= CATALYTIC REACTION MECHANISMS =

Potential of Supported Copper and Potassium Oxide Catalysts in the Combustion of Carbonaceous Particles¹

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Abstract—Different oxide carriers (TiO₂ and ZrO₂) as supports for low amounts of Cu²⁺ and K⁺ species (2 wt % as equivalent oxide) were tested in the catalytic oxidation of carbon black. The K–Cu/oxide catalysts were shown to have a lower soot combustion temperature than K/oxide, Cu/oxide, and pure oxide carriers. The K–Cu/ZrO₂ catalyst was found to be the most active; it exhibited activity in a loose contact nearly similar to that obtained in a tight contact mode. Physicochemical characterization by EPR, XPS, and TPR revealed the interaction of K⁺ species with Cu²⁺ species and the ZrO₂ carrier in K–Cu/ZrO₂ as well as a strongly distorted Cu²⁺ species on the ZrO₂ surface. The potassium ions ensure promoting effects towards the contact between the carbon black and the catalyst surface. Although potassium ions were found to lower the reducibility of the cupric oxide species, the oxidation rate of carbon black increased in the presence of K/oxide and K–Cu/oxide.

INTRODUCTION

Nowadays, worldwide research efforts are undertaken to lower particulate emissions from diesel engines. The small size of diesel particles ($\leq 2 \mu m$) may be linked to a number of health problems by its ability to penetrate the body through the respiratory system. Among the technologies considered for diesel particulate removal, one way is the use of filters carrying a suitable catalyst, which enables simultaneous soot filtration and combustion in the temperature range 350–400°C.

The catalytic combustion of diesel particles is in principle a solid–solid process where the contact between the catalyst and the soot to be burned out markedly influences the reaction kinetics. For example, Neeft *et al.* [1, 2] showed that Fe_2O_3 is an active catalyst in the "tight" contact mode but shows hardly any activity in "loose" contact. On the contrary, MoO₃ and Sb₂O₃ exhibit activity in loose contact that is only slightly less than what is observed in the tight contact mode. Laboratory preparation of soot–catalyst mixtures by milling yields "tight" contact will typically be loose [3].

In recent studies [4–6], the use of salts and mixed compounds such as Cu–K–Mo–Cl, Cu–K–V, Cu–K–V–Cl, or $K_{0.7}Cu_{0.3}VO_3$ + KCl was proposed. The high activity of these systems at temperatures lower than 400°C has been explained by the formation of low eutectics that melts at the operating temperature, which enables one to obtain a good contact between the active phase and the carbon particles. However, the stability of such catalytic systems is sometimes poor since vapors

of active components could be released from the catalyst under operating conditions.

In this work, we have investigated the potential of stable oxide systems based on supported Cu and/or K oxide species using titania TiO_2 or zirconia ZrO_2 as the oxide carriers. Even if the activity of these systems appeared to be lower than different salts, interesting properties could arise from their higher stability. Moreover, the Cu-K/TiO₂ and Cu-K/ZrO₂ catalysts studied in this work contain low equivalent amounts of CuO or/and K₂O (2 wt %) in order to keep a strong interaction between the oxide carrier surface and the active species after calcination. The activity of K-Cu/oxide was tested in the oxidation of carbon black following both "tight" and "loose" contact conditions. Their catalytic behavior has been correlated to the physicochemical properties, which were investigated by electron paramagnetic resonance (EPR), temperature programmed reduction (TPR), and X-ray pholoelectron spectroscopy (XPS).

EXPERIMENTAL

The titanium oxide carrier was prepared from the hydrolysis of titanium(IV) isopropoxide diluted in 2-propanol following a sol-gel method as described in [7]. Zirconium oxide carrier was obtained by the precipitation method adding an ammonia solution to a ZrOCl₂ solution. The precipitate was washed, filtered, and then dried at 100°C overnight. The resulting solids were calcined under a flow of dry air for 4 h at 600°C. After calcination treatment, ZrO₂ and TiO₂ possessed a specific area of 61 and 6 m²/g, respectively. Supported

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copper systems (Cu/oxide) and supported potassium systems (K/oxide) were obtained, respectively, by impregnation of a Cu(NO₃)₂ solution and a KHCO₃ solution onto the calcined supports (TiO₂ and ZrO₂). A coimpregnation procedure using the previous precursors was performed to prepare the K–Cu/oxide systems. After drying, all solids were calcined for 4 h at 600°C. The amounts of CuO or/and K₂O in the calcined catalysts reached almost 2 wt %.

