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Catalytic combustion of carbon particulate

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Abstract

The catalytic combustion of carbon particulate was investigated with the aim of developing a catalyst for the abatement of soot in diesel exhausts. In the presence of a Cu/V/K based catalyst a strong increase of the rate of carbon combustion and a marked decrease of the apparent activation energy were observed. The carbon reactivity showed a linear dependence upon the initial ratio of the mass of catalyst to the mass of carbon and a square root dependence upon the oxygen partial pressure. However, catalytic combustion of diesel soot and partially graphitized carbon black confirmed previous results obtained for other carbon materials. In particular, kinetic data follow a model proposed for the catalytic combustion of amorphous carbon black [1]. An extension of this model, incorporating the influence of carbon–catalyst contact on the catalyst performances, has been presented.

Keywords: Combustion; Carbon particulates

1. Introduction

Stringent standards for emissions from combustion systems require the development of new technologies to remove carbon particulate from exhausts. Depending on the combustion process application (diesel engine for vehicles or cogeneration systems, oil fuelled burners, etc.) the high content of unburned carbon (50–95%) makes the accomplishment of this operation through a catalytic post-combustion process attractive. Moreover, the physico-chemical features of carbon particulate as well as its reactivity depend on both the source and the operating conditions responsible for its formation. In the case of automotive diesel exhausts the process must be implemented with an efficient filtering system whose regeneration is accomplished by catalytic combustion of captured soot [2].

In previous works we reported on the performances of a Cu/V/K based catalyst (137AA) in the combustion of various carbon materials ranging from fullerene to graphite [1–3]. As this catalyst is active in the direct oxidation of the carbonaceous matrix of particulate [2], it is a candidate to be employed for the catalytic control of particulate emissions from diesel engines as well from oil fuelled power stations. In this work the catalytic combustion of partially graphitized carbon black and of soot collected at an automotive diesel engine exhaust has been investigated. A descriptive kinetic model for particulate catalytic oxidation has been proposed. It is the extension of

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a model developed for amorphous carbon black catalytic oxidation [1].

2. Experimental

The catalyst 137AA was prepared by impregnating α-Al_2O_3 powder (s.s.a. = 2.7 m^2/g,) with aqueous solution of the following salts: NH_4VO_3, $CuCl_2 \cdot 2H_2O$ and KCl (BAKER Chemicals). The catalyst was then dried at 393 K and calcined at 973 K overnight [4].

Two carbon materials were used, i.e., soot (DS) collected at the exhaust of a diesel engine (LOMBARDINI, single cylinder, D.I., 325 cm^3 displacement, 18:1 compression ratio) and partially graphitized carbon black (Graphpac GB, Table 1). Kinetic results of combustion of an amorphous carbon black (CB-330, Table 1) were also utilized for comparison.

A simultaneous thermoanalyser (NETZSCH STA 409) was employed to perform air flow temperature-programmed thermogravimetries of either the carbonaceous material alone (uncatalyzed combustion), or mixed with the catalyst (catalyzed combustion). In the latter case the initial mass ratio, Rm, of carbon particulate to catalyst was 0.1. Air flow rate was 21 Ncm^3/min, whereas the temperature was increased from 293 K to 1373 K at a rate of 10 $Kmin^{-1}$.

Tests of carbon combustion were carried out at constant temperature in a quartz flow reactor connected on-line with CO, CO_2 (NDIR, Uras 10E) and O_2 (paramagnetic, Magnos 6G) HARTMAN and BRAUN analyzers. Mixtures of carbon material and catalyst were prepared by thorough pounding of the two components in a mortar. Carbon particulate, either alone or mixed with the catalyst, was diluted with quartz particles and loaded in the central zone (3 cm) of the reactor, which operated as a differential reactor with respect to oxygen concentration. The gas feed flow rate was 500 Ncm^3/min and the operating pressure 101 kPa. The oxygen molar fraction in the gas feed ranged from 0.03 to 1. The temperature was varied in the range 573–673 K in the tests carried out in the presence of catalyst. In the absence of catalyst the ranges were 773–873 K with DS and 923–1023 K with Graphpac. The explored range of Rm was 0.033–0.4. Carbon oxidation rate and conversion degree were calculated from the concentrations of carbon oxides measured in the reactor outlet gas. Carbon mass balance was verified within a 5% tolerance for all tests.

