

# Simultaneous removal of soot and nitrogen oxides from diesel engine exhausts

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## Abstract

In this paper, previously reported findings and new results presented here are discussed with the main objective of establishing the reaction mechanism for soot oxidation on different supports and catalysts formulations. Catalysts containing Co, K and/or Ba supported on MgO, La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> have been studied for diesel soot catalytic combustion. Among them, K/La<sub>2</sub>O<sub>3</sub> and K/CeO<sub>2</sub> showed the best activity and stability for the combustion of soot with oxygen. A reaction mechanism involving the redox sites and the surface-carbonate species takes place on these catalysts. On the other hand, Co,K/La<sub>2</sub>O<sub>3</sub> and Co,K/CeO<sub>2</sub> catalysts display activity for the simultaneous removal of soot and nitric oxide. The soot–catalyst contacting phenomenon was also addressed. A synergic La–K effect was observed in which the mechanical mixtures of soot with K–La<sub>2</sub>O<sub>3</sub> showed higher combustion rates than those observed when K and La were directly deposited on the soot surface. The effect of the addition of Ba was explored with the aim of promoting the interaction of the solid with NO<sub>2</sub>, thus combining the NO<sub>x</sub> catalytic trap concept with the soot combustion for filter regeneration. Ba/CeO<sub>2</sub> and Ba,K/CeO<sub>2</sub> were effective in NO<sub>x</sub> absorption as shown in the microbalance experiments. However, the formation of stable nitrate species inhibits the soot combustion reaction. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Soot combustion; Nitric oxide removal; Co–K–Ba catalysts

## 1. Introduction

Particulate matter (soot) and NO<sub>x</sub> are the main pollutants in diesel engine emissions. The combination of a filter with oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [1]. Since the temperature in the exhaust gases may be as low as 200 °C for small engines, and can exceed 600 °C at full load for heavy engines, a useful catalyst has to operate efficiently at low tem-

peratures and be thermally stable. The reaction mechanism and therefore a rational catalyst design for this system has been studied only recently. Studies with a large number of formulations have been reported during the last few years, and the soot–catalyst contact appears to be one of the most important problems to be overcome [2]. In this paper, the reaction mechanisms of soot combustion with oxygen are compared using different supports (MgO, La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>) promoted with potassium and/or cobalt. The discussion is largely based on our previous results [3,5–7,9,10] and also the new results presented in this paper. The feasibility of the simultaneous removal of soot and nitric oxide is studied using Ba as a promoter. The contact problem between the soot and the catalyst is also addressed.

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## 2. Experimental

### 2.1. Soot and catalyst preparation

The soot was obtained by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel as described in [3]. After collecting from the vessel walls, it was dried in a stove for 24 h at 120 °C.

The catalysts were prepared from a support (MgO, La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>) suspension in water, to which Co(NO<sub>3</sub>)<sub>2</sub> and/or KOH solution was added to obtain 12 wt.% of Co and/or 4.5 wt.% of K. Barium acetate was used for the preparation of Ba/CeO<sub>2</sub> catalysts. The mixture was evaporated while being vigorously stirred until a paste was achieved, which was dried in a stove for 24 h at 120 °C, and calcined at different temperatures (400 and 700 °C).

### 2.2. Activity test

The catalytic activity for the combustion of soot was determined by temperature programmed oxidation (TPO) of carefully prepared mixtures of catalyst and soot (20:1). A gaseous flow (40 cm<sup>3</sup>/min) with 6% oxygen in nitrogen was used and the temperature was increased at a rate of 12 °C/min using 10 mg of the mechanical mixture. A modified TPO technique [4] was employed which consists of passing the gases coming from the reactor through a methanation reactor, where CO and CO<sub>2</sub> were converted into CH<sub>4</sub>. Afterwards, methane was measured continuously with an FID detector. The methanation reactor contained a nickel catalyst, and operated at 400 °C. Isothermal experiments were also performed including NO in the gaseous feed. In all TPO experiments, temperature is increased until all the soot is burnt off.

### 2.3. Catalyst characterization

The high frequency CO<sub>2</sub> pulses technique was carried out at 500, 400, and 25 °C by sending pulses of 0.135 μmol of CO<sub>2</sub> in He carrier for every 10 s. Thermal treatments between pulse cycles were also carried out. Typically, the catalyst (20 mg) was heated up to 700 °C, and cooled down to 500 °C where a new cycle of pulses was carried out. The CO<sub>2</sub> was detected with an FID after methanation as described above.

