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## CATALYTIC REACTION MECHANISMS

# Effects of Ozone on Catalytic and Physicochemical Properties of Cu–Ce–Al–O Catalysts for Soot Combustion[1]

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**Abstract**—The elimination of carbon particles at the level of the exhaust line is one of the present challenges of the car manufacturer. In this study, the catalytic combustion of carbon particles has been investigated in the presence of Cu–Ce–Al oxides. The influence of ozonation on the catalytic and physicochemical properties of Cu–Ce–Al oxides at the reaction of diesel soot combustion was examined by thermal analysis and EPR methods.

## INTRODUCTION

The elimination of carbon particles emitted into air from diesel engines is one of the main environmental problems. The elimination or, at least, the reduction of carbon particle emissions may be obtained by two distinct and complementary ways: the reduction of its formation during the combustion process and its removal downstream of the combustor. 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. Ceria ($CeO_2$) is widely used as a promoter in current based automobile catalysts. 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 stabilizing influence on alumina [2–4]. Moreover, literature data show that ceria is very active for catalytic soot combustion [5–7]. Copper oxide is considered as a possible substitute for noble metal in automobile exhaust converters. Copper oxide has already studied for catalytic combustion of soot [5, 6, 8–10]. The catalytic system may be active even in low oxygen concentration conditions. Indeed, an exhaust gases medium is sometimes poor in oxygen. But ozone, a high oxidation reagent, is also present in an exhaust gases medium and thus can enhance catalytic properties of solids. The purpose of this work is to investigate the influence of ozonation at the catalytic and physicochemical properties of Cu–Ce–Al oxides on the reaction of diesel soot combustion.

## EXPERIMENTAL

**Preparation of catalysts.** 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 [11]. Alumina is calcined at 500°C before being used as a support for preparing supported catalysts. With this method, the alumina is characterized by a specific area of 420 $m^2/g$ and a pore volume of 2.3 ml/g.

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°C/min.

Different Ce–Al oxides are prepared by incipient wetness of cerium nitrate solution onto alumina precalcined at 500°C. Then, the sample is dried at 100°C and calcined for 4 h in a flow of dry air at 500°C. Cerium containing solids are denoted 1Ce10Al, 3Ce10Al, and 10Ce10Al, where the number before the chemical symbol represents the atomic content in the solid.

Copper containing solids are prepared by incipient wetness of a support calcined at 500°C (alumina, ceria, or Ce–Al oxides) with aqueous solution of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, Prolabo, purity ≥99.0%). The mixture is dried at 100°C and calcined at 600°C for 4 h in a flow of dry air. Copper containing solids are denoted as supports: 1Cu10Al, 1Cu1Ce10Al, 1Cu3Ce10Al, 1Cu10Ce10Al, 5Cu3Ce10Al, and 1Cu10Ce.

The table summarizes the composition of supports and copper containing catalysts performed in the central elementary analysis office of the CNRS (Vernaison).

**Electronic paramagnetic resonance.** The electron paramagnetic resonance measurements are performed at –196°C on a EMX Bruker spectrometer with a cavity

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

Composition of solids

| Catalyst | wt % of CuO | wt % of $CeO_2$ | Atomic composition |
|---|---|---|---|
| $Al_2O_3$ | – | – | $Al_2O_3$ |
| $CeO_2$ | – | 100 | $CeO_2$ |
| 1Cu10Al | 16.4 | – | $Cu_{1.26}Al_{10}O_{16.26}$ |
| 1Cu1Ce10Al | 10.8 | 23.3 | $Cu_{1.05}Ce_{1.05}Al_{10}O_{18.15}$ |
| 1Cu3Ce10Al | 6.6 | 47.6 | $Cu_{0.92}Ce_{3.08}Al_{10}O_{22.08}$ |
| 5Cu3Ce10Al | 25.6 | 38.1 | $Cu_{4.53}Ce_{3.11}Al_{10}O_{25.75}$ |
| 1Cu10Ce10Al | 3.6 | 73.1 | $Cu_{0.98}Ce_{9.28}Al_{10}O_{34.54}$ |
| 1Cu10Ce | 4.4 | 95.6 | $Cu_{0.99}Ce_{10}O_{20.99}$ |

operating at a frequency of ~9.5 GHz (X band). The magnetic field was modulated at 100 kHz. The *g* values are determined from precise frequency and magnetic field values. EPR intensity is given by the double integration of the EPR signal.

