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Soot combustion and NO_x adsorption on Co,Ba,K/ZrO_2

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Abstract

The aim of this work was to study the Co,Ba,K/ZrO_2 catalyst for the removal of the most important pollutants emitted by diesel engines: soot and NO_x. The Ba(*x*)/ZrO_2 solids (with "*x*" varying between 0 and 16 wt.% Ba) and the Co,Ba,K/ZrO_2 system were prepared by wet impregnation and then calcined at 500 °C in air for 2 h. These solids were treated with NO + O_2 and the stability of the formed nitrates was analyzed under both oxidizing and inert atmospheres measuring the amount of NO_x adsorbed by the catalyst. Besides, the Co,Ba,K/ZrO_2 solid was studied as a catalyst for soot combustion. The soot/catalyst ratio was varied (1:1, 1:10, 1:15 and 1:20) and the NO_x content in the feed was also varied between 0 and 4%. From these results, an exploratory study concerning the reaction order with respect to NO was addressed; the reaction order was estimated at ca. 0.5 and the activation energy of the reaction was estimated at about 20 kcal/mol.

Keywords: Soot combustion; NO_x adsorption; ZrO_2-supported catalysts; Diesel exhaust pollutants

1. Introduction

Diesel engines are widely used as they combine high fuel economy, high durability and low maintenance costs. However, diesel engine exhausts have many adverse environmental effects due to the emission of nitrogen oxides (NO_x) and particulate matter (PM).

The use of TWC is an established technology for the catalytic reduction of NO_x produced by gasoline engines operating at stoichiometric conditions. However, there is still no appropriate catalytic technology for NO_x emission abatement in vehicles with diesel engines since TWC systems cannot work under rich conditions [1].

On the other hand, the best technical solution to the particulate emissions problem is to place a catalytic filter in line with the exhaust gases, capable of both filtering the material up to acceptable concentrations and oxidizing the retained particulate matter. In this context, the key challenge is to find a stable catalyst capable of decreasing the combustion temperature of soot down to diesel exhaust temperature [2].

Several catalysts have been investigated to fulfil this aim. Pioneering studies were carried out by Teraoka and co-workers [3–7] employing perovskite and spinel-type oxides. More recent studies are those carried out by Kureti et al. [8], who worked with iron oxide catalysts, Fino et al. [9], who did so with $La_{2-x}K_xCu_{1-y}V_yO_4$-type perovskites and Milt et al. [10], who tried with the $BaCoO_{3-y}$ perovskite. In order to overcome the soot-catalyst contacting problem, low-melting point metal salts have been employed [11]. In a recent publication [12], An and McGinn mixed soot with potassium catalysts in the presence of a liquid ("wet deposition"). They observed a high activity of potassium-rich catalysts in some wet-deposition routes due to the dissolution of potassium cations in the solvent, which led to tight contact between the soot and K cations. Moulijn and co-workers [13] suggested that the best way to test catalysts for soot oxidation at laboratory scale is working with loose contact between the soot and the catalyst particles. However, for fundamental studies, i.e. determination of reaction mechanisms, the loose contact is not appropriate since both thermal and mass transport phenomena become limiting, so that the tight contact is the right form to mix the catalysts and the soot.

Considering the pollutants emitted from diesel engines as a whole, the most feasible removal is the combination of NO_x traps and oxidation catalysts [14]. In previous works, we have found that the K/La_2O_3 and Co,K/CeO_2 solids were highly

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active and stable for soot combustion [15,16]. The addition of barium to the Co,K/CeO_2 catalyst enabled us to increase the NO_x adsorption capacity [17]. The objective of the present work is to obtain a catalyst active for the simultaneous NO_x and soot removal from the exhausts of diesel engines. For this purpose, the Co,Ba,K/ZrO_2 system is studied, characterizing the catalysts with different techniques: XRD, LRS and FTIR. Their properties are evaluated as a NO_x trap (using a thermogravimetric technique) and as a catalyst for soot combustion (varying both the NO_x amount present in the gaseous flow and the soot-catalyst ratio). From the kinetic data the reaction order with respect to NO is calculated and the reaction activation energy is estimated. Since it has been reported that zirconia readily adsorbs NO_x at low temperature [18], we have decided to use it as the support with the aim of improving NO_x trapping capacity.

