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Abatement of diesel exhaust pollutants: NO_x adsorption on Co,Ba,K/CeO_2 catalysts

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Abstract

The Co,Ba,K/CeO_2 system is a potential candidate to be used under the simultaneous abatement of soot and NO_x in diesel exhausts. In this work, we study the interactions of NO_x with the said solid. NO_2 is strongly adsorbed on the Ba,K/CeO_2 surface through the formation of Ba and K nitrate species which are stable under He atmosphere up to 490 °C. However, when Co is incorporated to the system (Co,Ba,K/CeO_2 catalyst), Ba nitrates become unstable at ca. 370 °C, under both $NO + O_2$ and He atmosphere. DRX, FTIR, and LRS characterization shows that potassium favors the formation of the $BaCoO_{2.93}$ perovskite in the Co,Ba,K/CeO_2 catalyst calcined at 400 °C. This perovskite structure is not detected when K is absent (Co,Ba/CeO_2 system). FTIR spectra of Co,Ba,K/CeO_2 treated with $NO + O_2$ indicate the formation of surface N-bound nitrate species (O–Ba- -NO_2), where NO_2 acts as a Lewis base. Since the said species are not detected in the samples without $BaCoO_{2.93}$, it is suggested that they are related to the Ba atoms of the perovskite structure. Microbalance experiments combined with FTIR and mass spectroscopy characterization show that the nitrate species formed in the Co,Ba,K/CeO_2 sample can be readily decomposed to N_2 under a reducing atmosphere, making this system very interesting to be used as a NO_x catalytic trap. On the other hand, under He atmosphere the decomposition of nitrates only produces gaseous NO_x. In addition, when the Co,Ba,K/CeO_2 catalyst previously treated under $NO + O_2$ atmosphere is intimately mixed with the soot and then heated in He up to 490 °C, the soot particulates are partially oxidized by the surface nitrate species.

Keywords: Diesel exhausts; NO_x storage; Co,Ba,K/CeO_2 catalysts

1. Introduction

The main pollutants emitted for diesel engines are soot particles and nitrogen oxides. The combination of traps and oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [1].

NO_x adsorbers (traps) constitute a new NO_x control technology, which is being developed for partial lean-burn gasoline engines and for diesel engines [2]. The adsorbers, which are incorporated into the catalyst washcoat, chemically bind nitrogen oxides during lean engine operation. After the adsorber capacity is saturated, the system is regenerated, and released NO_x is catalytically reduced during a period of rich engine operation [3]. In the case of diesel engines, since a rich operation is not feasible, periodic fuel injections are necessary. This topic is a challenge to meet the demands of future norms, and most of the studies have been performed with barium-supported catalysts [3–5].

In previous works [6,7] we reported that both Co,K/La_2O_3 and Co,K/CeO_2 are very active and stable catalysts for the combustion of soot with oxygen. In the case of the ceria support, a reaction mechanism involving redox sites from both Co and Ce oxides plus surface-carbonate species takes place on this catalyst. Potassium favors the surface mobility, thus improving the soot-catalyst contact and increasing the surface basicity. Moreover, the addition of NO to the gas phase results in a strong increase of the activity for soot combustion (reaction starts at ca. 250 °C and a maximum in TPO is obtained at ca. 350 °C). In this case, the soot combustion probably occurs via adsorbed NO_x species as intermediates. Also, a key role of the catalyst surface was found to be the oxidation of NO to NO_2. The oxidation of soot with NO_2 has been widely studied by other research teams and ours [8–11], and it is the basis of the Continuously Regenerating Trap (CRT) developed by Johnson Matthey.

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In this work we explore the effect of the addition of Ba to the Co,K/CeO_2 system, with the aim of improving the interaction with NO_x molecules. In this way, we are seeking two benefits: (i) to improve the catalytic activity for the soot combustion reaction by increasing the formation of surface NO_x intermediates, and (ii) to develop a bifunctional catalyst, which eliminates soot particles and is also able to store NO_x molecules, thus acting as a catalytic trap.

To this end, we characterized different solids (Co,Ba,K/CeO_2) using several techniques. The amount of NO_x stored was measured through thermogravimetric analysis and the surface species formed during these experiments were characterized by FTIR. XRD, Raman, and mass spectroscopies were applied to study the phase transformations occurring after different treatments of the solids.

2. Experimental

2.1. *Soot and catalysts preparation*

The soot used in this work 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 soot thus obtained contained 70 ppm of sulfur. Its specific surface area was 55 $m^2\,g^{-1}$. 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, the amount of carbon released as CO, CO_2, and hydrocarbons represents 9.3% of the soot [12].

The Ba,K/CeO_2 catalysts were prepared from a CeO_2 (Merck, p.a., specific surface area = 10 $m^2\,g^{-1}$) support suspension in water, to which a solution containing KNO_3 and/or barium acetate was added, in order to obtain a load of 7 wt% of K and/or 16 wt% of Ba. The mixture was heated while being vigorously stirred until a paste was achieved, which was dried in a stove for 24 h at 120 °C and calcined at 400 °C for 2 h. In the case of the cobalt-containing solids (Co,Ba,K/CeO_2 and Co,Ba/CeO_2), a $Co(NO_3)_2$ solution was added to the catalysts (prepared as described above) in order to obtain 12 wt% of Co. The soot and the different catalysts were mechanically mixed in an agate mortar so as to obtain a soot/catalyst = 1/20 (wt/wt) ratio.