**Activity tests.** 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. The catalytic tests towards the combustion of CB are studied by simultaneous gravimetric and differential thermal analysis (TG–DTA) with a Netzsch STA 409 apparatus. Before the catalytic test, CB (20 wt %) and catalyst (80 wt %) are mixed in an $Al_2O_3$ ball miller for 40 min; 40 or 20 mg of this mixture is loaded in an alumina crucible and heated from room temperature to 700°C (5°C/min) in air flow (75 ml/min). Figure 1 shows an example of TG–DTA curves. A weight loss of 20 wt % is observed, corresponding to the combustion of the total mass of carbon black. The TG curve allows one to obtain the temperature values $T_i$ (beginning of the carbon black combustion) and $T_f$ (complete conversion of carbon black). $T_{max}$ is the temperature of the maximum of the DTA curve and corresponds to the temperature of the highest combustion velocity. Catalytic properties of solids are evaluated by comparing these temperatures with those of CB combustion without a catalyst in the same conditions. For high reactive catalysts and 40 mg of analyzed mixture, TG–DTA curves reveal a fast oxidation of carbon black followed by a slower one. Thus, two temperatures $T_{max}$ are observed. This phenomenon can be explained by mass and heat transfer limitation [6, 12, 13]. The analysis of combustion products is performed evaluating the CO/(CO + $CO_2$) molar ratio from a Varian 3600 chromatograph.

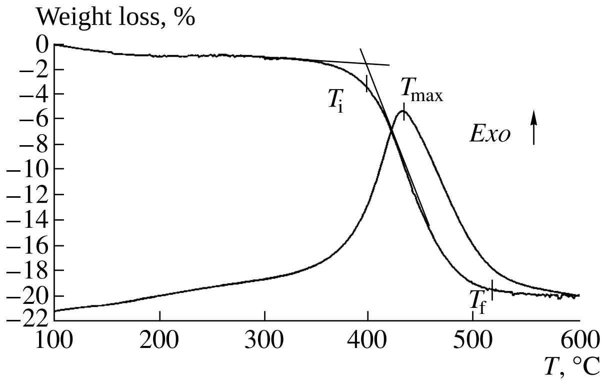

**Fig. 1.** Example of TG–DTA curve.

**Ozonation.** Ozonation of catalysts/carbon black samples is performed in the continuous gas flow reactor; the laboratory ozonizer produces approximately 2 vol % ozone in oxygen. Ozone concentration is determined in the gas phase inlet and outlet by UV-spectroscopy. The samples are allowed to react for 60 min in an oxygen/ozone flow of 75 ml/min at room temperature.

## RESULTS AND DISCUSSION

**1. Carbon black combustion before ozonation.** Figure 2 shows the reactivity of different catalysts before and after ozonation. The reactivity tests are performed on 20 mg of mixture. Combustion of carbon black alone takes place at high temperature ($T_{max}$ =

