



Redox properties of a TiO₂ supported Cu-V-K-Cl catalyst in low temperature soot oxidation

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Strong activity of a Cu-V-K-Cl/TiO₂ catalyst for soot oxidation was found by comparing results of constant temperature carbon oxidation tests in the presence and in the absence of catalyst. In addition, temperature programmed reductions (TPR) with different reductants (H₂ or soot) and re-oxidations (TPO) with air were carried out. Mass-spectrometric (MS) analyses of the gaseous products of the mentioned TPR and TPO processes were also performed on line. The aim was to investigate the behaviour of the catalyst under reducing and oxidising environments in order to draw indications on the role of the redox properties in the catalytic reaction mechanism.

Results showed that the catalyst can be reduced and re-oxidised under proper environments. In particular, the catalyst delivers oxygen in the whole range of temperatures from 480 to 1000 K when carbon or H₂ are employed as reducing substances. The relevant differences between the two cases are the main products of the reductions (H₂O with H₂ and CO₂ with soot) and the high HCl desorption in the case of reduction by H₂. In addition, the temperature range within which the catalyst re-oxidises after such a reduction is practically coincident with those where soot catalytic oxidation occurs.

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1. Introduction

In the last 50 years catalysis has played a key role in the development of new and more advantageous routes for the manufacture of traditional and novel chemicals. More recently catalysis has been more and more applied to carry out processes for solving environmental pollution problems [1]. The so called environmental catalysis has given a significant contribution to the reduction of air pollution in many cases, such as, for ex-

ample, NO_x reduction from power plant flue gas [2], three way catalysts at the automotive engine exhaust [3], VOC oxidation [4]. The goal of abating the pollutants present at the exhaust of a diesel engine has not yet fully achieved, due to the specific feature of that exhaust, i.e. the presence of particulate matter, especially as soot. Soot is the carbonaceous part of diesel particulate matter, which also contains other components, such as sulphates and heavy metals. Therefore, a diesel particulate matter removal process must include: (i) soot filtration by a suitable filter medium, since the residence time in the exhaust pipe is not long enough for particulate conversion; (ii) soot combustion on a specific oxidation catalyst, since the exhaust

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temperature is not as high as necessary for uncatalytic soot combustion.

Several investigations showed that transition metal oxides or their combinations are very active in the catalytic oxidation of soot [5,6], graphite [7,8], and char [9]. We showed that a Cu-V-K-Cl catalyst (catalyst 137AA) is able to strongly lower the ignition temperature of different carbon materials, from fullerene [10] to graphite [6], to carbon particulate from diesel engine and from oil fired power plants [6,11]. The same catalyst formulation was reported in [12], while Nb [13] and Mo [14] substitution for V were also investigated. The high performance of these catalysts was related to the presence of the copper chloride component, whose mobility would be responsible for the high activity [15], but whose volatility would be the cause of progressive catalyst deactivation [16,17]. Similar conclusions related to the enhanced mobility given by potassium in Co-K-MgO catalyst [18] and to the volatility of catalyst components in KI-KVO₃ [19] were reported. However, we never observed a so poor stability of our Cu-V-K-Cl catalyst, likely due to a very careful control of high temperature calcination in the last stage of preparation. Therefore, we deposited the catalyst on various structured supports in order to make prototypes of catalytic filters we tested at the exhaust of a domestic size gas oil burner (5 kW) [20], of a 5 kW mono-cylinder diesel engine [21] and of a new generation common rail four cylinders diesel engine [22].

