

NO_x trapping and soot combustion on BaCoO_{3–y} perovskite: LRS and FTIR characterization

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Received 19 March 2004; received in revised form 17 September 2004; accepted 24 September 2004
Available online 21 November 2004

Abstract

The BaCoO_{3–y} perovskite-type mixed oxide is studied for both trapping of NO_x and combustion of diesel soot. The starting material consists of a stoichiometric mixture of Ba and Co nitrates. Different crystalline phases are obtained when the solids are calcined at different temperatures (ranging from 400 to 1000 °C). After 400 °C calcination Ba(NO₃)₂ and Co₃O₄ crystalline phases are formed, while after calcination at 700 °C the BaCoO₃ stoichiometric perovskite is obtained. However, when the temperature is increased to 1000 °C, the structure loses oxygen and perovskite BaCoO_{2.74} is formed. The solids calcined at 700 and 1000 °C show high NO_x adsorption capacity, the latter being more effective. This solid shows weak IR bands in the 800 cm⁻¹ frequency region associated with the perovskite structure. After the catalyst interacts with NO_x, new bands associated with bulk nitrates and surface NO₃⁻ species are observed. Signals associated with surface N-bounded species of the O–Ba–NO₂ type could be masked by the intense Ba(NO₃)₂ signals. LRS characterization is in agreement with XRD and FTIR results. The Raman signal at 716 cm⁻¹ is associated with the BaCoO_{2.74} structure while a broad signal at 607 cm⁻¹ appears in samples containing BaCoO₃ and BaCoO_{2.94} phases. Nitrates formed upon NO + O₂ treatments show high thermal stability under He atmosphere up to 490 °C. However, reductive treatments either under H₂ atmosphere or with soot particles cause decomposition of the nitrates at temperatures lower than 400 °C. A reaction scheme is proposed involving the participation of perovskite structures, Co₃O₄, Ba(NO₃)₂, BaO and metallic Co particles.

The catalyst under study favors the reaction between the soot particles and the trapped NO_x species making this system promising for the simultaneous abatement of both contaminants. The addition of K decreases the soot combustion temperature.

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Keywords: BaCoO_{3–y} perovskite; Diesel pollutants; NO_x trapping; Soot combustion; Catalytic trap

1. Introduction

Soot particles and oxides of nitrogen (NO + NO₂) are the most important pollutants emitted by diesel engines. The filtration of particulate material and its combustion assisted by a catalyst deposited on the filter is the most studied alternative for the abatement of soot. The abatement of NO_x can be achieved in a second catalytic converter, by reaction with an adequate reducing agent (NH₃ or hydrocarbon SCR technology: selective catalytic reduction) [1]. Another alternative consists in the simultaneous abatement of soot

and NO_x. This solution is clearly much more ambitious and has been explored only recently [2]. According to Specchia and coworkers [1] the issue requiring urgent research is the development of an adequate catalyst capable of promoting both soot oxidation and NO_x reduction at relatively low temperatures and within the typical range of diesel engine exhaust gases (150–380 °C).

Pioneering studies on oxides with perovskite-type and spinel structures for this reaction were first carried out by Teraoka and co-workers [3–7]. In recent studies, Kureti et al. [8] have analyzed this reaction using iron oxides as catalysts while Fino et al. [1] did so with La_{2–x}K_xCu_{1–y}V_yO₄-type perovskites. However, further efforts should be made concerning the activity of the solids under conditions of

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loose contact, i.e., higher thermochemical stability, higher selectivity to CO₂, and higher selectivity to N₂ (particularly lower emissions of N₂O).

In a previous article [9], we reported that the Co,Ba,K/CeO₂ solid is an efficient trap of NO_x and, at the same time, an active catalyst for soot combustion. Traces of the BaCoO_{3-y} structure present in this solid could be involved in the NO₂ sorption–desorption capacity. In the present work, the BaCoO_{3-y} perovskite is synthesized and studied in order to simultaneously eliminate the two main pollutants emitted by diesel engines. In addition, potassium is added to the system in order to improve the activity of the catalysts and decrease the soot combustion temperature [7].

The Ba,Co,O system has been the subject of various studies. Boulahya et al. [10] recently synthesized BaCo₂O₄ by the ceramic method, which allowed them to establish a new relationship between this structure and BaCoO₃. In previous works, González-Calbet and coworkers [11,12] characterized different BaCoO_{3-y} phases upon different calcination temperatures. The application of the BaCoO_{3-y} perovskite to NO_x removal through sorption-desorption cycles was first reported by Machida et al. [13] and by Arai and Machida [14]. They made a thorough screening of metal oxides and zeolites and among them, BaCuO_{2.1} was the most effective system.

During the functioning of a catalytic trap, NO is oxidized to NO₂ and then adsorbed in the form of nitrates. In the present paper, the idea is to study the possibility of regenerating the trap by reducing the nitrates by oxidation of the soot particles to CO₂, so as to obtain a single catalytic system efficient for the simultaneous abatement of both pollutants. To this aim, the BaCoO_{3-y} system was characterized by means of XRD, LRS and FTIR. NO_x adsorption and soot combustion experiments were also performed.

2. Experimental

2.1. Materials preparation

The BaCoO_{3-y} solids were prepared by mixing Co(NO₃)₂ and Ba(NO₃)₂ solutions (0.25 M). In order to study the promotion effect of K in the soot oxidation, KOH (1 wt%) was added to the preparations. The mixed solution was heated while stirring continuously until a paste was achieved. It was dried at 110 °C and then calcined in an oven at different temperatures (400–1000 °C) for 17 h. The nomenclature adopted for the prepared mixed oxides was Ba,Co,O or Ba,Co,O,K (in the case of the solids containing K) followed by a number between parenthesis, which indicates the calcination temperature.