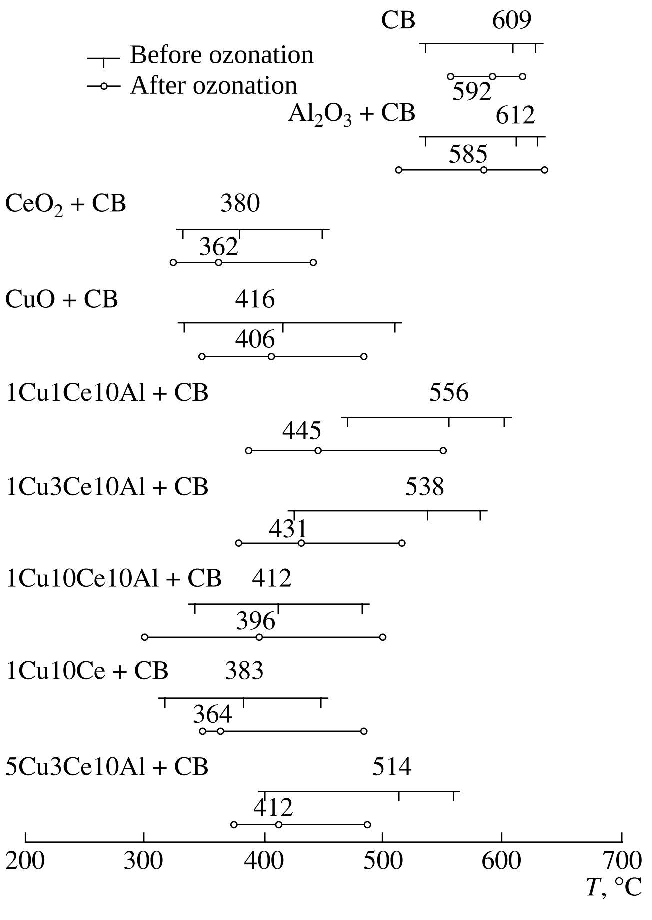

**Fig. 2.** Reactivity of solids for (20 wt % carbon + 80 wt % catalysts) before and after ozonation.

609°C). An insignificant difference is observed when the reaction is performed in the presence of $Al_2O_3$. For the other samples, combustion temperature decreases, showing the reactivity of copper- or ceria-based catalysts. Ceria and copper oxide are the most reactive samples with a combustion temperature of, respectively, 380 and 416°C. For the Cu–Ce–Al oxides, reactivity increases with increasing ceria content. Thus, the temperature $T_{max}$ decreases from 556°C for the 1Cu1Ce10Al sample to 538°C for the 1Cu3Ce10Al sample and to 412°C for the 1Cu10Ce10Al sample. For the 1Cu10Ce sample, the reactivity ($T_{max}$ = 383°C) and $CeO_2$ ($T_{max}$ = 380°C). Moreover, increasing copper content leads to higher reactivity. For the same support 3Ce10Al, the temperature $T_{max}$ decreases from 538°C for 1Cu3Ce10Al to 514°C for 5Cu3Ce10Al. Thus, it seems that copper oxide favors the reactivity when supported on alumina but has little effect on ceria reactivity, since this latter presents better reactivity than copper oxide.

**2. Carbon black combustion after ozonation.** Compared to untreated carbon black combustion, the ozonized carbon black combustion occurs at lower temperature (16°C) and with higher reaction velocity ($\Delta T = T_f - T_i$). Indeed, $\Delta T$ decreases from 92°C for untreated CB combustion to 60°C for ozonized CB combustion. For the $Al_2O_3$, $CeO_2$, and CuO catalysts, small differences for the combustion temperature (about 20–30°C) are observed. When the reaction is performed in the presence of Cu-based catalysts, the temperature of CB combustion is significantly lowered. Concerning the Cu–Ce–Al oxides, the increase of ceria content in the sample decreases the ozone influence on the catalysts' reactivity. Thus, for the 1Cu1Ce10Al catalyst, the $T_{max}$ temperature of the mixture after ozonation is 111°C lower than an untreated mixture, but for the 1Cu10Ce10Al system the temperature difference is only 16°C. On the other hand, the addition of copper does not affect the ozone influence on the catalyst reactivity: for the mixture of carbon black with 1Cu3Ce10Al and 5Cu3Ce10Al the difference in $T_{max}$ before and after ozonation is almost the same (~100°C). Thus, ozonation decreases the temperature $T_{max}$ of carbon black combustion. This effect is stable for all samples and the difference in $T_{max}$ for ozonized and initial CB is not less than 20°C. But the most important decrease of temperature is observed for the copper-based catalyst with the lowest ceria content (1Cu1Ce10Al). Thus, it seems important to study the influence of ozone on a copper-based catalyst without ceria.