2. Experimental

2.1. Catalyst preparation

The Ba loadings for Ba(x)/ZrO_2 catalysts were x = 3, 6, 9, 12 and 16% (expressed as Ba wt.%) whereas the Co,Ba,K/ZrO_2 sample had Co: 12 wt.%, Ba: 16 wt.% and K: 7 wt.%. The catalysts were prepared by impregnation from a ZrO_2 suspension to which a solution was added containing the desired cations so as to obtain the different loads mentioned above. The salts used were $Ba(Ac)_2$, $Co(Ac)_2$ and KNO_3. The mixture was evaporated until achieving a paste, which was dried at 120 °C for 24 h. The precursor thus obtained was calcined at 500 °C for 2 h in air flow.

2.2. Characterization

2.2.1. BET area

The surface area of the support and the different catalysts were determined in a Quantachrome Nova 1000 sorptometer using N_2 adsorption at liquid nitrogen temperature.

2.2.2. 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 $2\theta = 10°$ to 70°. The software package of the equipment was used for the phase identification.

2.2.3. IR spectroscopy (FTIR)

Infrared spectra were obtained using a Shimadzu 8101 M 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 charge coupled device (CCD) 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 with the laser power set at 30 mW.

2.2.5. Microbalance studies

Microbalance experiments were performed in a Cahn 2000 instrument in order to study the interaction of the solids with NO + O_2. Feeding O_2 was necessary to form NO_2. Previous work demonstrated that NO alone interacts very weakly with the solids under study [16]. Since the total gaseous flow was high, the concentrations at the microbalance exit remained almost unaltered compared to those in the feed. The FTIR analysis of downstream gases indicated that the NO_2/NO ratio was 1300 [17].

Before each experiment, 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%) + 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 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.

2.2.6. 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 the obtention and characterization of soot are reported elsewhere [15].

The soot/catalyst mixtures were heated at 5 °C/min from room temperature up to 600 °C in O_2(18%) + NO stream, helium balance (total flow 20 ml/min), in a flow equipment designed with this purpose. A high oxygen concentration was used in order to calculate the reaction order with respect to nitric oxide. Therefore, the oxygen concentration (O_2), remained unaltered during the kinetic experiments and it could be included in a global kinetic constant. The exhaust gases were analyzed with a Shimadzu GC-9A chromatograph (with TCD detector), the CO concentration being negligible. This fact is due to the presence of cobalt oxide, which is a good catalyst for CO oxidation. This is in agreement with results previously reported [19]. The soot/catalyst ratio was varied between 1:1 and 1:20 and the effect of the presence of NO was studied varying its concentration from 0 to 4%.

3. Results and discussion

3.1. Characterization

The incorporation of metal oxides to the ZrO_2 support did not alter the surface area, which was practically the same for all the catalysts prepared (42 $m^2\ g^{-1}$).

The Ba(x)/ZrO_2 catalysts were characterized both before and after the microbalance experiments. When the fresh catalysts were analyzed (before the microbalance treatment), the presence of monoclinic zirconia and barium carbonate was detected in all the samples. On the other hand, when the used

Table 1
Catalysts composition

Solid[a]	Crystalline phases[b]	Species detected by FTIR[b]
ZrO_2		
Fresh	ZrO_2 (m)	
$NO + O_2$, 70 °C[c]	ZrO_2 (m)	NO_3^- species
Used	ZrO_2 (m)	
Ba(x)/ZrO_2[d]		
Fresh	ZrO_2 (m), $BaCO_3$	$BaCO_3$
Used	ZrO_2 (m), $Ba(NO_3)_2$	$Ba(NO_3)_2$, NO_3^- species, [$BaCO_3$]
Co,Ba,K/ZrO_2		
Fresh	ZrO_2 (m), [$BaCO_3$]	$BaCO_3$, KNO_3, [K_2CO_3]
Used	ZrO_2 (m), [$Ba(NO_3)_2$]	$Ba(NO_3)_2$, $BaCO_3$, KNO_3, Co_3O_4

