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Catalytic combustion of diesel soot on Co, K supported catalysts

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Abstract

Catalysts containing 12% Co and 4.5% K, supported on MgO and CeO_2 have been studied for diesel soot catalytic combustion. It has been found that this reaction occurs by a redox mechanism when Co and K are deposited on any of the above-mentioned supports. On MgO-supported catalysts, CoO_x species are responsible for the supply of oxygen by a redox reaction. In this catalyst, K plays different roles, one of them being the stabilization of the CoO_x particles. On CeO_2-supported catalysts, Co does not significantly improve the activity of the K/CeO_2 catalyst, since in this case the support itself displays redox properties. XPS analyses indicate that the oxygen availability on the surface is much higher on CeO_2 than on MgO. On both CeO_2 and MgO-supported catalysts, K might provide a route for CO_2 release through a carbonate intermediate species. The presence of NO in the gas phase improves the catalytic activity for soot elimination. NO is oxidized to NO_2 on the Co, K/CeO_2 catalyst, and NO_2 is a stronger oxidizing agent than O_2, therefore decreasing the temperature needed to burn the soot. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Soot combustion; Cobalt/Magnesium oxide catalysts; Cobalt/Cerium oxide catalysts; Potassium promoter

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1. Introduction

Diesel-engined vehicles are becoming more popular due to the relatively high efficiency of the fuel and to the longer durability of the engines if compared to gasoline engines. Diesel engines use oxidating mixtures with air/fuel ratios higher than 20 which results in a relatively low-temperature combustion which produces lower emissions of NO_x, CO and hydrocarbons. Given the fuel economy, the CO_2 emission is also lower than in gasoline engines. Since the combustion process design yields high levels of particle emission, several efforts have been made in the last few years towards improving the fuel injector design. However, this has not been enough to reduce the particulate emission to values lower than the limits established by the present legislation, which makes post-combustion treatments quite necessary [1].

There are several commercial technologies for the treatment of diesel engines effluents. Among them we should mention the use of noble metals deposited on ceramic monoliths, which are active for the combustion of the liquid fraction (SOF), and for the oxidation of CO and volatile hydrocarbons. However, with this method it is not possible to abate the soot solid fraction (dry soot). The EGR technology [2] is efficient to decrease the nitrogen oxides emission and SOF but it increases the emission of solids. The most feasible way for the abatement of particles is the employment of filters which should be periodically regenerated [3]. The thermal regeneration by oxidation with air requires temperatures higher than 600°C which originates severe tensions in the materials employed. In order to

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decrease this temperature and perform the continuous regeneration in situ, it is possible to use catalysts which can be added to the fuel in the form of organometallic molecules, [4] or can be impregnated in the filter walls.

We have previously [5,6] shown that Co, K/MgO catalysts with 12 wt% of Co and 1.5, 4.5, 7.5 wt% of K, calcined at 400°C are active for the combustion of diesel soot. Among them, the one containing 4.5 wt% of K is that which burns soot at the lowest temperature (378°C). Coincidentally, this is the catalyst presenting the highest K/Mg and K/O surface ratios in XPS measurements. When the calcination temperature is increased at 500°C, both the solid containing 4.5% of K and the one containing 1.5%, as well as the unpromoted catalyst (Co/MgO), noticeably lose activity due to the formation of a solid solution (Co, Mg). However, the solid with the highest K content (7.5 wt%) presents a similar activity at different calcination temperatures (400, 500 and 700°C).

The aim of this work is to gain insight into the role of the support properties in the combustion of soot on Co, K supported catalysts. Cerium oxide, which has well-known oxygen storage properties, is compared with magnesium oxide. The effect of the addition of nitric oxide in the gaseous feed is also studied.

2. Experimental

2.1. Soot and catalysts sample preparation

The soot was obtained by burning commercial diesel fuel (YPF, Argentina) in a glass vessel, as described in Ref. [5]. 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.

The Co, K/MgO and Co, K/CeO_2 catalysts were prepared from a MgO or a CeO_2 (both Merck, p.a.) suspension in water, to which a $Co(NO_3)_2$ solution was added. The potassium was added to the suspension in the form of KOH. The mixture was evaporated while being vigorously stirred until achieving a paste which was dried in a stove for 24 h at 120°C, and calcined at 400°C. In this way, a catalyst with 12 wt% of Co and 4.5 wt% of K was obtained.

