it was H_2. Platinum seems to play a much more important role in decomposition than in the formation of the superficial nitrate species. It has also been proved that the presence of Pt decreases the thermal stability of $Ba(NO_3)_2$ and induces its catalytic decomposition, without being necessary to work under reducing atmosphere [17]. The nitrate decomposition occurs by a homogeneous catalytic reaction in the solid state.

Fig. 2 shows the NO_x adsorption profiles obtained with potassium containing catalysts. According to these results, adsorption capacity is not related to the presence of noble metals in the formulation, since with the K/La_2O_3 catalyst the relative mass values are the highest in the whole temperature range. Moreover, it does not seem to exist a correlation between catalysts formulation and their ability to adsorb NO_x, among the samples studied. This issue will be analyzed in Section 3.2.

As regards the NO_x species stability in inert atmosphere, the results obtained with the K/La_2O_3 catalyst showed that the trapped NO_x species are very stable and exhibit negligible decomposition up to 490 °C, in helium stream (not shown). This is in line with previous results obtained by our group concerning K_{OH}/La_2O_3 catalysts [12], as well as with the reports from other authors for different potassium containing catalysts [18,19].
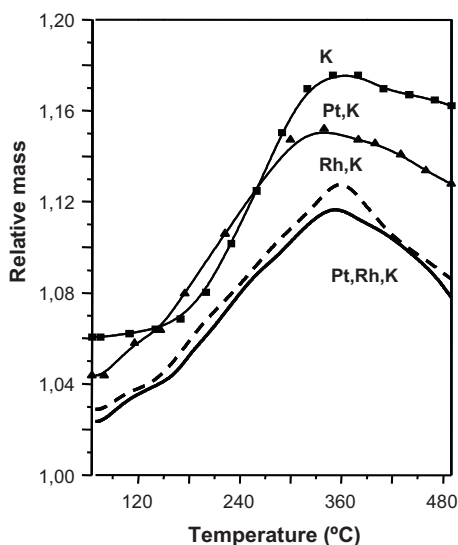
Fig. 2. NO(4%)+O_2(18%) adsorption in microbalance. K/La_2O_3 and NM,K/La_2O_3 catalysts.

The potassium effect on the ability of noble metals to decompose NO_x containing catalysts, is shown in Fig. 3. Each part of this figure compares the helium desorption profiles corresponding to a pair of catalysts which contain the same type and amount of noble metal, with and without potassium on their formulation. According to these results, the potassium addition to NM/La_2O_3 catalysts provokes different changes in their NO_x desorption behavior, depending on the type of noble metal. While the formulations without potassium exhibited similar ability to decompose the adsorbed nitrates, the NM,K/La_2O_3 catalysts showed marked differences.

It can be seen in Fig. 3 that for the same noble metal content, the temperatures at which nitrate decomposition starts are very similar. However, for the platinum catalysts (Fig. 3A), the amount of desorbed NO_x is much lower in the presence of potassium. On the contrary, for the Rh and Pt,Rh catalysts (Fig. 3B and C, respectively), the mass losses during the desorption step are not significantly affected by the addition of potassium to the catalytic formulation. This is also supported by the data presented in Table 2. Therefore, it can be concluded that platinum has an important effect on the NO_x species decomposition, but this effect is masked by the presence of potassium, which proves the existence of a strong interaction between the catalytic components of this formulation. This effect is further sustained by TPR results (not shown) from which it can be concluded that the noble metals Pt and Rh strongly interact both with potassium and with lanthanum oxide support, the interaction K–Pt being stronger than that of K–Rh.

Comparing the desorption profiles obtained with the Pt,K and Rh,K catalysts (Fig. 3A and B), it can be noticed that the amount of NO_x released is considerably higher for the rhodium catalyst. In NO_2 TPD experiments with M/BaO/Al_2O_3 catalysts, Abdulhamid et al. [20] observed that when M=Rh, the desorption peak occurred at lower temperature, compared to Pt or Pd. They attributed these results to the different mobility of the superficial NO_x species, depending on the type of noble metal. Besides, it has been previously stated that when Rh is in its oxidized form, it is capable of adsorbing NO_x at low temperature, forming a Rh$\cdots$NO$^+$ complex [21]. This compound is likely to decompose at high temperature. Therefore, the intermediate complex formed in the presence of NO could be responsible for nitrate decomposition both in NO+O_2 and in inert atmosphere.