Microbalance studies were performed in a Cahn 2000 equipment. The sample was stabilized at 70 °C and NO (5 vol.%) or NO (5 vol.%) + O<sub>2</sub> (5 vol.%) were fed. Afterwards, it was heated up to 490 °C (5 °C/min), maintained at this temperature for 1 h, and then cooled down. The procedure was repeated but with pure He feed.

The XPS spectra were obtained at room temperature with a Shimadzu ESCA 750 instrument using Mg Kα radiation. X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu Kα radiation.

## 3. Results and discussion

### 3.1. Catalytic soot combustion with oxygen (TPO experiments and high frequency CO<sub>2</sub> pulses)

The catalysts that contain potassium display good activity for soot combustion with a maximum in the TPO profile between 350 and 400 °C (Fig. 1). Isothermal experiments (not shown) indicate that the soot can be completely removed with diluted oxygen at 350 °C.

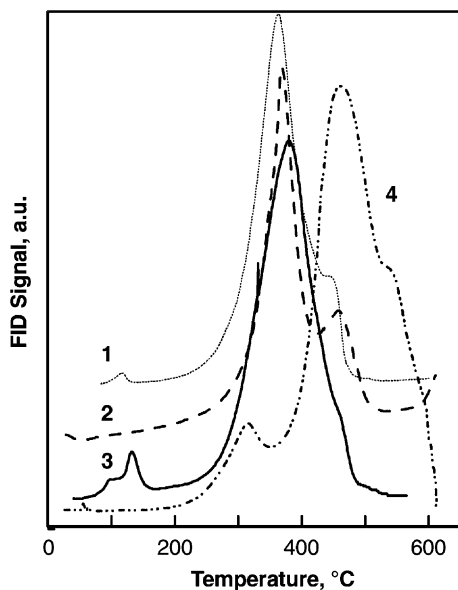


Fig. 1. TPO profiles of soot-catalyst mechanical mixture: (1) K(4.5)/CeO<sub>2</sub>; (2) K(4.5)/La<sub>2</sub>O<sub>3</sub>; (3) Ba(22),K(7)/CeO<sub>2</sub>; (4) Ba(22)/CeO<sub>2</sub>.

When lanthanum is the support, cobalt decreases the reaction rate due to the formation of a mixed oxide with a perovskite structure as seen by XRD [6]. This takes both the support and the  $\text{CoO}_x$  out of the reaction. This effect is more pronounced at high calcination temperatures and high K loading. XPS results show that higher the K/La surface ratio, higher the activity [6].

K and  $\text{La}_2\text{O}_3$  interact with  $\text{CO}_2$  at temperatures as high as  $500^\circ\text{C}$  [10]. As previously suggested [5], the reaction rate probably occurs via a carbonate-type intermediate, which is formed by consuming the C from the soot; then the intermediate decomposes releasing  $\text{CO}_2$ . This suggests that  $\text{La}_2\text{O}_3$  is playing a role in the reaction rate by forming a carbonate-type intermediate. Since the support modifies the activity of the active component (in this case potassium), it is important that the carbonate formed due to the interaction between the  $\text{CO}_2$  and the support decomposes at the reaction temperature. Otherwise, the surface of the support will be irreversibly deactivated due to the formation of carbonate. Experiments sending high frequency  $\text{CO}_2$  pulses were carried out (Fig. 2) to obtain information about the dynamics of the

adsorption–desorption process of the  $\text{CO}_2$ . Pulses were sent to the catalyst for every 10 s at different temperatures such as 30, 400 and  $500^\circ\text{C}$ . The smaller the amplitude of the signal, the higher the level of the interaction. Fig. 2A shows that  $\text{K}(4.5)/\text{La}_2\text{O}_3$  interacts with  $\text{CO}_2$  at high temperatures. Pure  $\text{La}_2\text{O}_3$  also interacts with the  $\text{CO}_2$  [10]. Therefore, both K and  $\text{La}_2\text{O}_3$  display a high level of interaction with the  $\text{CO}_2$  which is a product of the reaction, and therefore during the soot combustion, the formation of these carbonate-like intermediates can be expected. As observed in Fig. 2, the surface equilibrates reaching a pseudo-steady state, in which the average rate of desorption is equal to the average rate of injection of  $\text{CO}_2$ .

