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NOx adsorption and diesel soot combustion over La_2O_3 supported catalysts containing K, Rh and Pt

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ABSTRACT

In this work we report results of NO*x* adsorption and diesel soot combustion on a noble metal promoted K/La_2O_3 catalyst. The fresh-unpromoted solid is a complex mixture of hydroxide and carbonate compounds, but the addition of Rh favors the preferential formation of lanthanum oxycarbonate during the calcination step. K/La_2O_3 adsorbs NO*x* through the formation of La and K nitrate species when the solid is treated in NO + O_2 between 70 and 490 °C. Nitrates are stable in the same temperature range under helium flow. However, they become unstable at ca. 360 °C when either Rh and/or Pt are present, the effect of Rh being more pronounced. Nitrates decompose under different atmospheres: NO + O_2, He and H_2. The effect of Rh might be to form a thermally unstable complex (Rh–NO^+) which takes part both in the formation of the nitrates when the catalyst is exposed to NO*x* and in the nitrates decomposition at higher temperatures. Regarding soot combustion, nitrates react with soot with a temperature of maximun reaction rate of ca. 370 °C, under tight contact conditions. This temperature is not affected by the presence of Rh, which indicates that the stability of nitrates has little effect on their reaction with soot.

1. Introduction

Diesel engines have increased in popularity because of their superior fuel economy and durability. Particulate matter (soot) and NO_x are the diesel pollutants of major concern, the combination of a filter with oxidation catalysts being the most studied after-treatment process to eliminate soot particles. For NO_x abatement, NO_x adsorbers (traps) and NO_x SCR with ammonia or hydrocarbons constitute new technologies both for partial lean-burn gasoline engines and for diesel ones [1]. Interesting review articles on these subjects have been published, dealing with filters for particulate diesel emission control [2,3], NO_x abatement using sorbing catalytic materials [4] and fundamentals of oxidation of carbon by NO_x [5]. Some reviews [6–8] have recently offered updates on new technologies for diesel emission control.

NO_x adsorbers (traps) constitute a relatively new technology for NO_x abatement. The adsorber (usually containing Ba or K compounds) chemically binds nitrogen oxide during lean engine operation. After the adsorber capacity is saturated, the system is regenerated and released NO_x is reduced during a period of rich operation. In the case of diesel engines, since a rich operation is not feasible, periodic fuel injections are necessary.

On the other hand, a large number of catalyst formulations have been reported for soot combustion, and the contact between soot and the catalyst appears to be one of the most important problems to overcome. Another important problem that should be overcome is the deactivation of the catalysts when subjected to thermal shocks and poisons [9,10]. Van Setten et al. [11] proposed that, for laboratory studies, the most realistic method for bringing soot into physical contact with an oxidation catalyst is soot filtration from a diesel exhaust gas. Other convenient methods recommended by these authors are simply mixing with a spatula, shaking in a sample bottle, dipping in soot dispersion, or filtering from an artificial soot aerosol. Molten salt catalysts evaluated under realistic conditions gave promising results [12–14]. However, in this case, the catalyst design is restricted to compounds that melt at the temperature in which the soot combustion is going to be carried out. It means that the catalyst formulation is carried out first looking for materials that form a eutectic point around 300 °C or lower and then choosing according to the catalytic performance among these materials. Thus, something that is important in the catalyst formulation is to include active components with high mobility. In our previous studies [9,10,15–17], potassium plays that role, increasing the effective contact with the soot due to its high mobility. Particularly, we have found that potassium-loaded

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La_2O_3 catalysts calcined at 400 °C and mixed with soot are active and thermally stable, burning the soot at TPO maximum rates between 350 and 400 °C. Moreover, there is no difference in activity when they are either mixed in an agate mortar or separately grinded and mixed by shaking in a sample bottle (tight and loose conditions, respectively), making this system interesting to be investigated for practical applications [15]. When K/La_2O_3 was used as a monolith washcoat, similar results were obtained. It was possible to remove up to 90% of the soot holding the temperature at 405 °C, thus further suggesting the potentiality of this system for practical purposes.

Potassium has been largely investigated as an active component for soot combustion because its high mobility leads to active catalysts. In addition, due to its basic character potassium is good in order to be present in NO_x traps. However, the high mobility causes K to present a technological problem associated with its interaction with the monolith support. In spite of this, research and application developments using potassium keep coming out. The reason is that it is very important to study this compound in order to better understand the fundamentals of this very complex reaction system. This is demonstrated by recent publications, addressing the role of alkaline metals in the soot oxidation reaction. [18–23]. The patent literature also includes potassium in several devices developed for soot combustion [24,25] and also for simultaneous abatement of soot and NO_x [26–28]. In many cases, other alkaline metals are considered such as Li, Cs, Na, and included in basic studies or technological applications [29].

We have also found that NO_2 strongly interacts with both La_2O_3 and K/La_2O_3 solids, through the formation of monodentate nitrate species, which are stable under He, atmosphere until 490 °C. This surface species migrate inside the solid forming a bulk nitrate compound. This behavior also makes this system interesting to be used as a NO_x catalytic trap.

The reactions involved in the NO trapping process are the oxidation of NO–NO_2 and the reaction of the last compound with surface basic species, in our case K and La ones. This occurs under lean conditions and, when the trap is saturated, the adsorbed species are released and decomposed in a rich atmosphere. Thus, ingredients are necessary both to oxidize NO under lean conditions and to reduce NO_x–N_2 in the presence of a reductant. Usually, these roles are performed by Pt and Rh, respectively [30]. Accordingly, the objective of the present work is to study the interactions between NO_x and K/La_2O_3 also containing Pt and/or Rh. The soot combustion reaction on these catalysts is also adressed. To this end, a number of catalysts have been prepared: K/La_2O_3, Rh/La_2O_3, $Pt,K/La_2O_3$, $Rh,K/La_2O_3$ and $Pt,Rh,K/La_2O_3$ which were studied using a microbalance system to quantify the NO_x adsorption capacity and Temperature-programmed Oxidation (TPO) experiments to evaluate the soot combustion rate. In addition *in situ* FTIR measurements were performed to identify the different species formed after NO_x adsorption.

2. Experimental

2.1. Catalysts preparation

Catalysts were prepared by wet impregnation of the components over the La_2O_3 support (Strem Chemicals, 99.9%). $K(7.5)/La_2O_3$; $Rh(0.9)/La_2O_3$; $Pt(0.9),K(7.5)/La_2O_3$; $Rh(0.9),K(7.5)/La_2O_3$ and $Pt(0.9),Rh(0.9),K(7.5)/La_2O_3$ catalysts were prepared, where the numbers represent the wt. % of each component. KOH (1 M), $RhCl_3$ (40 g Rh/l) and H_2Cl_6Pt (8.4 g Pt/l) solutions were added to the support in order to obtain the required concentration of each metal. The suspensions were evaporated while being vigorously stirred until achieving a paste, which was dried in a stove at 120 °C for 24 h and then calcined at 500 °C for 2 h in air flow. For those catalysts which contain Pt, Rh, or both noble metals and K in their formulation, the impregnation was carried out in the following form: first, the corresponding noble metal(s) and after a calcination, potassium, followed by a second calcination step.