Carbonaceous particulate materials used for the tests were Carbon Black (CB) N330 provided by DEGUSSA. An elementary analysis revealed the following composition expressed in wt % [C, 97.23; H, 0.73; O, 1.16; N, 0.19; and S, 0.45]. In addition, CB possesses a BET surface area of 80 m²/g. Before the catalytic tests, CB (6 wt %) and catalyst (94 wt %) were mixed in a ball miller for 40 min, designating a tight contact between the carbon and the catalyst surface. To obtain another (CB-catalyst) mixture corresponding to the loose contact conditions, CB (6 wt %) and catalyst (94 wt %) were simply mixed inside a zirconia ball using a teflon stirring rod (light mixing). These latter conditions allowed us to evaluate the activity of oxide catalysts in experimental conditions similar to those of real application, since the soot particles emitted through the exhaust line can only be stopped by the catalyzed filter surface. This contact mode corresponds to loose contact conditions [2, 3].

The catalytic combustion was studied by simultaneous TG-DSC analysis with a NETZSCH STA 409 apparatus. About 50 mg of the CB-catalyst mixtures were loaded into an alumina crucible and heated from 25 to 800°C using a heating rate of 5°C/min in air flow (75 ml/min). As shown in Fig. 1a, by processing the experimental data, the onset temperature (T_i) could be derived (i.e., the temperature at which 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. Additional catalytic tests were performed under isothermal conditions considering the CB-catalyst mixtures in loose contact. Samples were kept under an air flow (75 ml/min) and heated to 400°C (5°C/min). The weight loss rate was used as a measure for the CB oxidation rate (Fig. 1b) in agreement with the experimental approach described by van Setten et al. [8]. Once the combustion starts, the oxidation rate progressively increases. Then, a part of the TG curve that is practically linear permits one to calculate the oxidation rate value that corresponds to a maximum (w, $\mu g/(g_{CB initial} s)$). The oxidation rate then decreases to zero. The analysis of combustion products was performed evaluating the $CO/(CO + CO_2)$ molar ratio from a Varian 3600 chromatograph coupled to the thermobalance.



Fig. 1. Examples of thermal analysis curves recorded for the catalytic test of (CB–catalyst) mixtures: (a) nonisothermal conditions, (b) isothermal conditions.

Electron paramagnetic resonance (EPR) measurements of the calcined catalysts were performed at -196° C on an EMX Bruker spectrometer, using a cavity operating with 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 saturation effects. The g values are determined from the precise frequency and magnetic field values.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Leybold–Heraeus LHS 10 spectrometer equipped with an Al K_{α} anticathode (hv =1486.6 eV). The binding energies were determined by using the Zr $3d_{5/2}$ peak at 182 eV as standardization for ZrO₂-based catalysts and the Ti2 $p_{3/2}$ peak at 458.5 eV for TiO₂-based catalysts.

Temperature programmed reduction experiments were performed on a Micromeritics Autochem 1900 apparatus. The catalyst sample (75 mg) was first treated *in situ* under O₂ diluted in argon flow at 450°C for 1 h. After cooling under argon flow, reduction treatment (3% H₂ in argon) was performed with a total flow of



Fig. 2. (a) TG-DSC curves obtained for the tests of (CB + TiO₂-based catalyst) mixtures in air flow: mixtures prepared following loose contact conditions: (*I*) TiO₂, (*2*) Cu/TiO₂, (*3*) K/TiO₂, (*4*) K–Cu/TiO₂; (b) TG-DSC curves obtained for the tests of (CB + ZrO₂-based catalyst) mixtures in air flow: mixtures prepared following loose contact conditions: (*I*') ZrO₂, (*2*') Cu/ZrO₂, (*3*') K/ZrO₂, (*4*') K–Cu/ZrO₂.