2.2. Solids characterization

2.2.1. X-ray diffraction (XRD)

The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using

Cu Kα radiation in the step mode with a step width of 0.02 °/step and a preset time of 0.4 s. The Shimadzu XD-D1 analysis software package was used for the phase identification.

2.2.2. Infrared 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.

2.2.3. Laser Raman spectroscopy (LRS)

The Raman spectra were recorded with a TRS-600-SZ-P Jasco Laser Raman instrument, equipped with a charge coupled device (CCD) with the detector cooled to about 153 K using liquid N₂. The excitation source was the 514.5 nm line of a Spectra 9000 Photometrics Ar ion laser with the laser power set at 30 mW.

For the spectroscopic techniques the intensity of the bands was characterized as: vs (very strong), s (strong), m (medium), w (weak), vw (very weak) and sh (shoulder).

2.2.4. Microbalance studies

Microbalance experiments were performed in a Cahn 2000 instrument in order to study the interaction of the solid with NO + O₂. Feeding O₂ is necessary to form NO₂. We have previously reported that NO alone interacts very weakly with the solids under study [9].

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%) + O₂ (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 down to 70 °C. At this temperature the feed was switched to He and after stabilization, the sample was weighed. Then the heating program was repeated in He flow, weighing the sample at the end of this treatment at 70 °C in He stream. The subscript “nit” after the adopted nomenclature indicates the solids after this microbalance treatment (nitrated catalysts).

Equation A was used for the calculation of the NO₂ storage capacities (%) (NSC) as ratios between the stored NO₂ (as Ba(NO₃)₂) and the maximum NO₂ storage capacity of Ba (which corresponds to 0.0146 mol NO₂/g Ba).

$$\% \text{ NO}_2 \text{ storage capacity} = \frac{((w(T)/w^\circ) - 1) \times 100}{\alpha + \beta - 1} \quad (1)$$

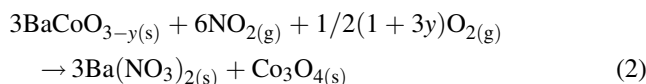
where *w*(*T*)/*w*[°] is the relative mass (i.e., sample weight at any temperature *T* divided by the initial weight obtained at 70 °C after the He treatment for 2 h at 400 °C),

$$\alpha = \frac{\text{MW}_{\text{Ba}(\text{NO}_3)_2}}{\text{MW}_{\text{BaCoO}_3}}$$

and

$$\beta = \frac{MW_{\text{Co}_3\text{O}_4}}{3MW_{\text{BaCoO}_3}}$$

Eq. (1) involves the molecular weights (MW) of $\text{Ba}(\text{NO}_3)_2$, BaCoO_3 and Co_3O_4 and it was obtained considering that the incorporation of NO_2 led to $\text{Ba}(\text{NO}_3)_2$ according to reaction (2):



In order to study the regeneration capacity of the NO_x trap, a microbalance experiment similar to those described above but feeding H_2 (10%) in He instead of pure He was done (making a purge of pure He during 30 min between the treatments of $\text{NO} + \text{O}_2$ and H_2/He).

2.3. Catalytic soot combustion

The soot was obtained by burning commercial diesel fuel (Repsol–YPF, Argentina) in a glass vessel. After being collected from the vessel walls, the soot was dried in a stove at 120°C for 24 h. More details about obtaining and characterization of soot are reported elsewhere [15].

The activity of the solids for the soot combustion was studied by TGA in a Mettler Toledo TGA/SDTA 851 instrument. The soot and the different catalysts were mechanically mixed in an agate mortar so as to obtain a soot/catalyst ratio = 1/20 (w/w). Usually, 10 mg of catalyst + soot mixtures were heated from 25 to 700°C at $10^\circ\text{C}/\text{min}$ in an air flow of 90 ml/min.

3. Results and discussion

3.1. Catalyst characterization: fresh catalysts

The XRD analysis was carried out on the solids calcined at different temperatures in order to observe (i) the decomposition of starting materials, $\text{Ba}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ and (ii) the formation of BaCoO_{3-y} perovskite (Table 1, Fig. 1). It is worth considering that the heating in

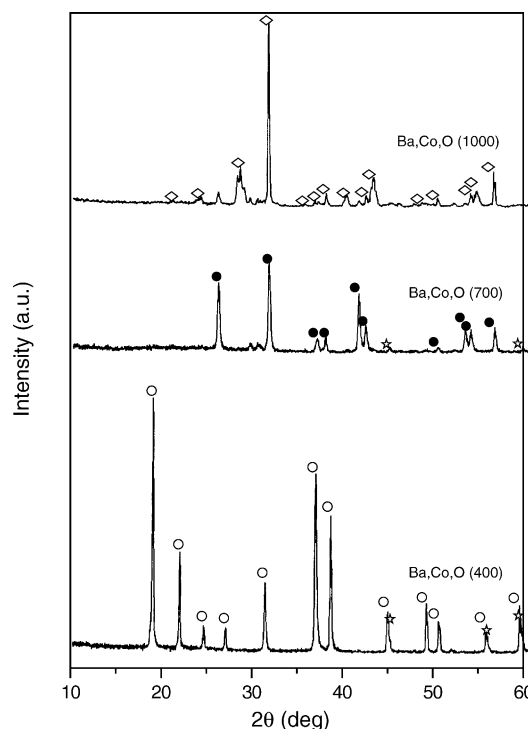


Fig. 1. Powder X-ray diffraction pattern of Ba,Co,O calcined at different temperatures. Ba,Co,O (400): \circ $\text{Ba}(\text{NO}_3)_2$; \star , Co_3O_4 . Ba,Co,O (700): \bullet , BaCoO_3 ; \star , Co_3O_4 . Ba,Co,O (1000): \diamond , $\text{BaCoO}_{2.74}$. No marked reflection peaks belong to phases reported in Table 1.