A $Rh(0.9)/SiO_2$ catalyst was also prepared. This catalyst was used to obtain a mechanical mixture with the $K(7.5)/La_2O_3$, with the aim of studying the effect of rhodium when it is not directly impregnated over the lanthanum support. The mixture was prepared weighting equal amounts of both catalysts and mixing them with a mortar, in order to homogenize the particle size.

2.2. X-ray diffraction (XRD)

The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu Kα radiation at a scan rate of 1 °/min, from $2\theta = 10$–$60°$.

2.3. Microbalance studies. NO_x adsorption cycles

They were performed in Cahn 2000 equipment with the objective of studying the interaction of the catalysts with NO + O_2. The samples were dried heating them at 450 °C in He for 30 min, followed by a second heating step, to 490 °C, for 10 min, after which samples were stabilised at 70 °C, where the weight was determined. This mass was considered to be the initial one, to guarantee that all samples were under the same conditions at the beginning of the experiments. All the weights subsequently obtained were divided by this value, and referred to as relative mass. After this, a mixture of NO (4%) + O_2 (18%) (He balance) was fed, and the samples were stabilised 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 repeated in this stream.

In order to assess the reversibility of the NO_x adsorption over different catalysts, some of them were selected to perform two cycles of adsorption and desorption. Such experiments were carried out repeating two consecutive times the heating treatments in NO + O_2 and He described above. Finally, the same adsorption–desorption cycles were performed but using a reducing atmosphere (H_2(0.1%)/He) in the regeneration step.

2.4. In situ FTIR studies

In situ FTIR studies were performed in order to investigate what species are formed over the catalysts surface when they are exposed to different gaseous feeds. For this purpose, the samples were placed into an infrared cell, provided with CaF_2 windows, where they were subjected to heating treatments in NO + O_2 and He. First, the samples were pre-treated at 400 °C for 30 min in He. After that, a spectrum was obtained, and used as reference to compare with those taken along the heating in NO + O_2. Then, the feed was changed to NO(4%) + O_2(18%) (balance He), and samples were heated at 200, 300, 400 and 450 °C, maintaining each temperature for 15 min. At the end of each heating, an IR spectrum was taken. The same procedure was repeated in He flow, to emulate the desorption step. After that, a second NO + O_2 treatment was performed. As in the microbalance experiments, another set of adsorption–desorption cycles were carried out using H_2(0.1%)/He to study the effect of the presence of a reductant gas. Additional experiments adding 10%CO_2 to the NO + O_2 stream were performed in order to evaluate the effect of this gas, which is present in diesel exhaust. All spectra were obtained using a Shimadzu IR Prestige 21 equipment, with an accumulation of 40 scans and a resolution of 8 cm^{-1}.

2.5. Soot combustion activity

In order to investigate the catalysts activity for soot combustion over a working NO_x trap, samples were previosuly treated in NO(4%) + O_2 (18%) flow, at 350 °C, for 1 h (except for the Rh/SiO_2 + K/La_2O_3 mixture, which was heated at 300 °C). Temperatures were selected taking into account the results obtained in the adsorption experiments, with the aim of achieving the maximum NO_x adsorption over catalysts surface. After this treatment, catalysts were mixed with soot in 20:1 weight ratio, in a mortar, for 6 min (tight contact). The soot was obtained by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. The catalytic activity was determined by heating these mixtures in N_2 flow, at a heating rate of 12 °C/min, 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 through a methanation reactor, where CO and CO_2 were converted to CH_4. Afterwards, methane was continuously measured with an FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C.

The same experiments were carried out employing soot-catalyst mixtures prepared with fresh catalysts (not pre-treated in NO). Finally, to complement the activity study, TPO experiments were performed, in O_2(6%)/N_2 stream, both with fresh and nitrated catalysts.

2.6. Temperature-programmed reduction (TPR)

TPR experiments were performed in an Okhura TP-2002S system. The TPR runs were conducted using a heating rate of 10 °C/min in a flow of 5% H_2/Ar (45 cm^3/min) up to 500 °C.

These experiments were carried out using the fresh Rh/SiO_2 and Rh,K/La_2O_3 catalysts pre-treated in N_2 and physical mixtures of Rh/SiO_2 and K/La_2O_3 with and without pre-treatment in N_2. The objective of these experiments is only to verify the mobility of K and if the interaction with Rh affects its properties. In addition we verified that on the Rh/La_2O_3 catalyst, there is no difference in the TPR profile whether it is pre-treated in N_2 or in O_2 (results not shown). On the other hand, we also found that when K is present, since this compound increases the oxygen adsorption, the TPR does not provide direct evidence of the H_2 consumption by the metal. This is another reason for choosing N_2 to pretreat the catalysts under analysis.

3. Results and discussion

3.1. NO + O_2 adsorption in microbalance

Fresh catalysts were characterized by XRD and FTIR (results not shown). All the lanthanum solids studied exhibit the presence of two phases, corresponding to the support: $La_2O_2CO_3$ and $La(OH)_3$. No XRD reflections or FTIR bands associated with the noble metals (Pt or Rh) were detected in the calcined catalysts. Rh/La_2O_3 showed the presence of $La_2O_2CO_3$ phase, with an almost negligible amount of $La(OH)_3$. Comparing results obtained for the potassium containing catalysts, a similarity was observed between K/La_2O_3 and Pt,K/La_2O_3 diffractograms, as well as in the FTIR spectra, both of them showing signals corresponding to lanthanum oxycarbonate and hydroxide, the latter being the major phase. On the contrary, Rh,K/La_2O_3 and Pt,Rh,K/La_2O_3 showed prevalence of the oxycarbonate compound. According to these results, the presence of rhodium in lanthanum supported catalysts could be favoring the predominance of the $La_2O_2CO_3$ phase, in agreement with Cornaglia et al. [31].

In order to study the interaction between the catalysts surface and NO_x, gravimetric studies were carried out. 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, corresponding to the NO_x stream, and the right 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 is represented. Results obtained for the K/La_2O_3 catalysts, as well as for the catalysts loaded with noble metals (Pt, Rh or both) are displayed.

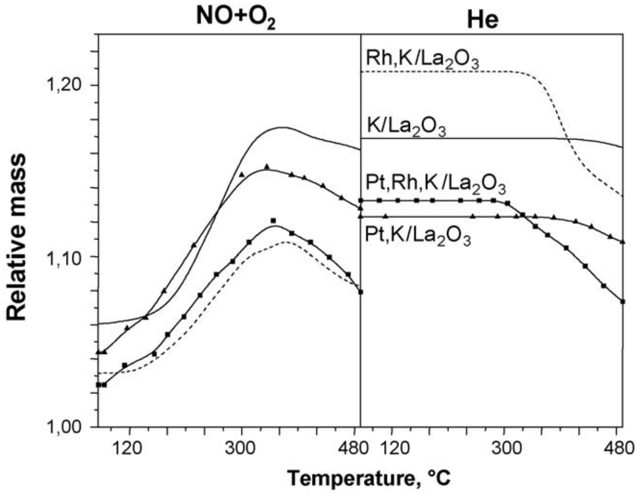

Fig. 1. NO(4%) + O_2(18%) adsorption (left) and decomposition in He (right) in microbalance. Pt,K–Rh,K–Pt,Rh,K and K lanthanum supported catalysts.