3.2. Catalyst characterization: Fourier transformed infrared spectroscopy (FTIR) and X-ray diffraction spectroscopy

The FTIR spectra of the mono and bimetallic catalysts without potassium (NM/La_2O_3) are shown in Fig. 4. All the signals observed are related to the lanthanum oxide support. No signals corresponding to the noble metals were detected, in agreement with Irusta et al. [22], who characterized La_2O_3 supported catalysts with various Pt and Rh contents, by FTIR and XRD. None of these methods allowed them to identify signals corresponding to Pt or Rh, even in catalysts with metal loadings in the 2–4% range.

According to the spectra, the main phases present are La(OH)$_3$ and $La_2O_2CO_3$. Lanthanum oxicarbonates can exist in three different polymorphic crystalline phases, identified as I, Ia and II. In these catalysts, the prevailing form is type II $La_2O_2CO_3$, with characteristic bands at 1508, 1465, 1087, 856 and 747 cm^{-1} [22]. Besides, a sharp band at 3608 cm^{-1}, and a wide one, at 644 cm^{-1} can be observed. These bands are characteristic of the stretching and bending vibrations, respectively, of the OH groups in La(OH)$_3$ [23]. The three catalysts exhibit the bands corresponding to type II $La_2O_2CO_3$. Besides, in the bimetallic and in the platinum catalysts, the signals characteristic of La(OH)$_3$ can be observed. However, in the rhodium catalyst these signals are not present.
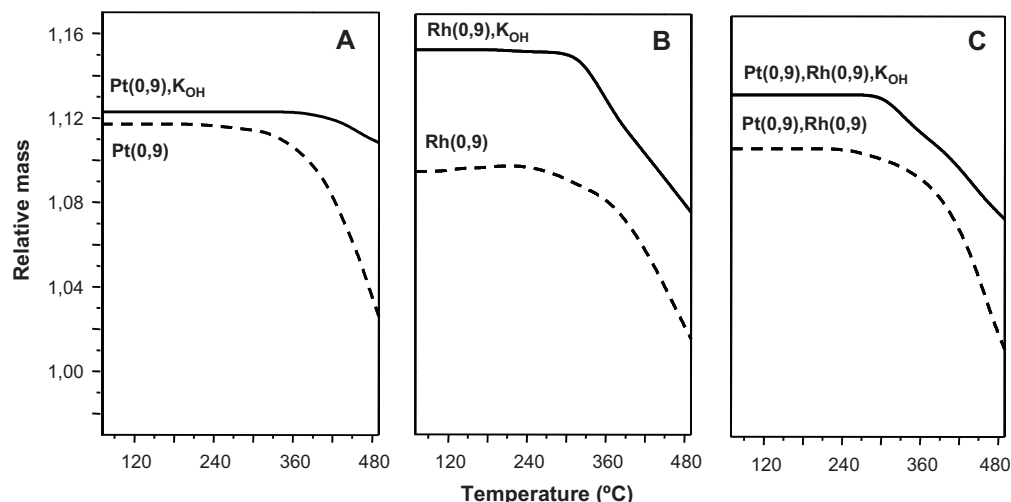

