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Investigation of the Cu–Zr–Y oxides activity in the carbon black catalytic oxidation by differential thermal analysis and temperature programmed reduction

M. Labaki, J.-F. Lamonier*, S. Siffert,
F. Wyrwalski, A. Aboukaïs

Laboratoire de Catalyse et Environnement, E.A. 2598, MREI, 145 Avenue Maurice Schumann, 59140 Dunkerque cedex, France

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Abstract

Different copper/zirconium-yttrium catalysts have been tested in carbon black oxidation reaction. Supported mainly on differential thermal analysis and temperature programmed reduction, two different mechanisms have been proposed to explain the catalytic results. In the absence of copper, it has been shown that Zr^{3+} ions and associated anionic vacancies are responsible to the catalytic enhancement observed in the mixed oxides, oxygen species being activated on these sites. Among mixed zirconia–yttria solids, ZrO_2-5 mol%Y_2O_3 is the most active catalyst. Copper impregnation on these oxides leads to the formation of different copper species. Small particles of CuO in low interaction with the support, induce a catalytic improvement due to the highest reducibility of these species. Moreover, in order to be more efficient, CuO species should have some interactions with the support, since impregnated samples are more active than the simple mechanical mixtures.

Keywords: Carbon black catalytic oxidation; Copper–zirconium–yttrium oxides; DTA and TPR measurements

1. Introduction

Soot emitted from diesel engines causes serious problems to human health and environment. The best option for the removal of soot from diesel exhaust is the collection of carbon black and its simultaneous oxidation at diesel exhaust gas temperatures (about 330 °C and even lower) in a monolithic filter coated by an oxidation catalyst. Indeed, the use of catalyst allows decreasing significantly the temperature of carbon black oxidation from around 600 °C (without catalyst) to 300 °C (in the presence of catalyst). Thus, several research groups have investigated catalytic oxidation of diesel soot or carbon black (model of soot) in air especially on molten metals and eutectic salts [1,2] and transition metal oxides [3–7]. Molten metals and eutectic salts were proven to be very active diesel soot oxidation catalysts but their stability and durability issues are not good and have to be enhanced. Recently, new researches have been focused on the catalytic properties of some metal oxides in the carbon black oxidation which present a lower activity in comparison with some salts but possess a much better stability. The ability of metal oxides to release active oxygen can be seen as an investigation route for catalytic performances improvement of such solids in the diesel soot oxidation [8].

Zirconium dioxide (or zirconia) is reported to be active in oxidation reactions [9–12]. Moreover, it is known that the stabilization of zirconia metastable tetragonal phase is determinant for a better catalytic activity [13–15]. In fact, introduction of yttrium into zirconia matrix should improve its catalytic behaviour because it stabilizes zirconia tetragonal phase and increases its oxygen mobility. Moreover, zirconia modified by yttrium impregnated with copper was found to be very active in deep propene and toluene oxidation reactions [16,17]. In this work, the activity of similar catalysts in the carbon black oxidation reaction is evaluated. The parameters such as the reactant–active phase contact and the reducibility of active phase are particularly considered in order to support mechanism able to explain the carbon black oxidation in the presence of transition metal oxides.

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* Corresponding author. Fax: +33 3 28 65 82 39.
E-mail address: lamonier@univ-littoral.fr (J.-F. Lamonier).

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2. Experimental

2.1. Catalysts preparation

Different simple and mixed zirconia–yttria supports impregnated or not by copper are prepared. Simple and mixed zirconia–yttria solid solutions are prepared by precipitation and coprecipitation of the respective precursor salts by ammonium. The samples are calcined under air flow at 600 °C and impregnated by the copper cations (using copper nitrate solution) with the subsequent drying in air at 100 °C (24 h) and calcining at 600 °C (4 h). Synthesis details are reported elsewhere [17]. The catalysts are denoted by Cu_m/Zr-*n*Y600, where "*m*" represents the copper weight content ($m = 0.5$ and 1) and "*n*" the molar percentage of yttrium in the support ($n = 1$, 5 and 10). A mechanical mixture of CuO (1 wt.%) and Y600 (99 wt.%) is also carried out (sample denoted MM (1%CuO + Y600)).