During the heating in NO_x stream, the K/La_2O_3 shows higher adsorption capacity than the other catalysts, in the whole temperature range. The formation of NO_2 is neccesary for the formation of both surface and bulk nitrate species. Such transformation of NO–NO_2 can be readily catalyzed by a noble metal. However, given the characteristics of the gravimetric equipment used in these experiments, there is enough residence time between the feed and the solid sample to guarantee the formation of NO_2 [16]. Thus, the formation of NO_2 is not a limiting step in our experiments, explaining why the K/La_2O_3 capacity is similar to the catalysts that also contain noble metals.

As it can be seen, for the K/La_2O_3 catalyst, the relative weight increases up to 330 °C approximately, and remains almost constant above this temperature. This indicates that stable nitrate species are formed over the catalyst surface. These species remain stable even after the heating treatment in helium. In the case of the rhodium containing catalysts (Rh,K/La_2O_3 and Pt,Rh,K/La_2O_3), on the contrary, the nitrate species formed during the NO_x treatment partially decompose at high temperatures (above 350 °C). During the cooling in NO + O_2, nitrates are re-adsorbed over the catalyst surface, this being represented by the discontinuity of the curves, which is almost negligible for those catalysts that do not contain rhodium.

During the gravimetric experiments, two types of species are formed through the interaction between NO_x and the solids: surface adsorbed species that can be formed at low temperatures, and bulk nitrate species that are formed due to the diffusion and reaction inside the solid when temperature increases. Surface species can form bulk nitrates, and vice-versa, depending on temperature.

At about 350 °C, bulk nitrates start to decompose, provoking a decrease in relative mass, as shown in Fig. 1. When 490 °C is reached, the heating is stopped, and the solid is cooled down maintaining NO + O_2 in the feed. From this point, the decrease in temperature provokes a continuous mass increase in both adsorbed and bulk nitrate species. There is no reason to expect that the increase in mass during the cool-down step should not be higher than the maximum mass gained during the heating step, because during the heating step nitrates previously adsorbed are decomposed after certain temperature, while during the cooling down, the adsorbed nitrates remain on the support. As a matter of fact, when Rh is present, the mass gained in the second step is clearly higher.

These results indicate that rhodium is playing a key role in modifying the adsorption strength of at least a fraction of the adsorbed NO-compounds in the presence of oxygen. Moreover, when rhodium catalysts are heated in helium atmosphere, an important fraction of the nitrate species is decomposed above 300 °C. Although the temperatures at which decomposition starts with Pt,K/La_2O_3 are similar to the rhodium containing catalysts, the fraction decomposed is much smaller than in the case of the rhodium catalysts. This is reasonable, because the temperature at which decomposition proceeds is mostly influenced by thermodynamic factors. On the contrary, the amount of nitrates decomposed both under NO + O_2 and He atmospheres is most probably kinetically controlled and, as a matter of fact, the presence of Rh as a catalyst increases the rate of the process.

According to these results, the presence of rhodium prevents the formation of stable species over the catalyst surface, enhancing nitrates decomposition, both in NO_x and inert atmosphere. It has been established that rhodium can adsorb NO_x at low temperature when it is in the oxidized form, forming Rh–NO^+ [32]. It is likely that this compound decomposed at higher temperatures, and therefore this could be the intermediate complex formed both in the presence of NO and during the decomposition/desorption of the nitrates at high temperatures under a helium atmosphere. The magnitude of mass gain in the cool-down step will depend on the storage capacity of the solid and on the formation rate of nitrate species. Thus, the presence of Rh explains that the Rh,K/La_2O_3 catalyst shows the lowest mass gain at the completion of the heating step (490 °C), and the highest mass gain after the completion of the cool-down step.

Taking the previous results into account, new catalysts formulations, all of them containing rhodium, were tested in the adsorption–desorption experiments. Fig. 2 shows the resulting profiles for three different rhodium containing catalysts. The effect of rhodium in the nitrates decomposition is observed for all of the catalysts prepared. In the Rh,K/La_2O_3 catalyst, both potassium and lanthanum are able to react with NO_2 forming nitrate species [15]. For this reason, the Rh/La_2O_3 catalyst displays lower adsorption capacity. However, as regards the species stability, the results are similar, since decomposition occurs both in NO_x and helium stream. Moreover, the weight decrease in helium is proportionally higher in the catalyst without K (compare the curves in the second part of the experiment for Rh/La_2O_3 and Rh,K/La_2O_3 catalysts, Fig. 2). This is related to the different basicity of these catalysts. According to Takahashi et al. [33], the stronger the catalyst basicity, the larger the quantity of NO_x stored and the more stable the nitrates formed on the surface. This effect was also observed even when rhodium was impregnated over SiO_2, forming a mechanical mixture with a K/La_2O_3 catalyst. Moreover, in this case the decomposition started at lower temperatures in both streams. This is a very interesting result, regarding both the catalytic filter-trap design and the understanding of the role of Rh in this mechanism. It can be speculated, according to these results, that the high mobility of K compounds might be the reason for this behavior. Rh favors the NO_x adsorption on K and on La_2O_3 through the formation of the Rh–NO^+ complex. At high enough temperature or under a helium stream, the nitrates formed on K and La_2O_3 are decomposed through the formation of the same intermediate compound (Rh–NO^+), this procedure being facilitated by the mobility of the potassium nitrates.

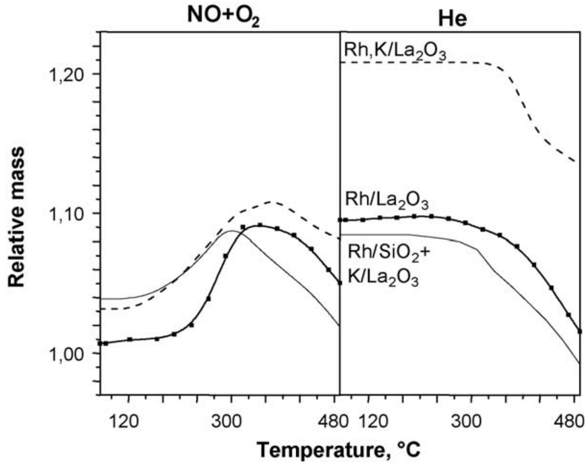

Fig. 2. NO(4%) + O_2(18%) adsorption (left) and decomposition in He (right) in microbalance. Rh and Rh,K–lanthanum supported catalysts and mechanical mixture Rh/SiO_2 + K/La_2O_3.

The regeneration capacity of the NO_x trap is an important item to be taken into account. Thus, the reversibilty of the adsorption–desorption process over different catalysts was evaluated. For this purpose, two cycles of NO_x adsorption and decomposition were carried out in the microbalance. The results are shown in Fig. 3.A. In order to study the effect of a reductant gas in the desorption step, the same experiments were performed using H_2(0.1%)/He (Fig. 3.B).