Fig. 3. NO_x decomposition in He stream. Catalysts with and without potassium in the formulation. (A) Pt catalysts; (B) Rh catalysts; (C) Pt and Rh catalysts.
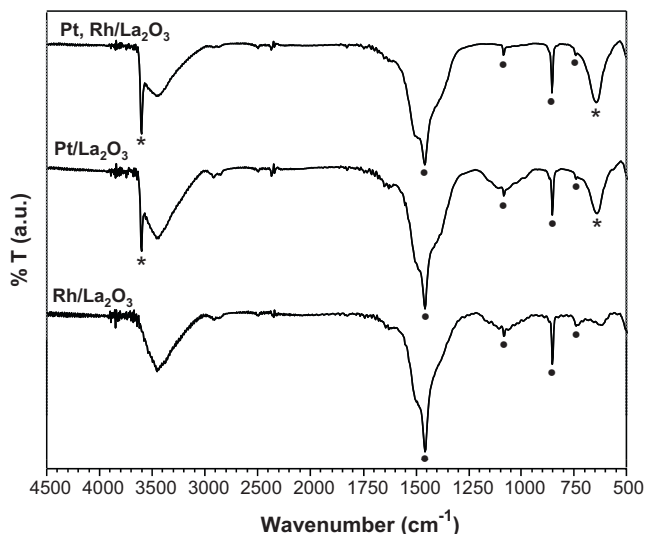
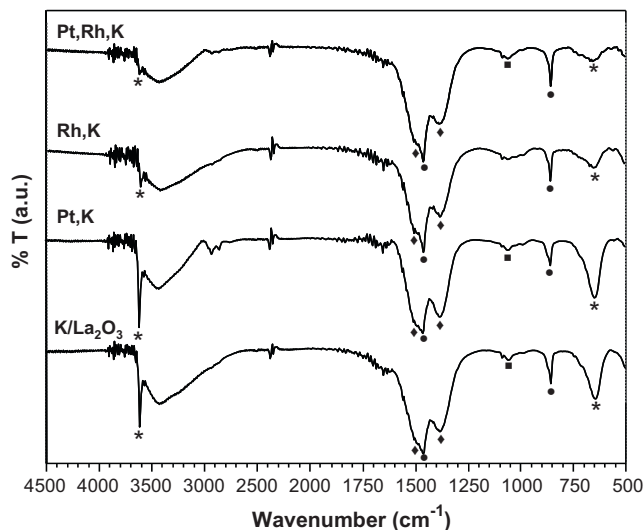Fig. 4. FTIR spectra of NM/La$_2$O$_3$ catalysts. (*) La(OH)$_3$; (●) La$_2$O$_2$CO$_3$.

Fig. 6. FTIR spectra of K/La$_2$O$_3$ and NM,K/La$_2$O$_3$ catalysts. (■) K$_2$CO$_3$; (*) La(OH)$_3$; (●) La$_2$O$_2$CO$_3$; (♦) La$_2$(CO$_3$)$_3$.

The X-ray diffraction technique was also employed in order to analyze the crystalline species present in the catalysts under study. Fig. 5 displays the X-ray spectra of the NM/La$_2$O$_3$ catalysts. These results are in agreement with the ones obtained by FTIR. In the three samples, only phases La$_2$O$_2$CO$_3$ (ASTMN° 37-804) and La(OH)$_3$ (ASTMN° 36-1481) were identified, which corresponded to the support. The FTIR bands associated with the lanthanum hydroxide phase could not be detected for the rhodium catalyst. In agreement, the XRD spectra show that these bands are much weaker in the Rh/La$_2$O$_3$ catalyst than in the other two samples.

Fig. 6 displays the FTIR spectra corresponding to potassium containing catalysts. The signals observed are mainly related to phases corresponding to the support, although weak bands can also be detected that can be assigned to potassium compounds. None of these catalysts exhibit signals associated with the noble metals. As regards the lanthanum oxide support, the main phases are La$_2$O$_2$CO$_3$ and La(OH)$_3$, and of lower importance, La$_2$(CO$_3$)$_3$.

The potassium precursor used to prepare these catalysts was KOH. Nevertheless, no FTIR signals corresponding to this compound were detected. The signal at 1060 cm^{-1} can be assigned to the K$_2$CO$_3$. This compound might be formed by reaction between

KOH and carbon dioxide during the calcination step of the catalysts in air flow, or due to their exposure to the atmosphere. In the Pt,K/La$_2$O$_3$ spectrum some signals between 2800 and 3000 cm^{-1} can be observed, which can be assigned to carbonate combination and overtone vibrations [24].

Comparing the spectra of the different potassium containing catalysts, it can be noticed that the main difference among them is the intensity of the La(OH)$_3$ signals. In the K and Pt,K catalysts these bands are very intense, while in the rhodium containing catalysts (Rh,K and Pt,Rh,K), they are of minor importance.

The XRD spectra of these catalysts are shown in Fig. 7. As in the catalysts without potassium, the main phases present are La$_2$O$_2$CO$_3$ and La(OH)$_3$. No XRD signals corresponding to La$_2$(CO$_3$)$_3$ were detected, despite the fact that this compound was identified by FTIR. This indicates either that lanthanum carbonate is a superficial species, or that the crystallites formed are too small to be detected by XRD.