Figure 3 presents the reactivity of the 1Cu10Al catalyst depending on ozone pretreatment. Five mixtures were studied: a mixture with CB/catalyst without any ozonation, an ozonized mixture, a mixture with ozonized catalyst and untreated CB, a mixture with untreated catalyst and ozonized CB, and a mixture with both separately ozonized catalyst and CB. These tests are expected to point out the role of ozonation on catalyst and carbon black. Without any ozone treatment, the carbon black combustion in the presence of 1Cu10Al shows a fast and slow oxidation process with a $T_{max}$ temperature of 513 and 529°C, respectively. When ozonation is carried out on a CB/catalyst mixture, the first $T_{max}$ is at 388°C, which is 135°C lower than the $T_{max}$ of an untreated mixture. The DTA-curve of ozonized 1Cu10Al catalyst with untreated carbon black has the same characteristic temperatures as the curve obtained for the untreated mixture. It means that the ozonation of 1Cu10Al does not influence its activity. Nevertheless, for the mixture of untreated catalyst/ozonized carbon black, the DTA-curve is significantly different: the decreases of $T_i$ and $T_{max}$ are, respectively, 70 and 33°C. Finally, the combustion of the mixture of separately ozonized catalyst and ozonized carbon black gives similar results to those of the mixture of untreated catalyst/ozonized carbon black. These data allow one to conclude that, when ozonized separately, $O_3$ influences the nature of carbon particles but does not affect the catalytic properties of the solids. Such an effect may be due to the formation of several oxygen complexes on the surface of carbon black [14, 15], which favors the catalytic oxidation of CB. Thus, due to the ozone pre-