[a] Fresh = calcined solids and Used = solids after the microbalance treatment with $NO + O_2$ and He.
[b] Crystalline phases or species detected at trace levels appear between brackets. m = monoclinic.
[c] Treated with $NO + O_2$ in the microbalance at 70 °C until a constant weight was achieved.
[d] "x" (3, 6, 9, 12 or 16) is the Ba wt.%.

catalysts were analyzed (after the microbalance treatment), the species detected were barium nitrate and adsorbed nitrate. In the case of the ZrO_2 support after exposure to NO (4%) + O_2 (18%) flow at 70 °C, adsorbed nitrate species were detected by FTIR (1384 cm^{-1} signal).

Table 1 shows a summary of the XRD and FTIR results obtained both for the Ba(x)/ZrO_2 system and for the system also containing cobalt and potassium (Co,Ba,K/ZrO_2). The presence of KNO_3 in the fresh Co,Ba,K/ZrO_2 solid was not surprising since it was the starting salt used in the preparation of the catalyst, which did not decompose during the calcination step. Previous studies of our group have demonstrated the stability of KNO_3 up to 600–700 °C [21]. Laser Raman spectroscopy results indicated the presence of Co_3O_4 (486, 523, 612 and 693 cm^{-1} signals) for the Co,Ba,K/ZrO_2 catalyst.

3.2. $NO + O_2$ adsorption

Fig. 1 shows results obtained with the microbalance for the Ba(3)/ZrO_2, Ba(6)/ZrO_2, Ba(9)/ZrO_2, Ba(12)/ZrO_2 and Ba(16)/ZrO_2 solids, besides those obtained for the support and for the Co, Ba and K containing catalysts. It can be observed that the support (ZrO_2) adsorbs NO_2 at low temperature due to the formation of adsorbed NO_3^- species (IR band at 1384 cm^{-1}). Nevertheless, these adsorbed nitrates are unstable at high temperature as they completely desorb when the temperature is increased up to 490 °C even in diluted $NO + O_2$ flow.

A similar behavior is observed for the catalysts containing 3 and 6% barium, adsorbing more NO_x than the support alone. However, the amount of adsorbed NO_x at low temperature increases with the barium loading increase. On the other hand, when the temperature rises these species are desorbed although at 490 °C, the desorption is not complete, as can be observed in the support (Fig. 1). The same occurs for the catalysts containing 9 and 12% barium, the decrease in weight being lower and taking place at higher temperatures.

In the case of the Ba(16)/ZrO_2 catalyst, a different behavior is observed: between 70 and 300 °C, the weight remains practically constant but from 300 °C upwards, the weight increases.

Under inert atmosphere, a similar behavior is observed for all the samples except for the difference in the desorption