air at high temperature of a perovskite can induce the formation of oxygen vacancies [16]. In this way, an interesting structural study of the stoichiometric BaCoO_3 and non-stoichiometric $\text{BaCoO}_{2.94}$ and $\text{BaCoO}_{2.74}$ is reported by González-Calbet and coworkers [11,12]. The XRD patterns of these perovskite-type solids point out that BaCoO_3 and $\text{BaCoO}_{2.94}$ present comparable patterns, the main difference being that the former has two pair of doublets at $2\theta = 41.5$ and 42.2° and 53.0 and 53.7° , respectively, that appear as singlets in the latter. Nevertheless, they are fairly different from that of $\text{BaCoO}_{2.74}$.

Samples treated at 400 and 500°C consist of a mixture of $\text{Ba}(\text{NO}_3)_2$ and Co_3O_4 . When the calcination temperature is increased up to 600°C , these two last crystalline phases

Table 1

Crystalline phases obtained when the Ba,Co,O system is calcined at different temperatures and NO_x storage capacities

System	XRD phases ^a	% NO_2 storage after the microbalance treatment ^b
Ba,Co,O (400) ^c	$\text{Ba}(\text{NO}_3)_2$, Co_3O_4	Negligible
Ba,Co,O (500) ^c	$\text{Ba}(\text{NO}_3)_2$, Co_3O_4	Negligible
Ba,Co,O (600) ^c	BaCoO_3 , $\text{BaCoO}_{2.94}$, [Co_3O_4 , $\text{Ba}(\text{NO}_3)_2$]	nd
Ba,Co,O (700)	BaCoO_3 , [Co_3O_4 , BaCo_2O_4]	12.6
Ba,Co,O,K (700)	BaCoO_3 , [Co_3O_4 , BaCo_2O_4]	12.9
Ba,Co,O (1000)	$\text{BaCoO}_{2.74}$, [BaCoO_3 , $\text{BaCoO}_{2.94}$]	22.9
Ba,Co,O,K (1000)	$\text{BaCoO}_{2.74}$, $\text{BaCoO}_{2.94}$, [BaCoO_3]	20.7

^a Phases between brackets appear at traces level.

^b % NO_2 storage capacities (NSC) were calculated using Eq. (1) (see text).

^c No different phases were detected for these systems containing K.

appear in minor proportions, with the major structures being BaCoO_3 and $\text{BaCoO}_{2.94}$. The XRD pattern of $\text{Ba}_x\text{Co}_x\text{O}$ (700) shows the characteristic signals of the stoichiometric BaCoO_3 with a small contribution of Co_3O_4 and BaCo_2O_4 (Fig. 1). The absence of $\text{Ba}(\text{NO}_3)_2$ in the solid calcined at 700 °C indicates that this temperature would be necessary to remove the nitrate species. This is in agreement with Querini et al. [15] who found that 700 °C was the temperature needed to completely decompose nitrates for the Co/MgO system. When the $\text{Ba}_x\text{Co}_x\text{O}$ system is calcined up to 1000 °C, $\text{BaCoO}_{2.74}$ is the principal structure present and the secondary phases are the two other mentioned perovskite-type structures: BaCoO_3 and $\text{BaCoO}_{2.94}$.

As far as we know, Raman spectra of $\text{Ba}_x\text{Co}_x\text{O}$ mixed oxides have not been reported in the literature. In order to further investigate the phases present in this interesting system, a LRS characterization has been performed. Results are combined with those obtained by XRD in order to make assignments of the observed LRS signals.

The LRS spectra of $\text{Ba}_x\text{Co}_x\text{O}$ system calcined at different temperatures (Fig. 2) show the evolution from the sample treated at 400 °C containing $\text{Ba}(\text{NO}_3)_2$ (bands at 1049 (vs) and 732 (m) cm^{-1}) and Co_3O_4 (signals at 688 (vs), 612 (vw), 524 (m) and 482 (m) cm^{-1}) to samples having perovskite phases, which are achieved at $T \geq 600$ °C. No changes between the Raman spectra of $\text{Ba}_x\text{Co}_x\text{O}$ (500) and $\text{Ba}_x\text{Co}_x\text{O}$ (400) are observed, in agreement with XRD results. As the calcination temperature increased to 600 °C, a new broad signal at 607 cm^{-1} appears along with those attributed to

$\text{Ba}(\text{NO}_3)_2$ and Co_3O_4 . This new signal is associated with perovskite structures, BaCoO_3 and $\text{BaCoO}_{2.94}$, which are both identified as the main crystalline phases in this sample (Table 1). In agreement with the above interpretation is the Raman spectrum of $\text{Ba}_x\text{Co}_x\text{O}$ (700) since this sample containing mainly BaCoO_3 has the most significant Raman peak at 607 cm^{-1} (Fig. 2). The two weak signals observed at 688 and 716 cm^{-1} are assigned to Co_3O_4 and $\text{BaCoO}_{2.74}$ respectively, which are present as secondary phases. The absence of nitrate species signals further confirms that temperatures as high as 700 °C are needed to remove these species. The assignment of 716 cm^{-1} signal to $\text{BaCoO}_{2.74}$ is substantiated by the $\text{Ba}_x\text{Co}_x\text{O}$ (1000) Raman spectrum (Fig. 2), because this is the major crystalline phase for the sample calcined at 1000 °C. The secondary phases, BaCoO_3 and $\text{BaCoO}_{2.94}$, are present in this spectrum as a broad peak at 607 cm^{-1} . Summarizing, the Raman signal at 716 cm^{-1} is associated with $\text{BaCoO}_{2.74}$ whereas the broad feature at 607 cm^{-1} is assigned to either BaCoO_3 or $\text{BaCoO}_{2.94}$. Those signals correspond to internal vibrations of perovskites where M–O bonds (M = Ba or Co) are involved.

