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Carbon black oxidation in the presence of Al_2O_3, CeO_2, and Mn oxide catalysts: An EPR study

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Abstract

Carbon black oxidation in the presence of CeO_2, Al_2O_3 and manganese oxide catalysts has been studied in tight contact conditions. In the presence of manganese based catalysts, the temperature gain is about 275 °C compared to the non-catalysed carbon black oxidation. The contribution of the manganese species to enhance the reactivity of carbon black oxidation has been evaluated by EPR technique. For Mn/Ce + CB mixtures the Mn^{2+} content considerably increases consequently to tight milled treatment indicating the reduction of some manganese species with higher oxidation states into Mn^{2+} ions. This phenomenon can be considered as the first step in the carbon black oxidation mechanism in the presence of Mn/Ce catalysts.

Keywords: Catalyst; Reactivity; Carbon black; CeO_2; Al_2O_3; Mn oxides; EPR

1. Introduction

In literature, various types of physical contact are used for catalytic soot oxidation. In general, the 'loose contact' mixtures present a high combustion temperature, while samples prepared with 'tight contact' show lower combustion temperature [1]. Since the degree of physical contact plays an important part in the oxidation process, the nature of this contact should be evidenced. It was shown that under practical conditions the contact between soot and catalyst is poor [2]. The preparation method of the carbon black mixtures with the catalyst gives more tight contact than the real conditions. However, the use of mechanical mill to establish close contact between soot and catalyst is necessary for the kinetics studies of carbon black oxidation in order to obtain reproducible and comparable results [3].

Among the metal oxide catalysts, manganese oxides have been used in many applications such as the oxidation reactions due to the ability of manganese to change valence in response to changing of oxygen environment [4]. Alumina (Al_2O_3) is often used as a support in oxidation catalysts due to its thermal stability and significant specific area surface [5]. Cerium oxide (CeO_2) is widely used as a promoter in automobile catalysts due to its oxygen storage capacity (OSC), its redox properties (Ce^{4+}/Ce^{3+}) and its thermal stabilizing influence on alumina [6,7]. The presence of cerium additives favours the reactivity of the doped soot and shifts the oxidation reaction towards low temperatures [8]. Cerium-coated traps are also found to be effective for catalytic soot oxidation [9].

Several studies have shown that carbon black and its derivatives show that an EPR signal constituted by a single line at different widths depending on the carbon and on the experimental treatment [10–13]. The EPR parameters of this signal are $g = 2.002$–2.005 and the line-width $\Delta H = 7$–100 G. The paramagnetic centres originate by mobile unpaired electrons within the carbon structure or at the surface forming free radicals. It was indicated that the EPR line-width and the unpaired spin density may be related to the surface area, molecular structure, particle size and defect characteristics. The increase in line-width is attributed to the formation of carbon–oxygen complexes. Thus, EPR technique can serve as a method for carbon black investigation.

In the present work, the EPR study is focused on the mixtures of carbon black with CeO_2, Al_2O_3, Mn/CeO_2 and Mn/Al_2O_3 in tight contact, to evaluate the consequences on the catalytic oxidation of carbon black.

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2. Experimental

2.1. Catalysts preparation

Cerium hydroxide $Ce(OH)_4$ was prepared from cerium(III) nitrate hexahydrated solution $Ce(NO_3)_3{\cdot}6H_2O$ (Prolabo) 0.232 M with an alkali solution of NaOH 1 M. The resulting hydroxide $Ce(OH)_4$ was filtered, washed and dried about 20 h in a drying oven at 100 °C and calcined at 500 °C under dried air (35 mL min^{-1}) for 4 h.

Alumina (Al_2O_3) was synthesized by sol–gel method [14]. Secondary aluminum butylate ($Al(OC_4H_9)_3$, Fluka, ~11.0 wt.% Al) was dissolved in butan-2-ol (Fluka, purity ≥99.5%) at 85 °C. Then, complexing agent (butan-1,3-diol, Fluka, purity ≥98%) preliminary heated at 60 °C was added before hydrolysis. Hydrolysis was performed by adding water to the solution at 85 °C. The gel was dried and calcined at 600 °C under oxygen flow (75 mL min^{-1}) for 4 h with a temperature rate of 0.5 °C/min.