In order to develop a catalytic filter for practical applications two more aspects must be taken into account: (i) the role of physical contact of deposited soot on the catalytic filter surface and (ii) the mechanism of soot catalytic oxidation. With this respect it must be remembered the complexity of the catalytic system due to the occurrence of a double heterogeneity involving a gas reactant (oxygen), a solid reactant (soot), and a solid catalyst. Macroscopic oxidation mechanisms of graphite have been proposed, such as deep channeling or edge recession [23]. The latter mechanism occurs when graphite is completely wetted by the catalyst resulting in higher activity [24]. In order to improve catalytic activity liquid catalysts, such as Cs₂SO₄·V₂O₅ were studied. Despite the relatively high activity exhibited by the catalyst it was concluded that the liquid state has no decisive influence on the catalytic performance [25].

Concerning the way of catalytic action on an atomic scale, the electronic mechanism [26] results in the enhanced reactivity of carbon substrate, while the oxygen transfer mechanism involves the catalyst reduction by carbon and reoxidation by gaseous oxygen [8,27]. Spillover mechanism was proposed to explain the coke catalytic oxidation in the absence of direct contact between catalyst and coke [28], while simultaneous occurrence of redox and spillover mechanism was evidenced in transition metal oxide catalysed carbon black oxidation [29].

The aim of this work was to give a contribution to the comprehension of the catalytic mechanisms of soot oxidation on Cu-V-K-Cl catalyst.

2. Experimental

2.1. Catalyst

Powder catalyst (named 137TF) was prepared by impregnating TiO₂ powder (DT51D, Rhône Poulenc) with aqueous solution of NH₄VO₃, CuCl₂·2H₂O and KCl (Baker Chemicals) [30,31]. The sample was then dried at 393 K and calcined at 973 K overnight. After calcination the amount of active species in the catalyst contributed for about 30 wt.%. TiO₂ powder had a specific surface area of 88 m²/g and a sulphate content, measured after chemical analysis, of 0.5 wt.% as SO₃.

2.2. Carbonaceous material

The carbonaceous material was soot collected at the exhaust of a gas oil burner operating at air/fuel mass feed ratios between 20 and 35. The soot specific surface area, measured by an area meter (SORP-TOMATIC, CARLO ERBA) through nitrogen adsorption at 77 K, was 90 m²/g (BET).

2.3. Experimental apparatus and procedures

The experimental apparatus used for performing constant temperature soot oxidation tests comprises a 300 mm height, 20 mm i.d. quartz tubular flow reactor, heated by an electrical furnace at controlled temperature (ASCÓN). Cylinder air and nitrogen (99.999% purity) were employed for obtaining 500 cm³/min

(STP) flow rate with 10 vol.% oxygen partial pressures of gas entering the reactor. Exhaust gas concentrations were determined by Hartmann and Braun continuous analysers: URAS 10E (for CO and CO₂) and MAGNOS 6G (for oxygen). The test started raising the temperature up to the desired value in nitrogen flow. Then the gas feed to the reactor was turned to the oxidising stream starting the oxidation. Carbon burn-off was followed by monitoring, through the continuous analysers, CO and CO₂ produced during gasification. The experiments were carried out under constant operating conditions. The temperature was investigated in the range 573–673 K in the case of catalytic tests and in the range 773–873 K in the case of uncatalytic tests. Mixtures of carbonaceous material and catalyst to be used in the experiments were prepared by properly pounding the two components in a mortar in order to assure a “tight” soot catalyst contact [14]. The initial mass ratio of soot and supported catalyst was 0.1. Further details of the apparatus and of the experimental procedure are reported elsewhere [32].

A two step process of catalyst reduction and subsequent re-oxidation was performed by employing a thermobalance coupled to a mass-spectrometer (TA-Instruments-2950 HR). In particular, the following tests were carried out:

- (i) Helium flow temperature-programmed reduction (TPR) of the catalyst by thermogravimetries (TGs) of soot-catalyst mixtures with a mass ratio of 0.1.
- (ii) Air flow temperature-programmed oxidation (TPO) of the above reduced soot-catalyst mixture.
- (iii) 5 vol.% hydrogen–helium flow TPR of the catalyst.
- (iv) Air flow TPO of the already reduced catalyst.

