## MECHANISMS
## OF CATALYTIC REACTIONS

# Carbon Black Oxidation Mechanism in Loose and Tight Contacts with Al₂O₃ and CeO₂ Catalysts[1]

**E. Saab, S. Aouad, E. Abi-Aad\*, M. N. Bokova, E. A. Zhilinskaya, and A. Aboukaïs**

*Laboratoire de Catalyse et Environnement E.A. 2598, Université du Littoral—Côte d'Opale,*
*MREI-1, 145 av. Maurice Schumann, Dunkerque, 59140 France*
*\*e-mail: abiaad@univ-littoral.fr*

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**Abstract**—The catalytic combustion of carbon black was investigated in the presence of $CeO_2$ and $Al_2O_3$. The influence of contact type between carbon particles and these oxides was examined by thermal analysis, the BET specific area, and EPR spectroscopy. For tight contact carbon black–catalyst mixtures, a new paramagnetic species is observed and can be considered as a fingerprint of the contact between the two solids. These new paramagnetic species increase the reactivity of the catalytic reaction of carbon black (CB) combustion and take part in the oxidation mechanism of CB.

## 1. INTRODUCTION

The particulate matter (soot) amount emitted by diesel engines is much larger than that emitted by these engines equipped with catalytic converters. This pollutant is hazardous to human health due to its potential mutagenic and carcinogenic activity and to their small size, which can penetrate into the lungs [1]. In order to reduce soot emissions, it is possible to use alternative combustibles or special devices to reduce particulates of exhaust gases [2]. As the particulate matter combustion temperature is much higher than the operational temperature found in the exhaust pipe, the combustion temperature must be decreased, and, consequently, active catalysts must be developed in such temperature levels [1, 2]. Catalysts can be used in a number of ways to accelerate the combustion of soot. It can be added either through the fuel, in which case it is incorporated into the soot spherules as they form, or physically mixed in after collection of soot. The latter way can be reached by impregnation of porous ceramic filters, such as ceramic honeycomb monoliths, placed through the exhaust stream with an oxidation catalyst. The contact between soot and catalyst is a very important parameter in the catalytic oxidation of soot. Only limited information is available on the intimacy of the solid–solid contact between the catalyst (solid) and the soot (solid) under real conditions [3–5]. However, it was shown that under practical conditions the contact between the soot and the catalyst is rather poor [4]. Nevertheless, the use of a mechanical mill is often chosen to establish close contact between the soot and the catalyst in order to define an intrinsic catalytic activity under optimal conditions and to obtain reproducible and comparable

results [3, 5]. In the same order, synthetic soot (carbon black, Printex U, fullerenes, etc.) is used as a model compound for diesel soot during simulated laboratory oxidation experiments [6, 7] since the chemical composition of real soot is variable and depends on several parameters (fuel composition, kind and state of engine, etc.).

Ceria ($CeO_2$) is widely used as a promoter in current-based automobile catalysts. In fact, one current application is the presence of cerium additives in diesel fuel which favors the reactivity of the doped soot and shifts the combustion reaction towards low temperatures [1]. Three main properties make ceria an essential component in such redox catalysts: its oxygen storage capacity (OSC) [1], its redox properties ($Ce^{4+}/Ce^{3+}$), and its thermal stability influence on alumina [3, 8]. Moreover, the literature data show that ceria is very active for catalytic soot combustion [4, 5]. According to the literature [6], ceria shows high activity due to the total oxidation of CB into $CeO_2$. It is related to the capacity of ceria to be easily reduced during the combustion reaction into nonstoichiometric oxides ($CeO_{2-x}$), which contribute to the formation of anionic vacancies on the surface. These vacancies are the active sites in the oxidation catalysis [7, 9, 10].

$Al_2O_3$ is often used as a support in the oxidation catalysts due to its thermal stability and significant specific area surface [10]. In addition, alumina and silica are the major components of the ceramic honeycomb monolith filters. Moreover, in a previous work [11] we studied the impact of $Al_2O_3$ and $CeO_2$ supports on manganese-based catalysts. It was clearly shown that for $Mn/CeO_2$ with CB mixtures, the $Mn^{2+}$ content considerably increases consequently to the contact between the two solids, indicating the reduction of some manganese

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[1] This article was submitted by the authors in English.

species with higher oxidation states into $Mn^{2+}$ ions. The reduction of the manganese species, in these conditions, is considered as an important factor in the carbon black oxidation mechanism. In parallel, the oxidation states of manganese, in $Mn/Al_2O_3$ catalysts, are not affected by such a treatment. These results have permitted us to explain the better reactivity of $Mn/CeO_2$ samples compared to $Mn/Al_2O_3$ catalysts.