2.2. *Catalyst characterization*

2.2.1. *X-ray diffraction (XRD)*

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

2.2.2. *Microbalance studies*

Microbalance studies were performed in a Cahn 2000 equipment with the objective of studying the interaction of the catalyst with NO and NO + O_2. The sample was dried for 2 h at 400 °C in He and then it was stabilized at 70 °C, at which point the sample weight was determined ($w°$). After this, a mixture of NO (4%) or NO (4%) + O_2 (18%) (He balance) was fed, and the sample was stabilized at 70 °C in this stream. When a constant weight value was obtained, the sample was heated up to 490 °C at 5 °C/min; then, it was maintained at this temperature for 10 min after which it was cooled to 70 °C. At this temperature, the feeding mixture was changed to He and after stabilization of the weight, the sample was weighed. Then the procedure was repeated with He (or 10% H_2 in He) feed, and the sample was weighed at the end of this treatment at 70 °C in a He stream.

Equation (A) was used for the calculation of the NO_2 storage capacity percentages as ratios between the stored NO_2 (as $Ba(NO_3)_2$) and the maximum NO_2 storage capacity of Ba ($b = 0.0146$ mol NO_2/g Ba).

$$\%\ \mathrm{NO_2\ storage\ capacity} = \frac{a(w(T)/w^\circ - 1)100}{b}, \tag{A}$$

where

$$a = \frac{2}{0.16(\mathrm{MW}_{\mathrm{Ba(NO_3)_2}} - \mathrm{MW}_{\mathrm{BaCO_3}})} = 0.1953\ \mathrm{mol\ NO_2/g\ Ba}.$$

The constant a involves the molecular weights (MW) of $BaCO_3$ and $Ba(NO_3)_2$ and it was calculated considering that: (i) all the barium (16 wt%) was as $BaCO_3$ for fresh catalysts, and (ii) the incorporation of NO_2 led to $Ba(NO_3)_2$ according to

$$\mathrm{BaCO_3(s)} + 2\mathrm{NO_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{Ba(NO_3)_2(s)} + \mathrm{CO_2(g)}, \tag{B}$$

$w(T)/w°$ is relative mass (i.e., sample weight at any temperature T divided by the initial weight obtained at 70 °C after the He treatment for 2 h at 400 °C).

Some of the experiments described above were performed in a flow-type reactor in order to analyze the gases evolved with (i) a Leybold quadrupole mass spectrometer able to monitor 10 components simultaneously as a function of temperature/time, and (ii) a IR gas cell (length: 15 cm) with KBr windows. These IR spectra were recorded by a Thermo Mattson Genesis II FTIR (scan, 20; resolution, 1 cm^{-1}).

In order to study the soot reaction with the adsorbed NO_x species, two different experiments were performed. (1) The Co,Ba,K/CeO_2 catalyst was pretreated with NO (4%) + O_2 (18%) up to 370 °C with a heating rate of 5 °C min^{-1}, and maintained at this temperature until a constant weight value was obtained. Then, the solid was mixed with soot in the proportion 20/1, and the weight changes during the heating in He in the microbalance up to 490 °C were recorded (as previously described). After this, a similar sequence was followed but with O_2 (18%) in He. (2) The Co,Ba,K/CeO_2 catalyst mixed with soot was treated first with He and then with O_2 (18%) in He with the corresponding heating sequences (as described in 1), the only difference being that the pretreatment of the catalyst in NO + O_2 was not performed.

2.2.3. *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 cm^{-1} resolution.

2.2.4. *Laser Raman spectroscopy (LRS)*

The Raman spectra were recorded with a TRS-600-SZ-P Jasco laser Raman instrument, equipped with a CCD (charge coupled device) with the detector cooled to about 153 K using liquid N_2. The excitation source was the 514.5-nm line of a Spectra 9000 Photometrics Ar ion laser, whereas the laser power was set at 30 mW.

3. Results and discussion

3.1. *Catalyst characterization*

The XRD patterns indicate that Ba/CeO_2 and Ba,K/CeO_2 are composed of CeO_2 and $BaCO_3$ crystalline phases (Table 1). In the case of Co,Ba,K/CeO_2, the main reflexion signals were those of the CeO_2 support. The low-intensity reflexions associated with $BaCoO_{2.93}$ perovskite, $BaCO_3$ and Co_3O_4 compounds were also detected. However, for Co,Ba/CeO_2, the perovskite structure was not detected, Co_3O_4 and $Ba(NO_3)_2$ being present instead. These results could indicate that potassium would favor the perovskite structure formation, which was also previously observed in the Co,K/La_2O_3 system [13].

In order to obtain further insight into this aspect, Raman spectra of Co-containing catalysts were recorded. Fig. 1 shows that the Co,Ba/CeO_2 solid presents the three characteristic vibrational signals of Co_3O_4: the sharp band at 693 cm^{-1} and the two bands at 523 and 486 cm^{-1} [14], in addition to a small signal at 464 cm^{-1} corresponding to the support (see the CeO_2 spectrum which was also included for comparison). However, in the K-containing solid (Co,Ba,K/CeO_2), although the Co_3O_4 vibrational bands appear, the support signal is magnified. This would probably imply a higher dispersion and smaller size of the Co_3O_4 crystals compared with the Co,Ba/CeO_2 solid. This is consistent with the XRD results: Co,Ba/CeO_2 presents Co_3O_4 as a segregated phase whereas Co,Ba,K/CeO_2 presents the cobalt oxide only at traces level.

