

COMPOSITION AND TEXTURAL PROPERTIES OF SOOT AND STUDY OF THEIR OXIDATIVE ELIMINATION BY CATALYTIC PROCESS

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ABSTRACT

Diesel soot and reference carbon black samples have been characterized by analysis of the organic compounds fraction and determination of textural characteristics (specific area). The potential to eliminate such carbonaceous particles has been investigated using a Cu/ZrO₂ solid catalyst promoted by potassium additives. The reactivity of soot samples depends on its organic compounds content. In general, Cu-K/ZrO₂ catalyst is able to lower significantly the soot oxidation temperature of almost 200°. This high activity is related to the ability of potassium to interact with copper species and to favour the release of active oxygen from the catalyst.

Key Words : soot, surface area, organic fraction, oxidation, Cu-K/ZrO₂ catalysts

1. INTRODUCTION

Soot particles correspond to a major fraction of atmospheric aerosols particularly in urban areas concerned by an important Diesel traffic density. Negative effects of soot are nowadays well-recognized on human health. The particle size appears to be the most influential factor (Schwartz and Meas, 2000) however specific organic compounds in soot could be one of the characteristics explaining that these airborne particles are more bioreactive than others (Adamson et al., 2000). During the last years, the awareness of the impacts of Diesel soot has lead to several works in catalysis research. In fact, among the technologies considered for soot removal, one way consists in the use of catalytic traps, corresponds to filters carrying a suitable catalyst, in view of simultaneous soot filtration and combustion. The catalyst should lower down soot ignition temperature of the non - catalytic combustion to the values characteristic of diesel exhaust: i.e. from almost 600°C to 200-350°C, respectively. The aim of this work is to undertake a study on both the chemical composition of different diesel soot samples and their textural properties (surface areas). These soot samples were then tested in an oxidative elimination reaction in presence of a Cu/ZrO₂ solid catalyst promoted by potassium additives. Different Cu and K

contents were considered for a better understanding of the effect of each active element on the oxidation reaction.

2. EXPERIMENTAL AND METHODS

The organic compounds of different Diesel soot DS (engine operating conditions in both low and high combustion temperatures) and reference carbon black samples (synthetic furnace soot NC330 Degussa and synthetic flame soot Printex U Degussa) were analyzed by chromatographic method coupled to mass spectrometry (GC-MS) for the qualitative/quantitative determination of polycyclic aromatic hydrocarbons and paraffins. Specific areas of soot and carbon black samples were determined by nitrogen adsorption.

The catalysts were prepared by co-impregnation in aqueous medium of given amounts of copper [Cu(NO₃)₂] and potassium [KHCO₃] onto a ZrO₂ carrier. After drying, all solids were calcined under dry air for 4h at 600°C. The equivalent amounts of CuO or/and K₂O in calcined catalysts were determined by chemical analysis. Catalysts were designated Cu_x-K_y/ZrO₂ where 0 < x < 4 and 0 < y < 4 correspond respectively to the amount expressed in wt% of CuO and K₂O in catalysts calcined at 600°C.

The catalytic tests were performed using a mixture of soot (6 wt%) and catalyst (94 wt %) corresponding to loose contact conditions (Neeft et al., 1997, Courcot et al., 2004). The latter permit to evaluate the activity of oxide catalysts in experimental conditions closely similar to those of real application, since the soot particles emitted through the exhaust line can only be stopped by the catalyzed filter surface. The catalytic oxidation was studied by simultaneous TG-DSC analysis (NETZSCH STA 409 apparatus). About 50 mg of the CB-catalyst mixtures were loaded in an alumina crucible and heated from 25 to 800°C using a heating rate of 5°.min⁻¹ in air flow (75ml.min⁻¹). As shown in Figure 1a, by processing the experimental data, the onset temperature (T_i) could be derived (i.e. temperature at which the combustion starts). The value of T_i is calculated from the TG curve as the intersection between the baseline and the tangent of the curve traced at the inflection point. Following a similar method, the temperature (T_f) at which the combustion of carbon is complete was obtained.