In the case of other supports such as  $\text{MgO}$  and  $\text{CeO}_2$ , the interaction with  $\text{CO}_2$  occurs only in the presence of K [5,7]. Fig. 2B displays the high frequency  $\text{CO}_2$  pulses results for  $\text{K}(4.5)/\text{CeO}_2$  support. The interaction between the catalyst and  $\text{CO}_2$  is noticeable at high temperature. This technique also provides an easy way of determining the stability of the surface. The amplitude of the signal before and after a treatment, e.g. temperature or water, indicates whether there is a change in the surface [10].

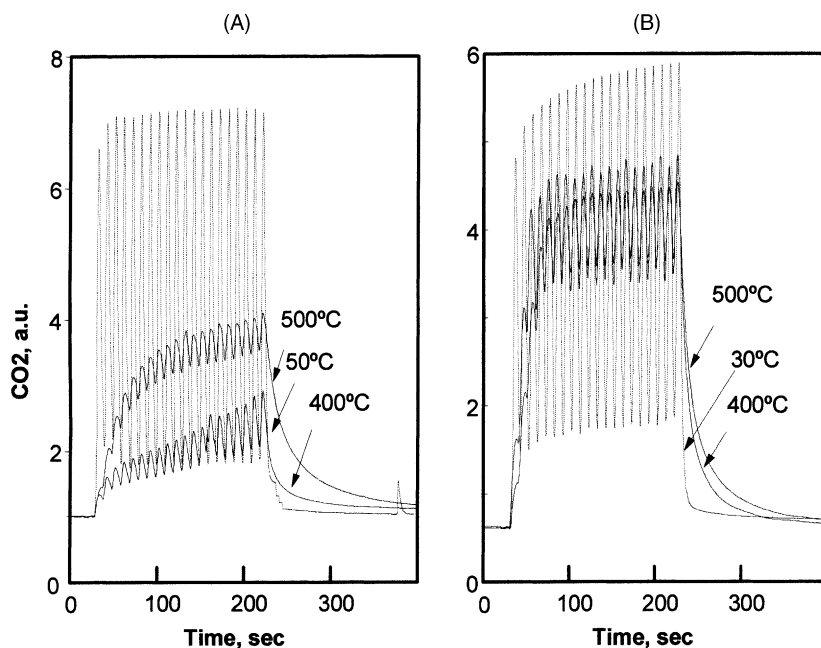


Fig. 2. High frequency  $\text{CO}_2$  pulses: (A)  $\text{K}(4.5)/\text{La}_2\text{O}_3$ ; (B)  $\text{K}(4.5)/\text{CeO}_2$ .

There exists a correlation between the amount of  $\text{Co}_3\text{O}_4$  and the activity for soot combustion when the support is  $\text{MgO}$ , which indicates that in the reaction mechanism, the redox property of the catalysts is of central importance. However, the  $\text{MgO}$  support fulfils no function, so the presence of  $\text{Co}$  and  $\text{K}$  is necessary.  $\text{Co}$  brings the redox property and  $\text{K}$  favours the formation of intermediate reaction carbonates [3,7].

When  $\text{CeO}_2$  is the support, the impregnation of cobalt does not contribute to the overall reaction rate since the redox property is provided by the support itself.  $\text{K/CeO}_2$  catalysts are equally active as the  $\text{La}_2\text{O}_3$ -supported catalysts [5,6].

Taking into account the results discussed above, the reaction mechanism for different supports is shown in the scheme (Fig. 3).  $\text{MgO}$  does not play any role.

$\text{CeO}_2$  provides a redox capacity by which oxygen is supplied in the reaction mechanism.  $\text{La}_2\text{O}_3$  plays a role in the reaction by forming a carbonate-type intermediate, same as  $\text{K}$ .  $\text{Co}$ , through its oxide, provides atomic oxygen for soot oxidation. It plays an important role in relatively inert supports like  $\text{MgO}$ .

