Study of Properties of a Catalyst for Soot Post-Combustion by Thermogravimetry−Mass Spectroscopy (TG−MS) Analysis

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The intent of this work is to study the performance of a catalyst for soot combustion under reducing and oxidizing environments, to draw indications on the catalytic mechanism and on the implications of the sulfation process. Thermogravimetric (TG) analyses of the sulfated catalyst in reducing and oxidizing environments and on-line mass spectrometry (MS) analyses of the gaseous products of the TG analyses have been performed. The catalyst is able to reduce and oxidize, when treated in suitable environments. Both H_2 and carbon reduce the catalyst within comparable ranges of temperature, although the main products of the reductions are different. In addition, the temperature ranges within which the catalysts reoxidize after the reductions are practically coincident with the catalyst threshold temperature. The aforementioned findings have led us to address the catalyst reduction as the rate-limiting step of the soot oxidation process. Sulfation decreases the catalyst activity through two different mechanisms that involve different catalytic components. One, which is irreversible, is due to the chlorine substitution with sulfur, and the other, which is reversible, is likely related to the physical or chemical covering of some other catalytic compounds that do not contain chlorine initially.

Introduction

Soot emissions from light- and heavy-duty diesel engines, either stationary or mobile, are responsible for most of the particulate pollution in large urban areas, which has serious repercussions on human health and the environment as a whole.[1−3] Soot, indeed, is respirable, because it is composed of relatively small particles (90 wt % are <1 μm in size) and consists of an amorphous carbonaceous matrix on which a soluble organic fraction (SOF), inorganic salts, sulfur compounds, and heavy metals may be adsorbed in quantities dependent on the fuel characteristics and of the combustion conditions.[4] The SOF, in turn, consists of unburned hydrocarbons, which are strongly suspected to be mutagenic and carcinogenic.[5,6] To match the progressively more stringent emission limits imposed in western countries, solutions to reduce soot emissions at the diesel exhausts have been proposed. They span from enhancements of the combustion systems (i.e., exhaust gas recirculation, turbulence improvement, common rail injection, etc.) to the use of after-treatment devices that are able to remove soot from the exhaust stream.[7−10] Among these, filtering systems coupled with oxidation catalysts seems to be the most suitable.[11]

Many catalysts that are potentially appropriate for the specific task were also proposed, because very different materials showed soot oxidation activity. They include (i) noble metals, which were thought to act essentially toward the SOF[12] but were found to trigger soot oxidation through the catalytic oxidation of NO to NO_2, which, in turn, oxidizes soot;[13,14] (ii) metal oxides;[15−18] (iii) some mixtures of them;[19,20] (iv) perovskite-type oxides;[21] (v) spinel-type copper-chromite,[22] which seem slightly more effective than noble-metal catalysts; and (vi) more-complex catalysts that, based on the synergistic effect of several constituents such as transition and alkaline metals, are capable of being active for soot oxidation at temperatures slightly above 580 K.[23−30] These latter materials are specifically active toward the oxidation of the carbonaceous matrix of soot and, as a result, they are capable of catalyzing the oxidation of substantially all carbonaceous matter.[31] Other parameters also affect the catalyst activity such as the support material,[32] the intensity of contact between soot and catalysts,[27] the catalyst preparation procedure, and the presence and the amount of promoters.[33]

Despite the significant activity and the relatively low threshold temperature of the mentioned catalysts, further studies are needed to make them suitable for practical applications. Indeed, the catalyst requirements for such an application must be high activity at low temperature (or low threshold temperature), high stability in the exhaust environment, and high stability to relatively high temperatures, which can be reached during trap regeneration. Such requirements are difficult to obtain and, in some respects, are in conflict with each other. In any case, they can be achieved only if a detailed knowledge of the reaction mechanism of the oxygen−carbon−catalyst reacting system and the catalyst resistance to possible poisons present in the exhausts become known. The knowledge of the mechanism is also relevant to the catalyst improvement and to the catalytic trap design, whereas the comprehension of the resistance to poisoning seems important for the process to be economically convenient.

Partially because of the catalysts complexity and partially because of the double heterogeneity of the system (gas reactant, solid catalyst, and solid reactant), the reaction mechanism of catalytic soot combustion of at least the most active and complex catalysts still remains unclear. In many cases, however, it has been suggested that the reaction occurs through a redox-type mechanism.[16,18,34] In contrast, it has been also reported that, in the case of a Co/Al_2O_3 catalyst, treatments at high temperature, which favor the formation of the

