Catalytic Combustion of Diesel Soot : The role of Ozone as Promoting Reactant

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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 physico-chemical properties of Cu-Ce-Al-oxides at the reaction of diesel soot combustion was examined by thermal analysis and EPR methods.**

Index Terms-- **Cu-Ce-Al-oxide catalysts, Diesel soot combustion, Ozone effect.**

I. INTRODUCTION

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 particles 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 stabilising 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 is already studied for catalytic combustion of soot [5], [6], [8]-[10]. The catalytic system may be active even in low oxygen concentration conditions. Indeed, exhaust gases medium is sometimes poor in oxygen. But ozone, high oxidation reagent, is also present in 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 physico-chemical properties of Cu-Ce-Al-oxydes on the reaction of diesel soot combustion.

II. EXPERIMENTAL SECTION

A. Catalysts preparation

Alumina is synthesized by sol-gel method. Secondary aluminum butylate ($Al(OC_4H_9)_3$, Fluka, ~11.0 wt% Al) is dissolved in butan-2-ol (Fluka, purity $\geq$ 99.5%). Then, complexing agent (Butan-1,3-diol, Fluka, purity $\geq$ 98%) is added before hydrolysis [11]. Alumina is calcined at 500°C before used as support for preparing supported catalysts. With this method, alumina is characterized with specific area of 420 m^2/g and pore volume of 2.3 mL per gram.

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 hours with a temperature rate of 0.5°C/min.

Different Ce-Al-O oxides are prepared by incipient wetness of cerium nitrate solution onto alumina pre-calcined at 500°C. Then, the sample is dried at 100°C and calcined for 4 hours in a flow of dry air at 500°C. Cerium containing solids are denoted 1Ce10Al, 3Ce10Al and 10Ce10Al where the number before 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-O oxides) with aqueous solution of copper nitrate ($Cu(NO_3)_3\cdot 3H_2O$, Prolabo, purity $\geq$ 99.0%). The mixture is dried at 100°C and calcined at 600°C for 4 hours in a flow of dry air. Copper containing solids are denoted as supports, 1Cu10Al, 1Cu1Ce10Al, 1Cu3Ce10Al, 1Cu10Ce10Al 5Cu3Ce10Al, and 1Cu10Ce.

Table 1 summarizes the composition of supports and copper containing catalysts performed in the central elementary analysis office of the CNRS (Vernaison).

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TABLE I
COMPOSITION OF THE SOLIDS

| Sample	wt% of CuO	wt% of ceria	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%	$Cu_{0.99}Ce_{10}O_{20.99}$

A. Electronic Paramagnetic Resonance

The electron paramagnetic resonance measurements are performed at −196°C on a EMX BRUKER spectrometer with a cavity 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. 40mg 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 (75mL/min). Fig. 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 to obtain the temperature values T_i (beginning of the carbon black combustion) and T_f (complete conversion of carbon black). The T_m 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 catalyst in the same conditions. For high reactive catalysts and 40mg of analysed mixture, TG-DTA curves reveal a fast oxidation of carbon black followed by a slower one. Thus, two T_m temperatures 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.

B. Activity Tests

Commercial 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 a Al_2O_3 ball miller for 40 minutes.

Fig. 1. Example of TG-DTA curve
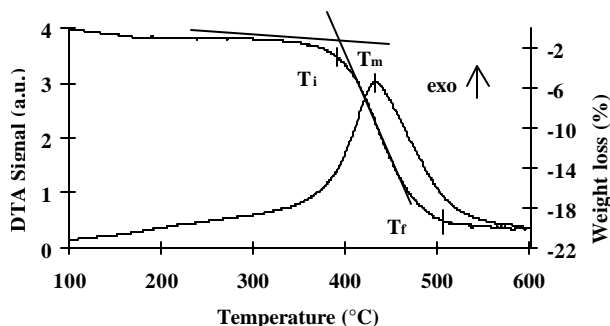
C. Ozonation