2.2. Carbon black combustion test

Commercially available carbon black is used as model soot in order to obtain reproducible and comparable results. The carbon black used is furnished by Degussa Society, NC330 (specific surface area (BET) of 80 m^2/g and apparent density of 370 kg/m^3). In order to establish a scale for the reactivity of the different oxides on one hand and to assure the reproducibility of the mechanical mixtures catalyst–carbon black on the other hand, the factors time of mixing, catalyst/carbon black ratio and catalyst weight are fixed and maintained constant for each test. The catalyst powders and carbon black are mixed together by a ball-miller (Retsch S 1000), containing 10 steel balls with 10 mm of diameter. The mixing time was of 40 min with a speed of 30 rotations/min. The catalyst/carbon black ratio in each mixture was 80/20 in weight. The reactant gas (dry air) passed through the catalyst–carbon black mixture (about 45 mg) at a flow rate of 75 mL min^{-1}. The temperature is raised by 5 °C min^{-1} from ambient to 600 °C. Differential Thermal and Thermo-Gravimetric Analyses (DTA-TGA) apparatus—Netzsch STA 409 C instrument is used for this aim.

2.3. Temperature programmed reduction (TPR)

H_2-TPR of the calcined catalysts was carried out in a conventional laboratory apparatus (Zeton Altamira AMI 200). Prior to the TPR experiments, all samples (100 or 200 mg) were activated under argon at 150 °C for 1 h. The samples were heated from ambient to 600 °C under H_2 flow (5 vol.% in argon—30 mL min^{-1}) at a heating rate of 5 °C min^{-1}.

3. Results and discussion

For all the tests, the TGA curves show a total mass loss of 20% corresponding to the complete combustion of carbon black mixed with the catalyst. Generally, DTA curves show exothermic peaks due to carbon black combustion.

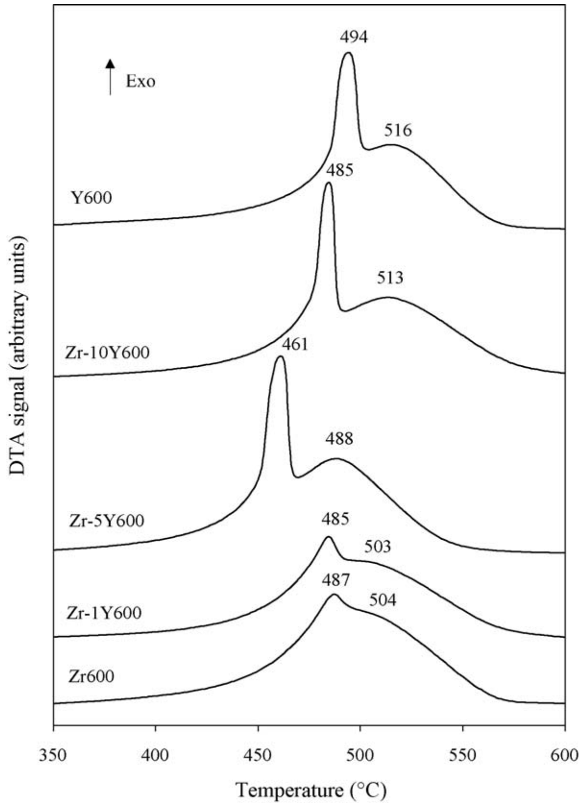

Fig. 1. Differential thermal analysis (DTA) curves of carbon black oxidation in the presence of different simple and mixed zirconia–yttria supports.

3.1. Carbon black oxidation on different simple and mixed zirconia–yttria supports

Fig. 1 shows the DTA curves corresponding to carbon black combustion in the presence of the different simple and mixed zirconia–yttria supports. Firstly, a catalytic reaction occurs in the presence of the supports since the carbon black oxidation takes place before 600 °C. Similar catalytic effects have been already observed. It is seen that both Zr600 and Zr-1Y600 have a combustion peak followed by a shoulder. For Zr-5Y600, Zr-10Y600 and Y600 two combustion peaks are observed; a first narrow one and a second large one. Many authors [18–20] have already observed both peaks. They assigned the first one to the combustion of carbon black in tight contact with the catalyst and the second one to the combustion of carbon black in loose contact with the catalyst. The second peak is also attributed to diffusion limitation of oxygen and reaction products which delays the combustion of a part of the carbon black which is oxidized later giving rise to the second peak.