2.2. Catalysts characterization

TPR experiments were carried out in an Okhura TS-2002 instrument. Typically, 50 mg of the precalcined solid were pretreated in an argon atmosphere by heating up to 200°C. Afterwards, the TPR was performed using 5% of hydrogen in argon, 40 cc/min, with a heating rate of 10°C/min, from 25° to 600°C.

The XPS spectra were obtained at room temperature with a computer-controlled Shimadzu ESCA 750 instrument, using MgK_α radiation. The surface atomic ratios were calculated using the area under the Mg 2*p*, Co $2p_{3/2}$, K *2p*, O *1s* and Ce *3d* peaks, the Scotfield photoionization cross-sections, the mean free paths of the electrons, and the instrument function which was given by the ESCA manufacturer. The fitting of the O 1s level has been carried out assuming two components. The O 1*s* peak at lower binding energy (530 eV) corresponds to lattice oxide ions, while at higher binding energy (532 eV) it can be attributed to a mixture of different species including $CO_3^{=}$ and OH^-. The contribution of this peak to the total area was $<$40%. The binding energy values are in agreement with the results reported by Praline et al. [7] for cerium oxides.

In order to study the interaction of the catalyst surface with CO_2, pulse experiments were carried out. Typically 50 mg of the solid were loaded in the cell and heated up to the desired temperature (usually the initial temperature was 400° or 500°C). After the temperature was stabilized, three consecutive pulses (0.25 cc) of 1.2% of CO_2 were sent to the cell. The carrier was 6% of oxygen in nitrogen, the same as that used during the activity test. The flow rate was 40 cc/min. After the three pulses, the temperature was changed and stabilized in another value. Pulses were carried out at 500°, 400°, 300°, 200°, 100° and 25°C. Experiments changing the CO_2 pulse frequency were also carried out at 400°C.

2.3. Catalytic activity

The catalytic activity for the combustion of soot was determined from peak-top temperature during temperature-programmed oxidation (TPO), of carefully prepared mixtures of catalyst and soot. The mixing of soot and catalyst was carried out during 10 min in an agata mortar. In this way, repetitive results were obtained in TPO experiments. Several experiments were carried out using 40 mg of catalyst and 2 mg of soot, which is a similar ratio to that used by Ahlstrom and Odenbrand [8]. A gaseous flow 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 [9] was employed which consisted in passing the gases coming from the reactor through a methanation reactor, where CO and CO_2 were converted into CH_4. Afterwards, methane was measured continuously with an FID detector. The methanation reactor contained a nickel catalyst and operated at 400°C.

To study the effect of nitric oxide, some experiments were carried out at constant temperature. These were performed by heating the sample under helium flow until the desired temperature was reached. Then, the feed was switched to the oxygen–helium or oxygen–nitric oxide (0.5%)–helium reacting mixtures. Samples were taken and stored in a 16-loop Valco valve for chromatographic TCD analysis.

3. Results and discussion

It has been previously [5,6] found that the activity of Co, K/MgO catalysts is directly related to the reducibility of cobalt, thus indicating that the reaction is carried out by a redox mechanism. Potassium plays different roles in these catalysts: (i) it increases the catalyst-soot contact by increasing surface mobility; (ii) it preserves the reducibility and dispersion of cobalt by improving stability against thermal treatments; and (iii) it favors the oxidation of soot by consuming the carbon to form carbonate species during soot combustion.

Table 1 shows comparative XPS results for Co and K catalysts supported on MgO and CeO_2. Results on CeO_2 support are also displayed. In the case of the Co, K/MgO catalyst, we observed [5,6] the formation of bulk mixed oxide phases, which results in the low surface ratios of Co/Mg and K/Mg obtained by XPS (bulk Co/Mg ratio = 0.10). For the catalysts in which CeO_2 was used as support, the Co/Ce ratio was higher for Co, K/CeO_2 if compared with Co/CeO_2. The O_L/Ce surface ratios observed are higher than the lattice O/Ce stoichiometric ratio of CeO_2, which is not the case for MgO-supported catalysts (see Table 1). This high availability of oxygen might play a key role in the catalyst activity for soot burning.