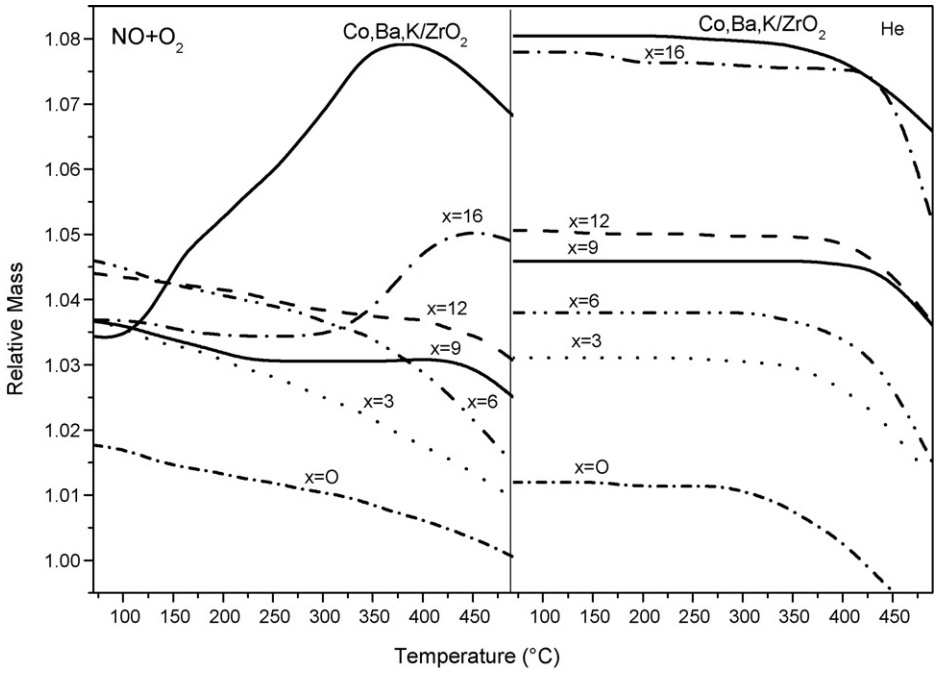

Fig. 1. Adsorption of NO_x during the microbalance experiments on Ba(x)/ZrO_2 and Co,Ba,K/ZrO_2 catalysts. Left-hand side: NO (4%) + O_2 (18%) (helium balance) and right-hand side: inert atmosphere (helium).

temperature. The desorption from the support begins at 300 °C whereas for the other catalysts it begins at ca. 400 °C. In contrast to what occurs with the support, the Ba-containing catalysts do not desorb all the adsorbed NO_x.

According to Eguchi and Kikuyama [22], at low temperature NO_x can be stored in a two-step reaction as NO_3^- species both on the surface and/or on the bulk of zirconia, whereas at high temperature sorbed nitrate species may either undergo reduction into gaseous NO_x or react with Ba to give bulk barium nitrate.

The XRD and IR characterization showed the presence of $Ba(NO_3)_2$ in the solids after the microbalance experiment, so that the following reactions could be proposed for the NO_x adsorption:

$$NO + 1/2O_2 \rightarrow NO_2$$

$$2NO_2 + 1/2O_2 + O^{2-} \rightarrow 2NO_3^- \text{(at low temperature)}$$

$$2NO_3^- + BaCO_3 \rightarrow Ba(NO_3)_2 + CO_2 + 1/2O_2 \quad \text{(at high temperature)}$$

$$BaCO_3 + 2NO_2 + 3/2O_2 \rightarrow Ba(NO_3)_2 + CO_2 \quad \text{(at high temperature)}$$

In the case of the Co,Ba,K/ZrO_2 system, the NO_x adsorption at low temperature is similar to that of the Ba(16)/ZrO_2 catalyst but as the temperature rises up to 370 °C, the cobalt-containing catalyst increases the amount of adsorbed NO_x. Nevertheless, from 370 to 490 °C decreasing weights are observed, which could be associated either to nitrates decomposition due to the presence of cobalt (as has been previously observed for the Co,Ba,K/CeO_2 system [17]) or to the desorption of NO_x over zirconia. Nevertheless, the maximum during the $NO + O_2$ adsorption appears at the same temperature for the Co,Ba,K—containing system either supported on ZrO_2 or on CeO_2. This suggests that the most probable reason for the observed decrease in weight could be associated with nitrate decomposition.

With respect to the stability of the potassium under rigorous conditions, in a previous work [20] we addressed this aspect with a similar solid (Ba,K/CeO_2), showing that potassium is highly stable against rigorous hydrothermal treatments.