30 mL/min from 25 to 700°C with a heating rate of 10° C/min.

RESULTS

Catalytic Combustion of Carbon Black

Figures 2a and 2b show TG-DSC curves obtained for the test of (CB-TiO₂-based catalysts) and (CB-ZrO₂-based catalysts) mixtures, respectively, which correspond to a loose contact mode. For the noncatalyzed reaction, we observed that the combustion of CB in air flow occurred regularly between $T_i = 530^{\circ}$ C and $T_{\rm f}$ = 635°C. The results obtained in the presence of pure titania or pure zirconia indicated the low reactivity of these oxide carriers. In the case of Cu/oxide catalysts, the presence of a copper oxide phase only slightly improved the reactivity of the corresponding systems. Nevertheless, we can observe (Fig. 2) that the lowering in reaction temperature is greater with the TiO₂-based catalyst than the ZrO₂-based catalyst. Indeed, the reaction temperature range for Cu/ZrO₂ and ZrO₂ exhibits only little difference.

In the case of K/oxide catalysts, we obtained that the oxidation reaction occurred between $T_i = 440^{\circ}$ C and $T_f = 500^{\circ}$ C for K/TiO₂ and between $T_i = 405^{\circ}$ C and $T_f = 505^{\circ}$ C for K/ZrO₂. These results indicate that the potassium oxide species provide nearly identical effects toward the reactivity in the oxidation of carbon black whatever the nature of oxide carrier ZrO₂ or TiO₂. The presence of a potassium oxide species leads to a high improvement of the reactivity of the catalytic systems. 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 observe the shift toward lower temperatures, which was

nearly 160°C between the test performed with $K-Cu/TiO_2$ and TiO_2 and nearly 200°C between the test performed with $K-Cu/ZrO_2$ and ZrO_2 . The catalyst $K-Cu/ZrO_2$ appeared then as the most reactive system for the oxidation of carbon particles studied in this work.

In addition, we have compared these catalytic test results with the ones obtained when CB–catalyst mixtures resulted from ball miller agitation ("tight contact"). The corresponding results are displayed in Fig. 3. In the case of pure oxide carrier and Cu/oxide systems (i.e., ZrO₂, TiO₂, Cu/TiO₂, and Cu/ZrO₂), the conversion of carbon black occurred in a lower temperature range for the mixtures (CB–catalyst) in tight contact than for the mixtures in loose contact. It indicates that the contact between carbon black and the catalyst surface has to be created by the physical force obtained from ball milling in order to obtain a lower reaction temperature.

For catalysts containing potassium ions, the results obtained revealed in each case higher activity in loose contact in comparison with copper-based catalysts (Cu/oxide) tested in tight contact conditions. Moreover, Fig. 3a shows a similar reactivity of K/TiO₂ toward the carbon oxidation whatever the contact mode; the reactivity in loose contact is nearly similar for Cu-K/TiO₂ and K/TiO₂. It can be seen that the conversion of carbon can be obtained at a lower temperature if the mixing of CB and the catalyst is performed by ball milling with K–Cu/TiO₂. On the contrary, the catalytic behavior of $K-Cu/ZrO_2$ is different since its reactivity is high and very similar whatever the contact mode. These comparisons clearly show that a high reactivity of potassiumcontaining catalysts can be obtained ($T_i = 370^{\circ}$ C, $T_f =$ 445°C) in this oxidation reaction even if a loose contact exists between the carbon black and the catalyst sur-



Fig. 3. Effect of metal oxide catalysts in tight (---) and loose (—) contact mode on the combustion temperature of carbon black: (a) TiO_2 -based catalysts, (b) ZrO_2 -based catalysts.

face. To sum up, Cu/TiO_2 and $Cu-K/TiO_2$ are active catalysts mainly in tight contact mode. The K–Cu/ZrO₂ catalyst, on the contrary, exhibits a high activity in loose contact mode that is closely similar to the activity in tight contact.