The crystalline phases are the same for the solids with and without K (Table 1). However, the XRD reflections of the $\text{Ba}_x\text{Co}_x\text{O}$ system were better defined in the case of the solids containing K, suggesting that K improves the interaction between Ba and Co to form the mixed oxide. A similar effect in the $\text{La}_x\text{Co}_x\text{O}$ system was observed by Moggia et al. [17]. They reported that as the K loading increased, a better crystallinity and a higher concentration of the out-layer perovskite were observed. In the case of the $\text{Ba}_x\text{Co}_x\text{O}$ solid calcined at 1000 °C (Fig. 3 and Table 1), the presence of K also induces the development of the $\text{BaCoO}_{2.94}$ phase.

Even though the incorporation of K into the perovskite lattice is possible [18–20] due to the similar ionic radii of Ba and K [18], in our samples the K/Ba atomic ratio is 0.06, and according to both Cortés Corberán and coworkers [20] and Shangguan et al. [7], for this low ratio no difference in the XRD pattern could be expected between the perovskite with and without potassium.

3.2. NO_2 interaction with the $\text{Ba}_x\text{Co}_x\text{O}$ catalysts

Table 1 also shows the NO_x storage capacities (NSC) obtained in the Cahn microbalance (as was explained in the experimental section). The best value is 22.9 at 490 °C, which is lower than that reported by Laurent et al. [21] for $\text{Pt}_x\text{Ba}_x/\text{Al}_2\text{O}_3$.

$\text{Ba}_x\text{Co}_x\text{O}$ solid calcined at 400 °C, which consists in a mixture of $\text{Ba}(\text{NO}_3)_2$ and Co_3O_4 , does not interact with NO_x . Thus, Co_3O_4 adsorbs rather small amounts of NO_x as was reported in our previous paper [9] and $\text{Ba}(\text{NO}_3)_2$ is already saturated in NO_x . The NSC values for $\text{Ba}_x\text{Co}_x\text{O}$ (700) and $\text{Ba}_x\text{Co}_x\text{O},\text{K}$ (700) are similar (Table 1). At this calcination temperature, barium nitrate coming from the preparation procedure is completely decomposed and the main phase is the stoichiometric perovskite BaCoO_3 (Figs. 1 and 2). The

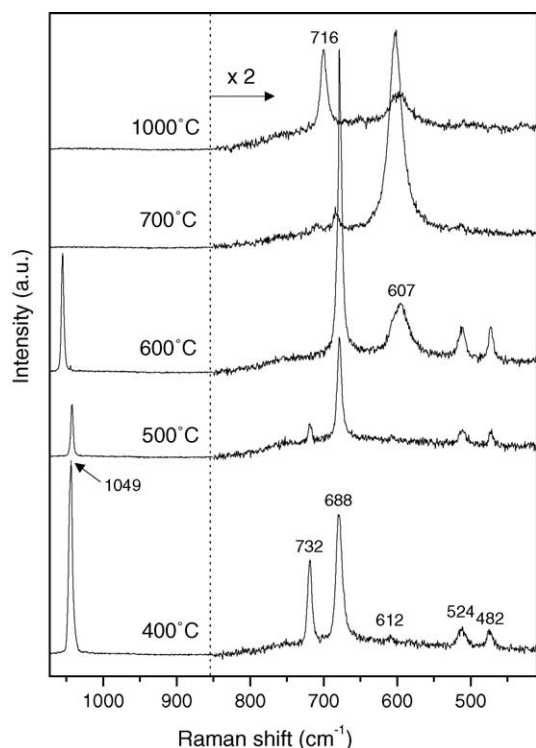


Fig. 2. Laser Raman spectra of $\text{Ba}_x\text{Co}_x\text{O}$ calcined at different temperatures.

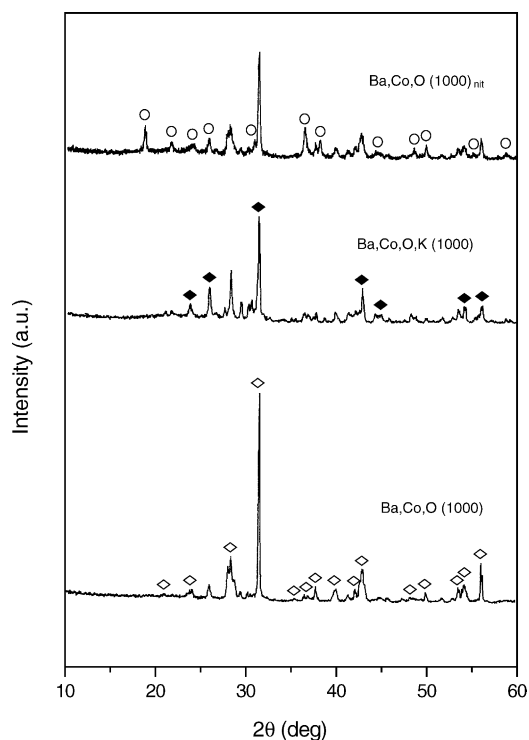


Fig. 3. Powder X-ray diffraction pattern of Ba,Co,O calcined at 1000 °C: effect of K addition and NO + O₂ treatment on the crystalline phases. Ba,Co,O (1000): ◊, BaCoO_{2.74}. Ba,Co,O,K (1000): ◆, BaCoO_{2.94}. Ba,Co,O (1000)_{nit}: ○, Ba(NO₃)₂. No marked reflection peaks belong to phases reported in Table 1.