The soot–catalyst contacting phenomenon was also analyzed. A synergic  $\text{La-K}$  effect was observed in which mechanical mixtures of soot with  $\text{K-La}_2\text{O}_3$  showed higher combustion rates than those observed when  $\text{K}$  and  $\text{La}$  were directly deposited on the soot surface [9]. This is in agreement with the mechanism proposed in which a cooperative action of the different components of a catalyst is important to obtain high activity.

### 3.2. Simultaneous removal of soot and $\text{NO}_x$

In order to simultaneously abate soot and  $\text{NO}$ , catalysts containing  $\text{Ba}$  were prepared. In the previous studies we have reported that  $\text{Co,K/CeO}_2$  and  $\text{Co,K/La}_2\text{O}_3$  catalysts are able to simultaneously remove  $\text{NO}_x$  and soot particles [5]. Since it has also been reported [8] that catalysts containing  $\text{Pt}$  and  $\text{BaO}$  are good  $\text{NO}$  traps by forming nitrates which then decompose, we explore in this work the possibility of combining this catalytic trap system with the soot combustion reaction. The mechanism of the  $\text{NO}$  trap is similar to the one proposed above for  $\text{CO}_2$  by forming carbonates that decompose at reaction temperature. With the above mentioned purpose,  $\text{Ba}$  catalysts supported in  $\text{CeO}_2$  were prepared. The  $\text{Ba}$  content was varied between 10 and 22 wt.%, and that of potassium among 4, 5 and 7 wt.%. By increasing the  $\text{Ba}$  content in  $\text{Ba/CeO}_2$  catalysts, a slight improvement in the activity of soot combustion is found. The maximum in the TPO profile is close to  $480^\circ\text{C}$  for  $\text{Ba}(10)/\text{CeO}_2$  and  $430^\circ\text{C}$  for  $\text{Ba}(22)/\text{CeO}_2$ . However, these catalysts are less active than those containing  $\text{K}$  (Fig. 1). This means that even though  $\text{Ba}$  presents a positive catalytic effect for soot burning, this effect is too small. By adding potassium to these catalysts, an increase in the activity can be observed. The  $\text{Ba}(22),\text{K}(7)/\text{CeO}_2$  catalyst, calcined at  $400^\circ\text{C}$ , presents an activity similar to  $\text{K/CeO}_2$  and  $\text{K/La}_2\text{O}_3$  (Fig. 1). The  $\text{CO}_2$  pulses carried out on the  $\text{Ba}(22)$  and  $\text{Ba}(22),\text{K}(7)$  catalysts indicated that while

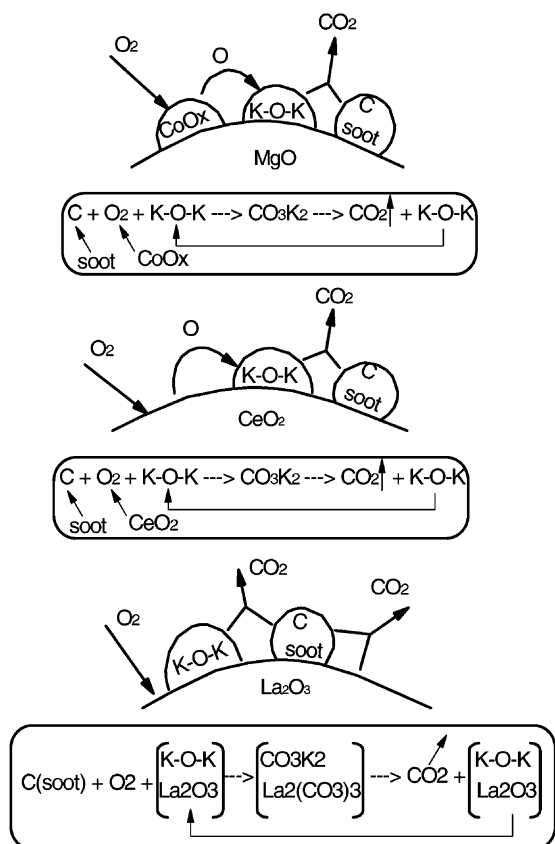


Fig. 3. Scheme of the reaction mechanism on different supports.