All the tests were carried out heating the samples at a rate of 5 K/min from ambient temperature to 973 K in a 60 cm³/min (STP) gas flow. In each test the amount of sample employed was about 50 mg.

3. Results and discussion

Data of concentrations of CO and CO₂ in the microreactor outlet gas were jointly integrated to determine the overall conversion of carbon X, defined as

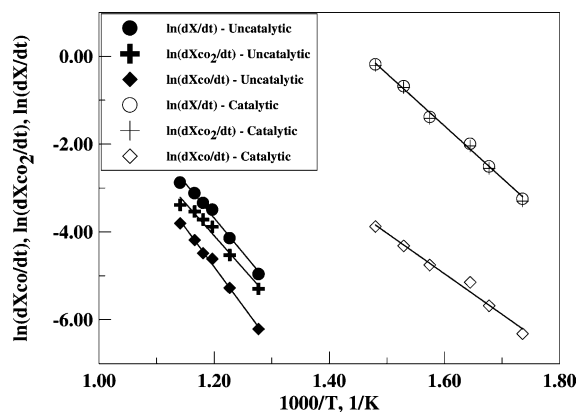


Fig. 1. Arrhenius plot for catalytic and uncatalytic oxidations of soot.

$(m_0 - m)/m_0$, m and m_0 being the current and the initial mass of soot, respectively. Also, they were separately processed to evaluate the partial conversions to CO (X_{CO}) and CO₂ (X_{CO_2}). Correspondingly, partial (dX_{CO}/dt and dX_{CO_2}/dt) and total (dX/dt) reactivity were also computed. The strong activity of the 137TF catalyst in the oxidation of soot appears from the comparison of the results of soot oxidation tests at constant temperature of soot/catalyst mixtures with mass ratio 0.1 and of soot alone. Such a comparison is made reporting data of carbon reactivity dX_{CO_2}/dt , dX_{CO}/dt , and dX/dt as Arrhenius plot in Fig. 1, from which the apparent activation energies E_a can be also evaluated. Reactivities, reported in Fig. 1, were computed at $X = 0.5$ but similar values were obtained in the range of X from 0.2 to 0.7. The observation of Fig. 1 suggests that in the case of catalytic oxidation the selectivity towards CO₂ is very high since dX_{CO_2}/dt practically coincides with dX/dt over the whole range of temperature explored. The apparent activation energies derived from the data in Fig. 1 are compared in Table 1 from which it appears that the presence of

Table 1
Apparent activation energy derived from data of Fig. 1

	E_a (kcal/mol)			ΔT (K)
	CO	CO ₂	TOT	
Uncatalytic	35	29	31	783–876
Catalytic	13	17	17	608–698

catalyst makes E_a about half of that evaluated in the absence of catalyst.

The dependence on the temperature of soot reactivities in the absence of catalyst conforms to that found previously with other carbonaceous materials [10,33] and is also in agreement with findings from literature [34–36]. Specifically, a slight prevalence of the slope of the straight line collecting $\ln(dX_{CO}/dt)$ points (E_{aco}) with respect to that related to $\ln(dX_{CO_2}/dt)$ (E_{aco_2}) (Table 1) suggests that the selectivity of the uncatalysed oxidation of soot toward CO_2 decreases exponentially with the temperature although, in the explored range of temperature (773–873 K), CO_2 yield remains higher than CO yield (Fig. 1).