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spinel phase and strongly decrease the catalyst redox capacity, do not affect the catalytic activity for soot combustion.[35] Other researchers suggested that the catalyst acts through the formation of liquid eutectic phases (from 330 °C to 480 °C, depending on the nature of the catalyst), which increases the activity of Cu−K−V catalysts by improving the soot−catalyst contact.[36] However, even in this case, the mechanism is likely to unfold according to a redox mechanism. Actually, some catalysts that are fairly active when in "tight contact" lose their catalytic activity almost completely when operated under "loose contact" conditions.[27,37] In contrast, other catalysts maintain their activity, even in loose contact mode.[26,38] Furthermore, it was determined that the carbon oxidation kinetics, with respect to the oxygen partial pressure in the presence of a $CuFe_2O_4$ catalyst, was half order, and so the formation of a rate-determining reactive oxygenated intermediate on the soot surface was proposed.[39] In addition, it has been reported that Co/MgO and the same catalyst promoted with 1.5 wt % of potassium show catalytic activity for soot combustion when calcined at 400 °C, but they become practically inactive if calcined at 500 °C or higher.[40] However, the same authors noted that this did not occur when the promoter amount was 7.5 wt %.[33]

For practical applications, among the others, it is necessary to assess the lifetime of the catalytic system of soot abatement. In this context, one of the factors that must be taken into consideration is the resistance to poisons inevitably contained in combustion exhausts. Indeed, as for many other catalysts, sulfur represents an undesirable poison, leading to a slow deactivation of the present catalyst.[41] However, as shown in previous work,[42] a complex interaction between gas exhaust components such as NO_x, SO_x, and H_2O may markedly limit such a problem.

This work was performed with a double purpose: (i) to acquire a better comprehension of the soot catalytic oxidation process and (ii) to investigate the consequences of sulfur poisoning. To this end, specific research activity has been conducted by performing thermogravimetric (TG) analysis, coupled with a mass spectrometry (MS) inquiry of the evolving gaseous products, of a sulfated catalyst in reducing and oxidizing environments with and without the presence of soot. Results are analyzed and compared with previously reported findings,[43] regarding the unsulfated catalyst, with the main objective of elucidating the reaction mechanism for soot oxidation in the presence of the specific catalyst.

Experimental Section

Catalyst. Powder catalyst (named 137TF) was prepared by impregnating TiO_2 powder (DT51D, Rhône Poulenc) with an aqueous solution of NH_4VO_3, $CuCl_2$-$2H_2O$, and KCl (Baker Chemicals).[42−44] The sample was then dried at 393 K and calcined at 973 K overnight.[25] The TiO_2 powder had a specific surface area of 88 m^2/g and a sulfate content, as measured after chemical analysis, of 0.5 wt %, in the form of SO_3. A further catalyst sulfation was achieved by treating, for 65 h at 683 K, the fresh catalyst with a 30 L/h (STP) stream that contained 1000 ppm SO_2, 3 vol % O_2, and 10 vol % H_2O in N_2. Such a composition was chosen to approximately simulate the composition of the main components of typical combustion exhaust gases. The relatively high SO_2 concentration was used to accelerate the sulfation process.

Table 1. Percentage Distribution of the Main Chemical Elements over the Catalyst Surface, as Determined by Energy-Dispersive X-ray Analysis (EDAX) of Fresh and Sulfated Powder Catalysts (137TF)

	Distribution (wt %)	
element	fresh	sulfated
Cu	8.2	10.5
V	7.8	6.3
K	6.9	8.0
Cl	5.3	0.0
S	0.8	8.9
Ti	71.0	66.3

Carbonaceous Material. The carbonaceous material was soot that had been collected at the exhaust of a gas oil burner operating at air/fuel mass feed ratios of 20−35. The Brunauer−Emmett−Teller (BET) specific surface area of the soot, as measured by an area meter (Sorptomatic, Carlo Erba) through nitrogen adsorption at 77 K, was 90 m^2/g.

Experimental Apparatus and Procedures. A thermobalance (Netzsch, model TA 209) was used to perform air flow temperature-programmed thermogravimetric analyses (TGs) of soot alone and of soot and catalyst mixtures with a soot-to-catalyst mass ratio of 0.1. Such tests were performed with both the fresh and sulfated catalysts. In addition, a thermobalance coupled to a mass spectrometer (TA Instruments, model 2950 HR) was used to perform (i) 5 vol % hydrogen−helium flow temperature-programmed reductions (TPRs) of the catalyst; (ii) air flow temperature-programmed oxidations (TPOs) of the already reduced catalyst; (iii) helium flow temperature-programmed TGs of soot−catalyst mixtures with a mass ratio of 0.1; and (iv) air flow TPOs of the already reduced soot−catalyst mixture.

Tests from items (i)−(iv) were performed with the sulfated catalysts. All the tests were performed by heating the samples from ambient temperature to 973 K in a 60 cm^3/min (STP) gas flow. The heating rate was 5 K/min in the tests from item (i) to item (iv) and was 10 K/min in the tests with the Netzsch TA 209 thermobalance.