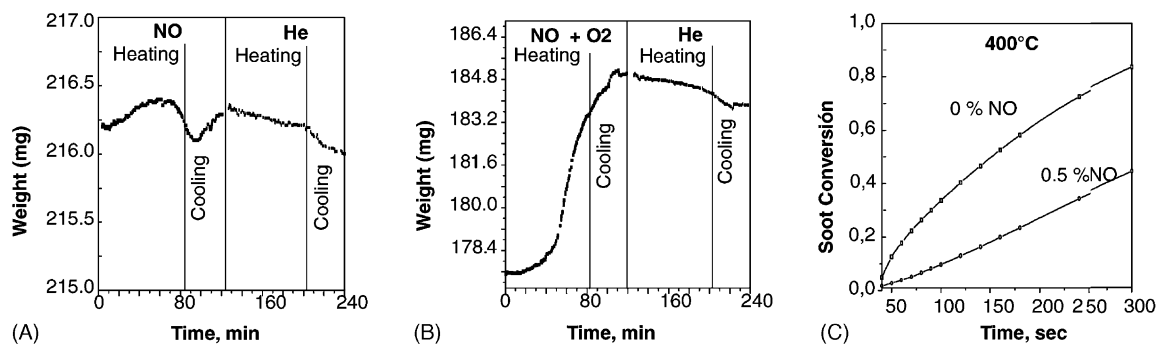


Fig. 4. Experiments with Ba(22)/CeO<sub>2</sub>: (A) using microbalance, heating up to 490 °C in NO and He; (B) using microbalance, heating up to 490 °C in NO and O<sub>2</sub>; (C) conversion of soot at 400 °C.

the Ba(22)/CeO<sub>2</sub> has little interaction with the CO<sub>2</sub>, the opposite occurs with the catalyst containing K which is in line with the mechanism described above [11].

In order to study the interaction between NO<sub>x</sub> and the surface of Ba-promoted catalysts (Ba/CeO<sub>2</sub> and Ba,K/CeO<sub>2</sub>), gravimetric studies were carried out. Fig. 4A displays microbalance experiments in which we measured the weight increase due to NO<sub>x</sub> adsorption on Ba/CeO<sub>2</sub> catalyst. It can be seen that when only 5 vol.% NO (in He) is fed, an increase in weight takes place due to NO adsorption. However, this effect is reversible when increasing the temperature (both with NO in the feed or in the pure He atmosphere). When the mixture of NO (5 vol.%) and O<sub>2</sub> (5 vol.%) was fed (Fig. 4B), the weight increase was higher and non-reversible due to the formation of stable nitrate species, as seen by FTIR [9]. The nitrate formation takes place due to the reaction of the NO<sub>2</sub> formed and the supported BaO. Similar results were obtained with Ba,K/CeO<sub>2</sub> catalyst.

Fig. 4C shows isothermal soot combustion experiments, with and without NO in the feed. It is observed that lower conversions of soot are obtained when NO is present in the gaseous feed. Even though still under study, we believe that barium nitrate inhibits the activity of soot combustion. Thus, the presence of Ba provides an efficient nitric oxide trap (as it was proved by microbalance results) but in the detriment of soot combustion activity. New formulations are under study with the objective of improving the soot combustion activity of Ba-containing catalysts. An interesting

approach would be to obtain a NO<sub>x</sub> catalytic trap in which the Ba(NO<sub>3</sub>)<sub>2</sub> formed is continuously decomposed to N<sub>2</sub> and BaO by the reducing action of the soot particles.

#### 4. Conclusions

K/La<sub>2</sub>O<sub>3</sub> and K/CeO<sub>2</sub> proved to be very active and stable catalysts for the combustion of soot with oxygen. A reaction mechanism involving the redox sites and the surface-carbonate species takes place on these catalysts. The support plays an important role in the combustion reaction. La<sub>2</sub>O<sub>3</sub> contributes to this with a reaction path leading to the formation of carbonate-type intermediates, which decomposes at the reaction temperature, in a similar way to the effect introduced by potassium in all the catalysts. CeO<sub>2</sub>, on the other hand, supplies the oxygen necessary for the redox mechanism to take place.

Ba/CeO<sub>2</sub> and Ba,K/CeO<sub>2</sub> were effective in NO<sub>x</sub> trapping due to the formation of stable nitrate species as shown in the microbalance experiments. However, the above said species inhibit the soot combustion reaction.

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