Owing to the important role played by the catalytic support on the carbon black oxidation process, we believed that it was necessary to study the reactivity of CB combustion in the presence of $CeO_2$ and $Al_2O_3$ in both loose and tight contact conditions. To elucidate the contribution of cerium and aluminium oxides in the carbon black oxidation process, thermal analysis, BET, and EPR techniques are used in this work.

## 2. EXPERIMENTAL

### 2.1. Preparation of Solids

Alumina is synthesized by the sol-gel method. Secondary aluminum butylate $(Al(OC_4H_9)_3$, Fluka, ~11.0 wt % Al) is dissolved in butan–2-ol (Fluka, purity ≥99.5%). Then, a complexing agent (Butan–1,3-diol, Fluka, purity ≥98%) is added before hydrolysis. Alumina is calcined at 500°C before use as a support for preparing supported catalysts.

Ceria is prepared by precipitation of $Ce(NO_3)_3 \cdot 6H_2O$ (Prolabo, total amount of rare earth oxides is 99.5%) in an ammonia aqueous solution (0.7 mol/l). The solid is filtered, washed, dried at 100°C, and calcined at 600°C for 4 h with a temperature rate of 0.5 K/min.

### 2.2. Preparation of Mixtures

Commercially available carbon black (CB) (N330 Degussa: 97.23 wt % C; 0.73 wt % H; 1.16 wt % O; 0.19 wt % N; 0.45 wt % S) is used as a model soot. Two types of mixtures of CB with the catalyst are prepared: (i) with a spatula—loose contact mixture and (ii) mixed in an $Al_2O_3$ ball miller for 40 min—tight contact mixture. Different weight percentages of CB and the catalyst are used: 1% CB + 99% Cat, 3% CB + 97% Cat, 5% CB + 95% Cat and 6% CB + 94% Cat.

### 2.3. Combustion Tests

The tests of the combustion of CB are studied by simultaneous gravimetric and differential thermal analysis (TG–DTA) with a NETZSCH STA 409 apparatus. Twenty milligrams of the sample is loaded in an alumina crucible and heated from room temperature to 750°C (5 K/min) in air flow (75 ml/min).

### 2.4. Specific Area

The BET surface areas of CB and mixtures were measured by a Quantasorb Junior (Ankerscmidt), through physisorption at liquid nitrogen temperature (77 K). This method consists of the measurement of the quantity of inert gas ($N_2$) physisorbed on the solid surface. The sample deposed in a U form cell was degased first at 130°C for thirty minutes under pure nitrogen N60. After cooling down to room temperature, a mixture of 30% of adsorbant gas (pure $N_2$) and 70% of porter inert gas (pure He) are physisorbed. The adsorption and desorption are produced respectively where the U cell containing the sample was immerged and then retired from a dewar of liquid nitrogen. With this method, alumina is characterized with a specific area of 360 $m^2\ g^{-1}$. The specific area of ceria is 91 $m^2\ g^{-1}$, and that of CB is 76 $m^2\ g^{-1}$.

### 2.5. Electron Paramagnetic Resonance

The electron paramagnetic resonance measurements are performed at room temperature on an EMX BRUKER spectrometer with a cavity operating at a frequency of ~9.5 GHz (X band). The magnetic field was modulated at 100 kHz, and the power supply was sufficiently small to avoid the saturation effect. Modulation amplitudes (Mod Am) from 0.5 to 10 G were used. The $g$-values were determined using the following relation: $h\nu = g\beta H$ where $h$ is the Planck constant, $\beta$ is the Bohr magneton, $H$ the magnetic field, and $\nu$ is the microwave frequency measured with high precision using a frequency-meter. All the thermal treatments (between 100 and 600°C) of the samples are carried out in a microflow reactor, which is assembled with a quartz EPR tube to allow the introduction of the sample into the resonance cavity.