addition of K only modified the sample crystallinity. As these samples were calcined at 1000 °C, the NSC values noticeable increased (Table 1). However, this rise is higher for the Ba,Co,O (1000) compared to the Ba,Co,O,K (1000). It is important to point out that the main crystalline phase of Ba,Co,O (1000) is BaCoO_{2.74} whose structure contains significant oxygen vacancies. When K was added, BaCoO_{2.94} was also formed and the lower NSC of the K-containing sample could be related to the smaller amount of oxygen vacancies of BaCoO_{2.94} in comparison with BaCoO_{2.74}.

Fig. 4 shows the Raman spectra of solids calcined at 700 and 1000 °C after microbalance experiments, in comparison with the fresh solids. After NO₂ treatments, the spectra of both samples, Ba,Co,O (700)_{nit} and Ba,Co,O (1000)_{nit}, show the characteristic vibrational bands of Ba(NO₃)₂ and Co₃O₄. On the other hand, the two bands attributed to BaCoO_{2.94} and BaCoO_{2.74} are less defined in contrast to those of fresh solids, suggesting that part of the perovskite structure could be destroyed owing to the interaction between Ba and NO₂. The formation of Ba(NO₃)₂ is confirmed as well by XRD, as shown in Fig. 3 for Ba,Co,O (1000)_{nit}.

Considering the 400–1000 °C calcination temperature range, an increase in the calcination temperature leads to an increase in the NO₂ storage capability. In this trend, samples with high oxygen vacancies considerably improve NSC. According to González-Calbet and coworkers [12] the non-

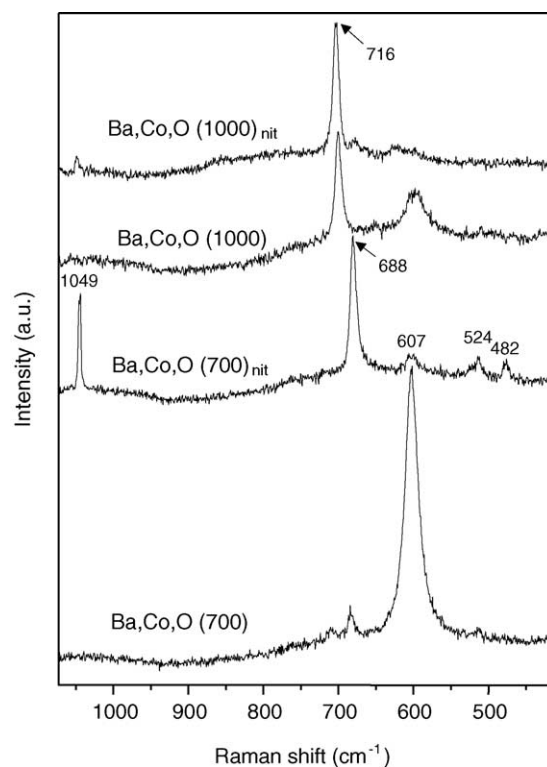


Fig. 4. Effect of the NO + O₂ treatment on the Laser Raman spectra of Ba,Co,O.

stoichiometric perovskite, BaCoO_{2.74}, contains high concentrations of anionic vacancies that are randomly distributed along the crystal. Besides, it is well known that those vacancies can act as Lewis bases and become adsorption sites for O₂ and NO₂ [22,23]. These adsorbed species can react with Ba to form bulk Ba(NO₃)₂ and Co₃O₄ through a shrinking core reaction mechanism as was proposed by Machida and coworkers [13,14] for Ba,Cu,O system. The gas–solid reaction involved is that denoted as (2) in Section 2. In the case of the stoichiometric perovskite, BaCoO₃, some surface Lewis base sites are expected.

These results imply the reversibility of the process of incorporation of NO_x and decomposition of nitrates: at high temperature and under an oxidizing atmosphere the perovskite-type structure is formed from Ba(NO₃)₂ and Co₃O₄ and after the NO₂ treatment, the initial species are recovered. The reversibility of the system is an important property to be considered for a working NO_x trap.

In order to substantiate the species formed after the NO + O₂ treatment, FTIR measurements were performed. Fig. 5 shows the spectra of the Ba,Co,O (1000) solid fresh (Fig. 5a) and after the NO + O₂ treatment in the microbalance (Fig. 5b). Ba,Co,O (1000) only shows weak bands in the low-frequency region (wavenumber lower to 800 cm⁻¹) associated with the perovskite structure. After the NO + O₂ treatment, Ba,Co,O (1000)_{nit} exhibits new bands associated with bulk Ba(NO₃)₂ (1416, 1358, 818 and 730 cm⁻¹) and