Table 1
XPS intensity ratio for the MgO- and CeO_2-supported catalysts

Catalysts[a]	Co/Ce	K/Ce	(O_T/Ce)[b]	(O_L/Ce)[c]	Co/Mg	K/Mg	O/Mg
CeO_2	–	–	6.2	4.1			
Co/CeO_2	0.90	–	11.0	7.0			
K/CeO_2	–	0.70	10.2	6.4			
Co, K/CeO_2	1.38	0.47	10.9	6.6			
Co/MgO					0.05	–	1.1
K /MgO					–	0.07	1.4
Co, K/MgO					0.06	0.03	1.0

[a] The samples were calcined at 400°C.
[b] Total oxygen.
[c] Lattice oxygen.

To study its surface reducibility, CeO_2 was analyzed before and after in situ reduction treatment with hydrogen at 400°C in the reaction chamber attached to the XPS instrument. Shyu et al [10] proposed that the area of the highest binding energy Ce satellite peak (915 eV) in the Ce 3*d* region, relative to the area of the entire Ce 3*d* region, determines the relative amounts of Ce^{+3} and Ce^{+4} in a given sample. In our oxidized CeO_2 sample the relative intensity of the Ce satellite peak was 12%, while after hydrogen treatment it decreased at 7.7%. This decrease indicates that ≈30% of the surface is present as Ce^{+3}. The sample was only partially reduced, probably because some reoxidation might occur during pumping down due to background oxygen. Similar results were reported by Schmieg and Belton [11] . Notwithstanding, the O_L/Ce intensity ratio decreases from 4.1 to 3.3 in the reduced sample, confirming the availability of surface oxygen at 400°C, temperature at which our catalysts based on CeO_2 are very active for soot combustion.

Fig. 1 shows TPR experiments for the catalysts studied in this work. For MgO-supported catalysts, reduction is carried out in an only peak located at 310°C for Co/MgO and 370°C for Co, K/MgO. Instead, for CeO_2 as support, two peaks are obtained for the reduction of Co (one at 310°C and another at 350°C) both for Co/CeO_2 and for Co, K/CeO_2, which is likely due to the presence of different surface CoO_x species [12]. It should be noticed that K/MgO and K/CeO_2 solids present H_2consumption peaks much smaller than those of Co containing catalysts in the above said temperature zones. Similar results were obtained with MgO and CeO_2 (not shown).

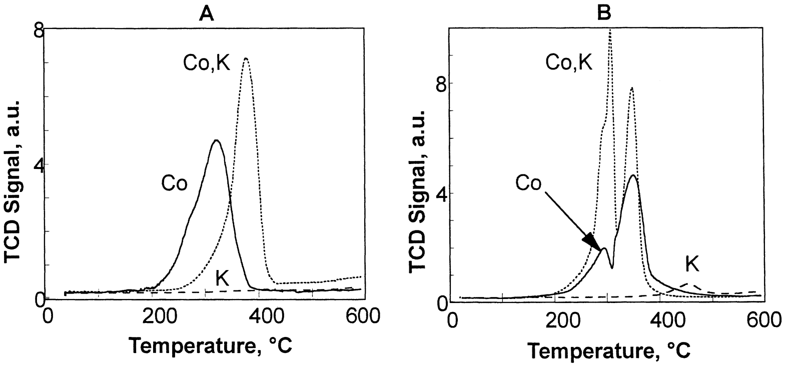

Fig. 1. TPR profiles for: (A) MgO-supported catalysts; (B) CeO_2-supported catalysts.