Carbon oxides temperature programmed desorption (TPD) was performed with the same experimental apparatus described above. TPD from carbon particulate, either alone or mixed with catalyst, was obtained by rising up the temperature from 293 K to 1373 K at a rate of 900 Kh^{-1} in nitrogen flow. The concentrations of CO and CO_2 evolved from the carbon surface were measured on line with the NDIR analyzers [5].

3. Results and discussion

Results of thermogravimetric tests in air flow are reported in Table 1 as values of the peak temperatures (Tm) of the thermogravimetric derivative curves. In the absence of catalyst soot is the most reactive material, showing the smallest value of Tm, compared to CB-330 and to Graphpac (Table 1). This trend suggests that the carbon

Table 1

Comparison of Tm and E_a for uncatalyzed and catalyzed combustion of carbon materials

Material	s.s.a. (m^2/g)	Source	Uncatalyzed		Catalyzed	
			Tm (K)	E_a (kcal/mol)	Tm (K)	E_a (kcal/mol)
DS	90	Diesel engine	903	36.0 ± 3	623	23.6 ± 2
Graphpac GB	110	ALLTECH	1073	49.9 ± 4	607	19.8 ± 2
CB-330	86	DEGUSSA	921	41.8 ± 3	617	17.9 ± 2

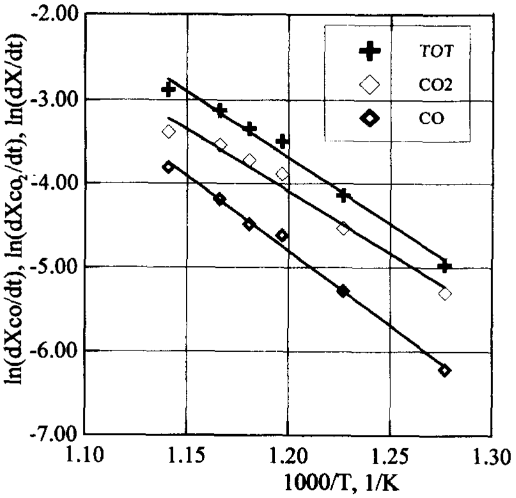

Fig. 1. Arrhenius plot for the uncatalyzed combustion of DS. $P_{O_2}=0.1$ atm and $X=0.5$.

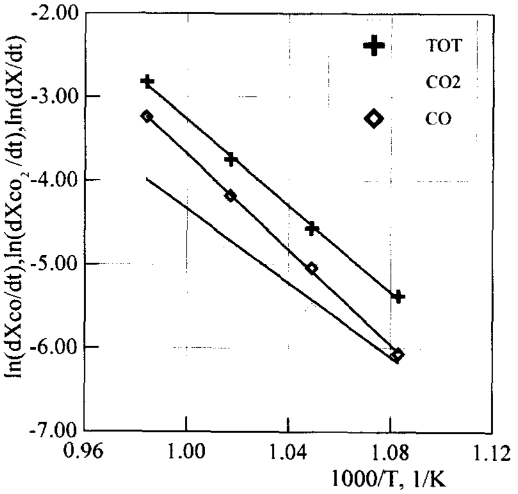

Fig. 2. Arrhenius plot for the uncatalyzed combustion of Graphpac. $P_{O_2}=0.1$ atm and $X=0.5$.

structure heavily affects the reactivity. The presence of catalyst significantly lowers the Tm values and flattens their differences, reducing them from about 170 K of the uncatalyzed case down to about 20 K (Table 1).

3.1. Kinetic measurements

Time integration of carbon monoxide and dioxide concentrations in the reactor outlet gas was performed in order to determine either the overall conversion of carbon $X=(m_0-m)/m_0$, where m and m_0 are the current and the initial mass of carbon, respectively, or the partial conversions to carbon monoxide (X_{CO}) and carbon dioxide (X_{CO_2}). Results of the uncatalyzed combustion of DS and Graphpac in the microreactor are shown in the Arrhenius plots of Fig. 1 and Fig. 2, respectively. It is worthwhile to note that the reactivity values reported in Fig. 1, Fig. 2, Fig. 3, Fig. 4 and Fig. 5 were all computed at $X=0.5$ but similar values were obtained in the range of X from 0.2 to 0.7. The trends of DS and Graphpac reactivities with the temperature are similar to that found with CB-330[5] and also agree with other findings from literature [6,7]. Specifically, the slightly