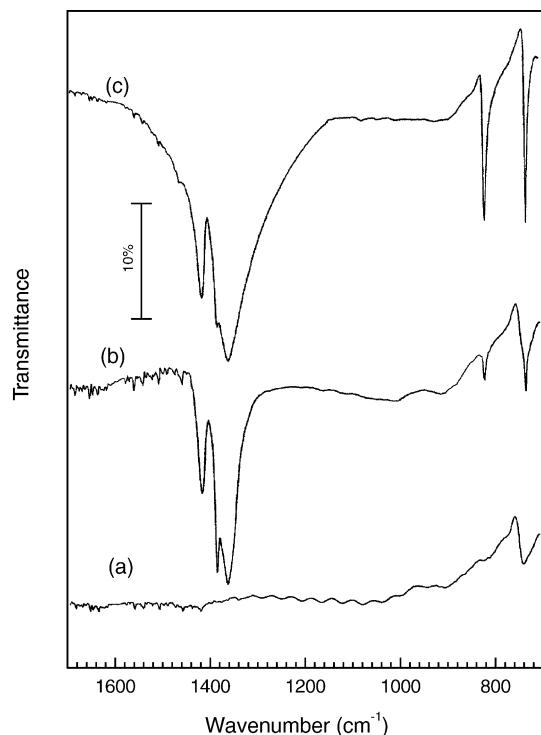


Fig. 5. Infrared spectra of Ba,Co,O (1000): (a) before and (b) after the NO + O₂ treatment. (c) Ba,Co,O (400) solid spectrum is included for comparison.

surface NO₃⁻ species (1385 cm⁻¹). The signals at 1405 cm⁻¹ (s) and 1352 cm⁻¹ (sh) associated with surface N-bounded nitrate species (O–Ba···NO₂) [9] could be masked by the intense Ba(NO₃)₂ signals. For comparison the spectrum of the Ba,Co,O (400) solid is also included (Fig. 5c), where the bands corresponding to Ba(NO₃)₂ are observed. These results are in agreement with those of XRD and Raman. The similarity in the FTIR spectrum of the Ba,Co,O (1000)_{nit} solid and the Ba,Co,O (400) further points out the reversibility of the process of NO_x trapping (Fig. 5b and c).

A working trap should be able to incorporate NO_x under oxidizing conditions and to release it under reducing conditions. Thus, the NSC of the solid is very important, but its ability to desorb and decompose the trapped NO_x is also very important. In order to study our catalyst under such conditions, an experiment was performed first by incorporating NO_x under excess oxygen atmosphere and then changing the atmosphere to reducing conditions (10% H₂ in Helium).

Fig. 6 displays changes in weight due to the NO_x storage under the NO + O₂ treatment and the nitrates decomposition under a reducing atmosphere for the Ba,Co,O,K (700) solid. The dotted line divides the graph into two sections: the left section corresponds to the heating in the NO + O₂ stream and the right section to the heating in H₂(10%)/He stream. Note that neither the cooling in the NO + O₂ flow nor the cooling in the H₂(10%)/He flow is represented in Fig. 6.

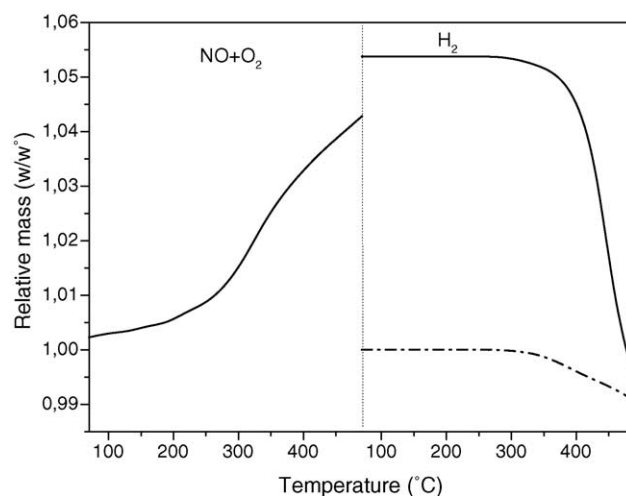


Fig. 6. Study of regeneration of the NO_x trap in the microbalance: Nitrates formation under NO + O₂ flow and decomposition under reducing atmosphere (continuous line). The dash-dotted line shows the reducibility of the perovskite. Solid: Ba,Co,O,K (700).

The discontinuity in weight observed for the curve represented by the solid line before and after the dotted line is due to the cooling in the NO + O₂ stream. As it can be inferred from Fig. 6, Ba,Co,O,K (700) behaves as a NO_x trap, retaining the NO_x in an oxidizing atmosphere and releasing it in a reducing one. Under the reducing atmosphere, nitrate species are completely decomposed and the initial weight is restored.

Heating the solid under a reducing atmosphere, ca. 300 °C metallic cobalt (Co⁰) is formed (it is well known that both Co₃O₄ and the Co-containing perovskite could produce Co⁰). The reducibility of the perovskite is shown in Fig. 6 with a dash-dotted line. These Co⁰ atoms would dissociate molecular H₂ (g) to atomic H, which would reduce the Ba(NO₃)₂ formed during the NO_x trapping process. A model of the decomposition of Ba(NO₃)₂ by a solid state, homogeneous catalytic reaction is presented by James et al. [24]. Fig. 7 summarizes the NO_x trapping process and the regeneration of the trap (under a reducing atmosphere).

3.3. Combustion of soot in the presence of nitrate species

The activity of the prepared solids for the combustion of diesel soot was studied by TGA. The profiles obtained for the solids calcined at 1000 °C are shown in Fig. 8a and those corresponding to the solids calcined at 700 °C are shown in Fig. 9a. The derivative curves, which represent the combustion reaction rate, are shown in Figs. 8b and 9b. It can be observed that the combustion of the soot particulates over Ba,Co,O (1000) (Fig. 8) begins at ca. 350 °C and the rate has a maximum at 450 °C. For the Ba,Co,O,K (1000) solid the combustion begins at ca. 300 °C and the maximum is at 420 °C, the difference being due to the promoting effect of potassium on the catalytic activity of the solids which has previously been reported [7,9].