As mentioned in the Section 2, a two step process of catalyst reduction (TPR), and subsequent re-oxidation (TPO) was carried out and the substances evolving from the sample were analysed by a mass spectrometer (MS). For the sake of clarity only major MS signals pertaining to the main detected species are shown in the figures. Specifically, for water only mass 18, for HCl only mass 36, for SO_2 only mass 64, for CO_2 only mass 44 and for H_2S only mass 34 are reported. In addition, when it was necessary to include signals of

different substances in the same figure, arbitrary scales not proportional to the original signals were employed. The reduction step was obtained by treating in helium flow a soot/catalyst mixture with a mass ratio of 0.1 in which the soot acted as reducing agent. The oxidation step, instead, was realised by treating in air flow the sample resulting from the previous step. Results of the reduction step are shown in Fig. 2 where the sample percentage weight with respect to the initial value and its changes (DTG) are reported as a function of temperature. The overall sample weight loss is 9% of the initial mass. The DTG curve presents a major peak at 825 K and minor peaks at 530, 625 and 895 K. When the mass spectrometry (MS) signals are considered, it appears that the major product of the reduction of the catalyst is, as expected, CO_2 . Therefore, the sample weight loss is mainly determined by carbon oxidation and the MS profile pertaining to CO_2 (mass 44) closely follows the DTG profile from 525 to 975 K (Fig. 2). SO_2 desorption starts at 775 K and presents a major peak at the same temperature at which DTG shows the major peak, and a minor peak at 880 K. Also a slight desorption of HCl (not shown in the figure) is observed after the major peak of combustion

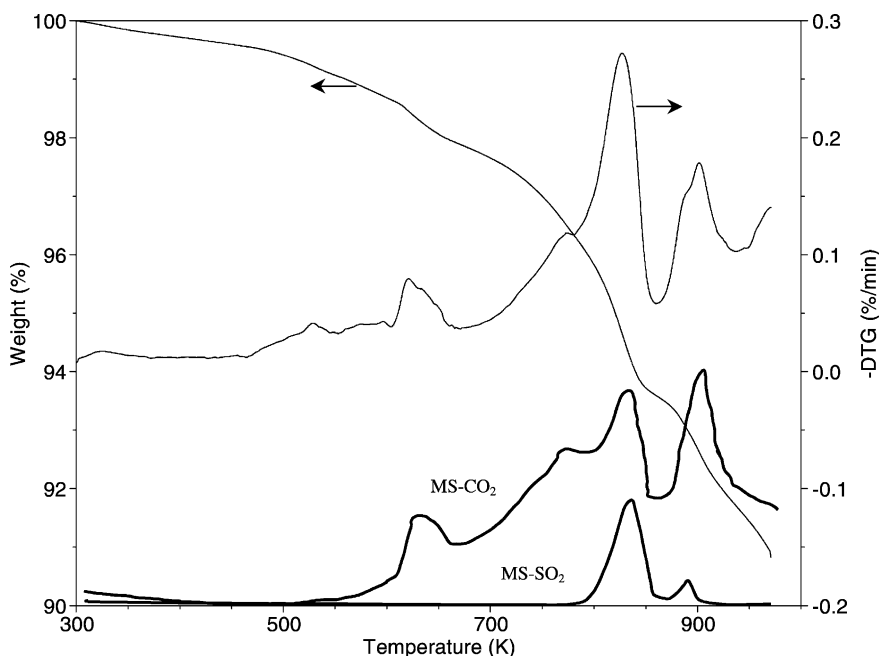


Fig. 2. Weight loss and DTG curves of a soot/catalyst mixture and the MS signals of substances evolved from it during the TPR in helium flow.

($T = 825$ K) ends (Fig. 2). Evolved CO profile (not shown) followed the CO_2 profile at much lower intensity. It is note worthy that in this test and in the others carried out on the fresh catalyst the presence of SO_2 and H_2S in the products stream derives from the decomposition of sulphates and sulphites present in the titania support. This, indeed, was partially sulphated and so contained some sulphur (see Section 2). As a result, TG analysis in air of the catalyst (not reported here) showed a 4% weight loss likely due to sulphites and/or sulphates decomposition in the range of temperature 625–975 K.