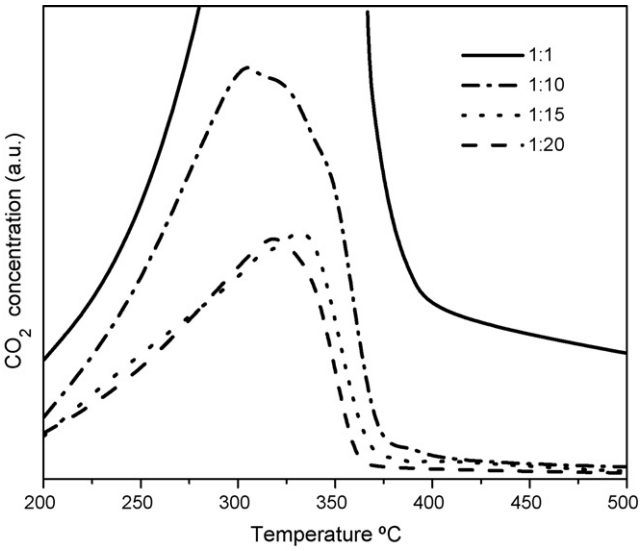

Fig. 2. Effect of the soot:catalyst ratio on the soot combustion rate. Catalyst: Co,Ba,K/ZrO_2. Feed composition: NO(4%) + O_2(18%) (helium balance).

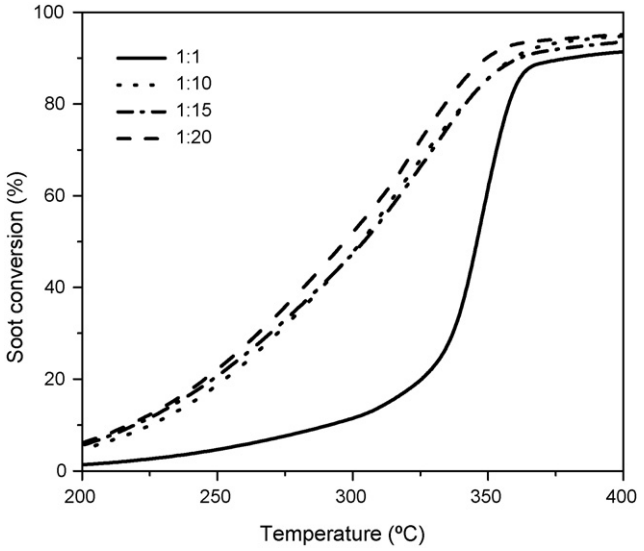

Fig. 3. Effect of the soot/catalyst ratio on the soot conversion calculated from data of Fig. 2.

3.3. Soot combustion

The Co,Ba,K/ZrO_2 system was studied as a catalyst for the soot combustion through experiments with different soot:catalyst ratios (1:1, 1:10, 1:15 and 1:20). The soot/catalyst mixtures were mechanically mixed in an agate mortar during 3 min so as to obtain a tight contact between the catalyst and the soot. Fifty milligrams of soot/catalyst mixture were used for the catalytic experiments.

During the heating treatment under reaction stream, samples were taken and stored in a 16-loop valve up to be analyzed by chromatography. Fig. 2 shows the results obtained. The temperature of maximum combustion rate decreases as the amount of soot in the mixtures is lower, being ca. 350 °C for the maximum soot/catalyst ratio (1:1), and ca. 300 °C for the other ratios. It is important to remark that the non-catalytic combustion of soot takes place at ca. 600 °C.

Fig. 3 was built from the calculus of the soot conversion by partially integrating the curves of Fig. 2. The lower conversion for the 1:1 soot/catalyst ratio could be associated with the need for the catalyst, the soot and the gaseous reactants to meet at one point (active site), situation difficult to achieve in this case due to the high amount of soot. For the other soot/catalyst ratios (1:10, 1:15 and 1:20), only a slight difference in the soot combustion rates is observed, which is in agreement with the existence of a low physical limitation in the soot-catalyst