The manganese was added by wet impregnation of Mn(II) nitrate solution over CeO_2 and Al_2O_3 oxides with different atomic ratios Mn/Ce = 10^{-4}; and 0.05 and Mn/Al = 10^{-4}; and 0.05. These catalysts were dried about 20 h in a drying oven at 100 °C and calcined at 500 °C under dried air (35 mL min^{-1}) for 4 h.

2.2. 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) was used as a model soot. The average diameter of the CB spherical particle is 0.08–0.25 μm. It was mixed with catalyst in an alumina ball miller for 40 min. The content of carbon black in the mixture was 5%.

Oxidation tests were studied by simultaneous gravimetric and differential thermal analysis (TG–DTA) with a NETZSCH STA 409 apparatus. About 10–50 mg of the CB/catalyst mixture was loaded in an alumina crucible and heated from room temperature to 600 °C (5 °C/min) in air flow (75 mL/min).

2.3. EPR measurements

The electron paramagnetic resonance (EPR) measurements were performed with 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 and the power supply was sufficently small to avoid saturation effect. The measurements were performed at room temperature and at 77 K. The *g* values were determined from precise frequency and magnetic field values. EPR intensity was given by the normalized double integration of the EPR signal.

3. Results and discussion

3.1. Catalytic oxidation of CB

Fig. 1 shows the TG–DTA curves of carbon black in the presence of different catalysts. The T_{max} in a DTA curve indicates the temperature at which the highest combustion rate is reached. In the absence of catalyst, 5% carbon black with SiC showed a T_{max} of 622 °C. Insignificant catalytic effect (T_{max} = 607 °C) was observed when the reaction was performed in the presence of Al_2O_3 due to the high stability of alumina. Comparable results have been observed in literature for CB with SiC and in the presence of alumina in similar experimental conditions [15,16]. When the manganese was impregnated with 10^{-4} of atomic ratio over Al_2O_3, the T_{max} decreased to 572 °C. With the increase of the manganese content until 5% atomic ratio, the combustion temperature decreased of about 53 °C. The characteristic temperatures of CB oxidation in the presence of cerium oxide are shifted to the low-temperature region (390 °C). With 10^{-4} Mn impregnated on ceria surface, the T_{max} decreases about 25 °C (T_{max} = 366 °C). When the percentage of impregnated manganese increases (5%), the T_{max} decreases to 346 °C. Thus the T_{max} depends on the type of the catalyst support and the percentage of manganese in the solid.

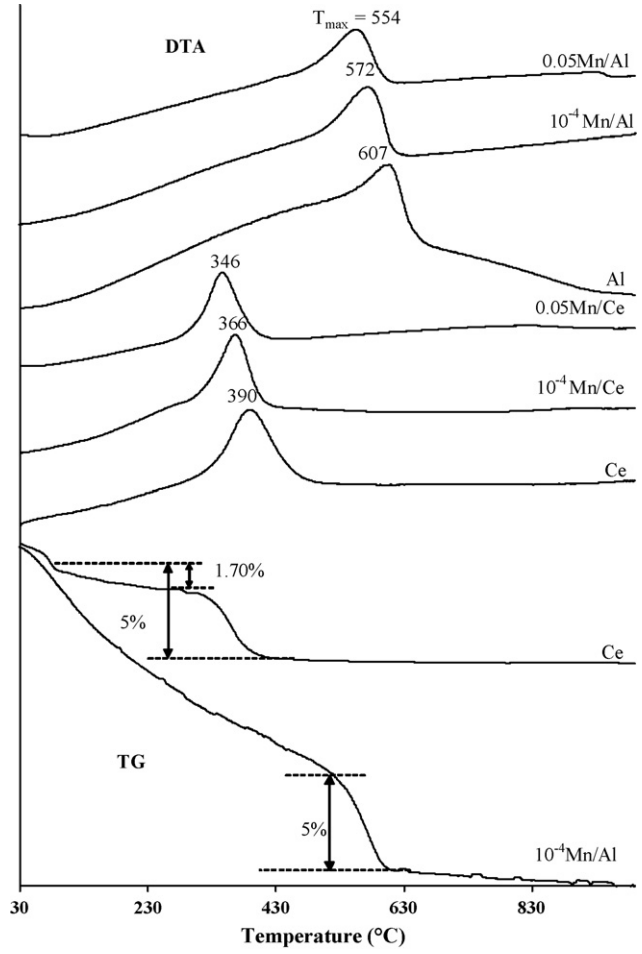

Fig. 1. TG–DTA curves of different catalyst + 5% CB mixtures in tight contact conditions.