In the tests involving carbonaceous material and catalyst mixtures, these latter mixtures were prepared by properly pounding the two components in a mortar, to ensure tight soot−catalyst contact.[27]

Results

As mentioned in the Experimental Section, titania powder that was used as support for the 137TF catalyst was already slightly sulfated. However, after the further forced sulfation in the SO_2-containing stream, the sulfur content increased. Indeed, TG analysis of the sulfated catalyst showed a 4% weight loss, likely due to sulfites and/or sulfates decomposition in the temperature range of 450−700 °C. Energy-dispersive X-ray analysis (EDAX), performed with a Philips model XL30 scanning electron microscope that was equipped with a LaB_6 filament, showed the presence of copper, vanadium, potassium, and chlorine in the fresh 137TF catalyst (see Table 1). After catalyst sulfation, EDAX analysis detected a complete substitution of chlorine by sulfur. A loss of chlorine by the mere thermal treatment must be excluded, given that the catalyst was calcined at 973 K overnight during the preparation. However, the relative amounts of the remaining significant elements are substantially unchanged, except for a slight enrichment of copper (see Table 1).

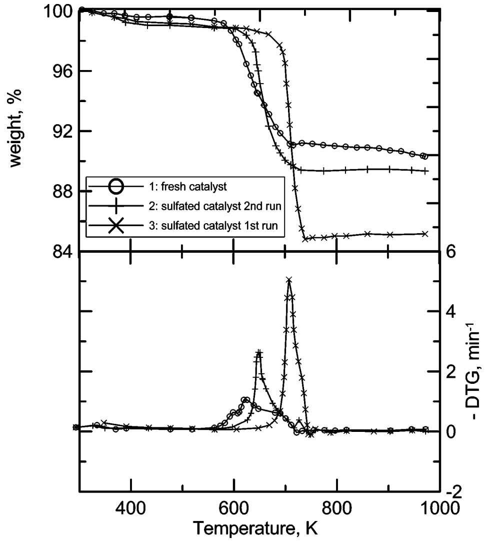

Figure 1. Percentage sample weight loss curve and its derivative (DTG) curve obtained during temperature-programmed oxidation (TPO) tests of (1) a mixture of soot and fresh catalyst, (2) a mixture of soot and sulfated catalyst (second run), and (3) a mixture of soot and sulfated catalyst (first run).

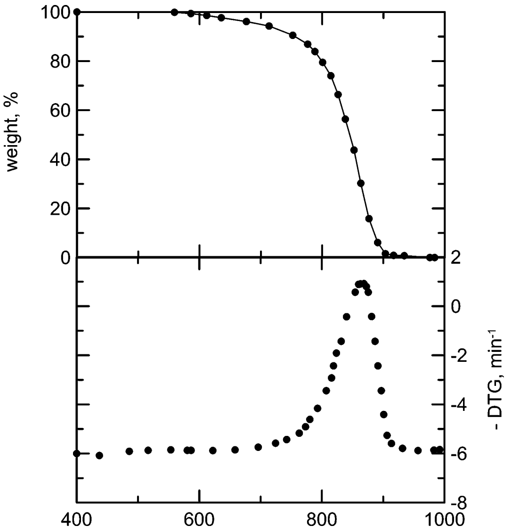

Figure 2. Percentage sample weight loss curve and its derivative (DTG) curve obtained during TPO tests of soot alone.

Catalytic Activity in Soot Combustion. The performances of the fresh and the sulfated 137TF catalyst in the oxidation of soot may be obtained by comparing the results of TG analyses of soot−catalyst mixtures with a mass ratio of 0.1, as reported in Figure 1 (curves 1 and 3, respectively), with the results of the TG analysis of soot alone, as shown in Figure 2. In Figure 1, for each sample, the residual weight, which is expressed as the percentage of the sample initial weight (TG curve), and the derivative of the percent sample residual weight (DTG curve) are plotted as functions of temperature (note that, in all figures in this paper, the data of the derivative of sample residual weight are reported with the sign inverted, because the ordinate is given as (−DTG, min^{-1})). From the comparison between the results in Figures 1 and 2, it is evident that both the fresh (curve 1) and the sulfated catalyst (curve 3) markedly lower the soot combustion temperature. However, the activity of the fresh catalyst is noticeably higher than that of the sulfated catalyst, with its threshold temperature and its combustion temperature (DTG peak) being ∼100 °C lower than that relevant to the sulfated catalyst (see Figure 1). The overall mass losses of the samples are different, being ∼9% in the case of the fresh catalyst and ∼15% in the other case. This suggests that the weight loss of the sulfated catalyst cannot be attributable only to soot combustion, because the overall amount of soot in the sample is only ∼9 wt %. Figure 1 also shows that the DTG curve of the fresh catalyst, besides the major peak at 620 K, has a significant shoulder at 650 K.

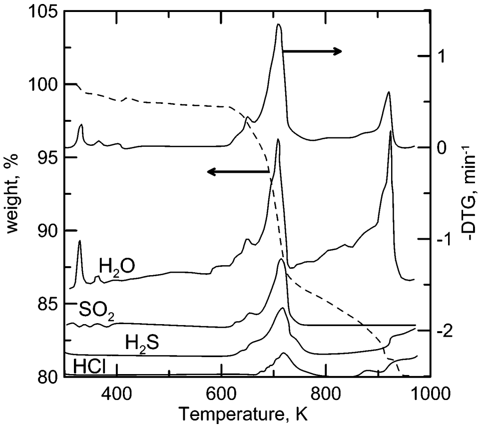

Figure 3. Percentage sample weight loss curve, its derivative (DTG) curve, and mass spectroscopy (MS) signals of substances evolved during the temperature-programmed reduction (TPR) of the sulfated catalyst in a 5% H_2−helium flow.