The following catalytic activity order could be given by the temperature of the first peak:

$$\text{Zr-5Y600} > \text{Zr-10Y600} \sim \text{Zr-1Y600} \sim \text{Zr600} > \text{Y600}.$$

It is generally assumed that hydrocarbons catalytic oxidation on metal oxides takes place via a redox mechanism in which the rate-determining step would be the oxygen removal of the oxidized catalyst (OC) to oxidize hydrocarbons. In a second step the reduced catalyst (RC) is reoxidized by the oxygen from the gas phase. The oxidation of carbon black in the presence of metal oxide is not a conventional heterogeneous catalysis reaction since a part of reactants is solid. Nevertheless, replacing hydrocarbons in the previous redox mechanism with carbon black, the following mechanism (*M1*) can be proposed:

$$\text{Carbon black} + \text{“OC”} \rightarrow \text{products}\,(\text{CO}_2\ \text{and/or CO}) + \text{“RC”} \tag{1}$$

$$\text{“RC”} + \text{“oxygen”} \rightarrow \text{“OC”} \tag{2}$$

This simplified mechanism evidences the importance of “carbon black–catalyst” interaction (step 1). The type of oxygen used for the oxidation of reduced catalyst is not detailed since ZrO_2–Y_2O_3 solids present lattice mobile oxygen species which can participate to the catalytic reoxidation process (step 2).

The study of metal oxides reducibility (corresponding to the first step) seems to be crucial in order to explain the catalytic results observed in the carbon black oxidation. Then, H_2-TPR experiments have been performed in the presence of Zr600, Zr-5Y600 and Y600 and the results are shown in Fig. 2.

In the temperature range of the catalytic activity (from 300 °C up to 600 °C), Y_2O_3 partially reduces since H_2 consumption is observed as soon as 450 °C and 550 °C for, respectively, Y600 and Zr-5Y600. Taking into account the previous mechanism (*M1*), this result well explains the reactivity of this oxide in the carbon black oxidation. But in the same temperature range, ZrO_2 solid is not reduced although Zr600 is active in the carbon black oxidation. This result can be explained by a redox mechanism involving anionic vacancies at the surface of zirconia. Indeed, electron paramagnetic resonance (EPR) measurement evidenced the presence of Zr^{3+} cations in the different zirconia systems [17]. Moreover, O_2^- anion radicals are considered by many investigators as intermediate species in the catalytic oxidation on the solid surfaces. On zirconia, the formation of these anionic oxygen species in the carbon black oxidation could be explained by the intervention of Zr^{3+} species and associated anionic vacancies ($\square_{surf}$) on the catalyst surface in the following mechanism (*M2*):

$$Zr^{3+}\square_{surf} + O_2 \rightarrow Zr^{4+}\square_{surf} - O_2^- \tag{3}$$

$$Zr^{4+}\square_{surf} - O_2^- + \text{carbon black} \rightarrow Zr^{3+}\square_{surf} + \text{products} \tag{4}$$

Furthermore, among zirconium-based supports, Zr-5Y600 is the most active one whereas the other supports present similar activities. In a previous study [17], it has been shown that the number of anionic vacancies, created by the substitution of Zr^{4+} by Y^{3+}, in yttria-stabilized zirconia solids depends on the yttrium contents (1, 5 or 10% of Y_2O_3). EPR measurements evidenced that Zr-5Y600 possesses the highest number of Zr^{3+} species compared to the other zirconium-based supports [17]. Then, in view of steps (3) and (4) of *M2*, the best activity of Zr-5Y600 catalyst is well explained by the highest number of Zr^{3+} and associated anionic vacancies in this sample.

Zirconium and yttrium oxides cannot be used directly for carbon black oxidation, since, for example, carbonaceous selectivity towards CO of 3.2% was measured in the presence of pure zirconia [12] (5.2% without catalyst [18]). In order to inhibit the CO formation, impregnation of copper on these supports was performed. Indeed, it is well known that copper oxide facilitates the CO oxidation into CO_2. Moreover it is expected that copper species activate also the carbon black oxidation since these species are identified as active in many total oxidation reactions.