The results of TG–MS analysis in air flow of the previous sample after the treatment in helium are reported in Fig. 3. The percent sample weight curve and its derivative (DTG) clearly show a combustion peak at 655 K. The total weight loss is only 3.5% but, before the combustion starts (from 475 to 625 K), there is a growth of the sample mass likely due to the catalyst oxidation, which also continues up to 775 K after the end of carbon combustion. MS signals clearly show that only CO_2 desorbs significantly with a peak correspondent to the DTG peak. CO was not detected in this case because of the presence of N_2 in the gas stream,

which caused strong interference with CO analysis. It is note worthy that the catalyst re-oxidation step was carried out under conditions that cannot be considered strictly oxidising. Actually, the presence of soot in the sample with its reducing capability interacts with the catalyst oxidation process, as evidenced by the sample weight gain, loss and regain during the re-oxidation step (Fig. 3). If the reducing agent were a gas, different features should be expected for both the reducing and the re-oxidising steps. However, since the reduction mechanism by a gas reducing substance may be significantly different from that occurring by a solid reducing material, the mere utilisation of the results of the reduction by gas to infer features of the catalyst when reduced by carbon could lead to misleading conclusions. In any event, for comparison with the previous results a catalyst reducing and re-oxidising process was carried out by employing H_2 as reducing agent.

Results of a TPR test in 5% H_2 –helium flow of the catalyst are shown in Fig. 4 where the data are shown in the usual way. In this case the total weight loss, mostly occurring above 625 K, results to be about 6%. The DTG curve shows three major peaks at 665, 755

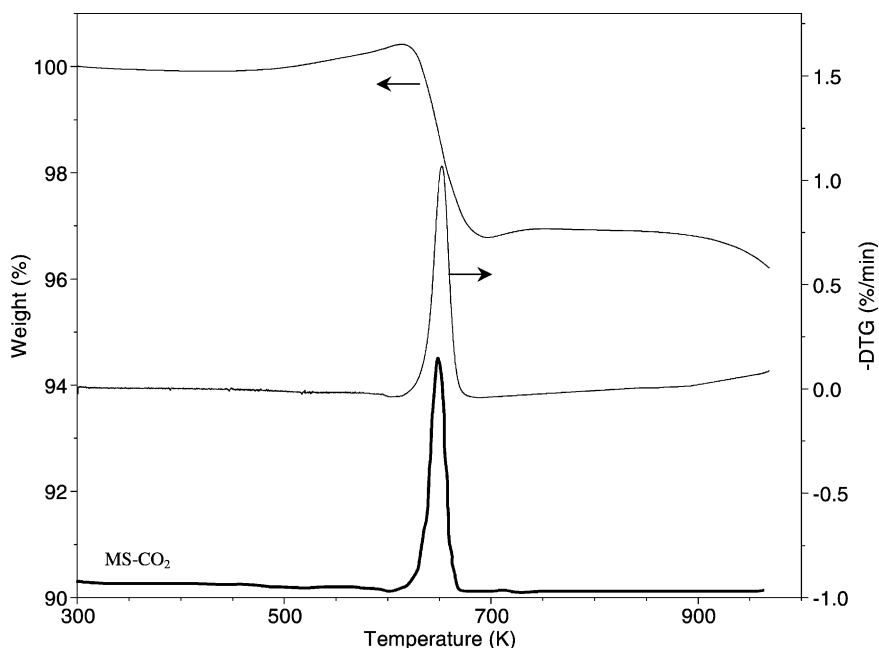


Fig. 3. Weight loss and DTG curves of a soot/catalyst mixture and the MS signals of substances evolved from it during the air flow TPO following TPR.