As regards the relative amount of each lanthanum phase, the XRD results confirm what was previously observed by FTIR. In this sense, Fig. 7 shows that in the spectra of the K/La$_2$O$_3$ and Pt,K/La$_2$O$_3$ catalysts the intensity of the signals corresponding to La(OH)$_3$ is considerably higher than in the spectra of the Rh,K and Pt,Rh,K cat-

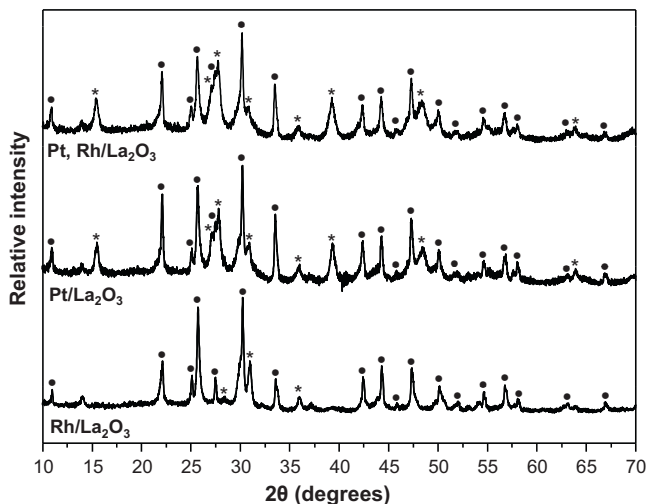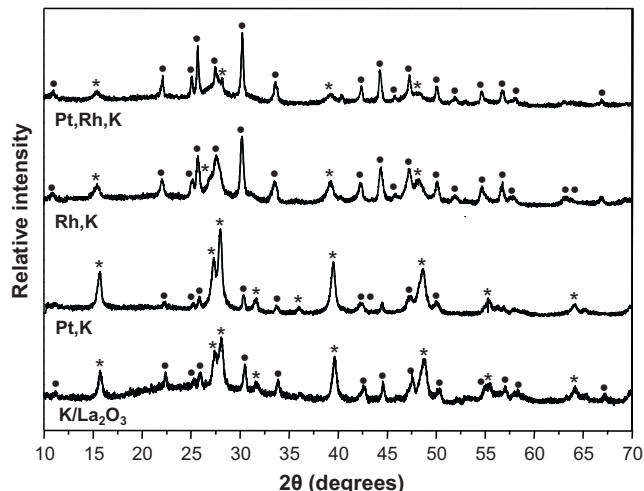Fig. 5. XRD spectra of NM/La$_2$O$_3$ catalysts. (*) La(OH)$_3$; (●) La$_2$O$_2$CO$_3$.

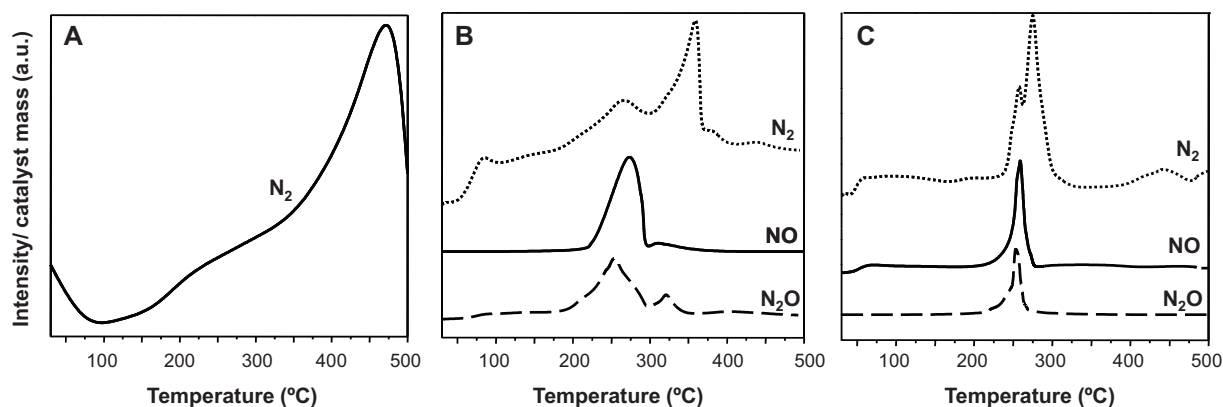Fig. 7. XRD spectra of K/La$_2$O$_3$ and NM,K/La$_2$O$_3$ catalysts. (*) La(OH)$_3$; (●) La$_2$O$_2$CO$_3$.