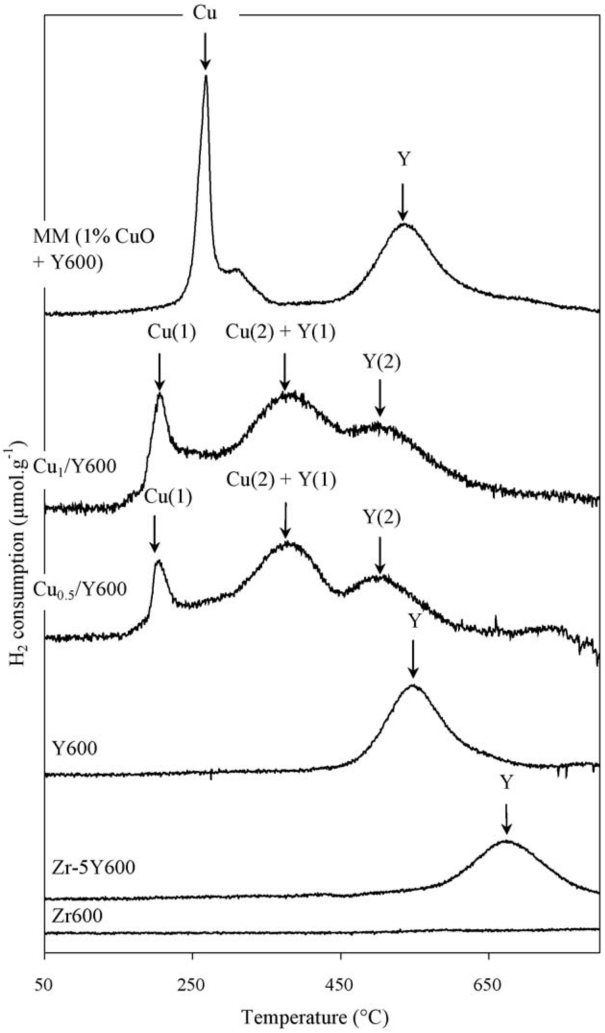

Fig. 2. Temperature programmed reduction (TPR) curves obtained in the presence of mixed oxides (Zr600, Zr-5Y600 and Y600) and in the presence of yttria modified by different copper loadings and mm (1%CuO + Y600) sample.

3.2. Carbon black combustion on different simple and mixed zirconia–yttria supports impregnated by copper

3.2.1. Support effect on 0.5 wt.% copper impregnated catalysts

Fig. 3 displays the DTA curves of carbon black oxidation reaction over 0.5 wt.% copper impregnated on different simple and mixed zirconia–yttria supports.

Two combustion peaks are observed and explained, as for the case of pure supports, by the carbon black combustion into two steps. Taking into account the different maximum peak temper-

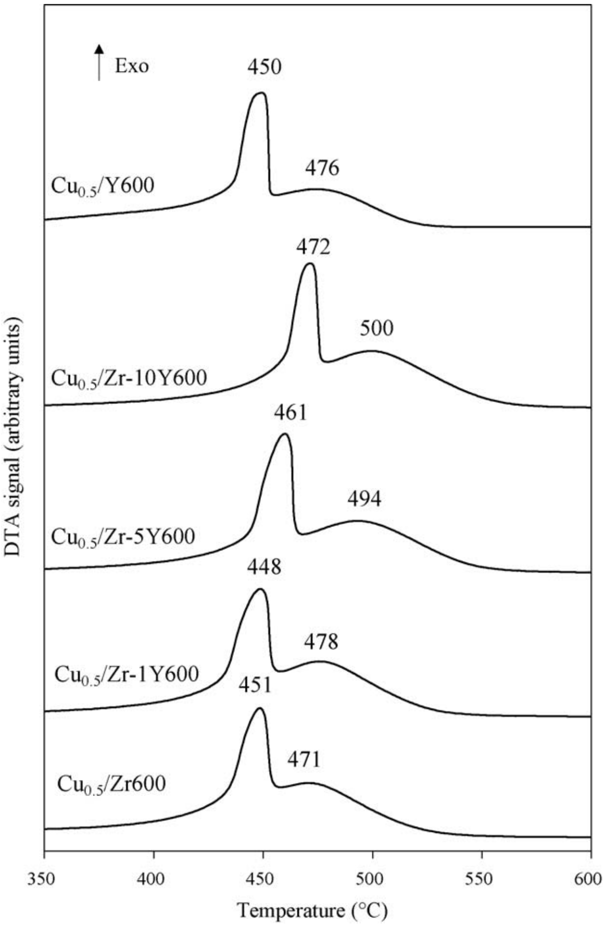

Fig. 3. Differential thermal analysis (DTA) curves of carbon black oxidation in the presence of 0.5 wt.%copper/zirconia–yttria supports.