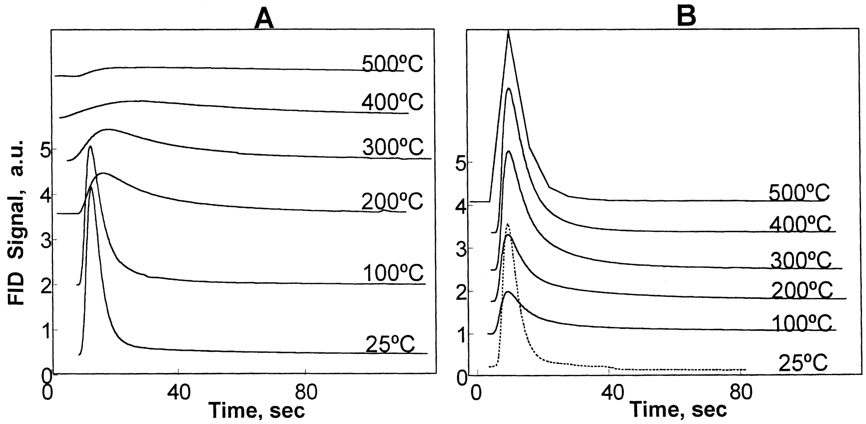

Fig. 2. CO_2 pulses at different temperatures on CeO_2-supported catalysts; (A) Co, K; (B) Co.

In the case of CeO_2, a large amount of information on the redox behavior has been collected by TPR [13], coinciding in that the TPR of CeO_2 shows primarily two peaks, at ≈450° and 830°C. The first, low-temperature peak is due to the reduction of the most easily reducible surface capping oxygen of the solid, while removal of bulk oxygen was suggested as the cause of the high-temperature signal [14,15]. In our TPR experiments, due to the low-surface area of the sample used ($<1\,m^2/g$) the low-temperature peak is very small, in agreement with results reported in Ref. [14]. Thus, taking into account the XPS results shown above, and literature data, it is concluded that surface oxygen of CeO_2 can act as an oxygen reservoir and/or active species during soot combustion, fact that is very well known in the case of three-way catalysts [13].

In order to study the interaction of CO_2 with the catalyst surfaces, CO_2 pulse experiments were performed at different temperatures. Fig. 2 shows these results, observing that in the potassium-containing catalysts the interaction is stronger, mainly in the range of temperatures in which the soot combustion occurs. This result, which is indicating the formation of surface carbonates, suggests that during combustion these could act as reaction intermediates.

The catalytic activity of potassium to gasify coal, when deposited directly on top of it, is well known. In our case, when potassium is impregnated both on MgO or on CeO_2, it notoriously increases the interaction with CO_2, and since this is the product of the coke combustion reaction, it can be expected that the formation and decomposition of potassium carbonate-like species really occur, thus providing a route for coke

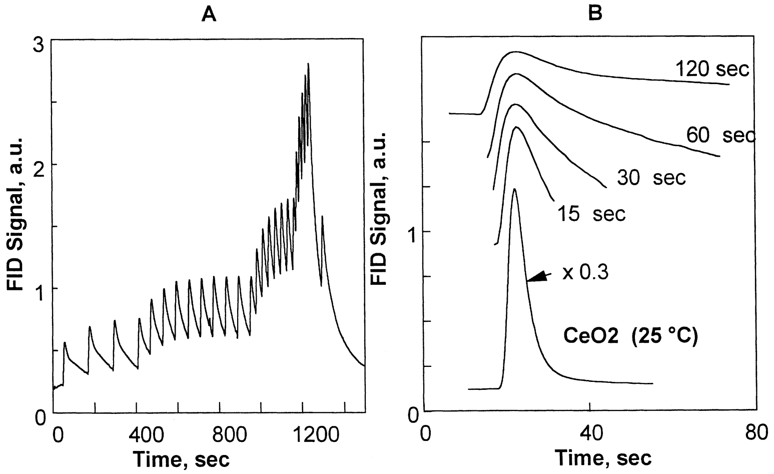

Fig. 3. CO_2 pulses at 500°C on K/CeO_2 catalyst. (A) Pulses at increasing frequency. (B) Detail of an pulse at each frequency. Labels indicate the time delay (s) between pulses.

burning. This has been previously suggested in reacting systems similar to ours. In the steam gasification of carbon, the $BaCO_3$ has a catalytic effect, which was interpreted in terms of a sequential series of reaction steps involving decomposition of the carbonate to oxide, followed by regeneration of the carbonate phase by reaction with the gaseous environment. Moreover, the graphite catalyzed the decomposition of the $BaCO_3$ through the $BaCO_3 + C = BaO + 2CO$ reaction [16]. In the soot oxidation, $CaCO_3$ is formed from the reaction between CaO and soot, which decomposes at higher temperatures to CaO and CO and CO_2 [17], in agreement with a mechanism as the one proposed for the calcium catalyzed CO_2 gasification of carbon [18].