In parallel, on the TG curve of CeO_2 + 5% CB a weight loss corresponding to the oxidation of the total mass of carbon black is observed. In addition, one can see that in the range of 100–250 °C, a weight loss equal to 1.7% occurs. This latter corresponds to 34% of total CB weight in the sample and can be related first to the effect of CeO_2 as an oxygen storage catalyst,

and second to the tight contact between CeO_2 and CB suggesting the first step in the mechanism of CB oxidation in the presence of cerium oxide. Similar data have been observed in such conditions and attributed to the high reactivity of ceria–CB interface species [17]. In addition, the catalytic reaction continue at higher temperatures taking advantage of heat diffusion related to the partial oxidation of CB in the range of 100–250 °C. Therefore, the catalytic proprieties of cerium oxide play an important role leading to important shift of CB combustion temperature particularly in tight contact conditions [17,18]. Two general mechanisms have been proposed to account the diversified catalytic effects of metals and oxides in carbon oxidation: electron-transfer and oxygen-transfer mechanisms [19,20]. Several experimental facts such as:

(i) CeO_2 is an active catalyst only in tight contact conditions with carbon black [16,18],
(ii) the formation of an interface reactive species between ceria and CB [17],
(iii) the presence of O_2^- species on ceria surface [21]

have already permit to conclude in favour of oxygen-transfer mechanisms.

TG curves relative to CB + Mn/Ce mixtures have similar shapes as CB + Ce sample. The weight loss in the case of alumina based samples; 10^{-4} Mn for example, is about 12.6%. A weight loss of 5% is due to the oxidation of CB and the rest (7.6%) may be related to the water desorption starting from ~50 °C. In fact, sol–gel alumina is a very hygroscopic material with high specific area (~320 $m^2\ g^{-1}$).

3.2. EPR measurements

EPR spectra of ions with $S > 1/2$ and $I \neq 0$ may be analyzed using an axial symmetry spin-Hamiltonian:

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2)$$

where D and E are the crystal-field parameters, S and I denote the total electron and nuclear spins, g is the g-factor and A is the hyper fine structure (HFS) constant.

Fig. 2 shows the EPR spectra of manganese (5%) supported on ceria and alumina catalysts in the absence of CB. For the 0.05Mn/Ce sample, the EPR spectrum is consistent with high spin Mn^{2+} ions with electronic configuration $3d^5$ (ground state $^6S_{5/2}$) where the six normal ($\Delta M_I = 0$) HFS transitions are observed. It has been attributed to Mn^{2+} ions with $S = 5/2$ and $I = 5/2$ (100% of ^{55}Mn) and characterized by the following EPR parameters: $g = 2.006$, $A = 92$ G. Similar results have been observed in the literature and have been assigned to Mn^{2+} ions located in a weak axially distorted octahedral crystal field ($D \ll g\beta H$) [22]. In addition, from the EPR parameters and the presence of the HFS, one can conclude that the latter signal is characteristic of Mn^{2+} isolated species. When 0.05Mn/Ce catalyst was mixed with 5% of CB in tight contact conditions, the EPR spectrum of the

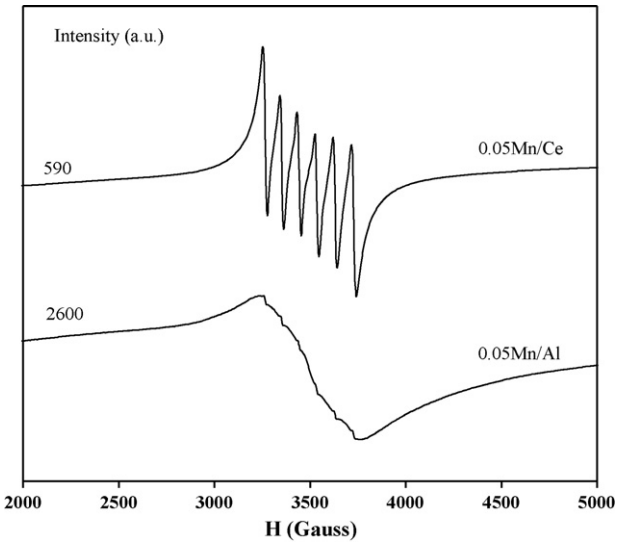

Fig. 2. EPR spectra, recorded at room temperature, of 0.05Mn/Ce and 0.05Mn/Al catalysts.