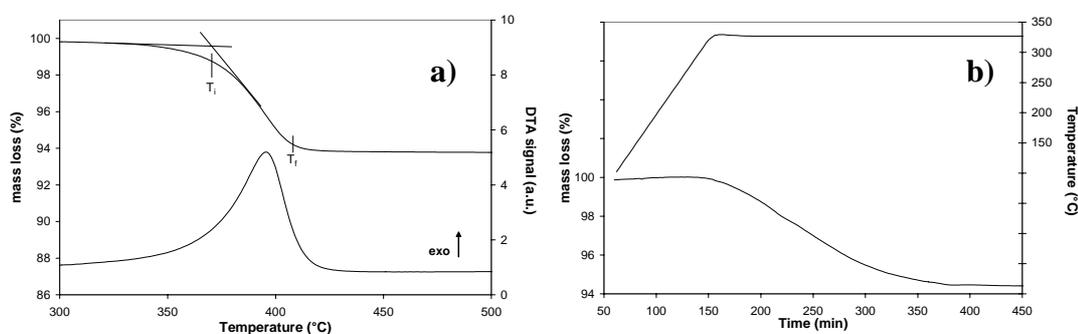


Figure 1 : Examples of thermal analysis curves recorded for the catalytic test of (CB-catalyst) mixtures. a) non-isothermal conditions; b) isothermal conditions.

Additional catalytic tests were performed under isothermal conditions considering the CB-catalyst mixtures in loose contact. Samples were kept under an air flow ($75\text{ml}\cdot\text{min}^{-1}$) and heated to 327°C ($5^\circ\cdot\text{min}^{-1}$). The weight loss rate was used as a measure for the CB oxidation rate (Figure 1b) in agreement with the experimental approach described by van Setten et al. (1999). Considering tangent of the mass curve at different carbon conversion values, oxidation rates were calculated. Once the combustion starts, it is observed that the oxidation rate progressively increases, reaches a maximum and then finally decreases to zero. The analysis of combustion products was performed evaluating the $\text{CO}/(\text{CO}+\text{CO}_2)$ molar ratio from a Varian 3600 chromatograph coupled to the thermobalance.

The reducibility of the catalysts was determined by Temperature Programmed Reduction (H_2 -TPR). The experiments were carried out in a conventional apparatus (AMI 200, Zeton Altamira). The catalysts (~ 75 mg) were previously treated *in-situ* under O_2 diluted in argon flow at 450°C for 1 h. After cooling under argon flow, reduction treatment (3% H_2 in argon) was performed with a total flow of $30\text{ mL}\cdot\text{min}^{-1}$ from 25°C to 700°C with a heating rate of $10^\circ\cdot\text{min}^{-1}$. Additional experiments consisted in H_2 -TPR measurements of (CB-catalysts) loose contact mixtures previously treated under argon ($30\text{ mL}\cdot\text{min}^{-1}$) at 400°C for 1 h. This treatment was considered to simulate the beginning of the CB conversion initiated by the participation of active catalytic species, normally contributing to a redox mechanism. Considering the difference in H_2 consumption for these two kinds of measurements for a given catalyst, quantitative information could be obtained on such oxygen species able to react with carbon during the Ar treatment at 400°C .

3. RESULTS AND DISCUSSION

3.1. Soot and Carbon Black characterization

The analysis of the nine PAHs given in Table 1 indicates that the diesel soot contains the higher content of PAHs. The synthetic flame CB (Printex U) contains higher amounts of PAHs than the synthetic furnace sample (NC 330).

Table 1. Concentration ranges ($\mu\text{g}/\text{g}$) of individual PAH in diesel soot and carbon black samples.

Compounds	Diesel soot DS	CB Printex U	CB NC 330
Phenanthrene	744.8	810.1	6.8
Anthracene	361.2	78.9	-
Fluoranthene	150.6	139.6	5.5
Pyrene	89.8	106.4	20.7
Benzo(a)anthracene	174.2	2.6	-
Chrysene	117.4	4.5	-
Benzo(a+e)pyrene	75.4	18.7	-
Indeno(123cd)pyrene	52.3	2.0	-
Benzo(ghi)perylene	138.1	1.4	-

Table 2. Textural characteristics of Diesel soot and carbon black .