To compare the oxidation rate of CB in the presence of the different catalysts, CB oxidation tests were performed under isothermal conditions at 400°C (Table 1). This temperature value was chosen taking into account the results obtained under nonisothermal conditions. At 400°C, although low oxidation rates should be expected for pure oxide supports, the effect of the copper and/or potassium species appeared to be of main interest. Table 1 gathers the CB oxidation rate values obtained in the presence of the different catalysts. It appeared that Cu/TiO₂ allows one to obtain a higher CB oxidation rate than Cu/ZrO₂. The two K/oxide catalysts provided a similar oxidation rate close to 110 $\mu g/(g_{CB initial} s)$. The results clearly show that the highest rates are obtained for catalysts containing both copper and potassium species. However, an important difference in the oxidation rate is revealed between K–Cu/TiO₂ (173 μ g/(g_{CB initial} s)) and K–Cu/ZrO₂ (379 μ g/(g_{CB initial} s)). Thus, these data show that potassium species have a role in providing high oxidation rates in the CB oxidation reaction. Finally, the interest in combining copper and potassium species in such oxide systems is clearly revealed.

Regarding the combustion products, it can be mentioned first that a selectivity of $CO/(CO + CO_2)$ of 5.2% was obtained for the combustion of CB performed in the absence of catalyst. In the case of loose contact and tight contact CB–catalyst mixtures, carbon monoxide (CO) was detected in low amounts in the presence of TiO₂ (loose, 4.5%; tight, 4.1%), ZrO₂ (loose, 3.6%; tight, 3.2%), and Cu/ZrO₂ (loose, 3.1%; tight, 2.8%). On the contrary, whatever the contact mode, the analysis of combustion products in the presence of Cu/TiO₂ and all potassium-containing catalysts revealed that only CO₂ was formed.

Due to the differences in catalytic behavior evidenced for the TiO_2 -based and ZrO_2 -based catalysts, investigations on the physicochemical properties of the catalysts will be undertaken in order to reveal eventual differences between the copper and potassium supported species stabilized in these systems and to get a better understanding of the reaction mechanism involved in the oxidation of carbon black in the presence of such catalysts.

Characterization of the Catalysts

1. Electron paramagnetic resonance (EPR). Figure 4a shows the *X*-band EPR spectra of Cu/TiO₂ and K–Cu/TiO₂ catalysts. For Cu/TiO₂, the spectra relative to Cu²⁺ species are the superimposition of three signals denoted *H*, *L*, and *I*. All these signals were studied and attributed earlier [7]. A signal with well-resolved hyperfine structure (*H* signal) is characterized by parameter values $g_{zz} = 2.32$, $g_{yy} = 2.09$, $g_{xx} = 2.10$, $A_{zz} = 75$ G, $A_{yy} = 26$ G, and $A_{xx} = 19$ G. This signal has been

 Table 1. Oxidation rates of CB determined from tests performed under isothermal conditions at 400°C: (CB-catalyst) mixtures in loose contact mode

TiO ₂ -based catalysts	Oxidation rate of CB, µg/(g _{CB initial} s)	ZrO ₂ -based catalysts	Oxidation rate of CB, µg/(g _{CB initial} s)
TiO ₂ support	12	ZrO ₂ support	6
Cu/TiO ₂	48	Cu/ZrO ₂	15
K/TiO ₂	109	K/ZrO ₂	116
K–Cu/TiO ₂	173	K-Cu/ZrO ₂	379

Sample	Binding energy, eV			Surface atomic ratio*			
	Cu 2p _{3/2}	K 2p _{3/2}	Ti 2p _{3/2}	Zr 3d _{5/2}	Cu/M	K/M	Cu/K
K–Cu/TiO ₂	933.9	293.1	458.5	-	0.075	0.19	0.39
K-Cu/ZrO ₂	933.9	293.5	-	182	0.15	0.17	0.88
* M = Ti or Zr.							