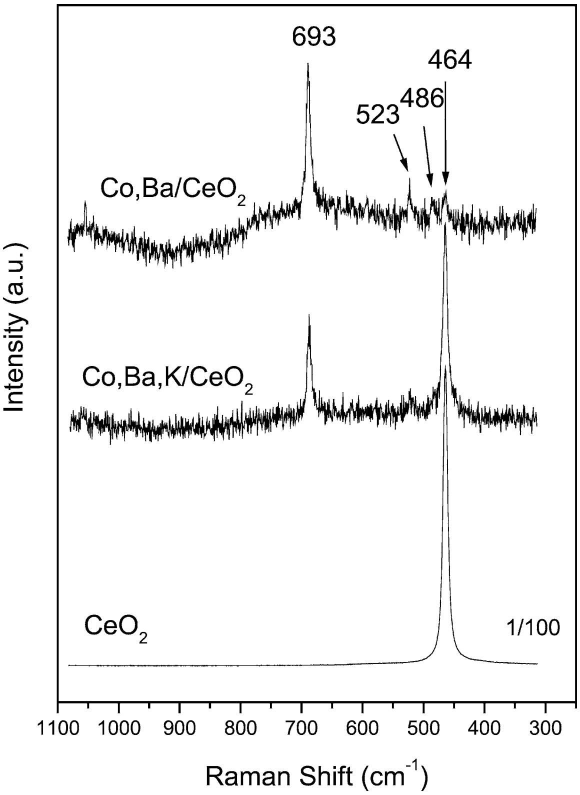

Fig. 1. Raman spectra of the Co-containing catalysts, including the support signal for comparison.

Table 1
XRD phases

Catalyst	Crystalline phases
Ba/CeO_2	CeO_2, $BaCO_3$
Ba,K/CeO_2	CeO_2, $BaCO_3$
Co,Ba/CeO_2	CeO_2, $Ba(NO_3)_2$, Co_3O_4[a]
Co,Ba,K/CeO_2	CeO_2, $BaCoO_{2.93}$,[b] Co_3O_4,[b] $BaCO_3$[b]

[a] Confirmed by laser Raman spectroscopy.
[b] Traces.

3.2. *NO_x interaction with the catalysts*

In order to study the NO_x storage capacity of the obtained catalysts, gravimetric studies were carried out. After saturation in NO + O_2 at 70 °C, several steps were taken: (1) the sample was heated in the same flow up to 490 °C at 5 °C/min, (2) it was cooled in the same flow to 70 °C, (3) it was heated in He until 490 °C, and (4) it was cooled to 70 °C in He.

Figs. 2 and 3 display the changes of weight due to the NO + O_2 adsorption for all the solids. The dotted line divides each graph into two sections: the left section corresponds to the heating in the NO + O_2 stream (step 1), and the right one to the heating in the He stream (step 3). Note that neither the cooling in the NO + O_2 stream (step 2) nor the cooling in the He flow (step 4) are represented. The discontinuity in weight observed for each curve before and after the dotted line is due to the cooling in the NO + O_2 stream.

Fig. 2 shows the microbalance experiments for Ba/CeO_2, K/CeO_2, Ba,K/CeO_2, and the support for comparison. Unloaded CeO_2 adsorbs some NO_x at 70 °C and the addition of Ba to the said support increases the amount of NO_x ad-

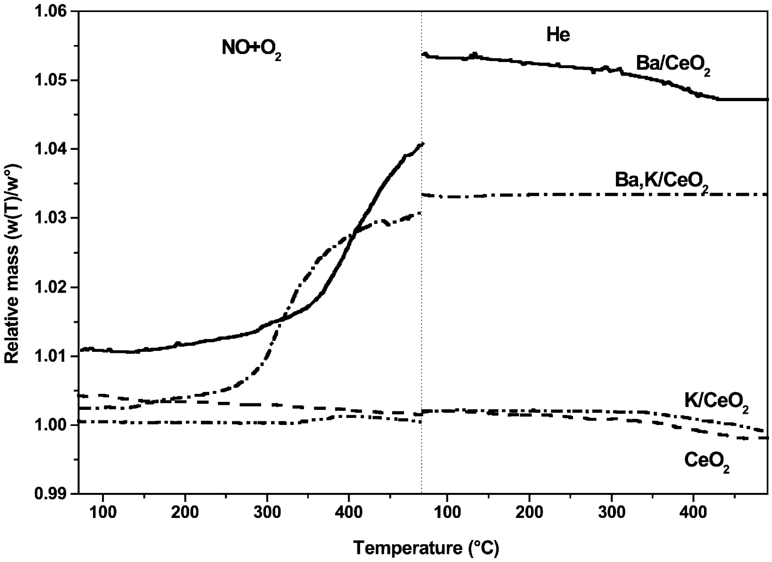

Fig. 2. NO_x adsorption in microbalance for the Ba,K/CeO_2 system. Gaseous feed: NO (4%) and O_2 (18%) (He balance).