Samples	Specific area (m ² /g)	
	outgassed at 100°C	outgassed at 500°C
Diesel soot DS	43	262
carbon black NC 330	80	82
carbon black Printex U	95	128

Table 2 gathers the specific areas values for samples outgassed at 100°C and 500°C. Except in the case of CB NC 330, a significant increase in specific area occurred after outgassing at 500°C, and particularly in the case of the diesel soot DS sample. More precisely, we observed a specific area increase reaching 73 m²/g after treating the diesel soot at 300°C. Then the main specific area increase is observed 300°C and 400°C, to reach 240 m²/g. Simultaneously, TG-DTA measurements performed under pure N₂ gas reveals a progressive desorption of organic compounds between 200° and 400°C (not shown). The evolution of the soot specific area versus the treatment temperature seems to be correlated to the departure of organics compounds from the soot. In fact, we evidenced the desorption of 8.2 % of volatile compounds between 200°C and 300°C among them alkylated benzene and alkylated naphthalene that are more generally found in the gaseous phase of the exhaust (Flandrin et al. 2002). Others main compounds desorbed were acenaphthylene, acenaphtene and fluorene. Hence the total organic fraction of the diesel soot include volatile compounds and the PAHs given in Table 1. The volatile compounds would be mainly adsorbed on soot surface sites. On the other hand, the nitrogen adsorption isotherm for the soot outgassed at 500°C was typical of a porous material, characterized by a pore width between 20 and 30 nm, obtained from density functional theory model. These data can be explained considering the departure of a part of the heavier organic compounds, probably occupying the inter-particle pore volume of the soot. This result appeared to be in good agreement with findings of Rockne et al. (2002) on the pore structure of soot.

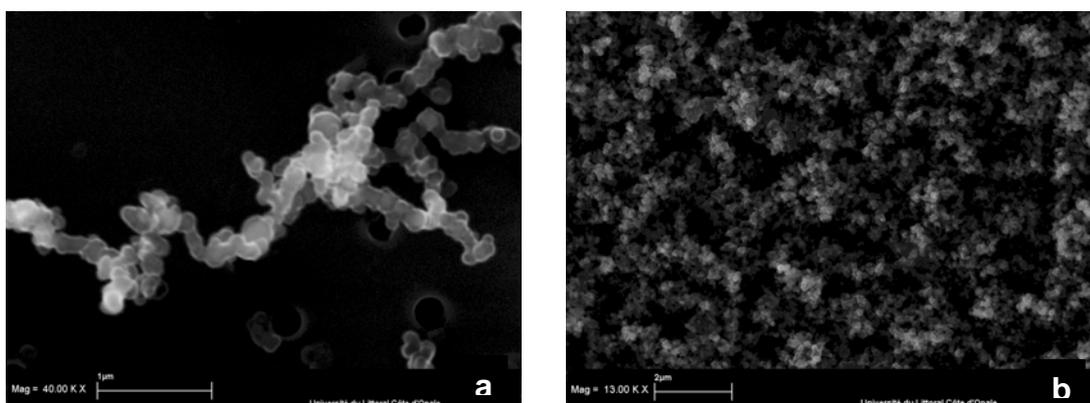


Figure 2: Secondary Electron images of diesel soot particles. a) structured chain with a low agglomeration ; b) highly structured and agglomerated soot.

The SEM analysis of the diesel soot particles (Figure 2) shows a typical chain-like structure of soot (Ambrogio et al. 2002). The latter corresponds to the agglomeration of elemental soot particles, with diameter close to 80 – 120 nm in our case. The soot sample also shows a high level of agglomeration. This high agglomeration can probably be considered to explain the presence of the inter-particle porosity of the soot.