Table 2. Binding energy (BE) for Cu $2p_{3/2}$, K $2p_{3/2}$, Ti $2p_{3/2}$, and Zr $3d_{5/2}$ levels and surface atomic ratio of different elements in K–Cu/oxide catalysts

attributed to Cu^{2+} ions located in orthorhombic symmetry sites [7]. Corresponding Cu^{2+} species could be Cu atoms in substitution positions of Ti⁴⁺ ions in the rutile structure. A second signal, designated as the *L* signal, is



Fig. 4. (a) X-band EPR spectra recorded at 77 K of Cu/TiO_2 and K–Cu/TiO₂ catalysts (M = Zr, Ti); (b) X-band EPR spectra recorded at 77 K of Cu/ZrO_2 and K–Cu/ZrO₂ catalysts.

relative to an axial symmetry ($g_{\parallel} = 2.25$ and $g_{\perp} = 2.06$) and can be ascribed to Cu²⁺ ions in interaction inside small aggregates [7]. Finally, a third signal (I signal) is broad and isotropic, centered at $g_{iso} = 2.65$ with $\Delta H =$ 1380 G. It can be attributed to Cu^{2+} species present in large agglomerates in Cu/TiO₂ solids [7]. In the case of K-Cu/TiO₂, only an intense axial symmetry signal, similar to the *L* signal ($g_{\parallel} = 2.25, g_{\perp} = 2.06$) is observed. Besides, the intensity of the EPR signal relative to the Cu²⁺ species is much higher for K-Cu/TiO₂ than Cu/TiO₂, although the two samples possess the same copper content. In fact, as mentioned in a previous study on different Cu/oxide systems [9], the formation of CuO crystallites, which are EPR silent, on the catalyst surface can explain the decrease of the effective intensity of the isolated Cu²⁺ species signal. Because of the low EPR signal intensity obtained for the Cu/TiO₂ sample, it has been suggested that this catalyst contains more CuO crystallites than the K–Cu/TiO₂ catalyst. In fact, Cu/TiO₂ and K-Cu/TiO₂ were prepared using a TiO₂ carrier, which possesses a low specific surface area (6 m^2/g). This parameter may account for the poor dispersion of Cu²⁺ ions and thus the formation of CuO crystallites in Cu/TiO₂. However, the EPR signal intensities indicate the presence of dispersed Cu²⁺ species in higher amounts in K–Cu/TiO₂ than in Cu/TiO₂. This observation reveals that potassium ions allow the dispersion of copper species on the TiO₂ surface to increase. In fact, according to Boccuzzi et al. [10], it has been suggested that the preparation method, and particularly the acido-basic medium of the impregnating solution, influences the dispersion degree of the copper species. In our case, the potassium salt used for the preparation of K-Cu/TiO₂ increases the pH value of the impregnating solution above the zero point charge of TiO_2 and hence, favors the dispersion of the copper species on the catalyst surface.

EPR signals obtained for Cu/ZrO₂ and K–Cu/ZrO₂, shown in Fig. 4b, are very similar. A signal at g = 4.27 was attributed to Fe³⁺ present as a minor impurity in the ZrO₂ carrier. A second signal, characterized apparently by $g_{\parallel} = 1.956$ and $g_{\perp} = 1.973$, was ascribed to Zr³⁺ ions isolated in octahedral sites and constituting defects of the ZrO₂ carrier. It should be noted that these signals were widely described in a previous work devoted to the study of undoped zirconium oxide treated at differ-

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ent temperatures [11]. The spectrum obtained also shows the presence of two intense signals, denoted H'and L, corresponding to Cu^{2+} species. An axial symmetry signal with hyperfine structure (H' signal) was characterized by $g_{\parallel} = 2.358$, $A_{\parallel} = 113$ G, and $g_{\perp} = 2.058$. From the parameter values, the H' signal corresponds to isolated Cu²⁺ ions situated in octahedral symmetry sites with strong distortions, in agreement with observations of Kulyova et al. [12]. The same observations were also mentioned by Liu et al. [13] for Cu/ZrO₂ systems containing low amounts of copper oxide similar to the Cu/ZrO_2 and K– Cu/ZrO_2 systems studied in this work. This high distortion of the Cu^{2+} sites (*H* signal) allows us to suggest the strong interaction of the corresponding copper species with the ZrO_2 carrier. The second signal relative to the Cu²⁺ species is nearly similar to the *L* signal centered at $g_{iso} = 2.12$, indicating the presence of small aggregates of the Cu²⁺ species. Finally, the EPR signal intensities appeared to be of the same order for the Cu/ZrO₂ and \overline{K} -Cu/ZrO₂ samples. The EPR data seem to show that the Cu²⁺ species could occupy the same sites in the two ZrO₂-based catalysts and that the presence of potassium does not modify the distribution of copper species on the surface. For these reasons, it has been suggested that the relatively high specific area of the ZrO_2 carrier (61 m²/g) should be a parameter accounting for the good dispersion degree of Cu^{2+} species, even in the case of the Cu/ZrO₂ sample.