To determine if the catalyst can reach a steady state in the process of carbonate formation and decomposition, an experiment was carried out sending pulses of CO_2 at increasing frequency, at 500°C. These experiments are measuring the CO_2 buffering capacity, in a similar manner to the experiments used to measure the oxygen buffering capacity [19].

Fig. 3 shows the results of these experiments on K/CeO_2, at 500°C. Fig. 3(A) shows all the pulses, and Fig. 3(B) one of the pulses at each frequency. The pulse obtained at 25°C, where no interaction is found, is included as a reference (multiplied by 0.3 to adjust to the same scale). At each frequency, the system reaches a pseudo-steady state, what indicates that the catalyst surface equilibrates with respect to the carbonate formation and decomposition. When increasing the pulse frequency, the interaction decreases (peaks become sharper), but the peaks still come out significantly distorted as compared to the pulse at low temperature. These results indicate that the interaction between the CO_2 and the catalyst is adequate to allow the formation and decomposition of the carbonate, being therefore a possible additional route for soot combustion.

In order to compare the activity of these catalysts for soot combustion, TPO experiments with soot/catalyst mixtures = 1/20 were performed. Fig. 4 shows the results obtained. While MgO is inactive for soot combustion, CeO_2 presents some activity, burning the soot at 500°C (not shown). The impregnation of Co and Co, K results in more active catalysts, obtaining the following order: Co, K/CeO_2 $\geq$ K/CeO_2 > Co, K/MgO $\geq$ Co/CeO_2 > Co/MgO > CeO_2 > K/MgO = MgO. It is interesting to observe that, while the addition of K to MgO does not significantly modify its activity, the addition of K to CeO_2 notably decreases the soot combustion temperature. This result agrees with the conclusions of our previous work in that the soot combustion in these solids is carried out through a redox mechanism [5] and in that K increases the soot-catalyst contact surface [6]. Cerium oxide has oxygen storage capacity and with the addition of K a highly active catalyst is obtained. This is not the case for MgO.

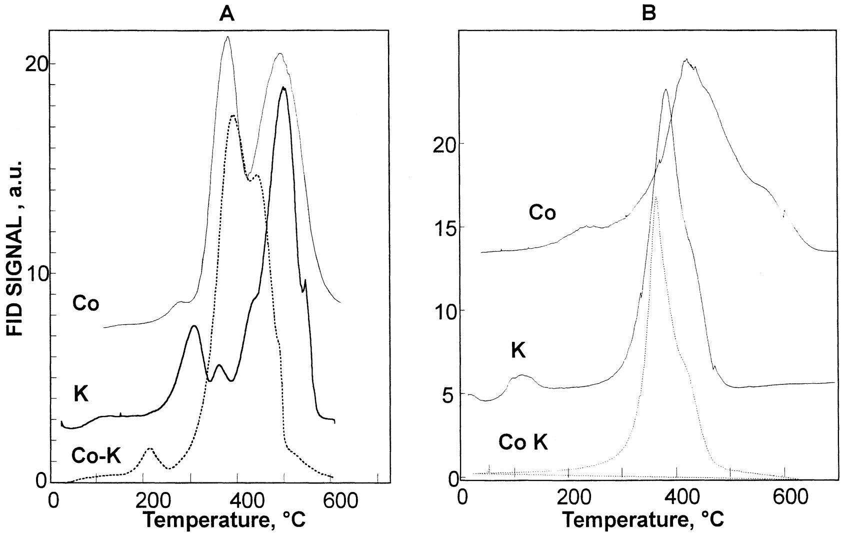

Fig. 4. TPO profiles for mechanical mixtures of catalysts and soot: (A) MgO-supported catalysts; (B) CeO_2-supported catalysts.

The experimental results obtained in this work and those we published before [5,6] show that the Co supported in MgO is active for diesel soot combustion and that its activity notably increases with the addition of potassium. On the other hand, as it has been previously said, we observed that the potassium deposited on the magnesium oxide presents low activity; hence, in the case of MgO-supported catalysts, the role of this alkaline metal is clearly to somehow promote the activity of cobalt, 4.5% being an optimum loading of the said metal. With higher potassium levels, the activity of these solids slightly decreases.