Catalyst Features. As reported in the Experimental Section, reductions (TPR), and subsequent reoxidation (TPO) of the samples were performed and the substances evolving from the sample were analyzed by a mass spectrometer (MS). The results of a TG−MS test in a 5% H_2−helium flow of the sulfated catalyst are shown in Figure 3, where the percentage sample weight (TG), with respect to the initial value, and its changes (DTG) are reported as a function of temperature. There is a significant weight loss of the sample for increasing temperatures (∼20%), which, primarily, is due to the H_2O formation. The TG curve is characterized by a 1% weight loss below 375 K, by a rapid loss (of ∼12 wt %) between 625 K and 725 K, and by a slow loss of ∼7 wt % between 725 K and 925 K. The DTG curve presents essentially two major peaks, at 710 K and 920 K, and very small peaks at low temperature (<375 K).

In Figure 3, the MS signal pertaining to the relevant compounds desorbed from the sample also is reported. The major product of the reduction of the catalyst is H_2O, followed in the order by SO_2, H_2S, and HCl, and to avoid ambiguity, only major MS signals pertaining to the mentioned species are shown in the figure. Specifically: for water, only mass 18; for SO_2, only mass 64; for H_2S, only mass 34; and for HCl, only mass 36 are reported. In addition, to include all the signals previously mentioned in the same figure, arbitrary scales not proportional to the original signals have been used. From Figure 3, it appears evident that the MS signals pertaining to H_2O follow the DTG curve in all the investigated temperature ranges, and so do the MS signals relative to SO_2, but only up to 745 K. The amount of HCl released is very small, with a peak at 715 K, where also SO_2 and H_2S show a peak and that corresponds to the major DTG peak (see Figure 3). At temperature of >825 K, a significant release of H_2S and HCl, increasing with the temperature, is also observed.

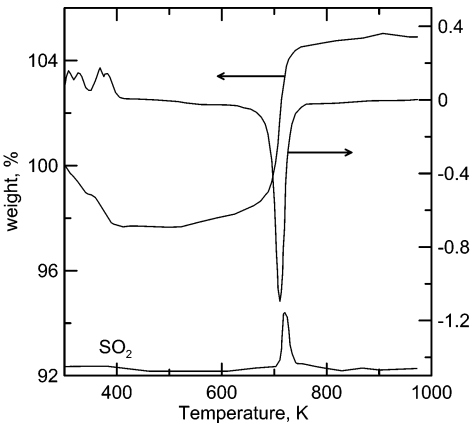

Figure 4. Percentage sample weight loss curve, its derivative (DTG) curve, and the MS signals of substances evolved from it during the air flow TPO of the sulfated catalyst, following the TPR in a 5% H_2−helium flow.

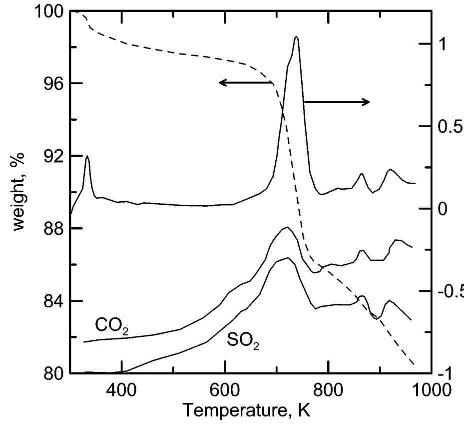

Figure 5. Percentage sample weight loss curve, its derivative (DTG) curve, and the relevant MS signals of evolved substances during the TPR in a helium flow of a mixture of soot and sulfated catalyst.

The results of the TG−MS test in an air flow of the previously reduced sulfated catalyst are shown in Figure 4 in the same way applied in Figure 3. The sample mass first decreases by ∼2 wt %, then rapidly increases at 675−745 K, gaining ∼7 wt %, with a net increase of ∼5 wt %, with respect to the initial mass. The slight weight loss that occurs at <375 K seems mainly due to CO_2 release, which, considering the fact that carbon should not be present on the catalyst, seems likely due to the desorption of atmospheric CO_2 previously adsorbed on the catalyst. A small release of SO_2 just after the end of the reoxidation process is observed (see Figure 4).

Results of a TG−MS test in a helium flow of a soot−catalyst (sulfated) mixture with a mass ratio of 0.1 are shown in Figure 5. In this case, H_2 has been omitted from the gas stream, because carbon itself may act as a reducing agent. The overall sample weight loss is ∼20% of the initial mass. The DTG curve presents a major peak at 735 K and minor peaks at 335, 865, and 925 K. The weight loss is determined by SO_2 desorption as well by carbon oxidation (i.e., CO_2), as shown by profiles pertaining to CO_2 and SO_2 that closely follow the DTG profile from 525 K (see Figure 5). In this case, there is no desorption of HCl, whereas H_2O is desorbed at temperatures of <375 K.