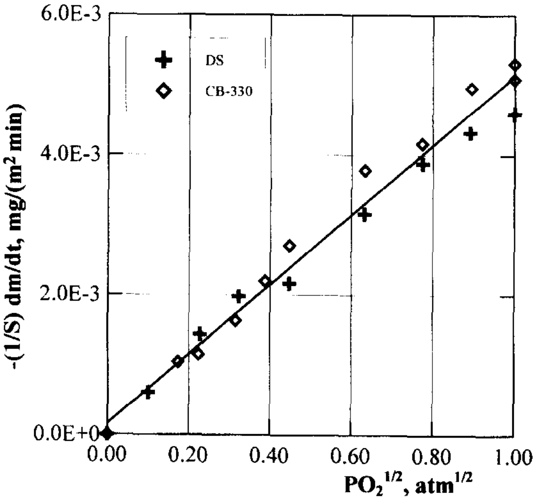

Fig. 3. Influence of oxygen molar fraction on reactivity of DS-catalyst and CB330-catalyst mixtures. Rm = 0.1, $X=0.5$ and $T=593$ K.

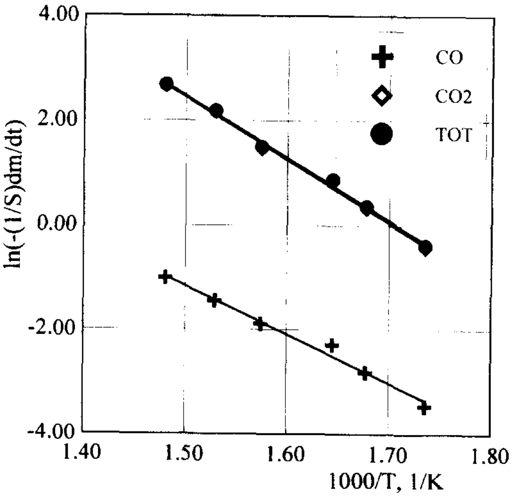

Fig. 4. Arrhenius plot for the catalytic combustion of DS. Rm = 0.1, $P_{O_2}=0.05$ atm and $X=0.5$.

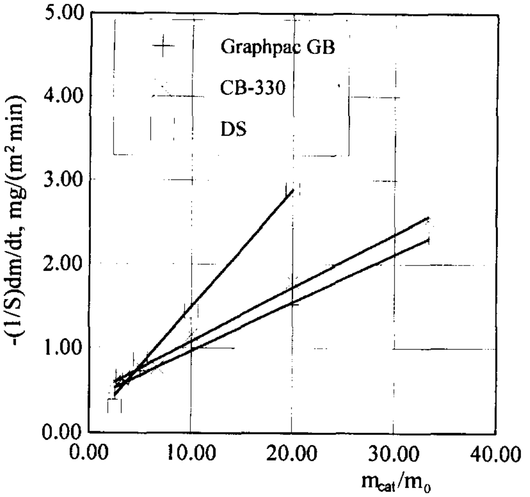

Fig. 5. Effect of m_{cat}/m_0 on catalytic combustion of DS, Graphpac and CB-330. $P_{O_2}=0.05$ atm, $X=0.5$ and $T=593$ K.

greater slope of the straight line collecting $\ln(dX_{CO}/dt)$ points with respect to that related to $\ln(dX_{CO_2}/dt)$ suggests that the selectivity towards CO_2 of the uncatalyzed oxidation of DS and Graphpac decreases exponentially with the temperature. However, the comparison of Fig. 1 and Fig. 2 shows that DS is more reactive than Graphpac, the latter showing values of dX/dt similar to that obtained with DS at temperature 100 K lower. DS appears more reactive even with respect to CB-330 [5] although in this case the differences are less marked. Moreover, the combustion of DS in the range of temperatures 773–873K favors the formation of CO_2 with respect to CO (Fig. 1), whereas the opposite is shown by Graphpac, even if in a different range of temperatures (923–1023 K). In the case of the combustion of CB-330 the amount of CO in the range of temperatures 773–873 K was substantially the same as CO_2 [5]. This suggests that impurities contained in DS act as catalysts of carbon oxidation since a high selectivity toward CO_2 formation is typical of the catalyzed oxidation [1,5]. This catalytic effect can explain why at a given temperature the overall carbon combustion rate of DS is higher than that of Graphpac (Fig. 1 and Fig. 2) and of CB-330 [5]. A further peculiarity of DS behavior is the tendency of the slope of the interpolating straight line to decrease as the temperature increases. Actually, this circumstance could be due to the likely increase of the carbon oxidation rate at relatively low temperature because of the catalytic effect above, that becomes progressively less influent as the temperature increases.