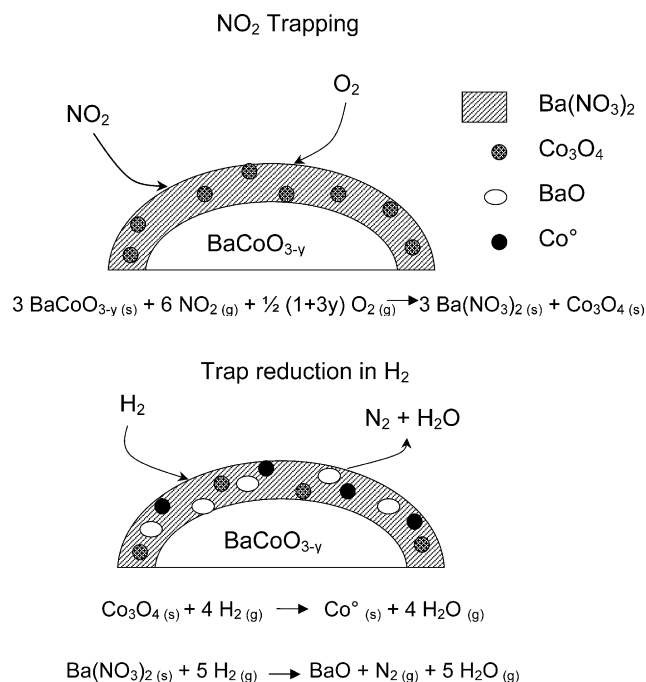


Fig. 7. Scheme for the NO_x trapping-regeneration process with the BaCoO_{3-y} perovskite.

The same figure shows the TGA curves corresponding to the soot combustion over Ba,Co,O (1000)_{nit} and Ba,Co,O,K (1000)_{nit} (whose NSC were reported in Table 1). It can be observed that the presence of nitrate species promotes the combustion, shifting the peaks of maximum rate to 370 and 360 °C for the catalysts with and without potassium, respectively. In this case the weight loss is considerably

higher compared with the untreated solids due to the decomposition of nitrates. The used soot/catalyst ratio was 1/20, so that the weight loss due to the combustion of soot is expected to be 5%, which in fact occurs for the untreated solids (Fig. 8). Nevertheless, for the same catalysts previously treated with NO + O₂, the weight loss observed is higher than 5% (ca. 8%). Considering that during the microbalance experiments in He atmosphere nitrate species are stable up to 500 °C and that excess oxygen is known to further stabilize these nitrates [25], it is concluded that the presence of soot particulates is responsible for the lower temperature of nitrates decomposition through the reaction C(soot) + surface NO₃⁻. At higher temperatures (ca. 500 °C) another weight loss is observed for the solids treated with NO + O₂ due to the decomposition of the fraction of nitrates that did not react with the soot particulates.

Comparing Figs. 8 and 9, there are no significant differences in the soot combustion rate temperatures. Nevertheless, the most important difference is the magnitude of the weight loss for the solids treated with NO + O₂: higher values are observed for solids calcined at higher temperature. It is important to remember the NSC values reported in Table 1 and thus TGA results correlate with NSC values: solids calcined at the higher temperature appear as better NO_x traps. However, note that the weight loss at ca. 500 °C is lower for the solids calcined at 700 °C, meaning that a higher fraction of nitrates is decomposed during the soot combustion.

In order to characterize the solid after the combustion of soot, the Ba,Co,O,K (700)_{nit} solid extracted after the TGA experiment (i.e., the Ba,Co,O,K (700)_{nit} solid mixed with soot and burned in the TGA apparatus) was analyzed by

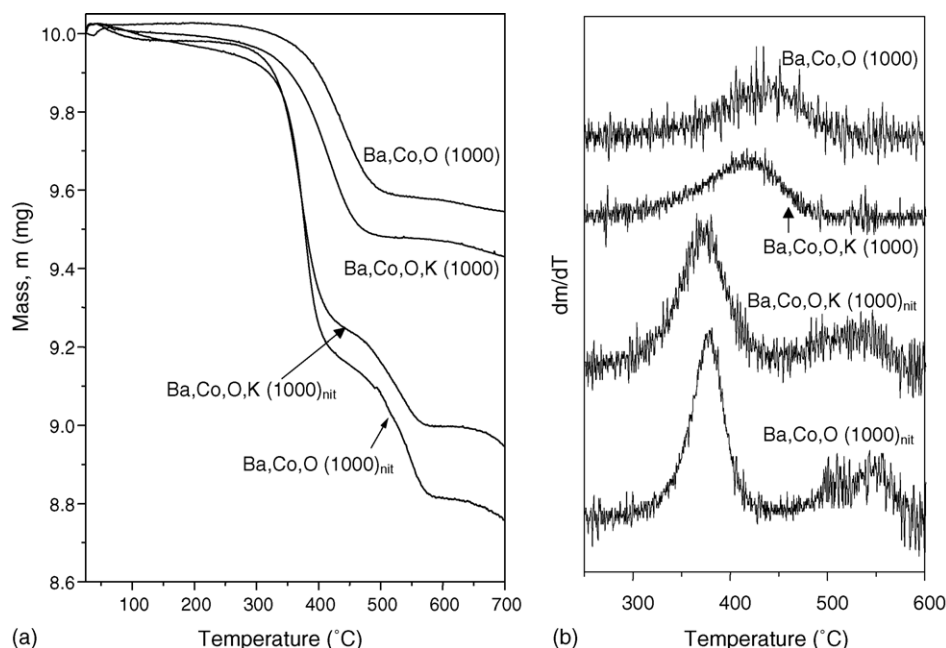


Fig. 8. TGA curves (a) and derivatives (b) for the solids calcined at 1000 °C mixed with soot: influence of the presence of nitrate species on the soot combustion.