2. X-ray photoelectron spectroscopy (XPS). Table 2 gathers the values of binding energies (BE) for different levels of elements contained in K-Cu/oxide catalysts as well as surface atomic ratios obtained from XPS analysis. The BE value of the principal photopeak (PP) of Cu $2p_{3/2}$ was 933.9 eV, which corresponds to the typical value reported for Cu²⁺ ions. In fact, the Cu $2p_{3/2}$ signal also possesses a satellite component (SAT), characteristic of Cu²⁺ species. According to D'huysser *et al.* [14], qualitative information on the environment of the Cu²⁺ ions can be obtained from the ratio between the intensities of the satellite component and the principal photopeak: $(I_{\text{SAT}}/I_{\text{PP}})$ Cu $2p_{3/2}$ ratio. To obtain this information, the spectra were smoothed by the Fourier method to improve the signal-to-noise ratio and the peaks were then integrated after linear background subtraction. The value of the (I_{SAT}/I_{PP}) Cu $2p_{3/2}$ ratio generally varies between 0.55 and 0.85 when the Cu^{2+} ion possesses an octahedral or a tetrahedral environment, respectively. In our case, for both the Cu-K/TiO₂ and Cu–K/ZrO₂ samples, the (I_{SAT}/I_{PP}) Cu $2p_{3/2}$ ratio value reached 0.57, which clearly corresponds to an octahedral environment. The BE value of the K $2p_{3/2}$ level reached a value superior to 293 eV for the two samples, and particularly in the case of K-Cu/ZrO₂ (293.5 eV), which reveals an important cationic character of the K⁺ ions. Similar BE values for the K $2p_{3/2}$ level have been reported in K/TiO₂ systems [15, 16] with different K contents. High BE values of the K $2p_{3/2}$ level were observed for dispersed K species interacting with the oxide carrier surface, whereas for a higher K content, a BE value of K $2p_{3/2}$ at 292.6 eV was attributed to a change in the dispersion mode and the presence of K–O–K bonds. In the present study, the BE values obtained suggest that potassium species are mainly interacting with the carrier surface in both Cu–K/TiO₂ and Cu–K/ZrO₂ samples.

The surface atomic ratio K/Ti reached 0.19 and appeared to be a value similar to that obtained for dispersed potassium species on the TiO₂ carrier surface, according to the results of our previous study [15]. In addition, an indication on the dispersion of copper species could be obtained from the value of the Cu/K atomic ratio, since copper and potassium were coimpregnated on the surface carrier previously calcined at 600°C. Whereas a homogeneous distribution of both Cu²⁺ and K⁺ on carrier surfaces would be characterized by a value Cu/K = 0.59, we noticed a surface atomic ratio deduced from XPS Cu/K = 0.39 for the K–Cu/TiO₂ sample. This result is due to the low intensity of the Cu $2p_{3/2}$ photopeak, which could be explained taking into account a "tower" model [17]. In this case, such an observation is in agreement with the presence of copper atoms inside copper oxide aggregates. In a K–Cu/ZrO₂ sample, on the contrary, a high intensity of the Cu $2p_{3/2}$ component implies that a Cu/K atomic ratio value of 0.88 was obtained. It means that Cu^{2+} ions could be well dispersed on the ZrO₂ surface. This result appeared in good agreement with the EPR data described above.