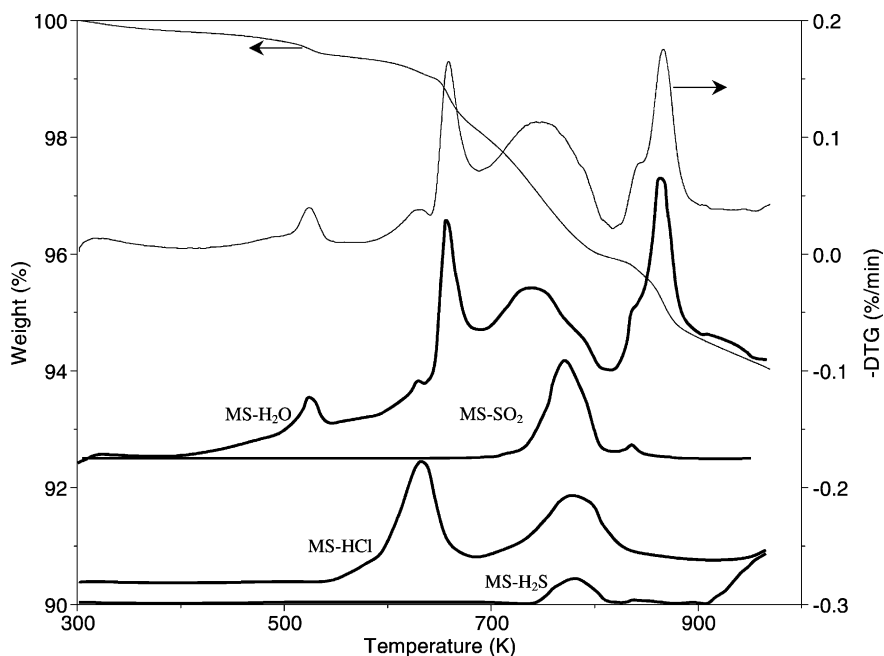


Fig. 4. Weight loss, DTG curves and MS signals of catalyst of substances evolved from it during the TPR in 5% H₂-helium flow.

and 865 K, the second of which is quite broad spanning from 695 to 815 K. There are also two minor peaks at 425 and 635 K. Considering the mass spectrometry (MS) signals, it appears that the major product of the reduction of the catalyst is H₂O followed in the order by HCl, CO₂, SO₂ and H₂S. The examination of Fig. 4 shows that MS signals pertaining to H₂O closely follow the DTG curve in all the investigated range of temperature. In contrast, HCl desorption starts at 525 K and continues up to 975 K with two peaks at 635 and 785 K. The first peak occurs in correspondence of one of the two minor peaks of the DTG curve while the second peak contributes to the formation of the broad DTG peak mentioned earlier. CO₂ evolution occurs between 375 and 665 K but the MS signals trend (not reported) does not recall any significant feature of the DTG curve. This CO₂ seems likely due to the desorption of atmospheric CO₂ adsorbed on the catalyst after the preparation. SO₂ is released from the catalyst from 673 to 883 K with a major peak at 780 K and a much minor peak at 845 K. Identical trend is shown by the MS signals related to H₂S but for a further growth of these signals from 915 to 975 K (Fig. 4).

Results of TPO test in air flow of the previously reduced catalyst are shown in Fig. 5 in the same way employed for the previous sample. The sample mass increases of about 4% between 525 and 655 K then loses about 1% above 825 K. The DTG curve presents one major peak at 615 K. The MS signals show that above 725 K there is a release of HCl and a smaller release of something with masses 49, 51 and 52, probably attributable to HClO.

Some indications, regarding the redox capability of the catalyst, the influence of the reducing substance on the reduction process, and their implications in the catalyst overall performances can be drawn from the set of results obtained in the present study. They may be useful for clarifying some relevant aspects of the mechanism and of the performances of the catalyst in the object.