The adsorption capacity of K/La_2O_3 is saturated during the first NO_x treatment, and nitrates formed over the catalyst surface are very stable in inert atmosphere, showing negligible decomposition. Therefore, NO_x adsorption over this catalyst is an irreversible process, in the temperature range studied. On the other hand, the Rh,K/La_2O_3 catalyst, which exhibits nitrates desorption above 350 °C in helium stream, recovers part of its initial adsorption capacity, although the amount of NO_x adsorbed during the second cycle is substantially smaller. The mechanical mixture K/La_2O_3 + Rh/SiO_2 shows the best performance among the three catalysts evaluated. The species formed over the catalyst surface start decomposing at 300 °C approximately, allowing NO_x re-adsorption during the second cycle. As shown in Fig. 3.A, the adsorption–desorption profiles are very similar between the two cycles; moreover, NO_x adsorption at 70 °C is higher in the second cycle. These results can also be explained following the model explained above. Potassium containig catalysts have higher basicity, which leads to formation of more stable nitrate species over their surfaces. Consequently, there is no important recovery of the adsorption capacity for the second cycle, both with the K/La_2O_3 and Rh,K/La_2O_3 catalysts. The reason why Rh cannot play the important role of decomposing a larger fraction of nitrate compounds is that it is partially blocked by K. A similar effect regarding a decrease in activity conversion for NO on Rh/La_2O_3 promoted with Na, was proposed by Feng-Yim Chang et al. [34], assigning this behavior to the block of the active Rh sites by Na, in line with studies by Macleod et al. [35]. In the case of the mechanical mixture, Rh is not blocked by K, since both components are initially on a different support.

Table 1 compares the weight losses calculated for the cycles performed in inert or reducing atmosphere. When the regeneration was carried out in a hydrogen containing stream, decomposition is higher for all the solids studied as compared to the use of pure helium. As shown in Fig. 3.B, in the case of the K/La_2O_3 catalyst, only a small portion of the adsorbed nitrates is released,

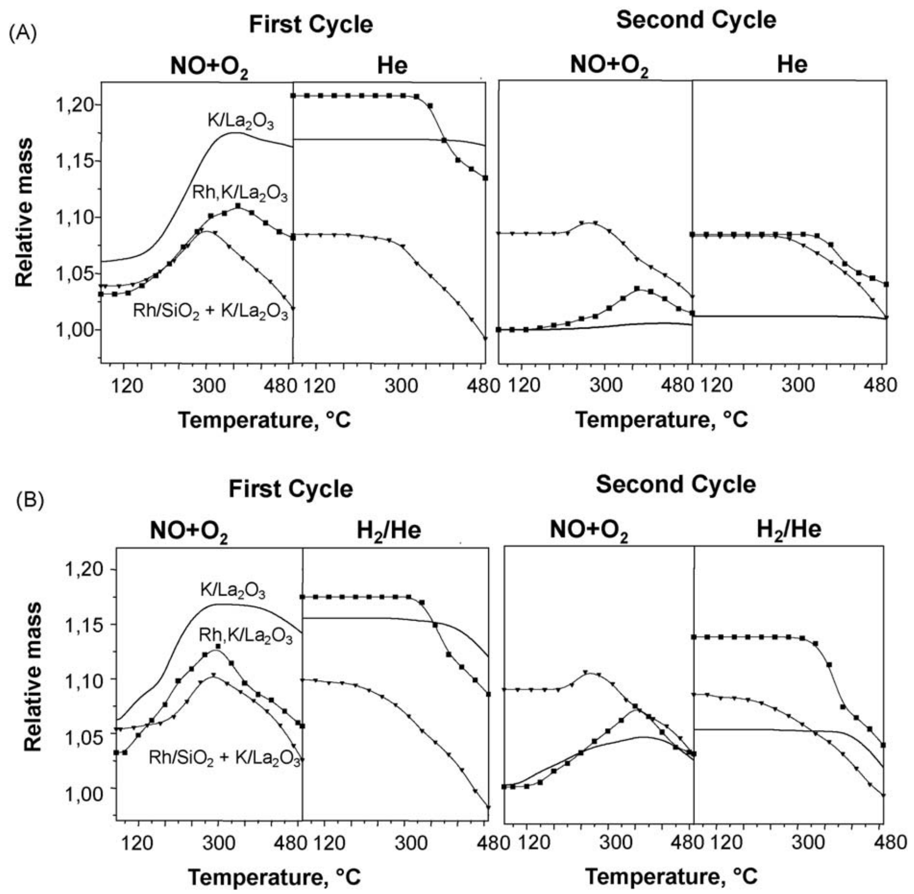

Fig. 3. NO_x adsorption–desorption cycles in microbalance. (A): Decomposition in He stream. (B): Decomposition in H_2(0.1%)/He stream.

but big enough to permit some adsorption in the second cycle. Moreover, according to the weight loss, this is the catalyst with a major difference in the desorption step when hydrogen is added to the gas flow. Rh,K/La_2O_3 exhibits a similar behavior, although the difference with regeneration in helium is smaller than in the case of the K/La_2O_3 catalyst. Finally, the mechanical mixture Rh/SiO_2 + K/La_2O_3 in hydrogen stream showed almost the same performance as in helium, with only a slight difference in the amount of nitrates decomposed in the different flows. This means that the decomposition of the nitrates, or in general the compounds formed during NO_x adsorption, occurs mainly due to temperature and involves Rh. The presence of H_2 in the gas phase is needed in order to reduce the NO_x formed upon decomposition at high temperatures, although in some cases such as K and Rh,K supported on La_2O_3, hydrogen favors the nitrates decomposition.

Table 1
Weight loss during desorption step in different gaseous streams in cyclic microbalance experiments.

Catalyst	Stream	Cycle	Δm (%)[a]
K/La_2O_3	He	1	0.46
		2	0.25
	H_2(0.1%)/He	1	3.03
		2	3.23
Rh,K/La_2O_3	He	1	6.07
		2	4.08
	H_2(0.1%)/He	1	7.6
		2	8.55
Rh/SiO_2 + K/La_2O_3	He	1	8.51
		2	6.61
	H_2(0.1%)/He	1	10.6
		2	9.13

m_2: Catalyst weight at the beginning of the desorption step (70 °C). m_3: Catalyst weight after desorption.

[a] Δm (%) = $(m_2 - m_3)/m_2 \times 100$.

3.2. Temperature-programmed reduction

Fig. 4 shows the TPR profile of selected samples. It can be seen that Rh/SiO_2 displays a well defined peak (curve a), with a complete reduction below 150 °C. On the other hand, Rh,K/La_2O_3 has a low reducibility, with a much lower H_2 consumption than Rh/SiO_2. This is a clear evidence of the interaction between Rh and the support La_2O_3 and/or with the K. The physical mixture Rh/SiO_2 and K/La_2O_3 that was not pre-treated at 500 °C, displays a TPR profile very similar to that of Rh/SiO_2, taking into account the dilution effect of this sample by the K/La_2O_3. A very interesting result is obtained when the physical mixture is pre-treated at 500 °C in nitrogen. At this temperature, potassium compounds have a high mobility, and because of this they can diffuse from La_2O_3 to SiO_2, interacting with Rh. The consequence of this is that the TPR profile is now very similar to that of Rh,K/La_2O_3.