3. Temperature programmed reduction (TPR) measurements. Copper-based catalysts were characterized by TPR with hydrogen as the reducing gas. The resulting TPR patterns are shown in Fig. 5. For Cu/oxide catalysts, peaks around 140°C (138°C for Cu/ZrO_2 and 146°C for Cu/TiO_2) were observed as well as a peak at 219°C, which was only obtained for the Cu/TiO_2 catalyst. The single type of copper species present in Cu/ZrO₂ is easily reducible. In fact, similar species still have been observed by Shimokawabe et al. [18] and Zhou et al. [19] in calcined systems with nearly the same equivalent CuO content. These authors ascribed these species to highly dispersed copper species. In the case of solid Cu/TiO₂, it has been suggested that the minor species leading to the peak at 146°C could correspond to Cu^{2+} dispersed species on the TiO₂ surface. The assignment of the species responsible for the peak at 219°C can be proposed taking into account the EPR results, which demonstrated that CuO crystallites were stabilized in a Cu/TiO₂ catalyst. In fact, the reduction of CuO generally occurred at a temperature close to 350°C in H₂ TPR experiments; however, the small size of the particle and/or the interaction of the particle with the carrier surface are parameters that could explain the reducibility. For this reason, it has been suggested that the peak at 219°C observed for Cu/TiO₂ could correspond to the presence of small CuO particles. The difference observed here between Cu/ZrO₂ and Cu/TiO₂ appeared in good agreement with the EPR data showing the presence of higher amounts



Fig. 5. H₂ TPR profiles of Cu-based catalysts: (1) Cu/TiO₂, (2) K–Cu/TiO₂, (3) Cu/ZrO₂, and (4) K–Cu/ZrO₂.

of isolated Cu^{2+} species in Cu/ZrO_2 , whereas the presence of CuO crystallites was put forward in the case of Cu/TiO₂.

In the presence of potassium, the peaks were globally obtained in a higher temperature range, centered around 270-275°C for the two K-Cu/oxides. The fact that the main peak for K-Cu/oxide was obtained at nearly the same temperature whatever the type of oxide carrier revealed the presence of copper species similarly influenced by potassium ions in the two catalysts. However, it is important to notice the presence of a shoulder in the main reduction peak of Cu-K/ZrO₂, which indicates the presence of a second peak at 202° C. Although potassium oxide species induced a strong decrease of the reducibility of copper species, it could be suggested that the peak at 202°C could correspond to dispersed copper species interacting with the ZrO_2 surface carrier. This attribution also appeared to be supported by the high Cu/Zr surface atomic ratio revealed by XPS measurements and the presence of isolated Cu^{2+} species in interaction with ZrO_2 evidenced by EPR for both Cu/ZrO₂ and Cu–K/ZrO₂.

Finally, we observed that the H₂ consumption was higher for the K–Cu/oxide than the Cu/oxide samples, which is visible in Fig. 5 from the profile of the peak centered at 270–275°C. In fact, for the Cu/oxide samples, it appeared that the H₂ consumption closely corresponds to the complete reduction of the Cu²⁺ species to give Cu⁰. Indeed, the H₂ consumption reached 247 μ mol/g_{catalyst} for Cu/TiO₂ and 240 μ mol/g for Cu/ZrO₂, whereas the theoretical H₂ consumption expected is 251 μ mol/g. In the case of K–Cu/oxide

samples, we found H_2 consumptions of 278 μ mol/g for K-Cu/TiO₂ and 374 µmol/g for K-Cu/ZrO₂, due mainly to the broad reduction peak at 270-275°C. However, such values cannot be explained only by the reduction of Cu²⁺ species. To explain the difference in H₂ consumption when potassium ions are present in Cu-based systems, K/oxide and pure oxide samples have been characterized by TPR. These experiments showed that a slight H₂ consumption started at a temperature higher than 400°C only in the case of the K/oxide samples. It demonstrates that potassium species could be responsible for the H₂ consumption, which could probably occur at a lower temperature in the presence of copper species. Consequently, it is suggested that the high H_2 consumption obtained for Cu–K/oxide could be explained not only by the reduction of Cu²⁺ species but also by the reduction of oxygen species stabilized by the chemical interactions between copper and potassium ions on the support surface. Moreover, the difference in H_2 consumption obtained for K-Cu/TiO₂ and K-Cu/ZrO₂ may be related to the difference in the specific area of the oxide supports. The influence of specific area on the amount of reducible species of potassium-copper-based oxide systems will be the subject of future studies.