The comparison of the Figs. 2 and 4 suggests that the catalyst reduction process, carried out by different reducing substances, presents differences but also similarities. An obvious difference is that the major product of the reduction is H₂O in one case and CO₂ in the other. It is note worthy that the catalyst is highly amorphous. Indeed, X-ray diffraction analysis of the

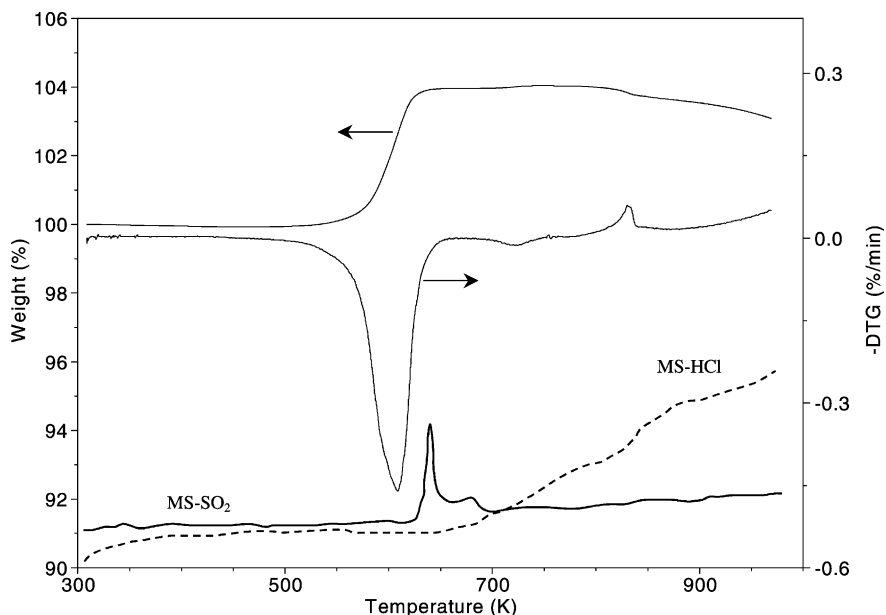


Fig. 5. Weight loss and DTG curves and the MS signals of catalyst of substances evolved from it during the air flow TPO following the TPR.

catalyst revealed the presence of KCl only while it did not reveal the presence of any specific oxides or oxygen containing compounds. However, it is clear that both H_2O and CO_2 derive, respectively, from the oxidation of H_2 and carbon by oxygen coming from the catalyst. An important difference is the marked desorption of HCl and the less significant desorption of H_2S in the case of reduction by H_2 with respect to the reduction by carbon. The HCl desorption means some loss of chlorine from the catalyst. The role of this element in this type of catalyst seems to be substantial for the activity of the catalyst when a “loose contact” [14] is realised with soot but does not seem to influence its activity when in the “tight contact” mode [37]. Therefore, in the specific context of the present work this difference should be of minor relevance. Another difference is the overall mass loss, which is 6% in the case of reduction by H_2 and 9% in the case of reduction by carbon. This discrepancy may be attributed to both the fact that in the case of reduction by carbon part of the mass of the reducing agent itself contributed to the weight loss, and the fact that HCl desorbs only during the reduction by H_2 . However, it appears evident that the general trend of the wt.% curves in Figs. 2 and 4 are comparable. In addition, the DTG curves as well

are fairly similar. Also the desorption of SO_2 , deriving from the titania support, is similar the only difference being a 50 K shift at higher temperatures of the MS signals in the case of catalyst reduction with soot.

In any event, even taking into account the due specificity, the comparison of the reducibility tests yielded substantially similar indications. That is the catalyst in the object, when exposed to a reducing environment, is able to deliver oxygen along the whole range of temperature from 480 to 1000 K, irrespective of the fact that the reducing substance is hydrogen or carbon.

Results show that the catalyst has marked capacity to reduce and oxidise when treated in proper environments. Indeed, the comparison between TPRs and TPOs tests carried out with the same catalyst sample shows that: a), even in the presence of desorption peaks, catalyst reduction occurs continuously within the whole investigated range of temperatures (Figs. 2 and 4); (b) in contrast, the re-oxidation appears as a strongly activated process. It occurs rapidly and within a relatively narrow range of temperatures, that is the region 545–675 K (Figs. 3 and 5). These findings were achieved either when the reducing substance was carbon or when it was H_2 . Actually, as we mentioned in

Section 3, in the case of the sample reduced by soot the re-oxidation endures, after the complete CO₂ release, up to 775 K. However, it is note worthy that in this instance during the catalyst re-oxidation a reduction process is also occurring because of the presence of soot for most of the test time.