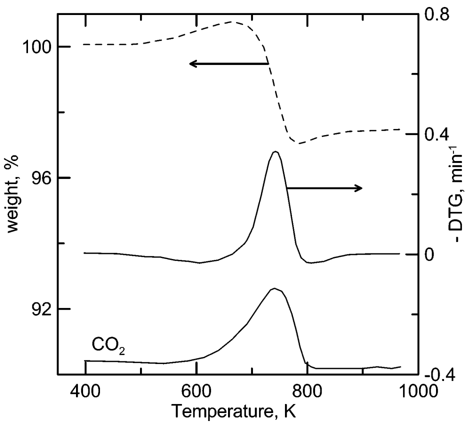

Figure 6. Percentage sample weight loss curve, its derivative (DTG) curve, and the relevant MS signals of evolved substances during the air flow TPO, following the TPR in a helium flow, of a mixture of soot and sulfated catalyst.

The results of TG−MS analysis in an air flow of the previous sample after the treatment in helium are reported in Figure 6. The percent sample weight (TG) curve and its derivative (DTG) clearly show a combustion peak at 750 K. The total weight loss is only 2.5%; however, before the combustion starts (from 475 K to 675 K), there is a growth of the sample mass, certainly due to the O_2 adsorption, which continues up to 875 K after the end of carbon oxidation. MS signals clearly show that only CO_2 desorbs significantly, with a peak correspondent to the DTG peak (see Figure 6).

Discussion

Catalyst Sulfation and Catalyst Redox Properties. In a recent work,[43] the results of tests similar to those presented in this paper but performed with the unsulfated catalyst were reported. For the purpose of comparison with the present findings, shown in Figures 1 and 3−6, such results are presented again in Figure 7a−d.

Comparison between data in Figures 7a and 3 suggests that sulfation apparently modifies the behavior of the catalyst under hydrogen reduction substantially. In particular, although in the case of the unsulfated catalyst, even in the presence of desorption peaks, the reduction occurs continuously along the entire investigated range of temperature, with the sulfated catalyst most (12 wt %) of the total weight loss (20 wt %) associated with the reduction process is concentrated between 630 and 730 K. Actually, in the case of the sulfated catalyst, the loss of SO_2, which is not a proper catalyst reduction process but rather a decomposition of sulfates and sulfites, is responsible for this phenomenon. This view is also supported by the fact that, unlike the case of the unsulfated catalyst (see Figure 7a),[43] the amount of desorbed SO_2 was relatively high, being poorer than that of H_2O only, and the SO_2 desorption profile closely follows the DTG profile peak (see Figure 3). In addition, the total weight loss in the cited range of temperature is much higher in the case of the sulfated catalyst (20 wt %, versus 6 wt %). A further significant difference between results in Figures 7 and 3 is the lack of a peak at ∼600 K in the H_2O desorption profile in this latter figure. The comparison between the reoxidation steps of the unsulfated and sulfated catalysts in Figures 7b and 4 shows that they appear very similar, except in the temperature range in which the rapid catalyst reoxidation occurs, i.e., 550−625 K for the unsulfated and 675−730 K for the sulfated catalysts.

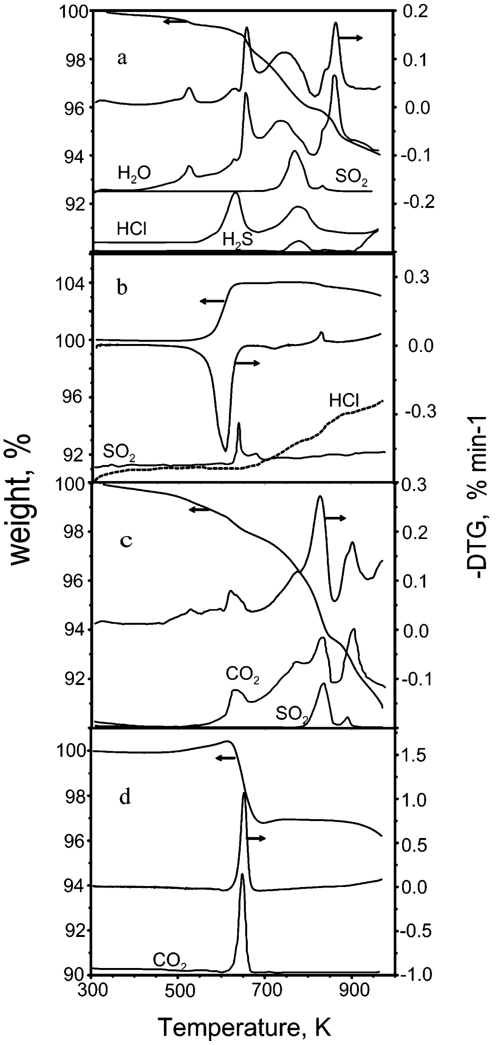

Figure 7. Percentage sample weight loss curve, its derivative (DTG) curve, and relevant MS signals of evolved substances during (a) the TPR of fresh catalyst in a 5% H_2−helium flow, (b) the TPO of the mixture of soot and fresh catalyst after the TPR in a 5% H_2−helium flow; (c) the TPR in a helium flow of a mixture of soot and fresh catalyst, and (d) the air flow TPO of the mixture of soot and fresh catalyst after the TPR in a helium flow.