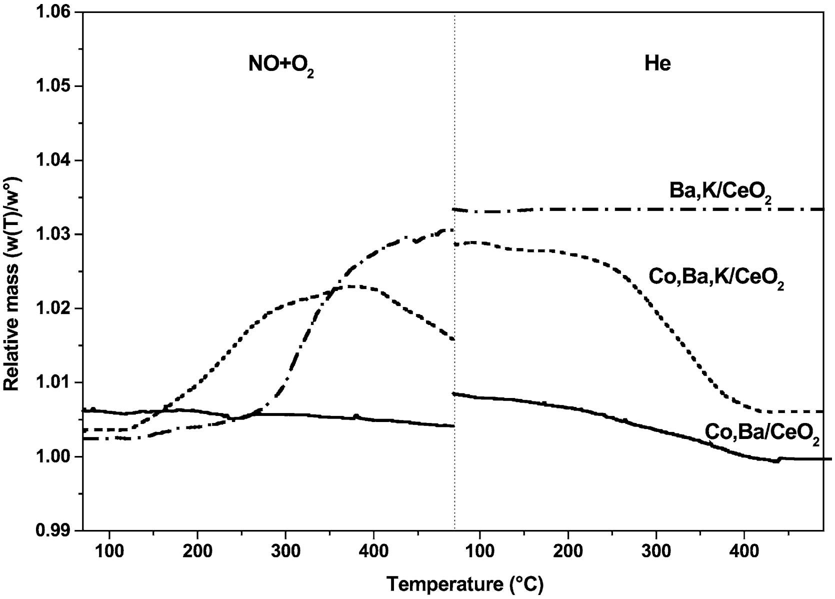

Fig. 3. Effect of the cobalt addition in the microbalance experiments. Gaseous feed: NO (4%) and O_2 (18%) (He balance).

sorbed at this low temperature. Probably, the effect of Ba is to increase the surface basicity. The presence of K provokes the opposite effect. K seems to cover the CeO_2 surface, thus preventing the NO_x adsorption.

The Ba/CeO_2 sample presents a significant increase in weight during the heating in the NO + O_2 stream and the final weight remains almost constant during the treatment in He (Fig. 2), suggesting a nonreversible NO_x incorporation to the solid. Its storage capacity is 63.1% at the end of the treatment. However, as the composition of the stream is NO, its storage capacity is insignificant (Table 2).

In order to consider the effect of NO_2, a NO + O_2 mixture was passed through a bed of Pt(1wt%)/Al_2O_3 before entering the microbalance. It is well known that Pt catalysts are effective in catalyzing the oxidation of NO to NO_2. On this particular occasion, the amount of NO_2 stored and the profile of the weight changes were comparable to those obtained for the NO + O_2 stream (Table 2). These results suggest that adsorbed NO_2 was the NO_x species which would react with Ba to give stable nitrate species. CeO_2 would act as oxidation catalyst promoting the NO_2 formation for NO + O_2 stream. In this trend, the downstream NO_2/NO ratio was 1300.

The potassium-containing sample (Ba,K/CeO_2) has a similar but not so pronounced behavior (Fig. 2). Its storage capacity is below the one observed for the Ba/CeO_2 sample (Table 2). Both potassium and barium are able to react with NO_2 forming nitrate species. But for the K-containing sample, K was added as KNO_3 and this substance was not

Table 2
NO_x storage capacities of different barium-containing materials[a]

Catalyst	NO_x feed	NO_2 % storage (NO_x treatment, 300 °C)[b]	NO_2 % storage (after cooling in NO_x, 70 °C)[b]	NO_2 % storage (after cooling in He, 70 °C)[b]
Ba/CeO_2	$NO + O_2$	19.1	72.6	63.1
Ba/CeO_2	NO_2	32.0	61.8	59.4
Ba/CeO_2	NO	4.4	3.7	0
$Ba,K/CeO_2$	$NO + O_2$	13.2	44.7	44.7
$Ba,K/CeO_2$	NO	1.0	4.2	2.2
$Co,Ba,K/CeO_2$	$NO + O_2$	27.1	39.1	1.0
$Co,Ba,K/CeO_2$	NO	6.8	5.9	0
$Co,Ba/CeO_2$	$NO + O_2$	7.5	12.3	0
$Pt,Ba/Al_2O_3$[c]	$NO + O_2$	26.8	–	–

[a] For the NO_2 % storage capacities equation, see Section 2.2.
[b] NO_x and He treatments are described in Section 3.2.
[c] [16].

decomposed during the calcination treatment. In fact, previous studies with K/La_2O_3 catalysts showed that KNO_3 decomposes above 600 °C during TGA experiments [15]. For K/CeO_2, KNO_3 was used as a source of K; therefore, weight changes during the treatment in $NO + O_2$ were negligible (Fig. 2). On the other hand, in the absence of O_2, part of NO is irreversibly adsorbed on $Ba,K/CeO_2$. However, its storage capacity is notably smaller than in the presence of $NO + O_2$ (Table 2).

The presence of O_2 enhances the NO_x adsorption due to the formation of NO_2 which is adsorbed on the O- - -M surface leading to nitrate species formation. Besides, NO_2 could diffuse through the catalyst particle producing bulk nitrate compound.

In order to study the effect of the addition of cobalt to Ba-containing catalysts and its relationship with NO_x interaction, microbalance studies were performed on $Co,Ba/CeO_2$ and $Co,Ba,K/CeO_2$ (12 wt% Co). Resulting profiles are shown in Fig. 3, in comparison with that obtained for $Ba,K/CeO_2$.