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

III. RESULTS AND DISCUSSION

A. Carbon black combustion before ozonation

Fig. 2 shows reactivity of different catalysts before and after ozonation. The reactivity tests are performed on 20 mg of mixture.
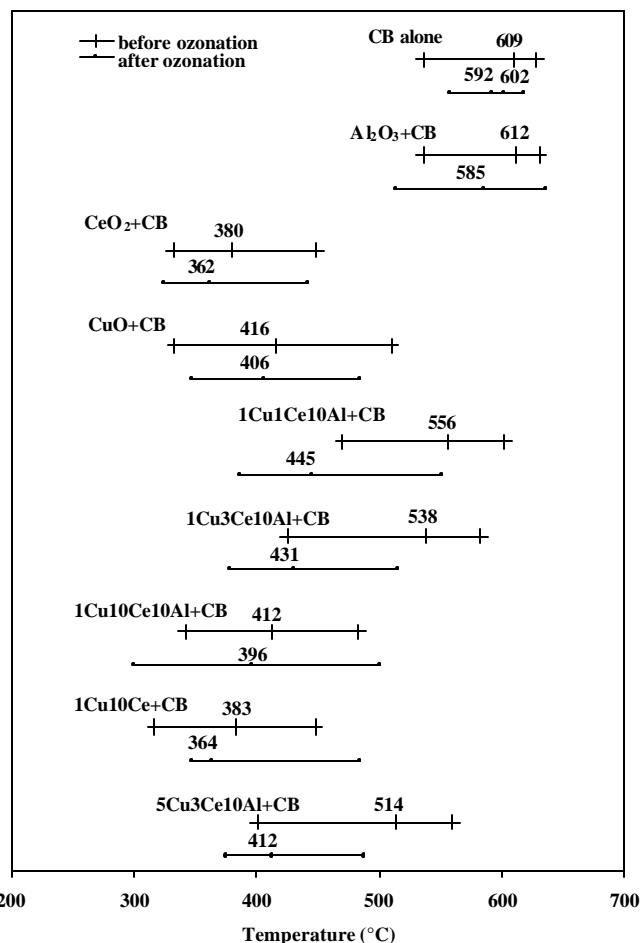

Fig. 2. Reactivity of solids for (20 wt% CB + 80 wt% catalysts) before and after ozonation

Combustion of carbon black alone takes place at high temperature (T_m = 609°C). 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°C and 416°C. For

the Cu-Ce-Al-O oxides, reactivity increases with increasing of ceria content. Thus, the temperature T_m decreases from 556°C for the 1Cu1Ce10Al sample to 538°C for the 1Cu3Ce10Al sample and to 412°C for 1Cu10Ce10Al sample. For 1Cu10Ce sample, the reactivity (T_m = 383°C) is quite the same as CeO_2 catalyst (T_m = 380°C). Moreover, increasing of copper content leads to higher reactivity. For the same support 3Ce10Al, the temperature T_m decreases from 538°C for 1Cu3Ce10Al to 514°C for 5Cu3Ce10Al. Thus, it seems that copper oxide favours the reactivity when supported on alumina but has a little effect on ceria reactivity, since this latter presents better reactivity than copper oxide.

B. 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, ΔT 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-O oxides, the increase of ceria content in the sample decreases the ozone influence on the catalysts reactivity. Thus, for 1Cu1Ce10Al catalyst, the T_m temperature of the mixture after ozonation is 111°C lower than 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_m before and after ozonation is almost the same (~100°C). Thus, ozonation decreases the temperature T_m of carbon black combustion. This effect is stable for all samples and difference in T_m 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.