## 3. RESULTS AND DISCUSSION

### 3.1. Carbon Black Oxidation

The TG curves of carbon black combustion in the presence of $Al_2O_3$ and $CeO_2$ are presented in Fig. 1. The observed weight loss corresponds to the combustion of the total mass of carbon black. The TG curve gives the temperature values $T_i$ (beginning of the carbon black combustion) and $T_f$ (complete conversion of carbon black). The $T_m$ shows the maximum temperature on the DTA curve and corresponds to the temperature of the highest combustion velocity. These specific temperatures ($T_i$, $T_m$, and $T_f$) are reported in Table 1 for CB without catalysts and in the presence of $Al_2O_3$ and $CeO_2$ in loose and tight contacts.
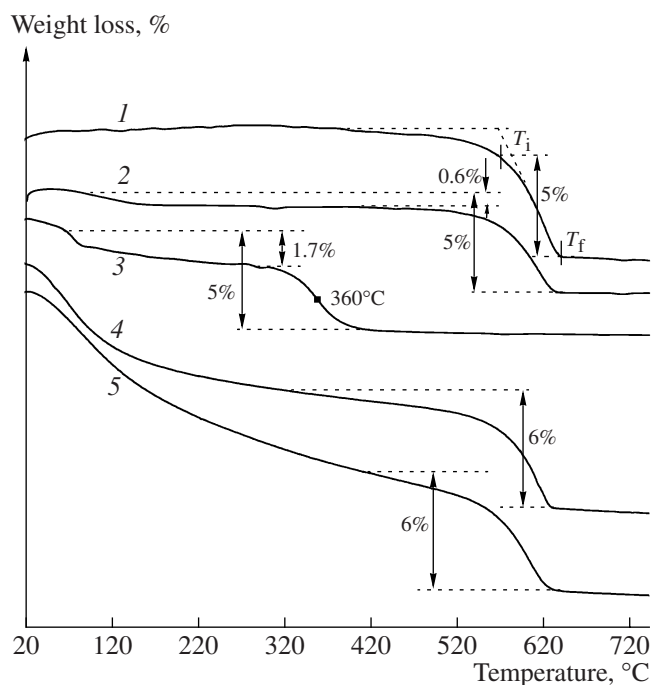
The carbon black combustion, in the absence of a catalyst, occurs at $T_m = 632°C$. An insignificant difference is observed when the reaction is performed in the presence of $Al_2O_3$. The drastic weight loss at low temperatures for $Al_2O_3$ + CB mixtures is usually attributed to water desorption. The entire quantity of CB (6%) is

oxidized from $T_i = 577°C$ up to $T_f = 628°C$ with $T_m = 625°C$ (loose contact) and from $T_i = 567°C$ up to $T_f = 629°C$ with $T_m = 607°C$ (tight contact) (see Fig. 1 and Table 1). From these data, one can conclude that the reactivity is higher in tight contact conditions than in loose conditions. In fact, the $T_m$ values are shifted to lower temperatures from 7 to 25°C when the reaction is performed in the presence of alumina in loose and tight contact, respectively (Table 1). However, in both cases, the reactivity ($T_i$, $T_m$, and $T_f$) seems not to be notably affected by the presence of alumina. These data are in accordance with literature showing that alumina is a nonactive catalyst in such a reaction [4, 10, 12–14]. The characteristic temperatures of CB combustion in the presence of cerium oxide depend on the nature of contact between the solids. For the loose contact mixture, $T_m$ is practically the same as for noncatalytic CB combustion. On the contrary, for the tight contact mixture, the characteristic temperatures are shifted to the low-temperature region. The temperature $T_m$ for the $CeO_2$ + CB mixture in tight contact (CeT) is 272°C lower than that for the initial CB. Thus, $CeO_2$ is an active catalyst only in tight contact with carbon black. This result is in accordance with previous studies and data presented in the literature [4, 11, 15, 16].