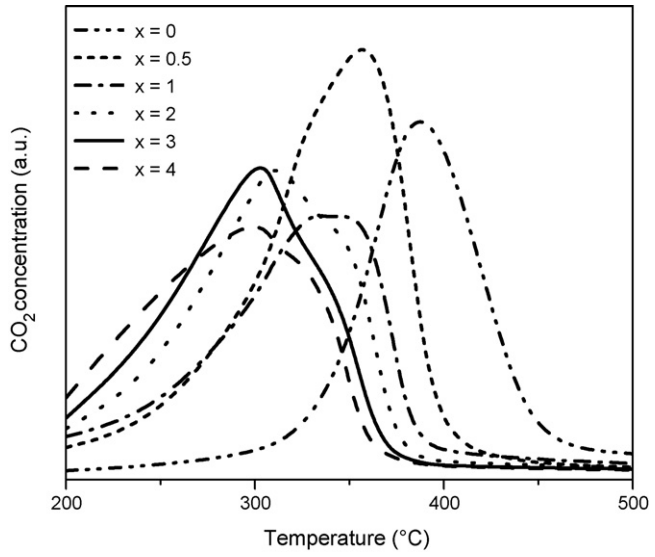

Fig. 4. Effect of NO concentration on soot combustion. Catalyst: Co,Ba,K/ZrO_2. Feed composition: NO(x%) + O_2(18%) (helium balance) and 1:20 soot:-catalyst ratio.

contact, which is possible due to the mobility given by potassium that favors this contact [12].

The effect of the addition of 4, 3, 2, 1, 0.5 and 0% NO in the feed was also studied and the results are depicted in Fig. 4. According to other authors [23], the lower the NO percentage, the higher the temperature of maximum soot combustion rate. The decrease in the maximum combustion rate temperature is better observed in Fig. 5, where the soot conversion was calculated by partially integrating the curves of Fig. 4.

The higher soot conversion obtained when the NO concentration was increased is due to the NO_2 formation, which oxidizes soot particles more easily than O_2. Shangguan et al. [6] proposed the following mechanism for the soot + O_2 reaction:

$$O_{2(g)} \rightarrow 2O_{(ads)}$$

$$C + O_{(ads)} \rightarrow C*(O)$$

$$C*(O) + O_{(ads)} \rightarrow CO_2$$

$$C*(O) + 1/2O_2 \rightarrow CO_2$$

These authors obtained a reaction order of 0.5 for O_2, which is in agreement with its dissociative adsorption. When NO is present, these steps must be considered:

$$NO + 1/2O_2 \rightarrow NO_2$$

$$NO_2 \rightarrow NO_{(ads)} + O_{(ads)}$$

$$C + O_{(ads)} \rightarrow C*(O)$$

The surface dissociation of NO_2 produces $O_{(ads)}$, which is the intermediary responsible for the soot particles oxidation.

In our case, the reaction between the soot and the surface nitrates is also possible [15], since as observed in the microbalance experiments with NO + O_2, when the Co,Ba,K/ZrO_2 system is heated in the presence of NO + O_2, different surface and bulk nitrate species are formed.

From the results presented in Figs. 2–5, a preliminary study was performed in order to obtain the reaction order with respect to NO. The soot combustion rate was considered as follows:

$$r = \mathrm{kg}(\mathrm{NO})^b(\mathrm{O_2})^c \quad (1)$$

where (NO) is the NO concentration, (O_2) the oxygen concentration and kg includes the functionality with the soot particles mass.

Considering the points where a low CO_2 evolution is observed, which means that the mass of soot is practically constant (kg = constant), and taking into account that the O_2 concentration does not change because it is present in excess, a new k' constant can be defined so that Eq. (1) results:

$$r = k'(\mathrm{NO})^b \quad (2)$$

We define the soot combustion rate as the derivative of the number of soot moles (nC) with respect to time:

$$r = \frac{\mathrm{d}nC}{\mathrm{d}t} \quad (3)$$

The following equations could also be considered:

$$nC = \int_0^t \mathrm{F}(\mathrm{CO_2})\mathrm{d}t \quad (4)$$

$$\frac{\mathrm{d}nC}{\mathrm{d}t} = F(\mathrm{CO_2}) \quad (5)$$

$$r = k'(\mathrm{NO})^b = F(\mathrm{CO_2}) \quad (6)$$

where F is the total flow (mol/cm^3) and (CO_2) is the CO_2 concentration (mol/cm^3). By comparing Eqs. (2)–(5), Eq. (6) can be obtained. As it can be observed, the reaction rate can be calculated as the product between the CO_2 (mol/cm^3) concen-