mixture is strictly the same ($g = 2.006$, $A = 92$ G). The only difference between the two spectra, before and after the addition of CB, is their intensities. In fact, the EPR intensity of the mixture is almost two times higher (×1.86) than that of the catalyst, indicating the increase of the Mn^{2+} ions content consequently to 0.05Mn/Ce + CB tight contact. It is important to note that the mill process doesn't show any effect on the EPR spectrum of the catalyst (without CB) treated in the same conditions as the mixture. It is well known that several manganese oxidation states exist Mn^0 (d^7), Mn^+ (d^6), Mn^{2+} (d^5), Mn^{3+} (d^4), Mn^{4+} (d^3). It is well known that Mn^+ and Mn^{3+} ions are EPR silent and Mn^{2+} cations are the most stable state of manganese ions and are widely studied by EPR. Thus, it can be suggested that consequently to the tight contact between the 0.05Mn/Ce catalyst and CB some manganese species with higher oxidation states are reduced into Mn^{2+} ions increasing the observed EPR intensity. It is important to note that this phenomenon can be considered as the first step in the carbon black oxidation mechanism in the presence of 0.05Mn/Ce catalyst. However, these observations are in agreement with the works of Carcium et al. [23] demonstrating that the active phases are pure MnO_2 or MnO_2 mixed with Mn_2O_3 in supported or unsupported MnO_x catalysts.

The 0.05Mn/Al sample gives a large EPR signal (ΔH_{pp} = 520 G, $g = 2.009$) with the presence of low intensity six lines HFS. This signal can be attributed, without ambiguity, to Mn^{2+} ions. However, in this case the interaction between the Mn^{2+} ions is considerably higher than for the 0.05Mn/Ce sample leading to the large signal and to the attenuation of the HFS resolution. In addition, the EPR intensity, related to the paramagnetic species content, is 4.4 times higher comparing to ceria-based catalyst (Fig. 2), which confirms the above statement. Consequently to tight contact with carbon black, neither EPR parameters nor intensity change indicating that no modifications occur on the oxidation state of 0.05Mn/Al catalyst. From these results, it clearly appears that manganese species on ceria surface are not exclusively in Mn^{2+} form whereas, the major part of manganese oxide on Al_2O_3 is consistent with Mn^{2+} ions, explaining the

differences between the reactivity of the two catalysts (Fig. 1). However, the participation of cerium compounds in the oxidation reaction by means of their well-known catalytic properties towards oxidation reactions should not be omitted. To elucidate these points, an EPR study was undertaken on mixture before and after catalytic test.

Fig. 3 shows the EPR spectra of CeO_2 and 10^{-4}Mn/Ce with 5% CB mixtures in different conditions, recorded at room temperature. For CeO_2 + CB tight contact sample, two EPR signals designed by S1 and S2 are observed. The S1 signal presents a slight axial distortion with EPR parameters: ΔH = 45–65 G and g_{iso} = 2.000. Whereas, the S2 signal is isotropic and sharp with stable EPR parameters $\Delta H \approx 3.5$ G and g_{iso} = 2.003. The S1 and S2 signals have been widely studied elsewhere and attributed to intrinsic paramagnetic centres on CB surface and to localised paramagnetic spins on the CB/catalyst interface, respectively [17]. In addition, we have demonstrated that paramagnetic species responsible for S2 signal can participate, at very low temperature, in the mechanism of CB oxidation in the presence of cerium oxide [17]. These results compared to those of thermal analysis permit to explain the origin of the 1.7% weight loss observed in a temperature range of 100–250 °C (Fig. 1).

The EPR spectrum of the 10^{-4}Mn/Ce catalyst shows a six lines hyperfine structure with g = 2.007 and A = 92 G characteristic of isolated Mn^{2+} ions. When 10^{-4}Mn/Ce was mixed with 5% of CB in loose contact conditions (Fig. 3), the EPR spectrum of the mixture is the strictly mathematical addition of the two signals corresponding to Mn^{2+} species and intrinsic paramagnetic centres of CB (S1 signal). When the mixture (10^{-4}Mn/Ce + 5% CB) is performed in tight contact conditions some essential modifications can be observed on the EPR spectrum. Indeed, Mn^{2+} signal as well as S1 and S2 signals are simultaneously present and the relative intensity of the Mn^{2+} signal is almost two times higher than initial 10^{-4}Mn/Ce catalyst (Fig. 3). It is important to note that, in this case, the contribution of the S1 and S2 signals, to the EPR intensity, is negligible. These results are in accordance with those observed for the 0.05Mn/Ce + CB catalyst and explained by the reduction of some Mn(IV) and Mn(III) species into Mn^{2+} ions, probably constituting the first step in the CB oxidation mechanism in the presence of Mn/Ce catalysts (tight contact). However, in the case of the 0.05Mn/Ce + CB sample S1 and S2 signals are probably masked by the high EPR intensity of the Mn^{2+} ions compared to 10^{-4}Mn/Ce + CB mixture (factor of 18.6).