Similarly to the one observed in Fig. 2, $Co,Ba/CeO_2$ presents some adsorption at 70 °C, probably on the support, which decreased with the addition of K. When temperature was increased, practically null adsorption of NO_x on $Co,Ba/CeO_2$ during the $NO + O_2$ treatment was observed. Note that the weight change curve is flat (Fig. 3). This is because barium is mainly as $Ba(NO_3)_2$ in the fresh solid. Furthermore, since Co_3O_4 is a crystalline structure identified by XRD for this sample (Table 1), this would imply that the NO_x trap capacity of this spinel is negligible.

It should be noted that the only fresh, calcined sample which shows barium nitrate XRD peaks is $Co,Ba/CeO_2$ (see Table 1). The source of the nitrates is the cobalt nitrate in the solution used for the impregnation method. Either during the solution stirring or during the calcination step, barium nitrate is formed which in this sample is stable up to 490 °C.

For the $Co,Ba,K/CeO_2$ solid, the nitrate species formed during the heating in $NO + O_2$ partially decompose at high temperatures (ca. 370–490 °C), although there is an increase in weight during the cooling in $NO + O_2$ (represented by the discontinuity of the curve in Fig. 3), the instability of the nitrate species is also observed in the He stream. In this way, the presence of the transition metal reduces the stability of nitrates at high temperatures. Note that the storage capacity of this sample at 300 °C is comparable to that of $Pt,Ba/Al_2O_3$ reported by Laurent et al. [16] (Table 2). Probably, the surface interaction between Co and Ba in the perovskite structure prevents the formation of stable nitrate species. FTIR experiments contributed to elucidate this aspect.

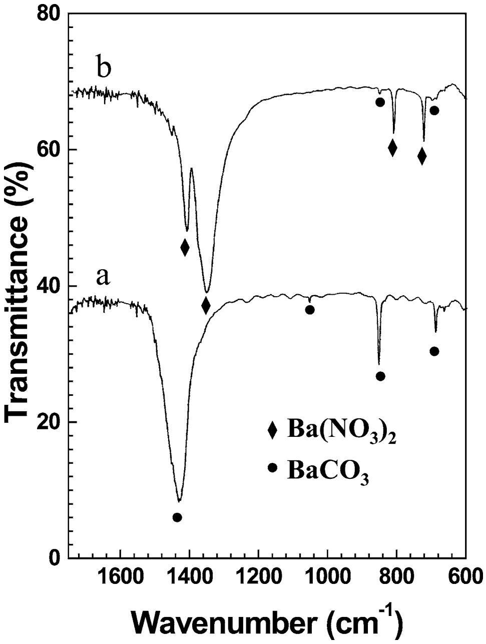

Fig. 4. Infrared spectra on Ba/CeO_2: (a) fresh solid and (b) after the microbalance experiment ($NO + O_2$ followed by He treatments with heatings up to 490 °C, i.e., steps 1–4). See experimental section for more details.

3.3. Characterization of NO_x species after $NO + O_2$ treatment

Figs. 4–6 show the IR spectra of the catalysts after being used on gravimetric studies. For comparison, fresh catalyst spectra are also reported.

The fresh Ba/CeO_2 spectrum (Fig. 4a) revealed the four characteristic vibrational frequencies of $BaCO_3$, a strong band at 1437 cm^{-1}, a small one at 1059 cm^{-1}, and two sharp bands at 858 and 694 cm^{-1} in agreement with XRD results (Table 1). Whereas, in the IR spectrum after the $NO + O_2$ treatment (Fig. 4b), $Ba(NO_3)_2$ was identified as the main compound (1416 (s), 1358 (s), 818 (m), and 730 (m) cm^{-1}). The presence of two small peaks at 858 and 694 cm^{-1} suggested that some $BaCO_3$ remained on the support. The heating in the $NO + O_2$ stream makes NO_2 replace CO_2 and the phase transformation occurs: $BaCO_3 \rightarrow Ba(NO_3)_2$ (reaction (B), Section 2.2). The observed increase in weight is due to the difference in the gravimetric factors between

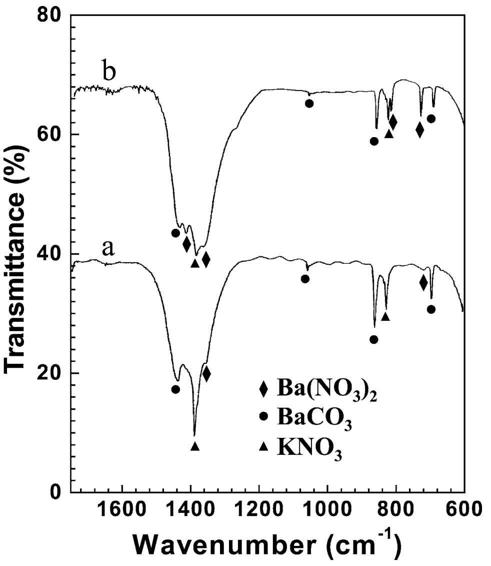

Fig. 5. Infrared spectra on Ba,K/CeO$_2$: (a) fresh solid and (b) after the microbalance experiment (NO + O$_2$ followed by He treatments with heatings up to 490 °C, steps 1–4).

Table 3
Characteristic IR vibrational frequencies

Species	IR vibrational frequencies (cm^{-1})
BaCO$_3$	1437 (s), 1059 (w), 858 (m), 694 (m)
Ba(NO$_3$)$_2$	1416 (s), 1358 (s), 818 (m), 730 (m)
KNO$_3$	1433 (sh), 1384 (s), 1354 (sh), 1273 (sh), 826 (m)
O–Ba- -NO$_2$	1405 (s), 1352 (sh)

BaCO$_3$ and Ba(NO$_3$)$_2$. This final compound is stable during the heating in He (Fig. 4b).