The differences, which have already been observed between the behaviors during reduction in a H_2−He flow of the sulfated and the unsulfated catalysts, also are confirmed when comparing the results in Figures 7c and 5, in regard to the TPR tests of a soot−catalyst mixture in helium flow with unsulfated and sulfated catalysts, respectively. Even in this case, indeed, the reduction of the sulfated catalyst shows a relatively rapid weight loss in the temperature range of 650−750 K, attributable to the sulfate and sulfites decomposition, and the total weight loss is ~20 wt %, compared to ~9 wt % measured with the unsulfated catalyst. Also for the reoxidation steps, which are reported in Figures 7d and 6, the comparison leads to considerations similar to those made for the assessment of results in Figures 7b and 4. The only remarkable difference is that, with the sulfated catalyst, the reoxidation involves a relatively larger temperature range, i.e., 600−800 K (see Figure 6).

A common feature to unsulfated and sulfated catalysts seems to be the SO_2 desorption during both the TPR in a H_2−He flow and the subsequent TPO in air. In addition, for both catalysts, SO_2 desorption occurs during TG in a helium flow of the soot−catalyst mixture, when the reducing agent is carbon, but it does not verify during the following TPO in air. Two possible hypotheses can be formulated to interpret such behavior. The first hypothesis is that, during TPR, in the presence of H_2, the desorption of SO_2 is coupled to the formation, either preventive (Figure 7a) or simultaneous (Figure 3), of H_2S. This suggests that the mechanism for SO_2 desorption could be the initial formation of H_2S during the TPR and the successive oxidization of part of it to SO_2 during the same TPR at the same or higher temperature or when the subsequent TPO step is performed (see Figures 4 and 7b). In any case, during TPO, SO_2 releases occur only after the catalyst reoxidation occurs (see Figures 4 and 7b). Against this hypothesis, there is the evidence that SO_2 release verify even without H_2S formation (see Figures 5 and 7c). A second hypothesis is that the SO_2 release would occur only when, at a given temperature, a particular oxidation state of the catalyst is reached. This, indeed, could occur during the TPR in a He−H_2 flow (see Figures 3 and 7a), during the subsequent reoxidation (see Figures 4 and 7b), and during the TG in a helium flow of the soot−catalyst mixtures (see Figures 5 and 7c). Finally, during the TPO of the already reduced soot−catalyst mixtures, the presence of carbon, most of the time, would not allow proper catalyst reoxidation. This prevents changes in the oxidation state of the catalyst components (see Figures 6 and 7d) while such changes would seem crucial for triggering SO_2 desorption.

Summarizing, the relevant differences between the behavior of the unsulfated catalyst, with respect to that of the sulfated catalyst during treatments in reducing and oxidizing environments are as follows:

(1) The reducing steps are characterized by a large weight loss that is primarily due to sulfate and sulfites decomposition;

(2) The peaks in the desorption profiles of H_2O or CO_2 (in the relevant tests) appear at higher temperatures; and

(3) The oxygen adsorption during the catalyst reoxidizing tests occurs, on the average, at temperatures that are 100 K higher.

Catalyst Redox Properties and Catalytic Activity. Present results, obtained with the sulfated catalyst, parallel those obtained previously,[43] in regard to the marked capacity of the catalyst to be reduced and oxidized, when treated in proper environments. In particular, the comparison between TPR and TPO tests performed on the sulfated catalyst in a H_2−He flow and then in an air flow (see Figures 3 and 4) or on soot−catalyst mixtures in a helium flow and then in an air flow (see Figures 5 and 6) confirm the findings obtained with the fresh catalyst[43] (see Figures 7a and 7b and Figures 7c and 7d). Conclusions related to this behavior were drawn in the cited paper and could be confirmed here. However, it is worthwhile to remark only that the ability of the catalyst (fresh or sulfated) to reduce during the TPR in a helium flow when mixed with soot and, hence, when the reducing agent is carbon means that the catalyst can withstand a carbothermic reduction, which is considered a prerequisite of metal oxides for catalytic activity toward oxidation reactions.[45]