Fig. 3 presents the reactivity of 1Cu10Al catalyst depending on ozone pre-treatment. Five mixtures are performed : 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 presence of 1Cu10Al shows a fast and slow oxidation processes with T_m temperature of 513°C and 529°C respectively. When ozonation is carried out on CB/catalyst mixture, the first T_m is at 388°C, which is 135°C lower than T_m of untreated mixture. DTA-curve of ozonized 1Cu10Al catalyst with untreated carbon black has the same characteristic temperatures than 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, DTA-curve is

significantly different : the decrease of T_i and Tm are respectively of 70°C 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.
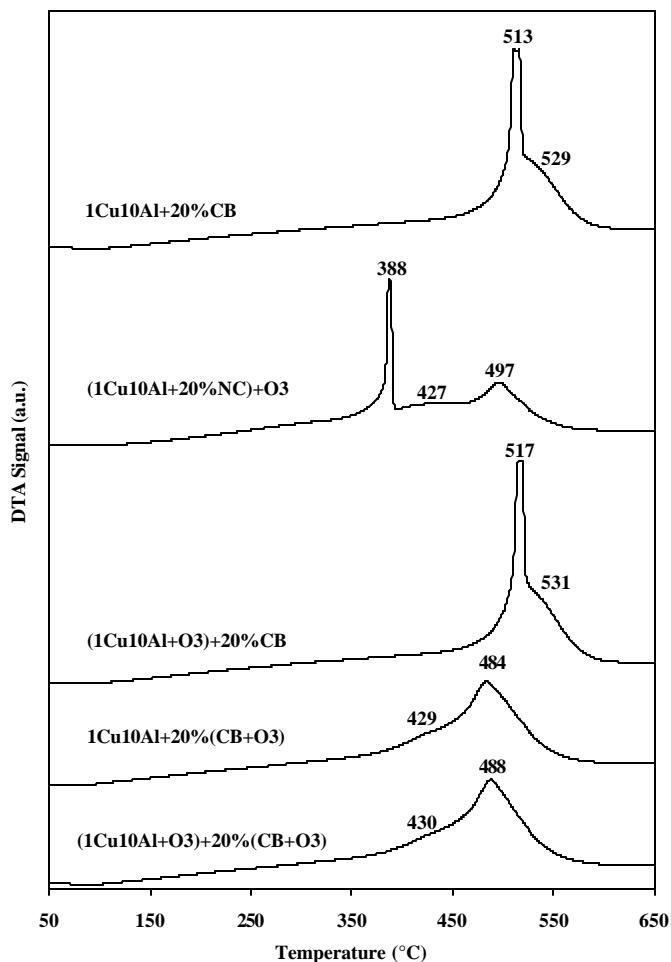

Fig. 3. Reactivity of 1Cu10Al for (20 wt% CB + 80 wt% catalysts) with or without ozonation step.

These data allow to conclude, that when ozonized separately, O_3 influences the nature of carbon particles, but does not effect the catalytic properties of the solids. Such effect may be due to formation of several oxygen complexes on the surface of carbon black [14], [15], which favours the catalytic oxidation of CB. Thus, due to the ozone pretreatment of CB, the catalytic combustion of CB passes at lower temperatures. However, ozone pre-treatment of carbon black/catalyst mixture gives the better result, showing a synergistic effect between CB and catalyst.