Rh,K/La_2O_3 exhibited much lower H_2 consumption than Rh/SiO_2. This is attributed to the fact that Rh is partially blocked by K, thus leading to lower H_2 chemisorption and to a slower reduction. Because of this, a second peak appeared at high temperature (not shown) with the catalyst that contains K in interaction with Rh.

These results are a strong support to the above discussion, in which the K mobility was considered to explain both the NO_x adsorption and nitrates decomposition on Rh-based catalysts, including physical mixtures where the Rh and the K are initially deposited on different supports.

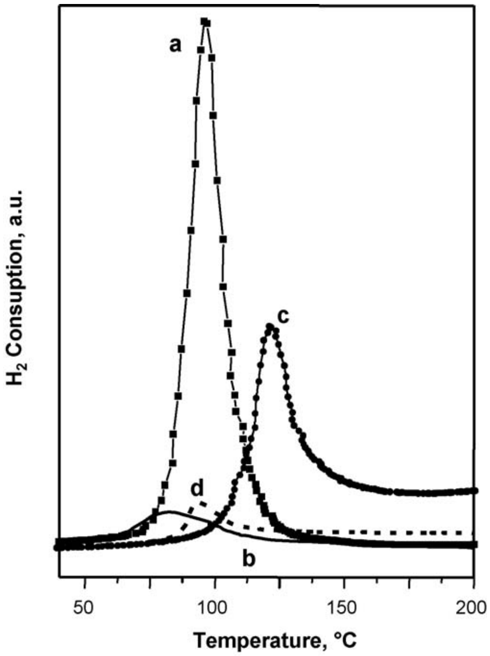

Fig. 4. TPR curves. (a): Rh/SiO_2 catalysts pre-treated in N_2. (b): $Rh/SiO_2 + K/La_2O_3$ pre-treated in N_2. (c): $Rh/SiO_2 + K/La_2O_3$ non-pre-treated. (d): $Rh,K/La_2O_3$ catalyst pre-treated in N_2.

3.3. *FTIR characterization of adsorbed species*

In order to assess the nature of the species that are formed over the catalysts surface during the microbalance experiments, FTIR studies were performed. An infrared cell was used, in which the catalysts were heated in different gaseous flows, trying to reproduce similar conditions as those employed in the microbalance. The catalysts selected for this study were $Rh,K/La_2O_3$ and K/La_2O_3, for comparative reasons, since they showed remarkable differences in their adsorption–desorption performances.

The spectra obtained for $Rh,K/La_2O_3$ are shown in Fig. 5. Lanthanum supported catalysts exhibit strong bands corresponding to lanthanum carbonates and oxicarbonates in the wavelength range 1200–1600 cm^{-1} (not shown). In addition to this, the experiment conditions prevent dilution of the samples with KBr. Therefore, the resulting spectra are saturated with these signals, which coincide with most of the ones corresponding to NO_x species adsorption. Nevertheless, two peaks were identified, one at 1778 cm^{-1}, attributed to NO adsorption [36], and the other at 1041 cm^{-1}, characteristic of lanthanum nitrates [37,38]. Fig. 5.A shows the IR spectra after the pretreatment of the catalyst in helium at 400 °C (curve a), and during the heating in $NO + O_2$ stream (curves b–e). By comparison with the pre-treated catalyst spectrum, it is clearly seen that the signals at 1041 and 1778 cm^{-1} arise as a consequence of NO_x species adsorption. When the flow is changed to helium (Fig. 5.B) the signals intensity decreases with increasing temperature, which is in agreement with the weight loss detected in the microbalance experiments. Finally, when the desorption is carried out in reducing atmosphere (Fig. 5.C), the nitrate peaks decrease at a higher rate, as compared to desorption under inert atmosphere. This is also in agreement with data shown in Fig. 3 and Table 1.

As regards the K/La_2O_3 catalyst (Fig. 6) the spectra obtained during the heating in $NO + O_2$ show the same characteristic signals observed for the rhodium containing catalyst corresponding to NO_x species adsorption. The major differences are found in the helium desorption spectra. For the $Rh,K/La_2O_3$ the signals at 1041 and 1778 cm^{-1} decreased their intensity as temperature became higher; on the contrary, the bands remain constant in the case of the K/La_2O_3 catalyst. This supports the different performances displayed by these catalysts in the microbalance experiments.

Since actual diesel exhaust contains in the order of 10% CO_2, additional experiments were carried out using a gaseous stream composed of NO (4%), O_2 (18%) and CO_2 (10%) during the adsorption step. Fig. 7 displays results corresponding to $Rh,K/La_2O_3$ (A) and K/La_2O_3 (B). For both catalysts, the bands corresponding to NO_x adsorption, at 1041 and 1778 cm^{-1}, start to arise at 200 °C and increase their intensity as temperature increases. According to this, the presence of CO_2 does not impair nitrates adsorption. Nevertheless, it can be expected that the amount of nitrates species adsorbed would be smaller since the catalysts contain great amounts of carbonates that are more

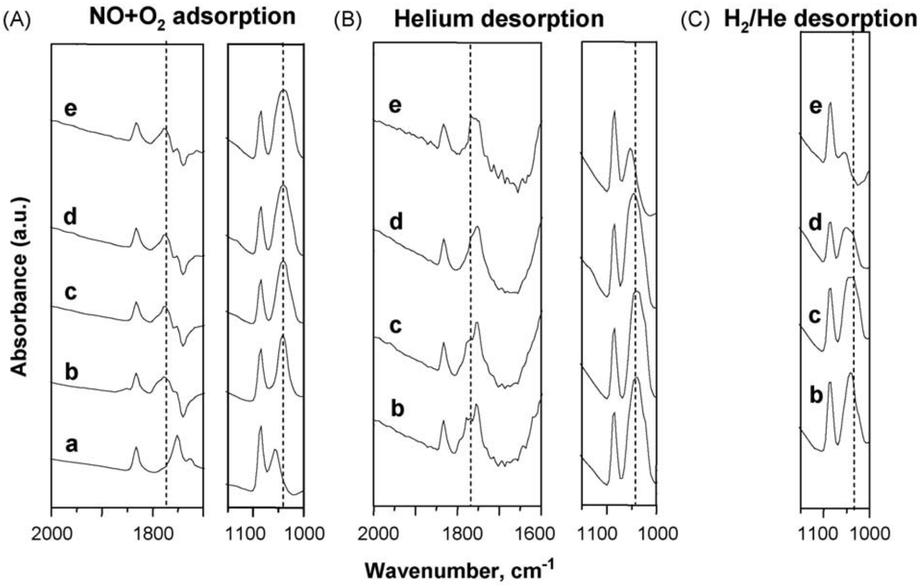

Fig. 5. *In situ* FTIR spectra, $Rh,K/La_2O_3$ catalyst. (A): NO(4%) + O_2(18%) stream. (B): He stream. (C): H_2(0.1%)/He stream. (a): catalyst pre-treated in Helium, 30 min at 400 °C, (b): 200 °C, (c): 300 °C, (d): 400 °C, (e): 450 °C.