The IR spectrum of the fresh K/CeO$_2$ catalyst (not shown) confirmed that KNO$_3$ is present on the surface causing a negligible adsorption of NO$_2$. As K was added to Ba/CeO$_2$, BaCO$_3$ and KNO$_3$ were the main compounds identified by IR (Fig. 5, Table 3). After the gravimetric studies, the IR spectrum indicated the presence of three compounds: KNO$_3$, Ba(NO$_3$)$_2$, and BaCO$_3$ (Fig. 5b). A significant portion of BaCO$_3$ seems to be occluded by K species during the NO + O$_2$ treatment, this being the cause for the smaller increase of weight in comparison with Ba/CeO$_2$ (Fig. 2). This phenomenon should be favored by the high mobility of potassium on the catalyst surface [17].

The bands associated with KNO$_3$ are present in the IR spectrum of the fresh Co,Ba,K/CeO$_2$ (Fig. 6) and a small contribution of Ba(NO$_3$)$_2$ species would be expected due to the signal at 730 cm^{-1}. The other three characteristic bands, 1416, 1358, and 818 cm^{-1}, are occluded by KNO$_3$ signals (Fig. 6a). In agreement with XRD results, a shoulder at 1437 cm^{-1} can be assigned to a small amount of BaCO$_3$. The weight reached after the Microbalance experiment (steps 1–4) was essentially the same as that of the starting solid (Fig. 3), which would lead one to expect no significant differences between the IR spectra before and after the microbalance experiences (Figs. 6a and 6c, respectively). The main vibrational signals of Ba(NO$_3$)$_2$ were not better resolved after the NO + O$_2$ treatment (Fig. 6c) in comparison with those of the fresh sample (Fig. 6a). However, a new band at 1405 cm^{-1} and a shoulder at 1352 cm^{-1} appeared, and they would be associated to surface N-bound nitrate species (O–Ba- -NO$_2$), where NO$_2$ would act as a Lewis base [18,19]. Ba would be chemically bound to either Co or Ce forming a mixed oxide so that the reaction between BaO and NO$_2$ to produce Ba(NO$_3$)$_2$ would not be allowed. According to the XRD results, BaCoO$_{2.93}$ was present in the fresh solid and this phase would be responsible for this interaction. Moreover, the IR spectrum of this sample after steps 1 and 2 (Fig. 6b), which means just after the treatment in NO + O$_2$, showed that the relative intensity of the band at 1405 cm^{-1} associated to the N-bounded NO$_2$ species was higher than that of the Co,Ba,K/CeO$_2$ after the complete microbalance experiment (steps 1–4) (Fig. 6c).

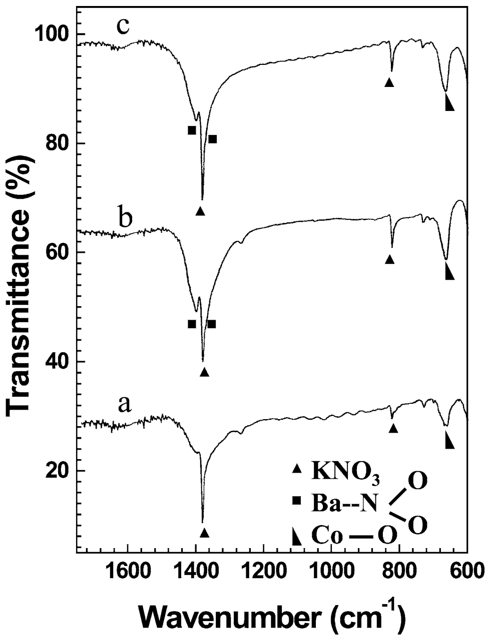

Fig. 6. Infrared spectra on Co,Ba,K/CeO$_2$: (a) fresh solid, (b) after the microbalance experiment (NO + O$_2$ with a heating up to 490 °C, steps 1 and 2 only) and (c) after the microbalance experiment (NO + O$_2$ followed by He treatments with heatings up to 490 °C, steps 1–4).

3.4. *Stability of the nitrate species under reducing atmosphere*

A working trap should be able to adsorb NO$_x$ under an oxidizing atmosphere and to release it as N$_2$ during the engine excursions under reducing conditions. Accordingly, the storage capacity of the solid and its ability to desorb and decompose the trapped NO$_x$ are important [6]. In order to study our catalyst under such conditions, an experiment was performed first by adsorbing NO$_x$ under an oxygen excess atmosphere at 370 °C and then changing the atmosphere to reducing conditions (10% of H$_2$ in helium), analyzing the composition of the gas phase with an on-line mass spec-