DISCUSSION

The catalytic results reported in this work can be discussed considering the nature of the copper and potassium species and their properties following the type of oxide support. First, we showed that TiO_2 and

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 ZrO_2 were practically inactive in the oxidation of carbon black under loose contact CB-catalyst conditions, i.e., the realistic conditions encountered in a soot oxidation reaction. In the case of Cu/oxide, a significant increase in catalyst activity in comparison with pure oxide was obtained only for Cu/TiO₂ tested in tight contact conditions. From the EPR and TPR data, it was shown that Cu/TiO_2 contains copper species in the form of copper oxide crystallites, whereas Cu/ZrO₂ contains well-dispersed Cu²⁺ species instead. In a previous study [9], we established a correlation between the catalytic behavior and the nature of Cu²⁺ species for different copper-based systems supported on CeO_2 , ZrO_2 , Al_2O_3 , and TiO_2 . It was shown that the presence of copper oxide crystallites in Cu/oxide systems could explain the increase in activity observed, partially due to the contact ensured by CuO particles with carbon black under tight contact conditions. In addition, copper oxide species are involved in the reaction via a redox mechanism in agreement with different works still reported in the literature for the oxidation of graphite [20] and in soot combustion [21]. In the present work, the low amount of copper in the samples is the main explanation of the relatively low activities of the Cu/oxide catalysts.

On the contrary, potassium ions induced promoting effects in the catalyst leading to increases in the activity and oxidation rates of carbon black (Fig. 2, Table 1). It appeared that potassium enables creation of a good contact between the catalyst and the carbon black under operating conditions. According to Querini et al. [22], the mobility of potassium oxide species can play a role in increasing the catalyst-soot contact. In our case, this phenomenon could occur at a temperature corresponding to the beginning of combustion, i.e., around 370 to 440°C following the different K-based catalysts. On the other hand, the interaction of potassium ions with the oxide carriers should be considered to explain the high reaction rates obtained. Indeed, in a previous study [15, 23], the role of potassium toward dissociative adsorption was investigated by means of surface potential measurements in the presence of oxygen performed on TiO_2 and K/TiO_2. Compared to pure TiO_2, we showed that potassium species lower the surface potential, which means that it decreases the energy required to obtain electron transfers with the oxide carrier. Consequently, it appeared that it was possible to detect the dissociation of gaseous oxygen to form surface O²⁻ species at relatively low temperatures (~310°C) for K/TiO₂, whereas it occurred from 400°C for pure TiO₂. Hence, potassium species were found to facilitate the dissociative adsorption of gaseous oxygen, which is known to be a parameter influencing oxidation reaction rates [24]. In our case, it has been suggested that such properties of the potassium species may be involved in the catalytic combustion of carbon black, at least in the presence of K/oxide systems. In addition, the contribution of the redox properties of copper oxide species in the catalytic combustion of carbon particles could also account for the high activity of K-Cu/oxide catalysts

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particularly evidenced for K–Cu/ZrO₂ in loose contact. Indeed, it cannot be excluded that potassium species introduced in copper-based catalysts can facilitate the reoxidation of active copper species involved in the catalytic reaction.

CONCLUSIONS

An investigation of the potential of stable systems based on Cu and K oxide species using TiO_2 and ZrO_2 as the carrier revealed the high reactivity of these systems in the catalytic combustion of carbon black. The high reactivity of K-based catalysts in loose contact is partially related to the interaction and the contact provided by the potassium species between the catalyst and the carbon black. In the case of K/oxide catalysts, potassium species are also responsible for an increase in the catalytic oxidation rate related to the fact that the dissociative adsorption of oxygen is facilitated on the catalyst surface.

Combining copper and potassium as an active phase in K–Cu/oxide systems leads to improvements in the catalytic properties in this reaction. Further investigations are in progress to optimize the copper and potassium contents of ZrO₂-based systems as well as to evaluate their stability in the catalytic combustion of carbon black.

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