Results of the catalytic combustion of DS and Graphpac in the microreactor, confirm previous findings obtained for CB-330 [2]. In the presence of catalyst the carbon reactivity depends linearly on the square root of the oxygen partial pressure as shown by comparing DS and CB-330 data of Fig. 3. In this figure the reactivity is the carbon mass change per unit time and per unit carbon surface S, i.e., $-dm/Sdt$. Results obtained with Graphpac follow the same trend.

Moreover, in the presence of catalyst the selectivity toward CO_2 formation approaches 100% and remains almost constant when temperature or carbon conversion change. This can be argued from the comparison of the Arrhenius plots for CO, CO_2 and $(CO+CO_2)$ formation reported in Fig. 4 in the case of soot oxidation.

The apparent activation energy E_a derived from the data of Fig. 4, is compared in Table 1 with those obtained with Graphpac, with CB-330, and with the corresponding values for the uncatalyzed oxidations. According to findings of thermogravimetric tests, the presence of catalyst heavily lowers E_a for all the materials and makes these values very close to each other in spite of their different structure, probably responsible of the marked differences of E_a values of the corresponding uncatalyzed reactions (Table 1). The influence of the catalyst is less pronounced in the case of DS with respect to CB-330 and Graphpac, although E_a of uncatalyzed soot oxidation has the lowest value. As shown in Fig. 5, DS and Graphpac catalytic reactivities, conforming to the behavior of CB-330 [1], depend linearly on the ratio of the initial mass of catalyst to the mass of carbon. Therefore, whereas straight lines collecting points related to CB-330 and Graphpac are almost coincident, the straight line corresponding to soot shows a greater slope. This suggests that with soot a more efficient carbon-catalyst contact is realized as Rm decreases.

The oxidation of carbon particulate in the presence of catalyst 137AA shows two features making the mechanism of oxidation different from that of the uncatalyzed case. The first is that the order of reaction with respect to P_{O_2} is 0.5 and the second that the differences in the apparent activation energies of the various carbon materials are almost nullified by the catalyst.

The order of reaction 0.5 with respect to P_{O_2} is clearly imposed by the presence of catalyst. Indeed, it must be considered that the main product of the catalyzed reaction is carbon dioxide (Fig. 4). The uncatalyzed oxidation of the same carbon materials leads to an 0.8 order of reaction, with respect to oxygen, for CO_2 formation. Moreover, the reaction order reported in literature [6–9] for the uncatalyzed carbon oxidation to carbon dioxide is almost 1, so that the order of reaction 0.5, found for the catalyzed conversion of carbon to carbon dioxide, reflects the presence of catalyst.

The smoothing of the differences in E_a of the various carbon materials suggests that the energies involved in the reaction do not depend on the nature and on the energetic state of carbon atoms in the carbon particle. This leads to the conclusion that the limiting step in the overall reaction mechanism should be related to the interaction between catalyst and carbon surface rather than to this latter alone. In particular, a redox mechanism involving the surface species of the catalyst containing Cu and V may be hypothesized [1].

3.2. TPD measurements

Results of carbon dioxide TPD are reported in Fig. 6 and Fig. 7. In Fig. 6 the rates of carbon mass desorbed as CO_2, from DS and CB-330 samples, normalized with respect to the initial mass of carbon m_0, are reported as functions of the temperature. For CB-330 the rate of desorption of surface complexes giving rise to carbon dioxide has a main peak ($T = 576$ K) with minor peaks at higher temperatures. The shape of the specific desorption rate of CO_2 versus temperature for soot sample is similar, but more clearly multimodal with peaks at 673, 920, 1086 and 1202 K (Fig. 6).