Fig. 8. Released species during nitrated catalysts treatment in reducing (H_2) atmosphere. (A) K/La_2O_3; (B) $Rh,K/La_2O_3$; (C) $Pt,K/La_2O_3$.

alysts. On the other hand, in these two catalysts, $La_2O_2CO_3$ is the main phase.

It is interesting to analyze the NO_x adsorption profiles displayed in Figs. 1 and 2, together with the FTIR and XRD spectra presented here. Based on these results, it can be concluded that among catalysts with the same general catalytic formulation, the samples which showed higher NO_x adsorption capacities are those containing a higher amount of the $La(OH)_3$ phase. On the one hand, $La(OH)_3$ decomposes at 380 °C, approximately, resulting in the formation of LaOOH [25]. Then, this compound decomposes to La_2O_3 in the 400–550 °C temperature range. Nevertheless, this transformation does not occur significantly in the presence of potassium [25]. According to this, during the catalysts pre-treatment, prior to the NO_x adsorption, the $La(OH)_3$ initially present on the samples suffers the transformation to LaOOH. On the other hand, the lanthanum carbonates start decomposing only above 550 °C [25], and hence, these species decomposition cannot take place during the catalysts pre-treatment, whose final temperature is 490 °C. Therefore, the higher the initial content of $La(OH)_3$ in the catalysts, the higher the amount of LaOOH at the beginning of the $NO + O_2$ treatment. These results indicate that the NO_x adsorption occurs more readily over this compound than on the $La_2O_2CO_3$. This causes that those catalysts with a higher initial content of $La(OH)_3$ have higher NO_x adsorption capacities. It has been reported that for K/La_2O_3 catalysts, the higher the $La(OH)_3$ phase content, the higher its interaction with CO_2 [25]. Such interaction capacity is related to the surface basicity, as in the case of the interaction with the nitrogen oxides. Thus, if the presence of $La(OH)_3$ increases the K/La_2O_3 capacity to adsorb CO_2, it could also result beneficial for the adsorption of NO_x. Similar results were obtained by Lietti et al. [26] with catalysts containing barium as the NO_x storage compound. Using $Pt–Ba/Al_2O_3$ catalysts, these authors were able to establish that NO_x storage takes place first on BaO, then on $Ba(OH)_2$ and finally on $BaCO_3$, in line with the decreasing basic character of the different NO_x storage barium sites. Also, the storage on $BaCO_3$ resulted of less importance. Toops et al. [27] found that NO_x adsorption occurs faster in the presence of H_2O than in a dry atmosphere, attributing this behavior to the promoting effect of the superficial hydroxyl groups.

3.3. Temperature-programmed reduction (TPR) of nitrated catalysts

The NO_x trap concept is based on the adsorption during the normal engine operation in oxygen excess, and then, when the adsorber capacity is saturated, the stored NO_x must be released and reduced to N_2, by the injection of a reducing agent. Thus, to study the catalytic system in more real conditions, NO_x decompo-

sition experiments were carried out in reducing atmosphere. The species generated during such reduction were determined by mass spectroscopy, as described in Section 2.2.3.

Fig. 8A shows results obtained with the K/La_2O_3 catalyst. Only the N_2 evolution is plotted, since no other nitrogen containing species was detected for this sample. Therefore, with the non-noble metal containing catalyst, although the reduction takes place at a rather high temperature, a complete reduction of NO_x to N_2 is achieved. Teraoka et al. [28] reported that during the simultaneous abatement of soot and NO_x using perovskite type based oxides (ABO_3), the substitution with K in the A sites promoted N_2 selectivity. In a subsequent work, using the $CuFe_2O_4$ spinel as a catalyst, they found similar results [29]. Furthermore, they also showed that Pt impregnation decreased N_2 selectivity.