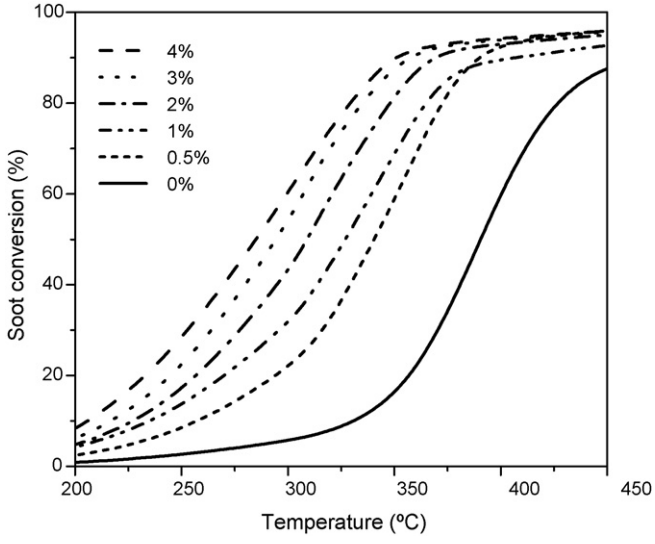

Fig. 5. Effect of NO concentration over soot conversion (data calculated from results shown in Fig. 4).

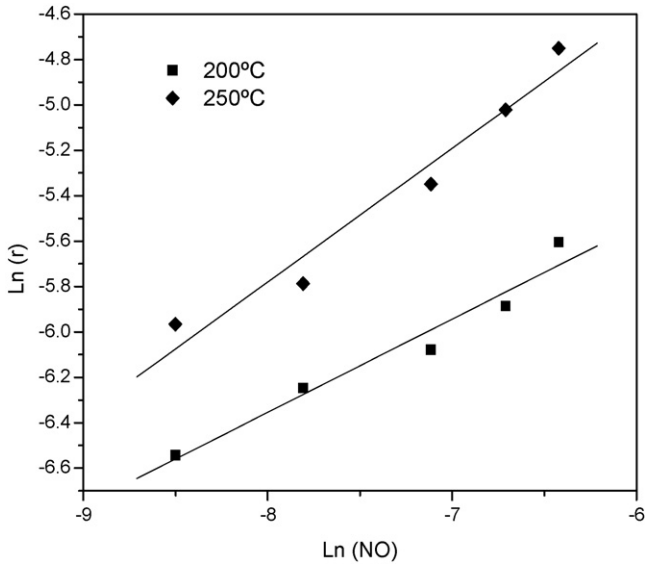

Fig. 6. Kinetic plots to calculate the reaction order with respect to NO from the data of Fig. 4.

tration and the total volumetric flow, so that:

$$\ln r = \ln k' + b \ln (\mathrm{NO}) \quad (7)$$

Fig. 6 shows the results obtained when ln r versus ln (NO) are plotted for 200 and 250 °C, temperatures at which the above conditions to simplify the reaction rate equation are complied. From these results, values of "b" were obtained by regression of the curves (0.41 for 200 °C and 0.59 for 250 °C, respectively). Taking into account Arrhenius law and considering the interception, the activation energy for the soot combustion was obtained: E_a = 19.6 kcal/mol.

4. Conclusions

The combination of BaO and ZrO_2 in the same catalyst allows one to expand the temperature range in which the solid is effective to adsorb NO_x. At low temperatures (from room temperature to 300 °C), the NO_x–ZrO_2 interaction prevails whereas at higher temperatures $Ba(NO_3)_2$ is formed. The incorporation of Co and K promotes the soot combustion activity, both from the Co redox properties and the potassium mobility, this latter advantage favoring the soot/catalyst contact.

Therefore, the Co,Ba,K/ZrO_2 solid is able to simultaneously remove both contaminants. In this catalyst, NO_x promotes the soot combustion, the reaction order being ca. 0.5 and the activation energy approximately 20 kcal/mol.

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