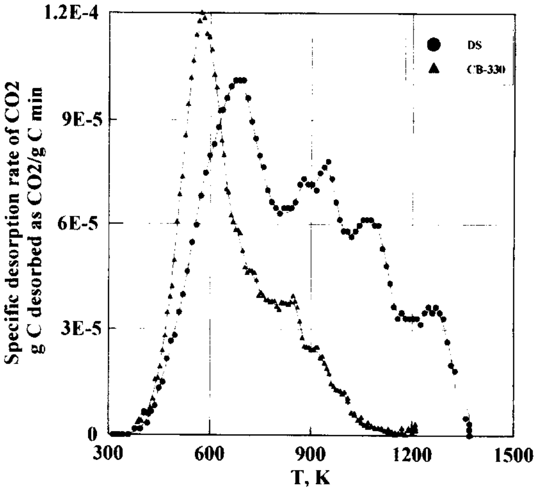

Fig. 6. TPD of CO_2 in nitrogen flow for CB-330 and DS. $dT/dt = 900$ Kh^{-1} and N_2 flow rate = 500 Ncm^3/min.

Moreover, for temperatures above 650 K, and hence also in the range of temperatures 773–873 K at which the data of Fig. 1 refer, the rate of CO_2 desorption from DS surface is markedly higher than that from CB-330. Therefore, the different reactivities of DS and CB-330 are parallel with the differences of the relevant CO_2 desorption rates.

When carbon particulate was mixed with the catalyst, the rate of CO_2 desorption was dramatically increased. Moreover, the differences between the rates of desorption from the two carbon materials level off. Indeed, both curves in

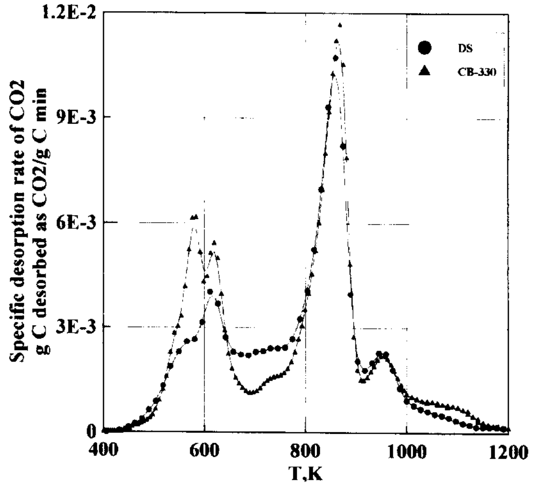

Fig. 7. TPD of CO_2 in nitrogen flow for CB-330 and DS. Samples mixed with catalyst, Rm = 0.1, $dT/dt = 900$ Kh^{-1} and N_2 flow rate = 500 Ncm^3/min.

Fig. 7 show a multimodal trend with a double peak at 543 and 608 K and a peak at about 931 K. From the literature [7,10,11], the presence of carbon dioxide in the outlet stream is related to the formation of (C–O_2) complexes on the sample surface. In this view, for both materials the first peak in Fig. 7 should indicate the presence of a conspicuous fraction of the total CO_2 that desorbs at relatively low temperatures.

In the presence of catalyst the overall amount of CO_2 evolved per unit carbon mass increases from 0.3 to 10.2 mmol/g in the case of DS and from 0.2 to 11 mmol/g in the case of CB-330. The high value of CO_2 desorption rate and consequently the large amount of CO_2 totally desorbed does not agree with the previous hypothesis. In fact a coverage degree of carbon surface greater than 100% is obtained in this case. A better explanation of this results could be obtained considering that, in the presence of catalyst, the CO_2 developed during TPD experiment is the product of a redox reaction between catalyst and carbon [1,12]. In this case the catalyst acts as oxygen donor to the carbon giving as products the reduced catalyst and gaseous CO_2. It is worth to note that the reduction of catalyst in hydrogen [1] results in the loss of about 1.25 mmol O_2 per gram of catalyst, or, for Rm = 0.1, about 12.5 mmol O_2 per gram carbon, in very good agreement with the amount of CO_2 detected in TPD tests. Therefore this result strongly supports a redox mechanism for the catalyzed combustion [1]. In the light of the previous explanation it is possible to give an interpretation of the attenuation of the differences between the reactivities of the various materials in the presence of catalyst (Table 1 and Fig. 3). Indeed, Fig. 7 shows that for both CB-330 and DS the formation of CO_2 at relatively low temperatures has almost the same rate. Therefore, only small differences in reactivity between the two materials should be expected, provided the enhanced formation of CO_2 is responsible for the marked increase of the oxidation rate with respect to the uncatalyzed reaction.