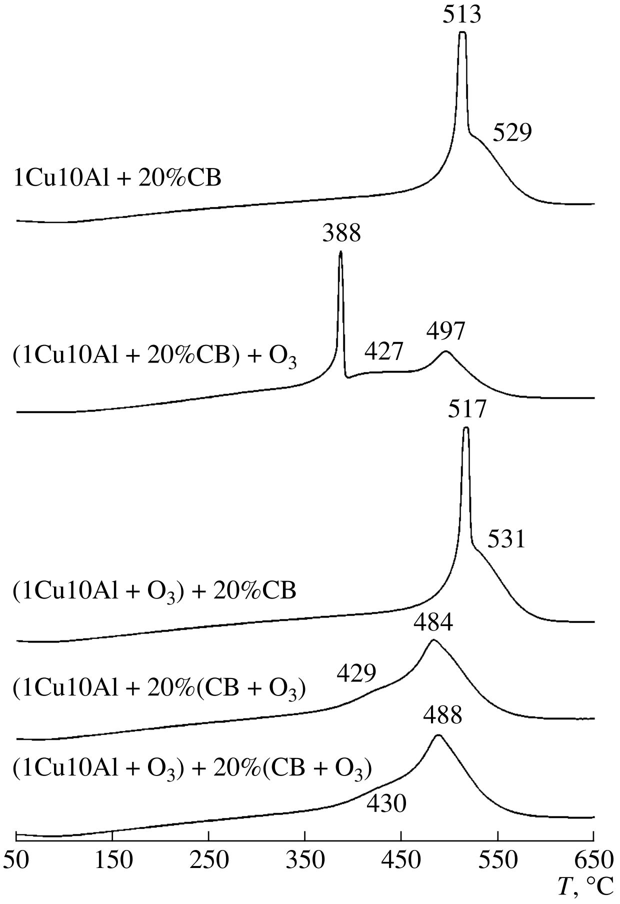

**Fig. 3.** Reactivity of 1Cu10Al for (20 wt % carbon + 80 wt % catalysts) with or without ozonation step.

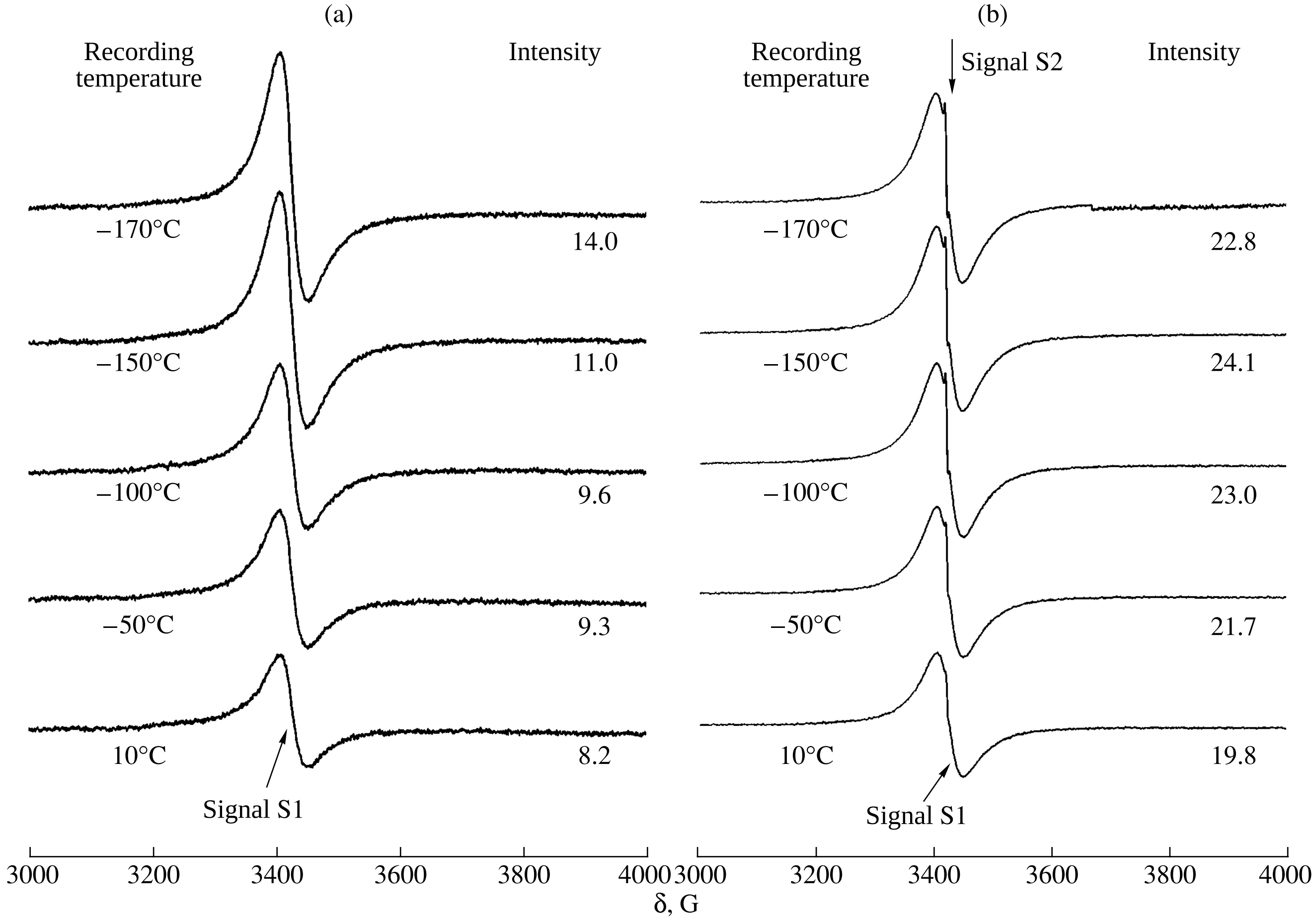

**Fig. 4.** EPR spectra of the CB recorded at different temperatures: (a) initial CB, (b) ozonized CB.

treatment of CB, the catalytic combustion of CB passes at lower temperatures. However, ozone pretreatment of carbon black/catalyst mixture gives a better result, showing a synergistic effect between CB and the catalyst.

Concerning the CO selectivity of the reaction, noncatalytic combustion of CB presents a CO selectivity of 14% ($CO/(CO + CO_2)$). The same value is obtained for a pure alumina-catalyzed reaction. However, pure ceria is totally selective in $CO_2$. Whatever the support is, the introduction of copper allows for total $CO_2$ selectivity. Finally, ozonation does not influence the selectivity of the CB combustion process.

**3. Characterization of carbon black before and after ozonation.** Untreated and ozonized carbon black are studied by EPR. Samples are subjected to vacuum ($5.2 \times 10^{-5}$ mbar, 3 h) treatment and EPR spectra are recorded at different temperatures from –170 to 10°C. Figure 4 shows the EPR spectra of initial and ozonized CB versus the recording temperature. From –170°C until 10°C for untreated CB only one signal S1 is evidenced but for ozonized CB two EPR signals S1 and S2 are detected.

The S1 signal presents a slight axial symmetry with a $g_{iso}$ value of ~2.000 and line width of 46 ± 1 G. Owing to the landscape and line width this signal can be attributed to free electrons in interaction with oxygen species despite the fact that the $g$-factor value is lower than those for free electrons ($g_e = 2.0023$). Moreover, the S1 intensity for CB before ozonation decreases with increasing recording temperature, while for CB after ozonation, this intensity is considerably higher and stable versus recording temperature. This phenomenon shows that these free electrons in interaction with oxygen species are more numerous and more stable for CB after ozonation.