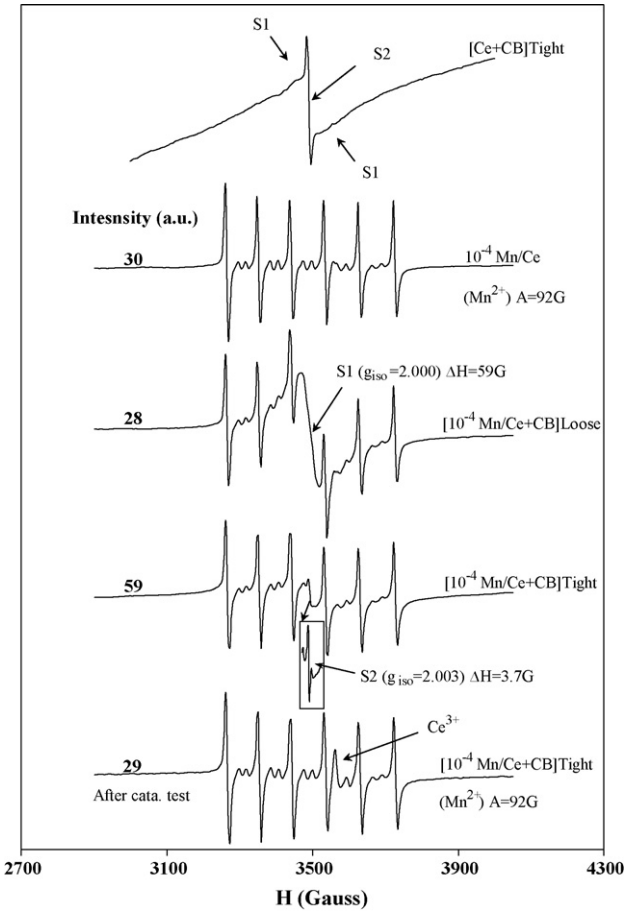

Fig. 3. EPR spectra, recorded at room temperature, of CeO_2 and 10^{-4}Mn/Ce with 5% CB mixtures in loose and tight contact conditions, before and after catalytic test.

After the catalytic test, the intensity of the EPR spectrum decreases about two times and regains the same value as the initial 10^{-4}Mn/Ce catalyst. In addition, no modifications in the EPR parameters of the Mn^{2+} ions were noted. Thus, after the catalytic oxidation of carbon black the manganese species find again their initial states. However, a new EPR signal with $g_{\perp}$ = 1.967; $g_{\|}$ = 1.943 is observed after test. It has already been demonstrated, in a previous work that such a signal can be attributed to the presence of defect sites "Ce^{3+}" in the CeO_2 matrix [24]. This result confirms the participation of ceria in the catalytic reaction. Finally, the disappearance of S1 and S2 signals after the catalytic test, at 600 °C, is predictable since these two signals are related to CB, which is totally burned in these conditions (Fig. 1). These results are in accordance with the DTA data showing the contribution of both ceria and manganese species in the catalytic oxidation of carbon black.

4. Conclusion

Owing to tight contact treatment with carbon black, the Mn^{2+} content considerably increases in Mn/Ce catalysts indicating the reduction of some manganese species with higher oxidation states into Mn^{2+} ions. Whereas, the oxidation states of manganese, in Mn/Al catalysts, are not affected by such a treatment. These results have permitted to partially explain the better reactivity of Mn/Ce samples comparing to Mn/Al catalysts. The reduction of the manganese species, in these conditions, is considered as an important factor in the carbon black oxidation mechanism. For the Mn/Ce catalysts, the contribution of both ceria and manganese species in the catalytic oxidation of carbon black are evidenced.

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