3.2. Soot oxidation by Cu-K/ZrO₂ catalysts

Catalytic tests were first performed using NC 330 CB since this sample contains a low amount of organic compounds and almost only a carbonaceous matrix. In this way, NC 330 can be used a reference to evaluate the ability of a catalyst to oxidize carbon. Figure 2 gives the temperature range in which the oxidation of NC 330 occurred for the test of (NC 330 - catalyst) mixtures. It is important to notice that the oxidation of non-catalyzed NC 330 in air flow occurred regularly between $T_i = 530^\circ\text{C}$ and $T_f = 635^\circ\text{C}$. The results obtained in the presence of pure ZrO₂ indicated the low reactivity of this oxide carrier. The reaction temperature range for Cu_x/ZrO₂ and ZrO₂ exhibits only little difference, revealing a slight improvement in catalytic properties, which depends on the copper content. The potassium oxide species leads to a high improvement of the reactivity of the catalytic systems, also depending on the K content. K_{3.50}/ZrO₂ catalyst permits to lower down soot ignition temperature between $T_i = 385^\circ\text{C}$ and $T_f = 475^\circ\text{C}$. For the catalytic tests performed in the presence of K-Cu/oxide, the conversion of carbon occurred in a low temperature range. In fact, it is noteworthy to obtain the shift toward lower temperatures of nearly 200° between the test performed with Cu_{1.96}-K_{3.45}/ZrO₂ and ZrO₂. The catalyst Cu_{1.96}-K_{3.45}/ZrO₂ ($T_i = 370^\circ\text{C}$ and $T_f = 445^\circ\text{C}$) appeared then as the most reactive system indicating synergistic effects related to the addition of both Cu and K on the ZrO₂ surface.

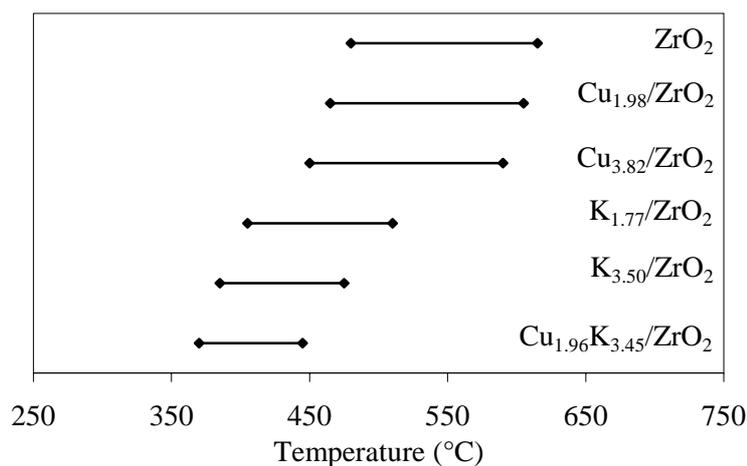


Figure 3 : Temperature ranges for NC 330 oxidation in the presence of Cu_x-K_y/ZrO₂ catalysts

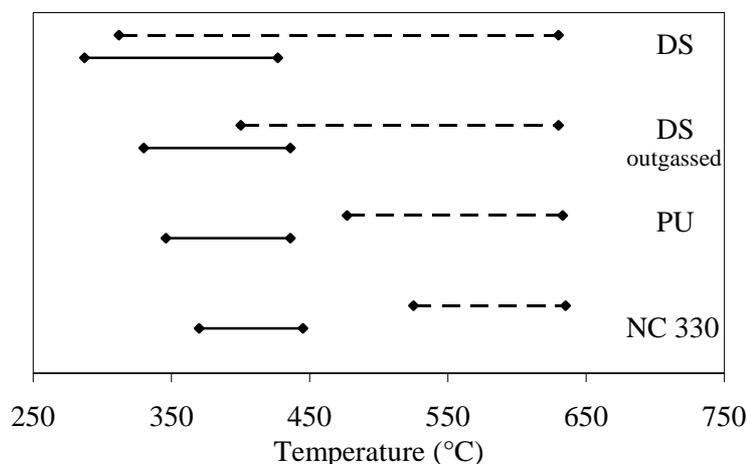


Figure 4 : Temperature ranges of Diesel soot and carbon black samples in the presence of $\text{Cu}_{1.96}\text{K}_{3.45}/\text{ZrO}_2$ catalyst.