The promoting effect of potassium has already been reported in this reaction on other catalysts [20,21]. Yuan et al. [21] explained the positive influence of potassium on the activity of Cu–K/TiO_2 catalysts by the stabilization of the TiO_2 support texture which increases the specific surface area of the catalysts. They argued that a higher specific surface area can favor the formation of the catalyst/soot interface during combustion. On the other hand, Mul et al. [22,23] explained the high activity of their Cu/K/Mo/Cl catalysts through the mobility and volatility of these compounds. With a similar idea, Serra et al. [24] by means of differential scanning calorimetry (DSC) determined that the presence of eutectic liquid phases dramatically improves the catalyst–carbon contact, thus constituting a key factor in determining the catalytic activity of Cu–K–V based catalysts. They also said that once liquid phases are formed at suitable temperatures (ranging from 330° to 480°C depending on the catalyst nature), most likely the catalytic combustion proceeds according to a redox mechanism.

Our results give additional evidence in order to establish the reaction mechanism. While on MgO-supported catalysts, Co is necessary in order to have a good activity, it is not so necessary in those supported with CeO_2. This is due to the fact that in the former Co introduces the redox property to the catalyst thus playing a distinctive role, whereas in the latter the support itself already has this property. Oxygen supply by a surface oxide with redox properties seems to be necessary in order to obtain a catalyst with high activity for soot combustion. It should be mentioned that the TPR profile indicates that the reducibility of K/CeO_2 below 500°C is much smaller than that for either Co/MgO or Co/CeO_2. Nevertheless, activity is higher. This indicates that even though the redox capacity is essential for the soot combustion activity, there is no direct correlation between the bulk reducibility as measured by TPR and the activity, when comparing different supports. This is because, in addition to the total reducibility of the active phase, its contact with the soot particle is needed for the reaction. It can be expected that this factor be much more favorable on CeO_2-supported

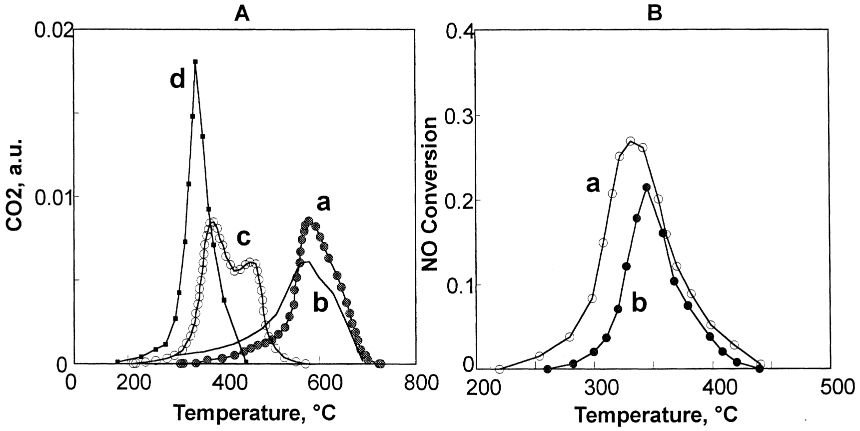

Fig. 5. TPO analyses of mechanical mixtures of Co–K/CeO_2 catalyst and soot: (A) CO_2 production plots: a: non-catalyzed soot + O_2 reaction; b: non-catalyzed soot + O_2 + NO reaction; c: catalyzed soot + O_2 reaction; d: catalyzed soot + O_2 + NO reaction; (B) NO conversion; a: to N_2; b: to N_2O. See Section 2 for reaction conditions.

catalysts, since in this case the whole surface of the support acts as an oxygen supplier, while on Co/MgO catalysts, only the CoO_x particles play this role.