Fig. 8B displays the evolution with temperature of the products obtained during reduction of NO_x adsorbed on the $Rh,K/La_2O_3$ catalyst. The reduction occurs at lower temperature than with the potassium catalyst, in agreement with the results obtained during NO_x decomposition in inert stream. However, a fraction of the decomposed nitrates does not complete its reduction to N_2, since peaks corresponding to NO and N_2O were also detected, with maximum at 250 °C, approximately. With the $Pt,K/La_2O_3$ catalyst (Fig. 8C), as with the rhodium sample, NO and N_2O were also detected as nitrate decomposition products. Nevertheless, the main product obtained was N_2.

The gravimetric experiments showed that the presence of noble metals allows nitrate decomposition to take place at lower temperature in inert atmosphere. In H_2 stream, both with the platinum and with the rhodium containing catalysts NO and N_2O are released at about 250 °C, while the main N_2 peaks are observed at higher temperatures. These results indicate that at low temperature, decomposition occurs at a higher rate than reduction. As a consequence, not all the released species can be reduced. As temperature increases, the reduction rate becomes high enough to completely transform the NO_x to N_2. With the non-noble metals containing catalyst, decomposition occurs at high temperature, with the reduction rate also being high, thus allowing all released species to be reduced to N_2. According to Ji et al. [30], it is important to establish a balance between nitrate decomposition and NO_x reduction in order to optimize the trap regeneration efficiency.

In Section 3.1, it was shown that in catalysts containing platinum and/or rhodium and potassium, the latter modifies the noble metals behavior, the effect being more notorious in the case of platinum. For this reason, in the NM-K formulations studied here, the most effective catalyst for NO_x decomposition in inert stream was the Rh,K one. However, according to the results presented in Fig. 8, with the $Pt,K/La_2O_3$ catalyst the reduction is completed below 300 °C, which is a lower temperature than the one achieved with
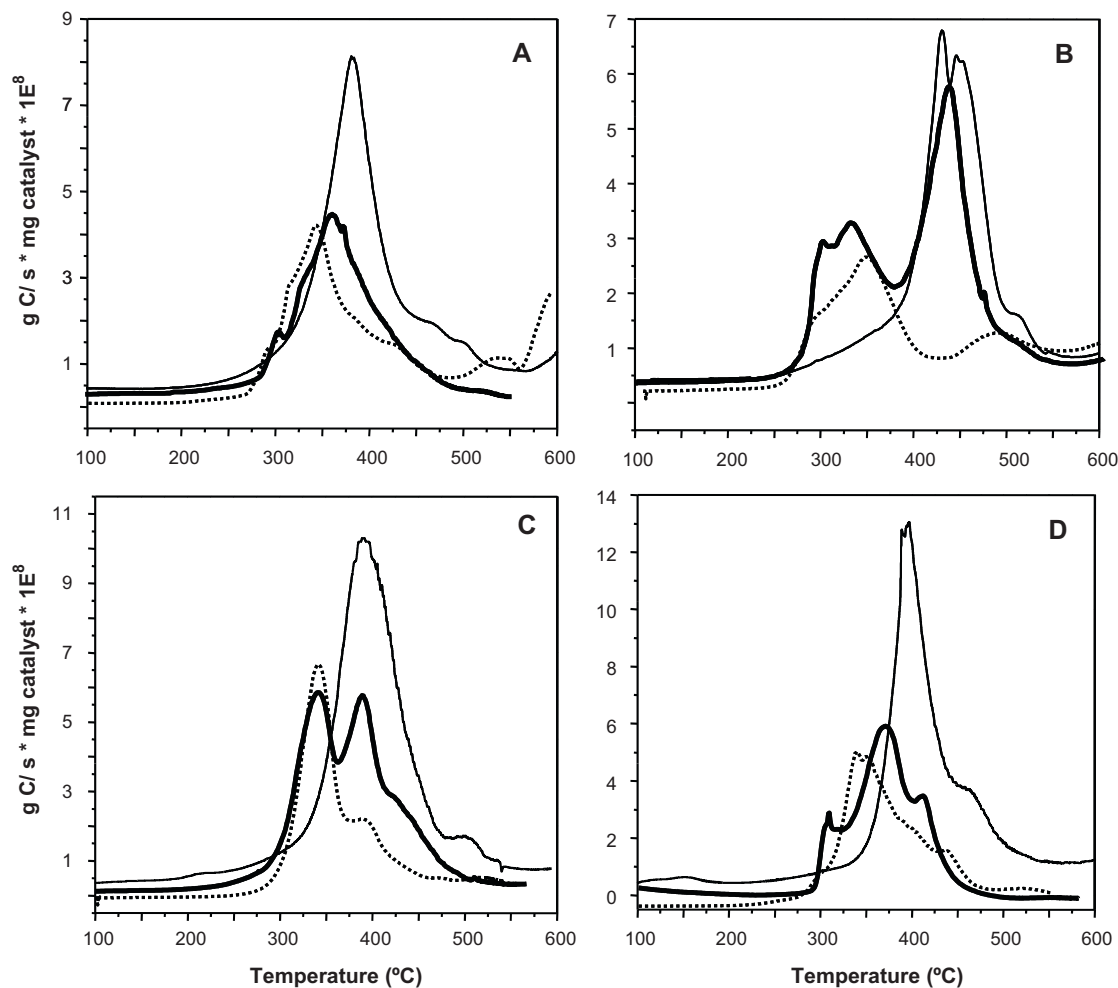
Fig. 9. Activity for soot combustion. Thick line: combustion in O_2(5%)/N_2; nitrated catalyst. Thin line: combustion in O_2(5%)/N_2; fresh catalyst. Dotted line: combustion in N_2 stream; nitrated catalyst. (A) K/La_2O_3 catalyst; (B) Rh/La_2O_3 catalyst; (C) Rh,K/La_2O_3 catalyst; (D) Pt,K/La_2O_3 catalyst.