The soot and carbon black samples were then tested in the oxidation reaction in the presence of the most active $\text{Cu}_{1.96}\text{-K}_{3.45}/\text{ZrO}_2$ catalyst and the catalytic effect can be appreciated by comparison with the non-catalytic oxidation data. First, the ignition of DS is observed at lower temperature than the DS outgassed due to the occurrence of organic compounds oxidation at a relatively low temperature in comparison with the carbon fraction. In this series, NC 330 appeared as the less reactive carbonaceous compound. It can be outlined that nearly same Tf values ($\sim 630^\circ\text{C}$) were obtained for the different samples, revealing similar properties towards the oxidation of the remaining carbon fraction after the organic compounds or/and surface functions reacted in the lower temperature range. A similar reactivity classification has been obtained when the oxidation is performed in the presence of $\text{Cu}_{1.96}\text{-K}_{3.45}/\text{ZrO}_2$ catalyst. Nevertheless, it appeared that the shift towards lower temperatures is more important on Tf values than Ti values. Considering at first the oxidation of organic compounds at low temperature (close to Ti) and rather the oxidation of carbon at higher temperature, this observation tends to show that such catalysts are more efficient in lowering the oxidation of carbon (almost $180 - 200^\circ$) than organic compounds in soot (between 30 and 150°).

Complementary information on the soot reactivity in the presence of the $\text{Cu}_{1.96}\text{-K}_{3.45}/\text{ZrO}_2$ catalyst were obtained from soot oxidation rates determined under isothermal conditions (Figure 5). The higher oxidation rates values were obtained after soot conversion of 20 or 30% for DS and Printex U, which correspond to samples containing the higher fraction of organic compounds. For these samples, oxidation rates values remain higher than DS outgassed and NC 330 till a conversion of 60% is reached. Such conversion levels are markedly higher than the organic compounds fraction in soot. Therefore, these observations show that the presence of organic compounds in soot enhances its reactivity and permit to oxidize a carbon fraction with a higher oxidation than in the case of a soot practically free of organic compounds.

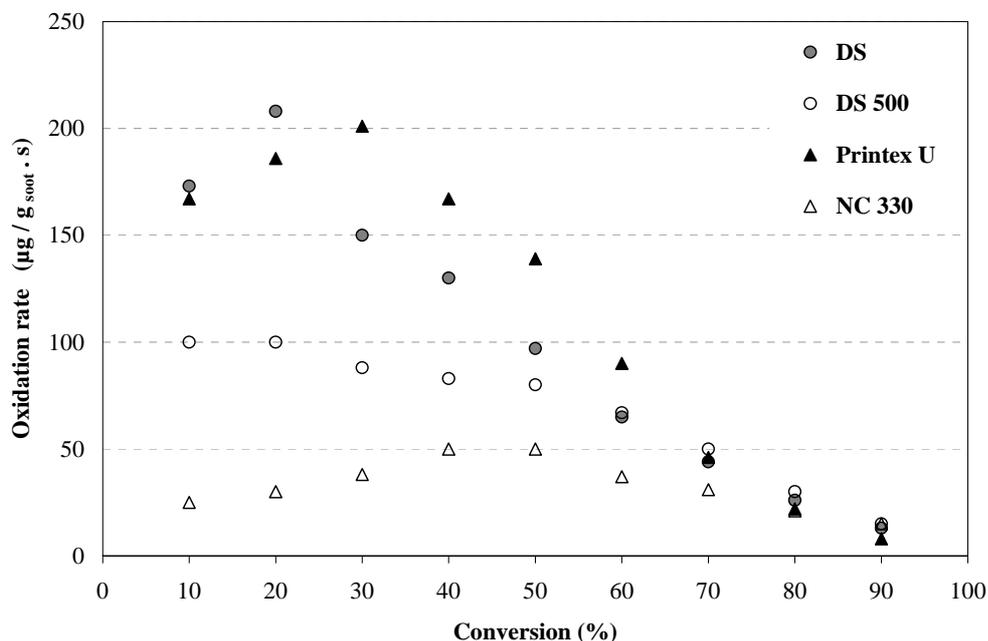


Figure 5 : Soot oxidation rate at 327°C as function of conversion in presence of $\text{Cu}_{1.96}\text{-K}_{3.45}/\text{ZrO}_2$ catalyst.