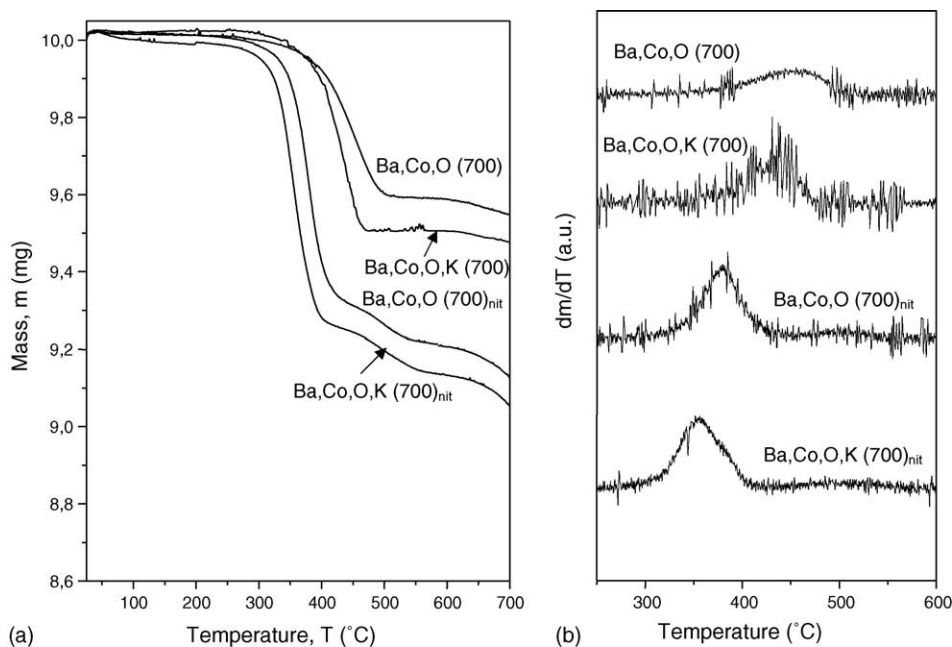


Fig. 9. TGA curves (a) and derivatives (b) for the solids calcined at 700 °C mixed with soot: influence of the presence of nitrate species on the soot combustion.

FTIR. Fig. 10 displays the spectrum obtained for this sample (Fig. 10c) in comparison to that obtained for the fresh solid (Ba,Co,O,K (700), Fig. 10a) and the NO₂ treated sample (Ba,Co,O,K (700)_{nit}, Fig. 10b). The transformation of

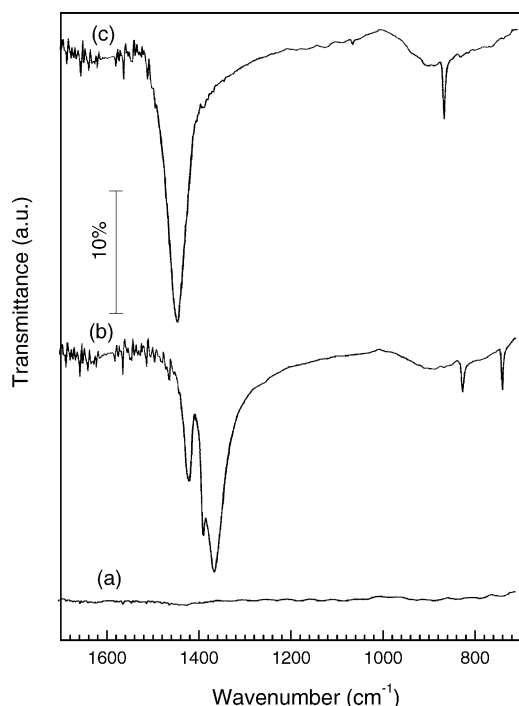


Fig. 10. FTIR spectra of the Ba,Co,O,K (700) system: (a) fresh solid, (b) Ba,Co,O,K (700) after the NO + O₂ treatment in the microbalance (Ba,Co,O,K (700)_{nit}) and (c) Ba,Co,O,K (700)_{nit} solid mixed with soot and burned in the TGA equipment.

Ba(NO₃)₂ into BaCO₃ (bands at 1437 (s), 1059 (w), 858 (m) and 694 (m) (not shown) is clearly evident. This indicates that during the combustion of soot, the generated CO₂ reacts with Ba(NO₃)₂ to form the corresponding carbonate. This result further confirms the reaction between C(soot) + nitrate species.

4. Conclusion

BaCoO_{3-y} is an active phase for both NO_x trapping and soot combustion in diesel exhausts. The addition of potassium decreases the temperature needed for the combustion.

Different crystalline perovskite-type phases are formed upon thermal treatments between 600 and 1000 °C. The solid calcined at the higher temperature is mainly composed of the non-stoichiometric perovskite BaCoO_{2.74}, and this phase shows the higher NO_x storage capacity.

Under NO + O₂ atmosphere, bulk Ba(NO₃)₂ and surface NO₃⁻ species were detected. These nitrate species are thermally stable under inert atmosphere until 490 °C. However, under reducing conditions, either contacting with H₂ or soot particles, nitrates decomposed at temperatures lower than 400 °C.

The studied catalyst favors the reaction between the nitrate species and the soot particulates, which makes this system promising for the simultaneous abatement of both contaminants. The soot combustion peak appears at lower temperatures for nitrated catalysts, suggesting that the reaction C(soot) + nitrate species occurs, in addition to the combustion with gaseous oxygen.

Acknowledgements

The financial support received from ANPCyT (PICT 14-6971) and from Universidad Nacional del Litoral (CAID program) is acknowledged. Thanks are also given to Prof. Elsa Grimaldi for the revision of the English manuscript.

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