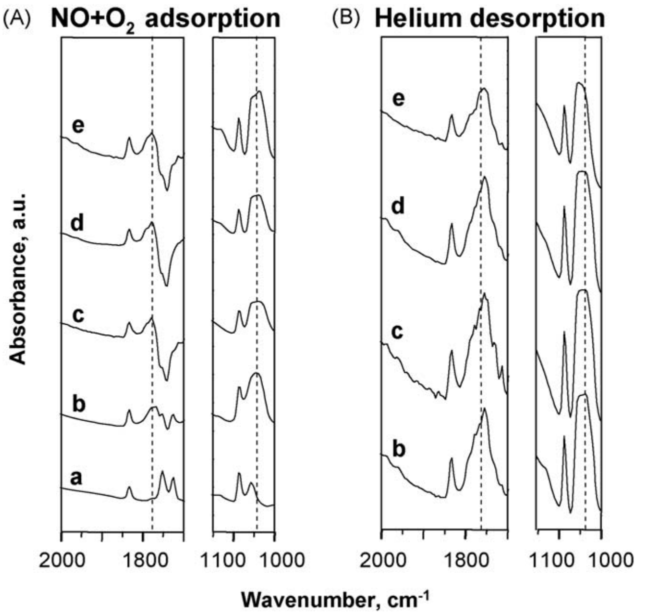

Fig. 6. *In situ* FTIR spectra, K/La$_2$O$_3$ catalyst. (A): NO(4%) + O$_2$(18%) stream. (B): He stream. (a): catalyst pre-treated in Helium, 30 min at 400 °C, (b): 200 °C, (c): 300 °C, (d): 400 °C, (e): 450 °C.

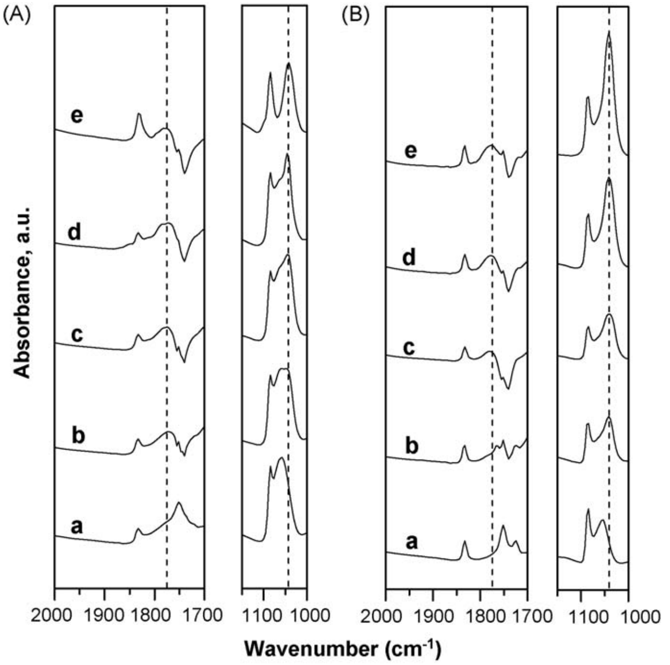

Fig. 7. *In situ* FTIR spectra, NO(4%) + O$_2$(18%) + CO$_2$(10%) stream. (A): Rh,K/La$_2$O$_3$ catalyst. (B): K/La$_2$O$_3$ catalyst. (a): catalyst pre-treated in Helium, 30 min at 400 °C, (b): 200 °C, (c): 300 °C, (d): 400 °C, (e): 450 °C.

difficult to decompose in the presence of CO$_2$, thus partially covering the support.

The results shown above indicate that impregnation of rhodium on lanthanum supported catalysts significantly enhances their performance as NO$_x$ traps, since it improves nitrates decomposition rate during the regeneration step. The other important contaminant present in diesel exhausts is particulate matter (soot). It is desirable that a system could have the ability to abate both contaminants. Hence, the catalysts were studied in relation with their activity to simultaneously eliminate soot and nitrogen oxides. The K/La$_2$O$_3$ catalyst was also used in the experiments, in order to establish a comparative study with the rhodium containing catalysts.

3.4. Soot reaction with adsorbed NO$_x$ species

Catalysts were pre-treated in NO + O$_2$ stream, selecting for each case the temperature that maximizes nitrates adsorption over the catalysts surface. Then, the nitrated catalysts were mixed with soot in 20:1 ratio and heated in nitrogen flow. Activity was continuously monitored measuring the CO$_2$ generated in soot combustion with a flame ionization detector.

Fig. 8 displays the profiles obtained for the different catalysts. The temperature at which CO$_2$ peaks are observed is similar among the evaluated catalysts, although they showed a different behavior in the NO$_x$ adsorption–desorption experiments (Figs. 1 and 2). Therefore, the activity for soot combustion of the nitrated catalysts does not depend on their ability to decompose adsorbed nitrates. If this were the case, the TPO profiles should correlate with the results shown in Figs. 1 and 2, i.e., the lower the nitrate decomposition, the lower the temperature at which the TPO profile is displayed. Thus, soot particles are probably oxidized directly with the nitrates species adsorbed on the catalysts surface, a previous decomposition of such species not being necessary.

Potassium is an active material for soot combustion mainly due to its high mobility, which improves the soot-catalyst contact. In Fig. 8 the CO$_2$ peaks areas are indicative of the amount of carbon being burnt in each case. As it is shown, the Rh/La$_2$O$_3$ catalyst burns soot at a similar temperature with the corresponding to potassium containing catalysts. However, the peak area is much lower, and hence, so is the amount of carbon reacted on this catalyst.

Although 50% in weight of the mechanical mixture Rh/SiO$_2$ + K/La$_2$O$_3$ is constituted by an inert material for soot combustion such as silica, it showed a similar performance in the reaction as lanthanum supported catalysts, burning the carbonaceous material at a temperature even slightly lower than them.