Results also show that the catalyst activity is certainly related to its redox properties. Indeed, it is significant that, whatever the reducing substance, the temperature ranges within which the catalysts re-oxidise (Figs. 3 and 5) are similar each other and practically coincident with those at which soot oxidation occurs during normal TPO of soot catalytic combustion in laboratory apparatus [10,11,33]. Actually, this circumstance was already pointed out by the authors in previous work [32,33] for catalyst reduced by H₂ but it is now confirmed also in the case of catalyst reduced by soot. This, taking also into account the considerations expressed earlier in the comparison between TPO and TPR, it is suggested that the catalyst threshold temperature is certainly related to the rate of catalyst re-oxidation while the rate of the soot catalytic oxidation is determined by the rate of catalyst reduction.

In previous work we correlated the catalytic activity in soot oxidation with the reducibility of the catalyst in hydrogen [32,33]. More recently, this correlation was also sustained by other researchers [38]. In contrast, the use of reducibility results in H₂ to make hypotheses of redox catalytic mechanism in carbon oxidation was criticised in literature because it was argued that the reduction of metal oxides by hydrogen follows a different mechanism with respect to the reduction by carbon [39]. The results and the consequent discussion presented in this paper seem to confirm the substantial correctness of the correlation above. Nonetheless, in the light of these considerations it could be more appropriate to refer the catalytic activity in soot oxidation to the oxidation step of the catalyst after reduction rather than with the reduction step. This because, as mentioned earlier, reducibility occurs in a wide range of temperatures while the oxidation verifies only in a narrow range.

In literature redox and oxygen spillover mechanisms of catalysis are reported as parallel but alternative ways of carbon attack of some transition metal oxides catalyst. The first mechanism would act only when physical contact between soot and catalyst is es-

tablished [8,27] while the second one also should occur for indirect contact [28]. On the one hand we have clear evidence of the redox property of the 137TF catalyst and on the other hand in previous work [32,40] we experienced complete involvement of the overall soot surface during soot oxidation tests that would suggest a spillover mechanism. Probably, as suggested by Mul et al. [29] both can act simultaneously and further investigations are needed to ascertain if in our case one or the other prevails and in which operating conditions.

An alternative reaction mechanism has been recently suggested [38] for some metal oxide catalysts for soot oxidation, specially when containing potassium [41]. This further mechanism, in any case associated with a redox capability of the catalyst, would unfold via the formation of carbonate-type intermediates, which may form on the catalyst-soot interface by subtraction of carbon from the soot and then may decompose releasing CO₂. This possible path was inferred from the capability of such catalysts to interact with gaseous CO₂ [41]. Although in principle the occurrence of this mechanism cannot be excluded also in the case of the 137TF catalyst, further experimental supports, besides the only propensity to adsorb and release CO₂, would be desirable to be confident with such a thesis.

4. Conclusions

The high activity of the Cu-V-K-Cl based catalyst and its peculiarities in the catalytic soot oxidation were confirmed by the results of the present work.

The redox properties of the catalyst were clearly demonstrated by TPR and TPO treatments. Under this respect the substantial equivalence of soot and 5 vol.% H₂ in He mixture in reducing the catalyst was shown. MS analysis of the gaseous exhaust from the TPR and TPO allowed the determination of the main species desorbing from the catalyst or from the soot-catalyst mixture.

Catalyst reduction occurs from low to high temperature, while the re-oxidation process appears strongly activated leading to the conclusion that the catalyst threshold temperature is practically the catalyst re-oxidation temperature while the carbon oxidation rate is closely dependent on the catalyst reduction rate.

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