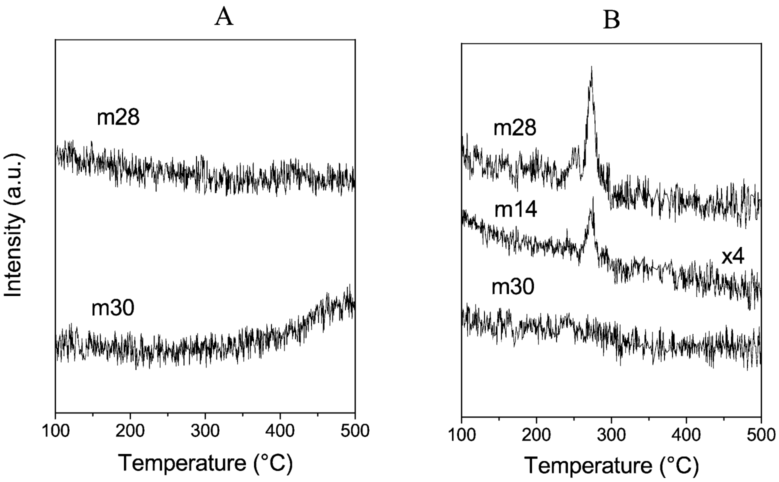

Fig. 7. Mass spectrometer analysis of products during heating in He stream (A) and H_2 (10%)/He (B). Catalyst: Co,Ba,K/CeO_2 (previously treated with NO + O_2 at 370 °C).

trometer. Results are shown in Fig. 7. It can be inferred that Co,Ba,K/CeO_2 behaves as a NO_x trap, retaining the NO_x in an oxidizing atmosphere and reducing NO_x to N_2 in diluted H_2 flow. The released N_2 is clearly observed through the 28 and the 14 mass fragments, besides the absence of NO_x fragments (30 mass). In this view, the NO_2 trapped on Ba sites was reduced by hydrogen, as reported by Balcon et al. [20].

For comparison, the evolution under He atmosphere was also recorded (left part of Fig. 7). This result shows that (i) the release of NO_x (30 mass profile) started around 350 °C, in clear concordance with the microbalance experiment (Fig. 3) and (ii) a flat curve was observed for a 28 mass profile, indicating that there was no N_2 evolution when heating under a nonreducing atmosphere.

3.5. Soot reaction with adsorbed NO_x species

As a tight contact mixture of fresh Co,Ba,K/CeO_2 catalyst and soot (catalyst/soot = 20) was heated in He up to 490 °C in the microbalance, soot particulates were partially burnt (Fig. 8A: dashed line). The reactant oxygen would be supplied by the catalyst surface taking into account the relevant characteristics of ceria-based materials: the oxygen storage ability of the ceria lattice and the high oxidizing power of Ce^{4+} ($Ce^{3+/4+}$ redox couple) [21,22]. The burning of the soot occurs in two steps (as can be clearly seen in the derivative of the curve, shown in the bottom of Fig. 8A, dashed line), similar to that observed during TPO (temperature-programmed oxidation) experiments [23]. This behavior would be associated to the contribution of Co surface species as active sites for soot oxidation [23,24]. The remaining soot is then totally burnt when O_2 is added to the He feed (Fig. 8B, dashed line). The surface oxygen vacancies originated during the catalytic oxidation of soot in He are readily regenerated via the incorporation of the gas-phase oxygen as lattice oxygen through the formation of superoxides (O_2^-) or peroxides (O_2^{2-}) [25–27] recovering the active sites for the reaction.

As the Co,Ba,K/CeO_2 catalyst previously pretreated with NO + O_2 (370 °C) was carefully mixed with soot (catalyst/soot = 20), placed in the microbalance, and heated in He flow up to 490 °C, the burning of the soot occurs in one step (Fig. 8A, solid line). In the absence of O_2, the soot particulates would be oxidized by reaction with the surface nitrate species. The main gaseous products in this case were NO and CO_2. Only trace amounts of NO_2, N_2O, and N_2 were detected, where the latter product was determined using a mass spectrometer analyzer. This result suggested that nitrate species decomposed toward NO_2, which underwent to NO after reaction with soot particles in the absence of O_2, as reported by Luré et al. [28].

Even though a contribution of the lattice oxygen could not be excluded, some unburnt soot remained after this treatment in He. The mechanistic nature of soot oxidation where the catalyst acts as a source of active oxidant agents demands a greater number of contact points between soot particulates and catalyst particles, specifically surface oxidant sites. These sites are reduced during the soot burning in the absence of O_2, and physical phenomena like mass and heat transfer become very important, thus decreasing the overall reaction rate.

In the presence of O_2, the burning of the remaining soot is completed at lower temperatures than in the fresh catalyst (Fig. 8B, solid line). This lower burning temperature was around 280 °C, suggesting that some active oxygen remains on the catalyst surface.

For comparison, the weight changes when fresh catalyst + soot (catalyst/soot = 20) were heated in NO + O_2 are included (Fig. 8C). The temperature at which the weight change rate became maximum is somehow lower than that of the catalyst (previously treated with NO + O_2 at 370 °C)+ soot (compare Figs. 8A and C). However, the tendencies of both curves are similar except that the soot was completely burnt because of the presence of the oxidant in the gas phase. After that, an increase in weight was observed due to the NO_2 incorporation to the solid (Fig. 8C).