With the purpose of verifying that particulate matter combustion in inert atmosphere takes place by reaction with the nitrates adsorbed on the catalyst surface, a set of experiments was carried out using fresh catalysts (i.e., not pre-treated). Fig. 9 displays results for the Rh,K/La$_2$O$_3$ catalyst, compared with the corresponding to the same catalyst, but previously treated in NO stream. When the catalyst surface does not contain nitrates, not only does

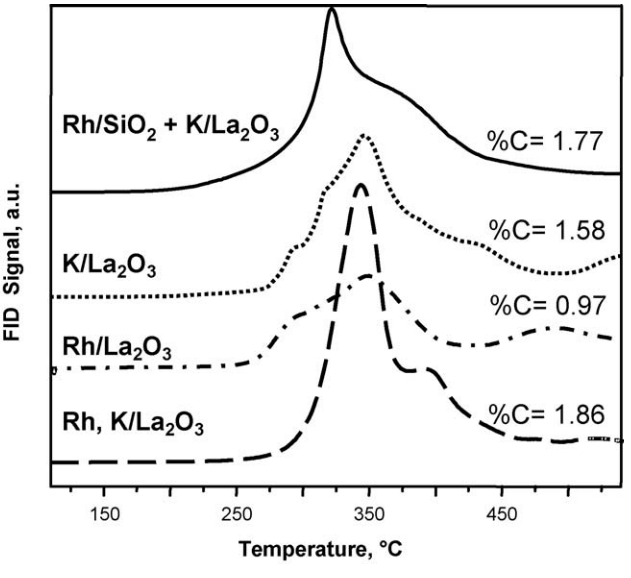

Fig. 8. Soot combustion in N$_2$ feed. Catalysts pre-treated in NO + O$_2$.

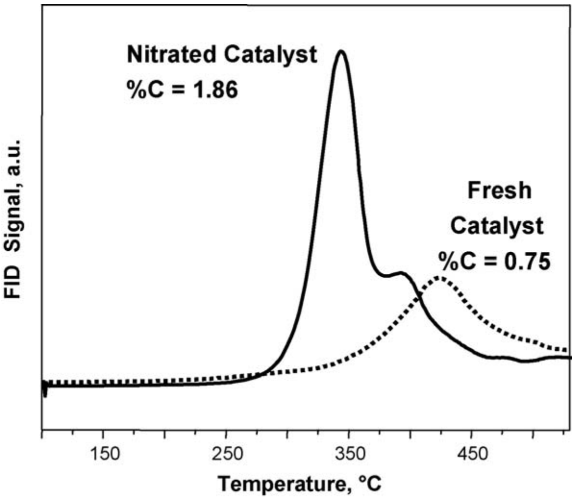

Fig. 9. Soot combustion in N_2 feed. Rh,K/La_2O_3 catalyst.

the soot gasification occur at higher temperature but also the amount of burnt carbon is remarkably lower. Other catalysts with different formulations showed a similar behavior (not shown).

Soot combustion experiments were also carried out in O_2(6%)/N_2 stream, using catalyst-soot mixtures prepared with both fresh and nitrated catalysts in order to evaluate the effect of the presence of nitrates on the catalyst surface in oxidative atmosphere. Results obtained with Rh,K/La_2O_3 are shown in Fig. 10.A, while those corresponding to K/La_2O_3 are shown in Fig. 10.B. For both samples, combustion begins at slightly lower temperatures when catalysts were previously treated in NO + O_2. Thus, the nitrates also have a beneficial effect when the reaction takes place in the presence of oxygen. On the other hand, CO_2 peaks corresponding to fresh catalysts are higher than those for nitrated catalysts. This could indicate that a higher amount of soot is burnt by non-treated catalysts. However, it has been reported that the simple manipulation of lanthana in air induces its hydration and its carbonation in bulk [39]. In previous works, the presence of $La_2O_2CO_3$ and $La(CO_3)_3$ phases on lanthanum supported catalysts was observed by X-ray diffraction and FTIR. It was also shown that parts of this species are replaced by $La(NO_3)_3$ and $LaONO_3$ when such catalysts are heated in NO_x stream [15]. Hence, the difference observed in the amount of carbon dioxide released between fresh and nitrated catalysts is attributed to the higher content of carbonate-type species on fresh samples.

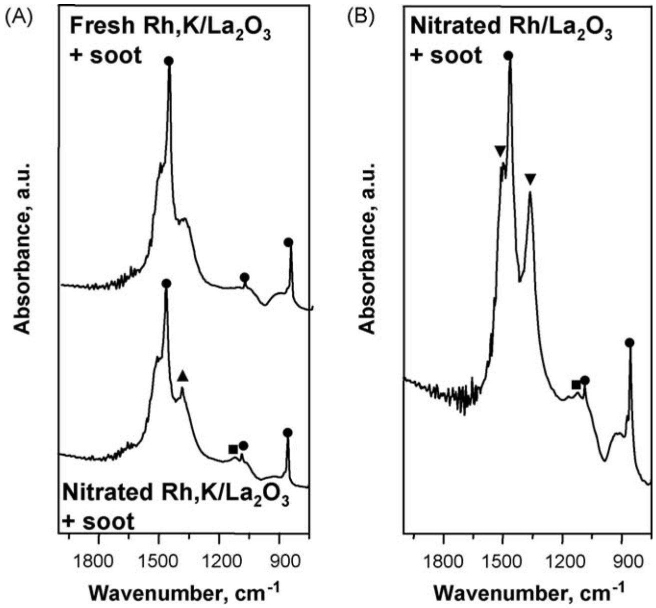

Fig. 11. Infrared spectra of the soot-catalyst mixtures after combustion in inert flow. ●: $La_2O_2CO_3$. ▲: NO^{3-} (sup.). ▼: NO^{3-} monodentate ■: NO^{2-}.

After being used in the combustion experiments in inert atmosphere soot-catalyst mixtures were characterized by infrared technique. Fig. 11.A shows spectra obtained for the Rh,K/La_2O_3 catalyst. For comparative reasons, both spectra corresponding to the soot-nitrated catalyst mixture and to the soot-fresh catalyst are shown. Both of them display the $La_2O_2CO_3$ signals (1470, 1093 and 863 cm^{-1}). The nitrated catalyst mixed with soot shows a signal at 1380 cm^{-1} attributed to superficial NO_3^- species. Thus, not all the adsorbed nitrates are consumed in the reaction with soot for this catalyst. A weak signal at 1120 cm^{-1} is also observed, which is attributed to NO_2^- species generated by reduction of the nitrates with the particulate matter which is mainly constituted by carbon.

Fig. 11.B shows the spectrum corresponding to the mixture prepared with the nitrated Rh/La_2O_3 catalyst after reaction in N_2 flow. As in the Rh,K/La_2O_3 spectrum, $La_2O_2CO_3$ signals are present. Signals at 1496 and 1363 cm^{-1} were attributed to monodentate nitrate species. These signals are very strong, since only a small fraction of soot is eliminated in the combustion with this catalyst (see Fig. 8). Therefore, most nitrates remain adsorbed to the catalyst surface without reacting. The signal corresponding to NO_2^- is also observed in this catalyst spectrum

3.5. Effect of Rh on catalytic behavior

As said before, the simple manipulation of La_2O_3 in air induces both its carbonation in bulk and its hydration [39], and different phases are also formed after calcination at different temperatures. In this vein, Taylor and Schrader [40] reported that, starting from