4. Model

In the previous investigation on the catalytic combustion of CB-330 [1] a general equation for the catalytic combustion of carbon particulates has been formulated:

$$-\mathrm{d}m/\mathrm{d}t = kS(m_{\mathrm{cat}}/m_0)P_{O_2}^{1/2} \qquad (1)$$

where k is the kinetic constant and S the total carbon surface whose change with the conversion degree of the reaction was computed assuming that carbon particles are agglomerates of small spheroidal (300 Å average diameter) grains. Such a model, which supposes that the reaction on the carbon surface is kinetically controlled and that all the exposed surface participates to the reaction, has been successfully employed for the uncatalyzed combustion of the soot produced in a flame [13]. The comparison of the measured reactivity of CB-330 and the prediction of Eq. (1) in the case of Rm = 0.1 is reported in Fig. 8. The agreement is satisfactory, but it becomes poor when results obtained at Rm higher than 0.1 are considered. Indeed, time profiles of reactivity obtained with Rm greater than 0.1 show a maximum that cannot be described by Eq. (1). The amplitude of the maximum increases as Rm increases eventually becoming higher than the initial value of the reactivity (Fig. 8, Rm = 0.4). This suggests that a

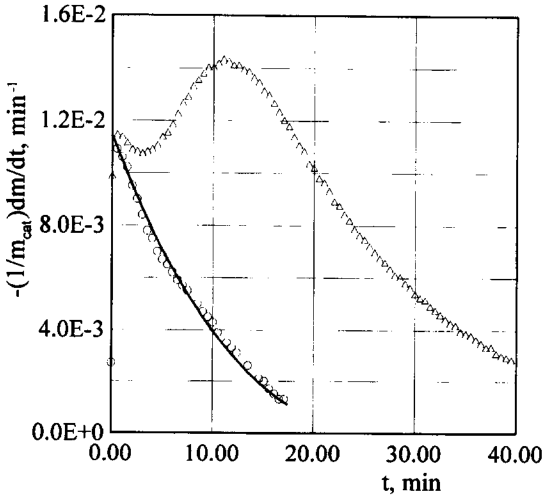

Fig. 8. Rates of CB-330 catalytic oxidation. P_{O_2} = 0.05 atm, T = 593 K and Rm = 0.1. ○ experimental data — Eq. (1); Rm = 0.4: △ experimental data.

more complex model must be hypothesized. Moreover, it must be taken into account that in the whole range of the Rm values there is always some segregation of carbon particles. Indeed at small values of Rm, a fraction of carbon is in contact with the fraction of inactive catalytic surface, while at great values of Rm a fraction of carbon is not in direct contact with the catalytic surface. In both cases a fraction of carbon will start to react only when the catalytic sites become available, as carbon covering these sites has reacted. A critical aspect of the present investigation is to define the effectiveness of carbon–catalyst contact, since it influences the catalytic performance. Experiments have confirmed that a given coverage of catalyst surface by carbon is reproducible by a standard sample preparation procedure by mechanical pounding.

The considerations above lead to the formulation of a model that takes into account the effectiveness of carbon–catalyst contact. The total amount of carbon is divided in two fractions reacting through different paths. The first fraction (m_{01}/m_0) is in direct contact with the catalyst active surface or anyhow contained in the field of activity of the catalyst. The other fraction (m_{02}/m_0) is segregated for the reasons described above and its reaction rate depends on the availability of active surface and, therefore, on the amount of the first fraction already reacted.