The S2 signal is isotropic and sharp with $g_{iso} \sim 2.003$ and a line width of ~3.5 G. The EPR parameters of the S2 signal are consistent with free hydrocarbon radicals strongly adsorbed on the carbon particles [16]. The interaction between free radicals and carbon gets weaker with an increase in temperature and the degree of liberty of these radicals increases. The intensity of the S2 signal decreases with an increase in recording temperature, and at 10°C this signal becomes slightly detectable. Thus, it can be assumed that at higher temperatures the mobility of these species is improved. This higher mobility affects the reactivity of the diesel soot, since these compounds participate in the combustion mechanism of CB [16]. Thus, ozonation favors the formation of free radicals on the surface of CB that, according to our DTA data, decreases the temperature of its combustion.

## CONCLUSION

The catalytic combustion of carbon particles has been investigated in the presence of Cu–Ce–Al oxides. Catalytic tests show that $Al_2O_3$ does not influence CB combustion. Ceria and copper oxide are the most reactive samples but ceria presents better reactivity than copper oxide. For the Cu–Ce–Al oxides, reactivity increases with increasing ceria content. Copper oxide favors the reactivity when supported on alumina but has little effect on ceria reactivity. Due to the ozone pretreatment, the catalytic combustion of CB passes to lower temperatures. This phenomenon is observed for all samples, but the most important decrease of temperature is evidenced for copper-based catalysts with the lowest ceria content. Moreover, catalytic tests show that ozonation does not change the catalytic properties of solids. Physicochemical characterization shows that ozonation influences the nature of carbon particles increasing the concentration and stability of free radicals. However, ozone pretreatment of carbon black in the mixture with a Cu–$Al_2O_3$ catalyst gives a better result, evidencing a synergistic effect between carbon black and catalyst.

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