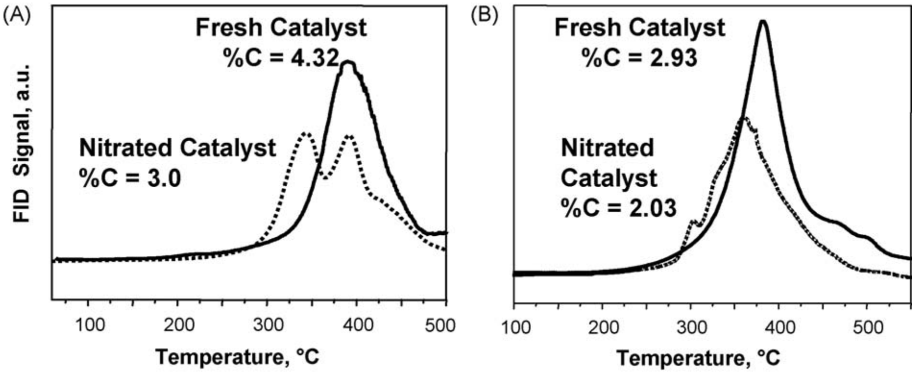

Fig. 10. Soot combustion in O_2(6%)/N_2 feed. (A): Rh,K/La_2O_3 catalyst. (B): K/La_2O_3 catalyst.

pure $La(OH)_3$ the following phases are obtained after heating in air: $La(OH)_3$ 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 $La_2O_2CO_3$ as starting material, no phase transformation occurred up to 700 °C [39]. As regards potassium species, 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 up to 1000 °C [41].

Typical NO_x catalytic traps consists of a high-surface-area support (Al_2O_3, TiO_2, ZrO_2), a NO_x storage component (Ba, K, Ca, La) and a noble metal (Pt,Rh). In this work, we used La_2O_3 both as the support and alkaline compound. Besides Ba, potassium is another key element that has shown potential as a storage component with significant benefits at higher temperatures; the K-based nitrate is more stable than the typical Ba-based nitrate [42]. Previous studies have demonstrated the good performance of K-based lean NO_x trap catalysts, even in the presence of CO_2 and H_2O in the feed. In this work, we also added K due to both the said NO_x trapping effect and its catalytic activity for soot combustion [43,44].

In most articles published in the literature, the catalytic effect of Pt and Rh takes place in different steps. The role of Pt is to oxidize NO into NO_2, which is subsequently trapped in the form of nitrate and nitrite species under lean conditions. The regeneration step, which occurs under rich conditions, involves the decomposition of nitrates releasing the stored NO_x, which is then reduced to N_2 over the Rh catalyst. Both steps, adsorption and regeneration, are important for a efficient NSR system. In this work, we found that not only does Rh have a fundamental role during the regeneration step but is also important during the NO_x adsorption one.

Taking into account the different basic species present on the surface of K/La_2O_3 catalysts, the interaction with NO is a rather complex process. Huang et al. [45] studied the adsorption and decomposition of NO on lanthanum oxide. They found that after La_2O_3 was pre-treated at 700 °C in He, exposure to NO at room temperature caused a brief reaction forming N_2O, and then gave three NO TPD peaks at 127, 427 and 527 °C, assigned to the decomposition of nitrito (ONO^-), nitro and bidentate nitrate species at 127 °C; desorption of NO^- and $(N_2O_2)^{2-}$ species at 427 °C; and decomposition of monodentate nitrate species into NO and O_2 at 527 °C. Chemisorption of O_2 prior to NO admission inhibits the formation of N_2O and blocks sites for the NO desorption at 427 °C, but enhances the 527 °C peak.

In our experiments, the presence of O_2 enhances the NO_x adsorption due to the formation of NO_2 which is adsorbed on the $O\cdots M$ surface leading to nitrate species formation. Besides, NO_2 could diffuse through the catalyst particle producing bulk nitrate compounds. Taking into account the results of Huang et al. [45], the majority of the mentioned species should be monodentate nitrate ones, since only a small fraction decomposed in He during microbalance experiments up to 490 °C. Moreover, estimations made in a previous work with the amount of NO_x consumed and the solids surface-area indicate that NO_x readily reacts with lanthana to form a bulk nitrate compound [15].

The addition of Pt and/or Rh to the K/La_2O_3 solid decreases the stability of nitrate species, this effect being stronger for Rh. A working trap should be able to adsorb NO_x under oxidizing conditions and to release it in the form of N_2 during the engine excursions under reducing conditions or the injection of a reductant in the case of diesel engines. Thus, the retention capacity of the solid is very important but its ability to desorb and decompose the trapped NO_x is also very important. Rhodium is usually included in the catalytic trap to promote the reaction between released NO_x and a reductant molecule, to give N_2 and CO_2 as products. The effect observed in this work when Rh is included in the formulation is important because it also promotes the rate of NO_x release during the regeneration step on La_2O_3 and K/La_2O_3 catalysts.

Another effect of rhodium is the preferential formation of $La_2O_2CO_3$ instead of hydroxide species. This effect would be related to the lack in stability of nitrates when Rh is present; the nitrates formed by reaction with carbonates are probably more easily decomposed than those formed with hydroxides. However, the experiments performed with the mechanical mixture $Rh/SiO_2 + K/La_2O_3$ also show the same effect on nitrate stability. Thus, the structural change in lanthana when Rh is present is not the origin of the phenomenon. Moreover, since in the mechanical mixture Rh is not in intimate contact with nitrates, the effect of Rh might be to form a thermally unstable complex ($Rh–NO^+$) which takes part both in the formation of the nitrates when the catalyst is exposed to NO_x, just by transferring this compound to K or La_2O_3. Then, under helium or hydrogen, the mobility of potassium compound transports the nitrates towards the Rh where they are decomposed. With regards to soot reaction with nitrate species, results show that the addition of Rh has a small positive effect but only for the $Rh/SiO_2 + K/La_2O_3$. Thus, it is inferred that the stability of nitrates does not play a role in the soot combustion reaction.

4. Conclusions

NO_x strongly interacts with the K/La_2O_3 solid through the formation of La and K nitrate species which are stable under He atmosphere up to 490 °C. This NO_x surface species migrates inside the solid forming a bulk nitrate compound when temperature increases. When either Rh or Pt are incorporated to the system nitrates become unstable at ca. 360 °C both under $NO + O_2$ and He (or H_2) atmosphere, the effect of Rh being stronger. The presence of Rh favors the formation of lanthanum oxycarbonate species during the calcination of the catalyst but it is shown that this fact is not responsible for the low stability of nitrates.

The role of Rh on the formation and decomposition of nitrates is to provide a reaction path by forming a thermally unstable intermediate. The presence of K on the formulation is also an important factor since it is involved in such mechanism by increasing the adsorption capacity and providing the mobility needed to contact the nitrates with the Rh, where they are decomposed. The insights gained in this work about the behavior of Rh when incorporated to basic supports could be useful to modulate the strength of the basicity and the Rh loading in order to optimize the window size for LNT operation.

The reaction between trapped NO_x and diesel soot readily proceeds under nitrogen atmosphere. However, the temperature at which the maximum rate is reached (ca. 370 °C) is not affected by the stability of nitrates. As a matter of fact, the presence of Rh, which favors nitrates decomposition, has little effect on this temperature. This is a key issue and indicates that the reaction proceeds between the soot and the nitrates on the surface before they decompose.

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