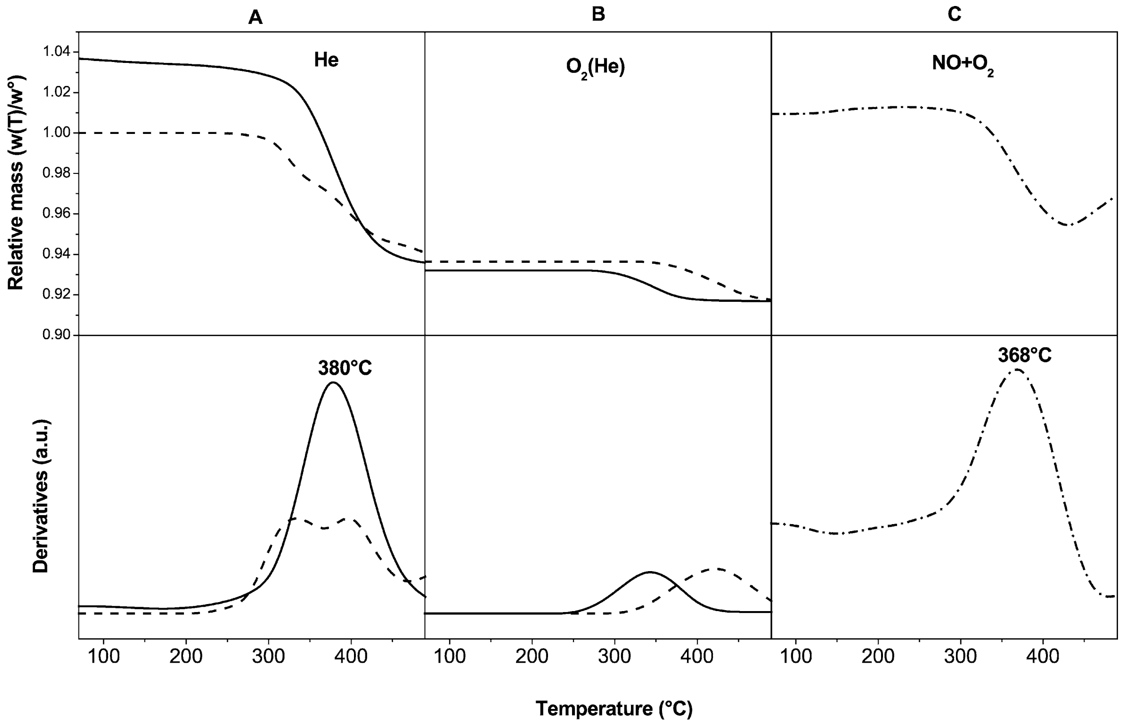

Fig. 8. Study of the reaction between soot and adsorbed NO_x species. (A) He stream, (B) O_2 (18%) in He, and (C) NO (4%) + O_2 (18%) (He balance). Solid line: Catalyst pre-treated with NO (4%) + O_2 (18%) up to 370 °C and then mixed with soot (20/1). Dashed and dashed dotted lines: Catalysts mixed with soot. The derivative curves are shown at the bottom.

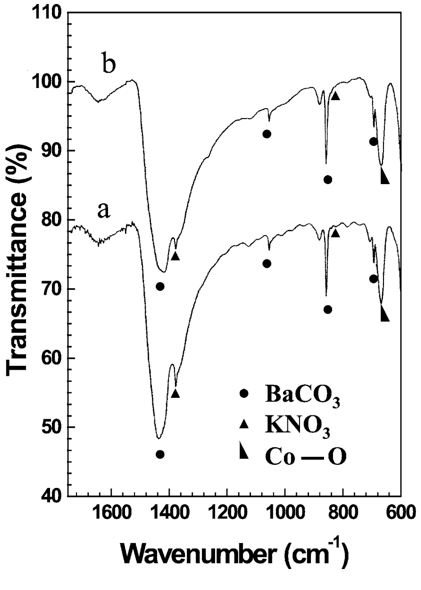

Fig. 9. Infrared spectra of the Co,Ba,K/CeO_2 after the combustion of soot in the absence of oxygen. (a) See dashed line in Fig. 8; (b) see solid line in Fig. 8.

The IR spectra of the Co,Ba,K/CeO_2 catalyst + soot (Fig. 9a) and Co,Ba,K/CeO_2 catalyst pretreated with NO + O_2 + soot (Fig. 9b), after the soot combustion, showed the characteristic bands of $BaCO_3$ and KNO_3 in both cases, thus indicating that during the combustion process there was a restructuring of Ba species and the formation of some bulk Ba carbonate. Moreover, the relative intensities of KNO_3 were less compared with those of the fresh catalyst (Fig. 6a), suggesting that those species could also act as a source of NO_2. Besides, one of the products of this reaction was CO_2 which competes with NO_2 for the same storage Ba sites promoting the release of the latter.

4. Conclusions

Barium oxide, a well-known NO_x trap, is incorporated in this work to a soot combustion catalyst (Co,K/CeO_2), looking for a system for the simultaneous soot combustion and NO_x abatement in diesel exhausts.

NO + O_2 strongly interacts with Ba,K/CeO_2 through the formation of Ba and K nitrate species which are stable under He atmosphere until 490 °C. This NO_2 surface species migrate inside the solid forming a bulk nitrate compound. When Co is incorporated to the system (Co,Ba,K/CeO_2 catalyst) nitrates become unstable at ca. 370 °C both under NO + O_2 and He atmosphere.

In the Co,Ba,K/CeO_2 catalyst the formation of the $BaCoO_{2.93}$ perovskite was detected, which is not present in the Co,Ba/CeO_2 system, indicating that potassium decreases the temperature necessary for the formation of the said structure. The perovskite would be responsible for the instability of nitrate species, due to the formation of surface N-bound nitrate species (O–Ba- -NO_2), where NO_2 acts as a Lewis base.

Nitrate species can be readily decomposed under a reducing atmosphere, making this system very interesting to be used as a NO_x catalytic trap. However, under He atmosphere, only nitrogen oxides are released during nitrates decomposition.

Soot particles can be oxidized by surface nitrate species trapped in the catalyst, this reaction being probably catalyzed by cobalt.

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