the rhodium catalyst, of about 350 °C. This is in line with the results obtained by Abdulhamid et al. [20], who worked with Pt/BaO/Al_2O_3 and Rh/BaO/Al_2O_3 catalysts. They found that, although with the rhodium catalyst NO_x desorption in TPD experiments took place at lower temperature, the platinum sample showed higher efficiency for NO_x reduction. In addition, Chambers et al. [31] studied the NO reduction reaction over SiO_2 supported metallic catalysts containing Pt, Pd or Rh. According to their results, the order of activity for the NO + CO reaction is Rh > Pd > Pt, but Pt > Pd > Rh for the reduction with H_2.

3.4. Soot combustion activity

In a previous work [32], we studied the reaction between soot and the NO_x adsorbed over different lanthanum supported catalysts, containing noble metals and potassium, in inert stream (N_2). It was found that the activity of the catalysts is not related to their ability to decompose the trapped nitrated species. When the combustion reaction with nitrated catalysts takes place in oxidant atmosphere, the situation is more complex since in the presence of O_2 the soot can be oxidized both by the gaseous reactant and by the nitrates adsorbed on the catalysts. Taking this into account, this section presents soot combustion results obtained under different conditions. The experiments were performed in oxidant or inert flow using fresh or nitrated catalysts, in order to determine which is the contribution of each oxidant agent by comparison of the different combustion profiles. Besides, it is interesting to study

the effect of the NO_x species adsorbed on the catalysts regarding their activity for soot combustion in O_2 stream. This allows evaluating the possibility of using these catalysts for the simultaneous abatement of soot and nitrogen oxides.

Fig. 9 presents the combustion results obtained with four different catalytic formulations. For each catalyst, two experiments were performed in O_2/N_2 stream: with the nitrated catalyst (thick line), and with the fresh sample (thin line). Finally, another soot combustion experiment was carried out in N_2 stream using the nitrated catalyst (dotted line). Comparing the combustion temperatures obtained with both the nitrated and the fresh catalysts in oxidant atmosphere, it can be concluded that for all the samples under study, the activity for soot combustion was increased by the presence of nitrate species previously adsorbed on the catalysts. However, according to the results discussed in Section 3.1, some of these samples were not very effective for NO_x desorption. Therefore, similarly to what was observed in inert atmosphere [32], NO_x species are capable of reacting with soot in O_2 stream without the necessity of their previous decomposition. These results are also in agreement with those obtained by other authors [3–7], who have previously shown that the soot can be oxidized at significantly lower temperatures over different catalysts treated in NO_x, in comparison with the fresh samples.