3.3. Temperature Programmed Reduction characterization of Cu-K/ZrO₂ catalysts

Table 3 gives the H₂ consumptions obtained for the TPR experiments of ZrO₂, Cu_x/ZrO₂ and Cu_x-K_y/ZrO₂ catalysts. First, it appeared that no H₂-consumption occurred for the ZrO₂ support while a slight H₂-consumption was observed from 400°C for K_y/ZrO₂. Following the copper content in Cu_x/ZrO₂ solids, the H₂ consumption increases which was ascribed to the reduction of the Cu(II) species ($\text{CuO} + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}_2\text{O}$) supported on the ZrO₂ surface. (Shimokawabe et al., 1990 ; Zhou et al. 1999). In the case of Cu_x-K_y/ZrO₂ samples, H₂ consumptions are markedly higher than the amounts required for the copper oxide phase reduction. Hence, it was suggested that the Cu(II) species not only interact with potassium species but also with the ZrO₂ support so that the TPR data could be explained by both the reduction of Cu(II) and species stabilized on the ZrO₂ surface. For the same Cu content (~2 wt% CuO), the H₂ over-consumption increases with the K content (Table 3) showing that the potassium species in the presence of copper favour the reduction of catalyst species. On the contrary, the sample with a high copper content (Cu_{4.02}-K_{1.85}/ZrO₂) is characterized by a relatively low H₂ over-consumption probably due to a stronger interaction of potassium species with Cu(II) than the entire solid including both Cu(II) and the ZrO₂ support.

A second step of the TPR characterization was carried out specifically to evidence if some active oxygen species of the catalysts are able to react to oxidize carbon. Such catalysts properties could account for explaining the high activity of Cu_x-K_y/ZrO₂. Assuming that some reducible species pointed out in the catalysts TPR profiles are active species contributing to a redox mechanism, (CB- catalysts) loose contact

mixtures previously treated *in-situ* under argon at 400°C were analyzed by TPR (see experimental part). In this case, catalysts species reduced by the carbon black during the Ar treatment could not be reduced during the subsequent H₂-TPR measurement. For solids containing only a low copper content, the H₂ consumption is unchanged. For a higher Cu content (Cu_{3,82}/ZrO₂), a decrease was obtained indicating that active oxygen species of the catalyst have reacted with carbon during the treatment of CB-catalyst mixture at 400°C. This phenomenon was ascribed to the presence of CuO crystallites considered as active species in the oxidation of carbon (Neeft et al., 1996, Pruvost et al. 2000).

Table 3: Quantitative data from TPR experiments of Cu_x-K_y/ZrO₂ catalysts.

Catalyst	Cu _{1,98} /ZrO ₂	Cu _{3,82} /ZrO ₂	Cu _{2,08} -K _{1,07} /ZrO ₂	Cu _{1,89} -K _{2,22} /ZrO ₂	Cu _{1,96} -K _{3,45} /ZrO ₂	Cu _{4,02} - K _{1,85} /ZrO ₂
H ₂ consumption (μmol H ₂ /g)	241	466	483	616	1219	679
theoretical H ₂ consumption CuO into Cu ⁰ (μmol H ₂ /g)	249	479	261	237	246	505
oxygen species released during (soot-catalyst) treatment under Ar (μmol espèces O/g)	0	131	222	379	973	174

For solids containing both potassium and copper, an important H₂ consumption decrease was recorded. These species were then reduced by carbon during the pre-treatment and this reduction is markedly high for the Cu_x-K_y/ZrO₂ with high K content. In parallel, catalytic tests performed under Ar permitted to evidence the higher conversion of carbon with higher K content in Cu_x-K_y/ZrO₂ catalysts. Our observations clearly demonstrate that potassium act as a promoter able to enhance the participation of oxygen species from the solid. Furthermore, the synergistic effects related to the addition of both Cu and K on the ZrO₂ surface could be related to the fact that potassium species facilitate the re-oxidation of active copper species involved in the catalytic reaction.

4. CONCLUSION

The characterization of diesel soot and carbon black samples show a dependence between the stabilization of particulate organic compounds and the textural properties of soots. Specific areas and porosity appears as parameters explaining the stability of organic compounds on the soot carbonaceous matrix.

The catalytic oxidation of carbonaceous samples has been investigated considering Cu and K containing ZrO₂ solids. Such catalysts are highly active systems for the oxidative elimination of soot. The organic compounds present in soot have an influence on both the soot reactivity and the catalytic reaction, as revealed by the

higher oxidation rate obtained for the Diesel soot in comparison with carbon black. Due to the presence of potassium promoter in the catalyst, the activity is related to the ability of the solid system to release active oxygen species involved in the oxidation reaction.

5. ACKNOWLEDGMENTS

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