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

C. Characterisation of carbon black before and after ozonation

Untreated and ozonized carbon black are studied by EPR. Samples are subjected to vacuum (5.2×10^{-5} mbar, 3h) treatment and EPR spectra are recorded at different temperatures from -170°C to 10°C. Fig. 4 and 5 show the EPR spectra of initial and ozonized CB versus the recording temperature.
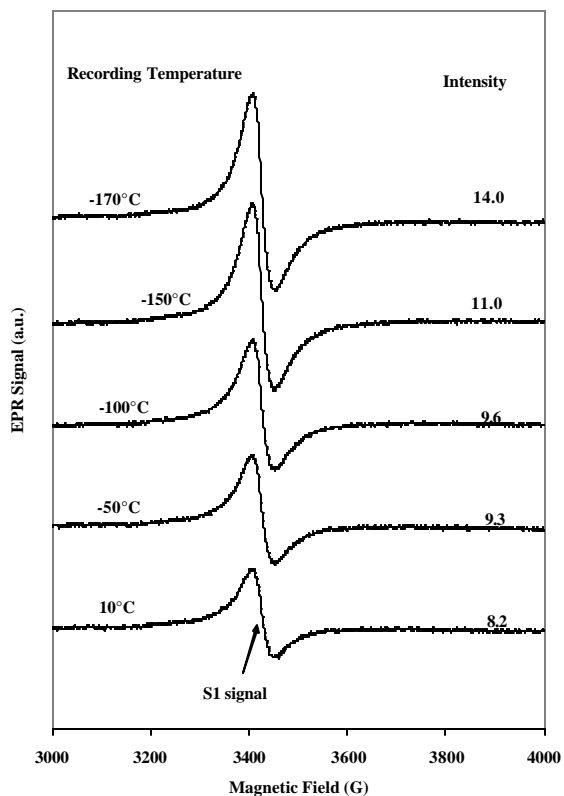
gets weaker with the increase of temperature and liberty degree of these radicals increases. The intensity of S2 signal decreases with the increase of recording temperature and at 10°C this signal becomes slightly detectable. Thus, it can be assumed that at higher temperatures the mobility of these species is improved. This higher mobility affects the
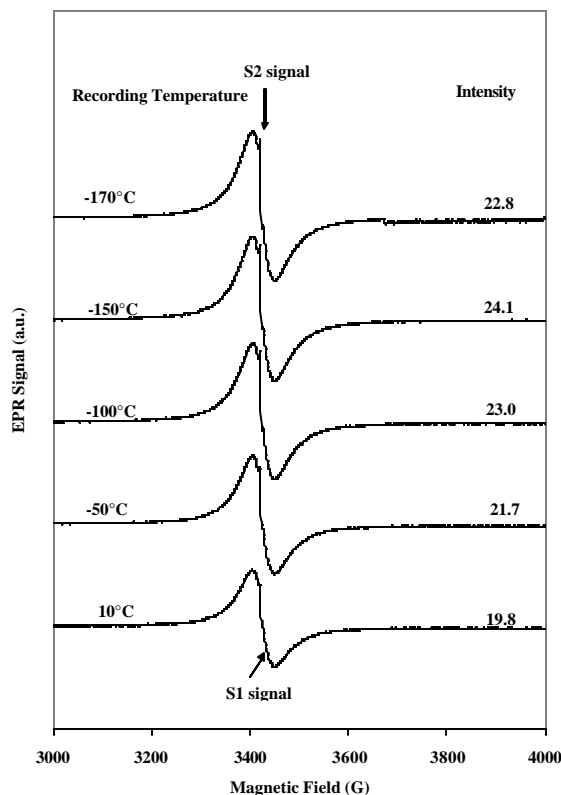

Fig. 4. EPR spectra of the CB recorded at different temperatures for initial CB

Fig. 5. EPR spectra of the CB recorded at different temperatures for ozonized CB

From -170°C until 10°C for untreated CB only on signal S1 is evidenced but for ozonized CB two EPR signals S1 and S2 are detected. S1 signal presents a slight axial symmetry with 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 g-factor value is lower than those for free electrons ($g_e = 2.0023$). Moreover, S1 intensity for CB before ozonation decreases with increasing of 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. S2 signal is isotropic and sharp with $g_{iso} = 2.003$ and line width of ~ 3.5G. 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

reactivity of the diesel soot since these compounds participate in the combustion mechanism of CB [16]. Thus, ozonation favours the formation of free radicals on the surface of CB, that according to our DTA data decreases the temperature of its combustion.

IV. 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-O oxides, reactivity increases with increasing of ceria content. Copper oxide favours the reactivity when supported on alumina but has a little effect on ceria reactivity. Due to the ozone pre-treatment, 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. Physico-chemical characterisation shows that ozonation influences the nature of carbon particles. However, ozone pre-treatment of carbon black in the mixture with catalyst gives the better result, evidencing a synergistic effect between carbon black and catalyst.

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