Catalyst Sulfation and Catalytic Activity. As shown in Figure 1, the sulfated catalyst is less active than the fresh catalyst. In addition, the sulfation process leads to, among other things, a complete loss (or substitution with sulfur) of chlorine (see Table 1). In the literature, it has been suggested that the role of chlorine in this type of catalyst is to enhance the capability of the catalyst to act in “loose” contact mode with soot.[46] In other words, it, together with copper, would increase the catalyst mobility or at least that of those compounds of the catalyst in which it is present. Such mobility seems essential, on one hand, to explain the high catalytic activity and, on the other hand, to justify the fact that, despite the highly heterogeneous nature of the system, the entire soot surface participates in the reaction simultaneously. As a consequence, the loss of chlorine after sulfation would definitely seem to compromise the catalyst activity. However, when the sulfated catalyst used for the TPO is re-mixed with soot and subjected to another TPO test, the resulting DTG profile (curve 2 in Figure 1) presents a peak at temperatures intermediate between those pertaining to the fresh and sulfated catalysts. This would suggest that the fresh catalyst might have been deactivated by sulfation through two different routes. One is a permanent deactivation, likely due to chemical catalyst modification, consequent to chlorine loss, and the other is a reversible deactivation that is probably due to physical or chemical covering of some catalytically active compounds, which can be reactivated by a simple thermal treatment. In other words, beyond the chlorine-containing compounds, which, as previously mentioned, are likely capable to enhance the catalytic activity when the soot−catalyst mixture is in loose contact mode, other active components are present in the catalyst and their relevance appears when those already containing chlorine are deactivated by chlorine loss or by substitution with sulfur. This interpretation is also supported by the fact that the DTG profile pertaining to the fresh catalyst in Figure 1 (curve 3) shows a shoulder at 645 K, just where the DTG peak of the sulfated and then desulfated catalyst shows the only relevant peak (see curve 2 in Figure 1). This, indeed, would mean that such active compounds also are present in the fresh catalyst, but their role is partially hidden by the presence of the much more active chlorine-containing compounds. When, because of the loss of chlorine, such compounds are not active anymore, the less-active compounds become more evident.

It is worth noting that the overall weight loss of the sulfated catalyst during TPR in a H_2−He flow is ~20%, whereas that pertaining to the fresh catalyst is 6%. Taking into account that the main product of the reduction in both cases is H_2O, the amount of oxygen yielded by the sulfated catalyst is higher than that yielded by the unsulfated catalyst, under the same operating conditions. However, such a finding does not necessarily mean that the activity of the sulfated catalyst is higher, because this oxygen is not recoverable anymore. This is shown by the results in Figure 6, relative to the reoxidation test after TPR treatment of such a catalyst, from which it seems that the weight gain (due to oxygen adsorption) of the sulfated catalyst is only 4%. Hence, it is likely that some oxygen for H_2O formation during the catalyst reduction in the H_2−He flow was derived from the sulfate and sulfite decomposition and not from the catalytically active species.

Catalytic Mechanism. The composite nature of the present catalyst formulation and the intrinsically high complexity of the catalytic process, which involves one gaseous reactant, one solid reactant, and the solid catalyst, make its study difficult and the comprehension of the catalysis mechanism very hard. The 137TF catalyst is, in fact, a mixture of several highly amorphous compounds, which seem to act synergetically as a catalyst.[28] Although many research groups studied the catalyst in the object or very similar catalysts, only few compounds were recognized among the many that are possible.[24,26,28,30,46,47] In any case, it should pertain to the wide category of mixed transition-metal and alkaline-metal oxides. This could also mean that, as underlined in the aforementioned discussion on the sulfated catalyst, many different catalytic substances in an highly amorphous state, acting at different temperatures, could be simultaneously present on the catalyst. However, an attempt to elucidate the possible mechanism of carbon oxidation by the 137TF catalyst with the support of the present results and of previous findings can be made. With reference to the classification proposed by Mul et al.,[48] on the basis of a study performed with $^{18}O_2$ on the oxidation of carbonaceous material catalyzed by transition-metal oxides, there would be three types of oxygen coming from such oxides that are useful for the formation of gaseous carbon oxides: adsorbed surface oxygen, surface oxygen, and lattice (or bulk) oxygen. The first, which is defined as activated oxygen on the surface of a metal oxide, is not incorporated in the oxide surface layer. The second is activated oxygen that is incorporated in the oxide surface (the first oxygen layer). The third is oxygen that is associated with the bulk of metal oxide, below the surface oxygen. Mul et al. proposed at least three models for the carbon oxidation mechanism that are dependent of the type and mode of oxygen that is involved.[48] Of these models, the one designated as “C”, which is a combination of a redox and a spill-over mechanism,[49,50] seems to apply to our catalyst. Based on such a model, a redox mechanism would act at the soot/metal oxide contact interface involving surface and bulk metal oxide oxygen, because of a fast exchange between these two oxygen types. Besides such an oxygen, another type of oxygen seems to participate in the process. This type of oxygen, not incorporated into the metal oxide surface oxygen but present as adsorbed surface oxygen, moves in an activated state over the surface, spills over, and forms surface oxygen complexes onto the carbon surface. The requisites that the system has to possess to be classified as acting according to the cited model C are as follows:

(1) It must enhance the formation of surface carbon oxygen complexes (SOCs) (mainly related to the oxygen spill-over mechanism);

(2) It must be able to reduce and oxidize in the proper environments;

(3) It must result in catalyst carbothermic reduction (which means a high capacity to withstand strong reduction by acting as an oxygen donor).