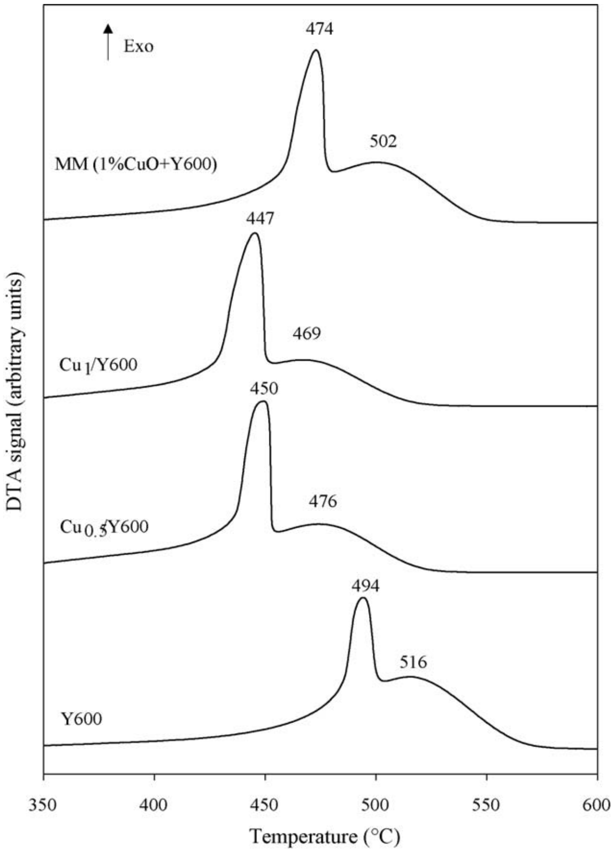

Fig. 4. Differential thermal analysis (DTA) curves of carbon black oxidation on pure yttria support and on yttria modified by different copper loadings.

atures, the following order of catalytic activity can be stated:

$$\mathrm{Cu_{0.5}/Y600} \sim \mathrm{Cu_{0.5}/Zr\text{-}1Y600} \sim \mathrm{Cu_{0.5}/Zr600}$$
$$> \mathrm{Cu_{0.5}/Zr\text{-}5Y600} > \mathrm{Cu_{0.5}/Zr\text{-}10Y600}.$$

The good activity of $Cu_{0.5}$/Y600 could be explained by the relatively low specific surface area of yttria (45 m^2/g), compared to the other supports, which could favour the formation of large particles of CuO. Indeed, many authors have evidenced that CuO species are the copper active species in carbon black oxidation reaction [18,21,22]. It is suggested that CuO species are more accessible to carbon black than dispersed copper species (isolated and clusters) which are rather inactive in this reaction [22].

The mixed supports having higher specific surface areas (respectively of 90 m^2/g, 98 m^2/g and 92 m^2/g for Zr-10Y600, Zr-5Y600 and Zr-1Y600) than pure yttria, large particles of CuO are not formed in these solids [23]. Previous TPR studies [23] evidence the presence of dispersed copper species (isolated and clusters) and of small CuO particles in low interaction with Zr600 and Zr-aY600 supports. Taking into account the step (1) of the first mechanism, $Cu_{0.5}$/Zr600 and/Zr-aY600 catalysts should be more active than $Cu_{0.5}$/Y600 since the reduction of small particles of CuO takes place at lower temperatures than those required to the larger ones reduction [23]. The relative lowest activity observed in the presence of $Cu_{0.5}$/Zr600 and $Cu_{0.5}$/Zr-aY600 is explained by the lowest quantity of CuO species since dispersed copper species like isolated and clusters copper are also formed on these supports [23]. Furthermore, it has been shown that the CuO particles quantity is higher in Zr-1Y600 sample than in Zr-10Y600 and Zr-5Y600: this result is in very good agreement with catalytic activity results which showed that among the Zr-aY600 supports, Zr-1Y600 led to the highest catalytic performance in the carbon black oxidation (Fig. 3).

It must be noticed that taking into consideration the high specific surface area values of the supports and the low copper content in the samples, the carrier surface is certainly partially covered by copper species and therefore we can not exclude the participation of Zr^{3+} sites (according to the second mechanism) in the carbon black oxidation in the presence of $Cu_{0.5}$/Zr600 or $Cu_{0.5}$/Zr-aY600 catalysts.

3.2.2. *Copper content effect on copper impregnated yttria*

Fig. 4 depicts the DTA curves of carbon black combustion on different catalysts yttria modified by copper. It is inferred that catalytic activity of Y600 is enhanced by copper impregnation and the higher the copper content, the better the enhancement. This is explained by the higher quantity of CuO species on the catalyst surface with increasing copper content.