### 3.2. Specific Surface Area ($S_{sp}$)

Table 2 summarizes the BET specific area of the CB and CeT after different thermal treatments. At 25°C, CB $S_{sp}$ was about 76 m$^2$ g$^{-1}$. This $S_{sp}$ is approximately the same between 25 and 300°C (~80 m$^2$ g$^{-1}$). At 400°C, the $S_{sp}$ of CB (133 m$^2$ g$^{-1}$) increases, which can be related to the formation of pores with the increase of temperature. In fact, adsorbed hydrocarbons on the CB surface can be oxidized at this temperature in the presence of oxygen. At 450°C, this phenomenon is more pronounced ($S_{sp}$ = 311 m$^2$ g$^{-1}$) and reached the highest values of $S_{sp}$ = 595 m$^2$ g$^{-1}$ for a calcination temperature of 500°C. From the chemical composition of the CB used for these experiments (97.23 wt % C) and the TG curve for the mixture 5% CB + 95% SiC (Fig. 1) showing a negligible variation of the weight loss at 500°C, one can conclude that the first step of the CB oxidation process is the oxidation of the adsorbed hydrocarbons leading to the increase of the specific area, which facilitates the adsorption of $O_2$ in order to oxidize the pure CB particulate.

The same study was carried out on the $CeO_2$ + CB mixture in tight contact (CeT). The specific area of the mixture CeT is constant between room temperature and 200°C (83 m$^2$ g$^{-1}$). For calcination temperatures of 300 and 400°C, a slight increase of the $S_{sp}$ is observed (Table 2). However, this increase should be compared to the 5% weight of CB in the mixture since the $S_{sp}$ of calcined ceria could be considered as a constant until 500°C. This increase reported to CB would represent a variation of 80 m$^2$ g$^{-1}$. This behavior could be attributed

Weight loss, %



**Fig. 1.** TG curves of carbon black combustion in the presence of $Al_2O_3$ and $CeO_2$. (*2*, *4*) Loose contact, (*3*, *5*) tight contact.

to the catalytic oxidation of the adsorbed hydrocarbons and then to CB combustion leading to the increase in the number of pores on the CB surface. In parallel, the TG curve on Fig. 1 clearly shows that the CB combustion takes place in this range of temperature (329–392°C; Table 1). At 500°C, the catalytic oxidation of CB is finished and the measured $S_{sp}$ (54 m$^2$ g$^{-1}$) is that of the $CeO_2$ catalyst. The decrease in $S_{sp}$ revealed after the catalytic test may be related to

(i) the effect on $CeO_2$ of the mechanical mill used to establish the tight contact,

(ii) the increase of the local temperature after the combustion of the CB particulate,

**Table 1.** Characteristic temperatures of carbon black combustion

| Sample | $T_i$, °C | $T_m$, °C | $T_f$, °C |
|---|---|---|---|
| 5% CB + 95% SiC | 580 | 632 | 640 |
| 5% CB + 95% $CeO_2$ (loose contact) | 571 | 618 | 629 |
| 5% CB + 95% $CeO_2$ (tight contact) | 329 | 360 | 392 |
| 6% CB + 94% $Al_2O_3$ (loose contact) | 577 | 625 | 628 |
| 6% CB + 94% $Al_2O_3$ (tight contact) | 567 | 607 | 629 |

**Table 2.** $S_{sp}$ of CB and CeT treated at different temperatures

| Temperature, °C | 25 | 100 | 200 | 300 | 400 | 450 | 500 |
|---|---|---|---|---|---|---|---|
| CB $S_{sp}$, m$^2$ g$^{-1}$ | 76 | 76 | 84 | 81 | 133 | 311 | 595 |
| CeT $S_{sp}$, m$^2$ g$^{-1}$ | 83 | 83 | 83 | 87 | 86 | – | 54 |

(iii) the catalytic effect of $CeO_2$ on this mixture after thermal treatment.

Since the $S_{sp}$ of the milled $CeO_2$ treated at 600°C is about 62 m$^2$ g$^{-1}$, the difference between the two values is probably related to the two last effects. In fact, due to its oxygen storage capacity, and under tight contact conditions, $CeO_2$ can accelerate CB combustion by using its own oxygen species. By comparison with the literature results, $O^{2-}$ species bound to $Ce^{4+}$ ions can react with CB to form $CO_2$ and consequently $Ce^{4+}$ ions are reduced to $Ce^{3+}$ species [17, 18].

### 3.3. EPR Study

Figures 2a and 2b show the evolution of the X-band EPR spectra of respectively mixtures 95% $CeO_2$ + 5% CB in loose contact (CeL) and 95% $CeO_2$ + 5% CB in tight contact (CeT) recorded at 25°C.