Since nitrogen oxides and particulate matter emissions are the main pollutants present in Diesel engine emissions, it is interesting to explore the possibility of the simultaneous NO_x-soot removal reaction. Shangguan et al. [25,26] have reported that perovskite-related oxides and spinel-type oxides are active for the above-mentioned reaction. The superiority of mixed metal oxides has been demonstrated from the fact that they are more selective to the reduction of NO_x into N_2 than simple oxides of constituent transition metals and their mechanical mixtures. The same authors [27] found that the doping of potassium to $CuFe_2O_4$ was effective in promoting the catalytic performance for the above-mentioned reaction. The catalytic performance of $Cu_{1-x}K_xFe_2O_4$ significantly depends on the doping amount of potassium, and the highest activity and selectivity were simultaneously attained at $x = 0.05$. In order to investigate the activity of our catalysts for the simultaneous NO_x-soot removal reaction, the effect of the addition of NO (0.5%) in the gaseous flow was studied using the Co, K/CeO_2 catalyst (which is, the most active catalyst for soot combustion with oxygen of all the catalysts studied in this work).

Fig. 5(a) shows that there is a decrease of c.a. 40°C in the combustion temperature when NO is introduced in the feed, if compared with the soot combustion with oxygen. This is probably due to the fact that NO_2 is a better oxidant than O_2, and in this case the fundamental role of the catalyst surface would be to increase the oxidation rate of NO to NO_2, as suggested by Teraoka et al. [25,26]. From this figure, it can also be seen that our catalyst shows similar soot ignition temperature (c.a. 250°C) if compared with the best potassium promoted $CuFe_2O_4$ studied by Shangguan et al. [27].

Fig. 5(b) shows the products of the NO reduction, these being N_2O and N_2, in agreement with the latter authors. Fig. 6 shows the isothermal combustion of the soot mixed with Co, K/CeO_2 where NO is introduced after some minutes on stream an increase in the rate of reaction being clearly observed.

According to this study, Co, K/CeO_2 catalyst has good activity for both soot and soot + NO elimination. Therefore, additional studies are now being carried out in our laboratory, in order to determine the thermal stability of the catalyst and the influence of potassium content on the catalytic properties.

4. Conclusions

- The results of this work confirm that for these catalysts, the activity for soot combustion is directly related to surface reducibility. The role of potassium

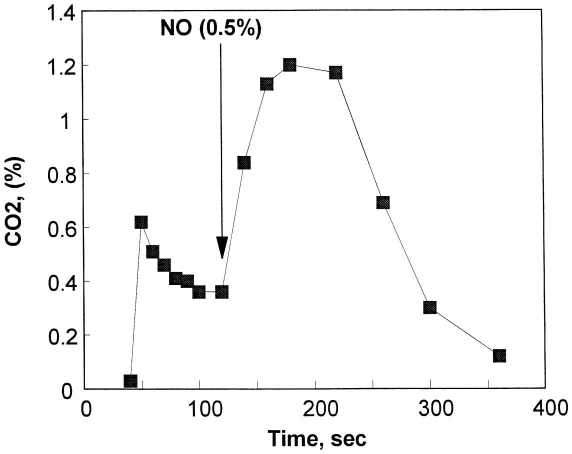

Fig. 6. Isothermal combustion of soot. Mechanical mixtures of Co–K/CeO$_2$ and soot. During the first 100 s on stream O_2 + He were fed. After that period of time, NO (0.5%) was introduced in the feed.

is a function of the support. While K/CeO$_2$ burns the soot at temperatures lower than 400°C, K/MgO is inactive for soot combustion.

- Among the solids studied, Co, K/CeO$_2$and K/CeO$_2$ are those which present higher activity for the combustion of diesel soot, probably due to the surface oxygen availability of CeO$_2$, and the increase of the catalyst–soot contact provided by potassium loading. Results also suggest that K introduces an alternative route for soot combustion by forming carbonate intermediates.
- When MgO is used as a support of Co and K, bulk mixed oxides are formed, resulting in low Co/Mg and K/Mg surface ratios. This phenomenon is not observed when CeO$_2$ is used as support.
- The simultaneous elimination of soot and NO can be effectively carried out in Co, K/CeO$_2$ at relatively low temperatures (reaction starts at c.a. 250°C and a maximum in TPO is obtained at c.a. 350°C). In this case, the soot combustion probably occurs with NO$_2$ as oxidizing agent. A fundamental role of the catalyst surface should be the oxidation of NO to NO$_2$.

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