Besides, addition of copper oxide to Y600 by mechanical mixture also enhances its activity, since the maxima of the two combustion peaks of MM (1%CuO + Y600) are, respectively,

Table 1
H_2 consumption (μmol g^{-1}) measured in the presence of different samples during TPR experiments

Samples	Cu		Y	
	Cu(1)	Cu(2)	Y(1)	Y(2)
Zr-5Y600	/		134	
Y600	/		144	
mm (1%CuO + Y600)	140		146	
$Cu_{0.5}$/Y600	32	127		71
Cu_1/Y600	48	134		98

at 474 °C and 502 °C (versus 494 °C and 516 °C for Y600). However, copper impregnation on Y600 even in a lower content leads to better catalytic activity than the mechanical mixture since $Cu_{0.5}$/Y600 is more active than MM (1%CuO + Y600).

As previously mentioned the carbon black oxidation reaction is ruled by two factors. The first one is ascribed to the contact between carbon black and the active phase (CuO). Since CuO surface from the mechanical mixture sample is probably lower than that obtained from the impregnated samples, then the lower activity of MM(1%CuO + Y600) can be firstly clarified by a lower contact between the reactant and CuO. The second factor concerns the reducibility of the active phase. The different TPR curves of copper yttrium samples are depicted in Fig. 2 and the quantitative results of peaks integration are listed in Table 1.

For all the samples, total experimental hydrogen consumption matches well with that required to the total reduction of copper ions into metallic copper (80 and 157 μmol g^{-1} for, respectively, 0.5 and 1 wt.% copper loading samples) and to the partial reduction of Y_2O_3 (experimental value of 144 μmol g^{-1} for pure Y600). For MM (1%CuO + Y600) sample, the first peak (Cu peak) can be attributed to the CuO reduction into Cu whereas the second one corresponds to the support reduction (Y peak). In Cu/Y600 samples, the maximum temperature of copper species reduction peak is lower (Cu(1)) than that of CuO species in the MM (CuO + Y600) sample. Moreover, the quantitative analysis reveals that at low temperatures (around 200 °C) only a part of copper species (Cu(1)) reduced to metallic copper, the remaining Cu^{2+} being reduced at much higher temperatures (Cu(2)). The presence of copper influences the Y_2O_3 reduction when this transition metal is impregnated on this oxide. Indeed, Fig. 2 evidences a support reduction at lower temperatures (Y(1)). This result can be explained by some Y^{3+} ions nearby Cu^{2+} ions when copper is impregnated on Y_2O_3. In fact, H_2 dissociation can be enhanced on copper metal particles previously formed (from Cu(1)) and reduction of some Y^{3+} ions can occur more quickly (Y(1)).

According to the first mechanism in which the step (1) is the rate-determining step, the reducibility of CuO species at lower temperatures but also the easier reduction of Y_2O_3 in Cu/Y600 samples well explains the better catalytic performances of impregnated samples in comparison with that of the mechanical mixture of oxides.

4. Conclusion

For the different zirconium–yttrium solids modified or not by copper addition, evaluated for the oxidation of carbon black, the whole amount of carbon black (20 wt.%) is oxidized before 600 °C. It is shown that zirconia sites are more active than yttria ones for carbon black combustion reaction. Indeed, the presence of original Zr^{3+} sites on the surface of the zirconium-based oxides explains the catalytic results via a redox mechanism involving anionic vacancies: Zr-5Y600 is the most active catalyst because the highest Zr^{3+} defects quantity was detected in this sample. In addition, it is found that the addition of copper (0.5 wt.%) improves mixed and pure oxides activities. It is assumed that the formation of CuO phase, under the form of large or small particles, is responsible for this activity enhancement, CuO species being more active than isolated copper and copper clusters for carbon black oxidation reaction. The highest quantity but also reducibility of the small particles of CuO well explain the difference in the catalytic activity of the mixed oxides impregnated by copper. Besides, addition of copper in different amounts has a beneficial effect on the activity of Y600: the more the quantity of CuO on the catalyst surface, the better the catalytic activity. Nevertheless, this copper oxide should have some interaction with yttria support in order to be more active since simple mixture of copper oxide and yttria is less active than $Cu_{0.5}$/Y600. This interaction increases the reducibility of copper species because the mechanical mixture of copper oxide and pure yttria is also the less reducible copper-based sample.

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