In previous works, EPR analysis of the initial carbon black showed an $S1$ signal attributed to intrinsic paramagnetic centers on CB. The $S1$ signal presents a slight axial distortion with a $g_{iso}$ value of ≈2.000 and a line-width of $\Delta H_{pp} = 63 \pm 4$ G. This signal has been attributed to unpaired electrons in the CB structure or to free CB radicals consistent with intrinsic paramagnetic species of CB [11, 17]. It was shown that these paramagnetic species ($S1$ signal) correspond to weakly interacting Curie spins but they are movable and obviously interact with the paramagnetic oxygen molecules inducing EPR line-width broadening [11].

Figure 2a shows the evolution of EPR spectra of the mixture CeL in the presence of air versus the heating temperature. The CB signal ($S1$) is present until 500°C, and its intensity decreases as calcination temperatures increase. $S1$ is not detected at 600°C, showing the total combustion of the CB. Another signal was detected from 200 until 600°C. This signal is characterized by $g_\perp = 1.965$, $g_\parallel = 1.942$, and $g_{iso} = 1.957$ and was widely investigated and attributed to $Ce^{3+}$ ions or to the interaction between conduction electrons and the $4f$ orbital of $Ce^{4+}$ ions in the $CeO_2$ matrix [19].

Figure 2b shows the EPR spectra of the mixture CeT treated at different temperatures and recorded at room temperature. For this mixture, the $S1$ signal attributed to intrinsic paramagnetic centers on CB is detectable from room temperature until 300°C. At 400°C this signal is not observable. The disappearance of this signal is in accordance with the weight loss on the TG curve
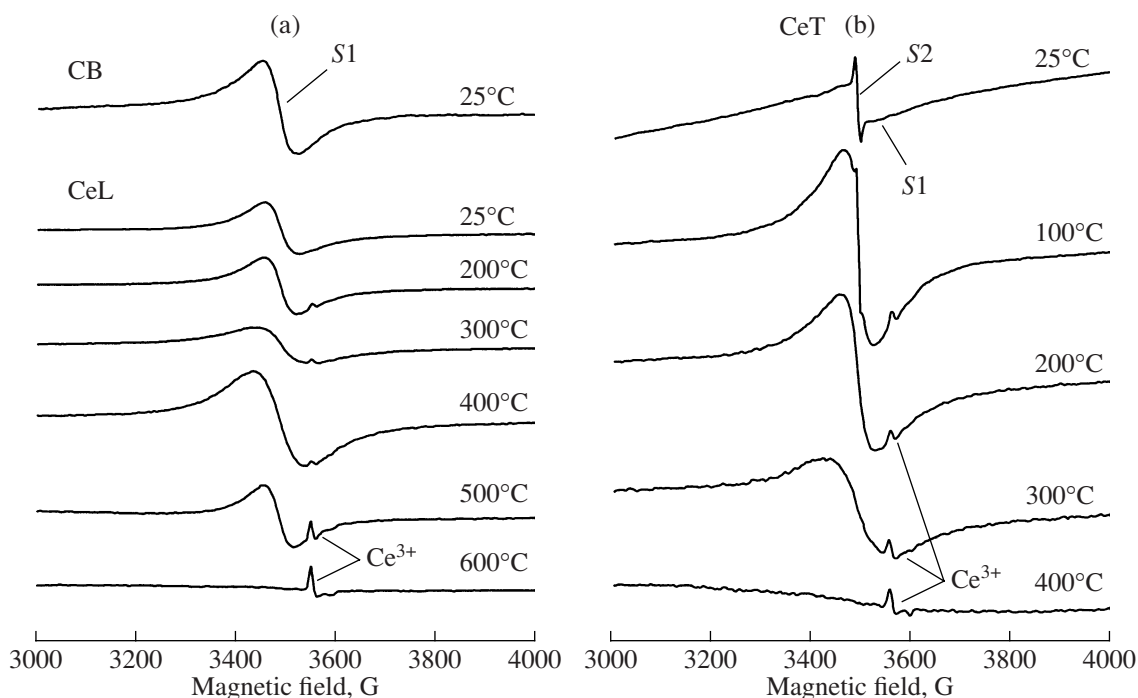


**Fig. 2.** EPR spectra recorded at 25°C, in the presence of air, for 5% CB + 95% $CeO_2$ samples: (a) in loose contact; (b) in tight contact.

(Fig. 1). At 392°C total CB combustion is observed during the catalytic test.