The combustion profiles obtained with the catalysts treated in NO + O_2 are very different from those corresponding to the fresh samples, except for the case of the K/La_2O_3 catalyst (Fig. 9A). However, as with the other solids, the maximum reaction rate is also

reached at lower temperature with the nitrated catalyst. The reason for this behavior can be attributed to the fact that this formulation has a high activity. This prevents the discrimination in the combustion profile obtained with the nitrated sample, of the fraction corresponding to the reaction between soot and the adsorbed nitrates from the fraction originated by the combustion with the gaseous O_2. Very similar results were obtained when the reaction using the nitrated catalyst was carried out in inert atmosphere (dotted line). Therefore, the catalyst treated in $NO + O_2$ also has a high activity in an inert flow, and it is not significantly affected by the presence of O_2 in the gaseous feed.

The combustion profile obtained with the nitrated Rh/La_2O_3 catalyst in O_2/N_2 stream (Fig. 9B, thick line) presents two distinct zones. According to the curve corresponding to the fresh catalyst (thin line), the second peak can be assigned to the fraction of soot being burnt with the O_2 of the gaseous stream. Moreover, taking into account the combustion profile obtained with the nitrated catalyst in inert atmosphere (dotted line), it can be concluded that the low temperature peak is originated by the reaction between soot and the nitrates adsorbed on the catalyst surface.

A similar analysis can be applied to the $Rh,K/La_2O_3$ catalyst (Fig. 9C). The combustion profile of the nitrated sample in O_2/N_2 stream (thick line) presents two peaks. According to the results obtained with the nitrated catalyst in inert atmosphere (dotted line), the low temperature peak corresponds to the reaction between soot and the adsorbed NO_x. On the other hand, the oxidation of soot on the fresh catalyst in O_2/N_2 flow (thin line) allows assigning the higher temperature peak to the combustion of the remaining soot with the gaseous oxygen.

The combustion profile exhibited by the nitrated $Pt,K/La_2O_3$ catalyst (Fig. 9D, thick line) also presents and additional low temperature peak, compared with the one corresponding to the fresh sample (thin line). This peak appears during the reaction of soot with the adsorbed nitrates. Besides, it is interesting to notice that the fraction of the curve assigned to the combustion with O_2 shifts to lower temperatures when the catalyst is previously treated in $NO + O_2$. As with the rhodium samples, the results obtained with the nitrated catalyst in inert atmosphere (dotted line) confirm that the fraction of the carbonaceous material that burns at lower temperature in O_2 stream corresponds to the reaction between soot and NO_x.

The results presented above show that the lanthanum supported catalysts here studied, which present good NO_x adsorption capacity, are active for the oxidation of soot. Moreover, the nitrogen compounds adsorbed enhance the activity of the solids for the combustion of the particulate material. These characteristics make them suitable to be used to eliminate soot according to the DPNR system. Further research is needed in order to evaluate the elimination of both contaminants, soot and nitrogen oxides, under conditions closer to the real ones.

4. Conclusions

Lanthanum supported catalysts containing noble metals (Pt and/or Rh) proved to be very effective NO_x traps. The lanthanum oxide support acts as the NO_x storing component, while the noble metals allow the decomposition of the nitrate species to take place at relatively low temperature, in inert atmosphere. In order to use these catalysts for the simultaneous abatement of soot and NO_x, the addition of potassium to the formulation, as the active material for particulate matter combustion, is necessary. NO_x desorption results obtained with the catalysts containing noble metals and potassium showed the existence of a strong interaction between the components. Although the NO_x desorption temperatures are not significantly modified, the amount of species decomposed in inert atmosphere decreased in the presence of potassium, this effect being much more notorious for the platinum catalyst.

The high ability of platinum and rhodium to decompose the adsorbed nitrates causes that in reducing atmosphere, the stored NO_x species are transformed to N_2 at lower temperature but with less selectivity with catalysts that contain noble metals and potassium than with the potassium sample. This is because at low temperature, in the presence of noble metals, the decomposition rate is higher than the reducing one, and the released species under these conditions cannot complete their reduction to N_2.

As regards the activity for soot combustion of these NO_x storing materials, it was shown that it is improved by the presence of adsorbed nitrate species. It was found that the soot combustion temperature is not related to the NO_x desorption temperature. Therefore, it is concluded that soot reacts with the adsorbed nitrogen oxides on the catalyst surface, their previous decomposition not being necessary. Therefore, lanthanum supported catalysts containing noble metals and potassium are not only effective as NO_x traps but also active for the simultaneous particulate matter abatement.

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