Our catalyst has all of the aforementioned requisites. Indeed, results presented in this paper and in previous work[43] demonstrated its strong propensity to act as an oxygen donor by withstanding carbothermic reduction. Furthermore, in previous work, on one hand, we experienced complete involvement of the overall soot surface during soot oxidation tests,[8,34] and, on the other hand, it was shown that this catalyst strongly influences the quality and the quantity of SOCs.[25] In particular, it enhances the overall number of SOCs and especially of those evolving as CO_2 with low desorption energy that, as stated in the literature, would sustain a spill-over mechanism.[48] Finally, it cannot be excluded that, given the complexity of the catalyst in the object, different components of the catalyst could have only one of the aforementioned requisites or that there would be the occurrence of synergetic effects of the various components on each other.[28,49]

For the completeness of the discussion, it is worthwhile to recall at least two other alternative oxidation mechanisms that have been proposed in the literature for catalysts similar to the 137TF catalyst: one is related to the possible formation of low-melting eutectic phases in the catalyst,[26,27,30,36] and the other is related to the formation of carbonates triggered by the presence of alkaline metals, along with transition metals.[33,43] The possibility of the occurrence of the latter mechanisms was discussed in a previous paper.[43] Instead, the first of these mechanisms was hypothesized for justifying the relatively strong activity of the catalyst under study and of similar catalysts, even in "loose" soot−catalyst contact mode,[27] and the involvement of the entire carbon surface during the reaction, despite the double heterogeneity of the system. Specifically, the occurrence of a wetting process of the solid reactant by the catalyst was assumed.[26,27,36] This assumption was supported by the fact that, with some transition-metal oxide catalysts (much simpler than the catalyst under study), differential scanning calorimetry (DSC) analysis showed that a melting process occurred at temperatures comparable to those at which the catalyst was active for soot combustion.[27,30,36] However, the melting phenomenon actually was only partially verified in the case of the catalyst used in this study. Indeed, the direct correspondence between the melting of some catalyst component and the activity toward soot combustion was not observed, although some fusion occurred in the temperature range (quite broad) within which the catalyst soot oxidation occurred. Doubts about the validity of such an hypothesis can also be raised, considering the fact that all the experiments, in which the formation of low-melting eutectics in catalysts with the same[36] or with similar composition[26,27] was observed, were performed by DSC under oxidizing conditions. Therefore, it may be argued that, during DSC experiments, the operating environment was not the same as those encountered by the catalyst under real operating conditions, i.e., in the presence of soot. In dependence of such conditions, if the catalyst is able to easily oxidize or reduce, as shown exhaustively in this work, the formation of particular compounds on the catalyst may occur, especially when, as in the case in the object, it has a complex formulation. Hence, it seems deceptive to consider the formation of a low-melting eutectic, detected by DSC analysis, as proof of the catalysis mechanism that should unfold through the wetting of the surface of the soot.

Conclusions

The applied technique of reduction and reoxidation of the catalyst with on-line mass spectroscopy (MS) analysis of evolving products allowed the determination of the main species desorbing from the catalyst or from the soot−catalyst mixture and has been demonstrated to be useful for determining some characteristics of the catalyst.

The application of such a technique to the sulfated catalyst substantially confirmed the findings already observed with the unsulfated catalyst. In particular, the sulfated catalyst is able to reduce and oxidize when treated in proper environments. The substantial equivalence of reduction processes performed by soot or by 5 vol % H_2 in a helium mixture was also confirmed. Actually, either H_2 or carbon reduce the catalyst, within comparable ranges of temperature, although the main products of the reductions are different. In addition, although the catalyst reduction occurs over the entire range of temperature, the reoxidation appears as an activated process that occurs rapidly in a relatively narrow range of temperature. Such a range is practically coincident with the catalyst threshold temperature.

The results lead to the conclusion that the catalyst reduction should be addressed as the rate-limiting step of the soot oxidation process.

Sulfation decreases the catalyst activity through two different mechanisms, likely involving different catalytic components. One, which is irreversible, is due to the chlorine substitution with sulfur, and the other, which is reversible, is likely related to a physical or chemical covering of some other catalytic compounds that do not contain chlorine initially.

The discussion on the catalytic mechanism led to the conclusion that the catalyst 137TF would act via a spillover mechanism, because it shows a strong propensity to act as an oxygen donor, to withstand carbothermic reductions, to completely involve the overall soot surface during soot oxidation tests, and to influence the quality and the quantity of surface carbon oxygen complexes (SOCs). Other possible catalytic mechanisms, which have been proposed in the literature, were also considered in the discussion; however, none of them seem to comply with the features of such a catalyst, although their occurrence, also in a synergetic way, cannot be completely excluded.

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