Another signal denoted $S2$ is observed. The $S2$ signal is isotropic with $g_{iso}$ = 2.003 and a line width of $\Delta H_{pp}$ = 3.5 G. The appearance of the S2 signal indicates the formation of new paramagnetic species consistent with localized paramagnetic spins on the carbon particles and catalyst interface and can be considered as a fingerprint of the contact between the two solids [11]. It is important to note that neither compressed carbon black nor the catalyst, treated alone in the mixing conditions, provides the $S2$ signal. This result supports the above attribution of the $S2$ signal. The $S2$ signal is observed only for the samples heated up to 100°C. For the mixture calcined at 200°C, the $S2$ signal, attributed to CB–catalyst contact, is not detectable. In parallel, on the TG curve and in the range of 100–200°C, we observe a weight loss equal to 1.7%, whereas, in the loose contact condition (absence of the $S2$ signal), this weight loss is equal to 0.6%. Thus, the difference in the weight losses at low temperature, due to contact conditions, is 1.1% (corresponding to 22% of the total CB weight in the sample). This latter can be related first to the effect of $CeO_2$ as an oxygen storage catalyst and second to the tight contact between $CeO_2$ and CB suggesting the first step in the mechanism of CB oxidation in the presence of cerium oxide. Similar data have been observed in such conditions and attributed to the high reactivity of ceria–CB interface species [17]. In addition, the catalytic reaction continues at higher temperatures taking advantage of heat diffusion related to the partial oxidation of CB in the range of 100 and 200°C. Therefore, the catalytic proprieties of cerium oxide play an important role leading to an important shift in the CB combustion temperature particularly in tight contact conditions [17, 18]. Two general mechanisms have been proposed to account for the diversified catalytic effects of metals and oxides in carbon oxidation: electron-transfer and oxygen-transfer mechanisms [19, 20]. Several experimental facts have already permitted us to conclude in favor of oxygen-transfer mechanisms. These facts are the following:

(i) $CeO_2$ is an active catalyst only in tight contact conditions with carbon black [16, 18],

(ii) the formation of an interface reactive species between ceria and CB [17],

(iii) the presence of $O_2^-$ species on the ceria surface [13]. Thus, it is evident to conclude that paramagnetic species responsible for the $S2$ signal can participate, at very low temperature, in the mechanism of CB combustion in the presence of cerium oxide. However, the possibility that cerium oxide participates in the combustion reaction by means of its well-known catalytic properties towards oxidation reactions should not be omitted. In fact, in both cases, loose and tight contacts, one can observe the increase of the intensity of the EPR signal relative to $Ce^{3+}$ ions with the increase of the reaction temperature (Figs. 2a, 2b). These data clearly show the reduction of $Ce^{4+}$ ions into $Ce^{3+}$ ions with the reaction advance. Thus, the increase of the EPR intensity relative to the $Ce^{3+}$ signal is more pronounced between 500–600°C for loose contact and 300–400°C for tight contact mixtures, respectively (Fig. 1 and Table 1), in accordance with the temperature ranges for catalytic oxidation of CB in the presence of $CeO_2$ in loose and tight contacts.

## CONCLUSIONS

The catalytic oxidation of carbon black was investigated in the presence of $CeO_2$ and $Al_2O_3$. The rate of carbon black combustion increases considerably in tight contact conditions. The CB oxidation process starts by the elimination of the adsorbed hydrocarbons leading to the formation of pores and to the increase of the specific area with the calcination temperature. This phenomenon would facilitate the adsorption of $O_2$ molecules in order to oxidize the CB particulate. For tight contact CB–catalyst mixtures, a new EPR signal, designated by $S2$, is observed. The appearance of the $S2$ signal indicates the formation of new paramagnetic species consistent with localized paramagnetic spins on the carbon particles and catalyst interface and can be considered as a fingerprint of the contact between the two solids. These new species increase the reactivity of the tight contact CB + $CeO_2$ mixtures in the catalytic reaction of CB combustion. In addition, reduction of $Ce^{4+}$ ions into $Ce^{3+}$ is evidenced simultaneously in the catalytic oxidation process showing the participation of ceria by means of its catalytic properties in the combustion reaction of CB. These results may be considered an important step in the elaboration of a general mechanism explaining the catalytic oxidation process of diesel soot.

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