The equations of this model are:

$$-\mathrm{d}\frac{y_1}{\mathrm{d}t} = k_y\, y_1^{2/3} \frac{m_{\mathrm{cat}}}{m_{01}} P_{O_2}^{1/2} \tag{2}$$

$$-\mathrm{d}\frac{y_2}{\mathrm{d}t} = k_y (1 - y_1)^n y_2^{2/3} \frac{m_{\mathrm{cat}}}{m_{01}} P_{O_2}^{1/2} \tag{3}$$

$$m_{01} + m_{02} = m_0 \tag{4}$$

where y_1 and y_2 are, respectively, the ratios of the current masses m_1 and m_2 to the initial masses m_{01} and m_{02} of carbon pertaining to the first and the second fraction defined above and implicitly contained in the model as parameters. The kinetic constants k_y in Eqs. (2) and (3) are substantially the constant k of Eq. (1) although they appear formally different. Indeed, according to the structural model for carbon particles introduced above, it is possible to transform the dependence from S in the dependence from $m^{2/3}$ at less of constants incorporated in k_y. Moreover an Arrhenius type law:

$$k_y = A_y \exp(-E_a/RT) \tag{5}$$

has been considered. The model parameters (A_y, E_a, n and m_{01}/m_{cat}) have been estimated making use of a numerical code available in literature [14], arranged for the case in object and tested with experimental data collected with CB-330. First the values of A_y and E_a have been estimated at Rm = 0.1 from Eq. (5). Then, the effect of Rm on CB-330 reactivity has been modelled with Eqs. (2) and (3) and the values of n and m_{01}/m_{cat} estimated (Table 2).

Table 2
Estimated model parameters for CB-330 catalytic combustion

Rm	n	m_{01}/m_{cat}	m_{01}/m_0
0.1	2.5	0.085	0.850
0.2	2.5	0.061	0.305
0.3	2.5	0.074	0.246
0.4	2.5	0.078	0.195

$T = 593$ K, $A_y = 7.8 \times 10^4$ $g_{\mathrm{CB\text{-}330}}/g_{\mathrm{cat}}$ min atm and $E_a = 17.4$ kcal/mol, estimated by the model.

The values of the parameters have been obtained minimizing the differences between model predictions and experimental points. The calculated value for E_a agrees very well with the experimental value in Table 1. The exponent n found by calculation should reflect the rapidity by which the segregated fraction of carbon gains access to the active catalyst surface. Presently, the estimated value of n does not allow a satisfactory explanation, so this aspect requires more investigation. The fraction m_{02}/m_0 of the overall carbon increases as Rm increases: it is relatively small when Rm is 0.1 but becomes dominant already at Rm = 0.2.

Altogether, preliminary results are satisfactory, the experimental time profiles of the reactivity being well described, as shown in Fig. 9 in the case of Rm = 0.3. In this figure the single contributions of the Eqs. (2) and (3) are also shown.

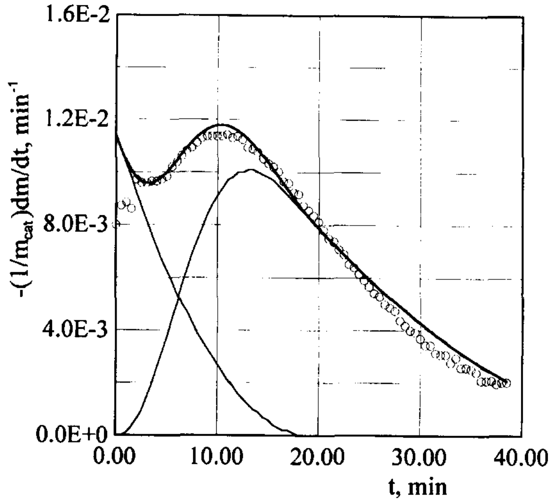

Fig. 9. Rates of CB-330 catalytic oxidation. $P_{O_2}=0.05$ atm, $T=593$ K and Rm = 0.3. O experimental data, — Eqs. (2) and (3), - - - Eq. (2), · · · Eq. (3).

It is worth noting that the contribution of Eq. (2) is practically the same of the prediction of Eq. (1) in the case of Rm = 0.1 reported in Fig. 7.

5. Conclusions

The rates of oxidation of diesel soot and carbon black in the presence of catalyst 137AA show linear dependencies of the carbon surface and of the ratio of the mass of catalyst to the initial mass of carbon while they depend on the square root of the oxygen partial pressure. However, diesel soot exhibits greater reactivity than the other carbon materials, likely due to catalytic effects of impurities.

The rate of catalyzed reaction depends on the temperature according to the Arrhenius equation. The catalyst significantly increases the rate of combustion, lowers the apparent energy of activation E_a and attenuates the reactivity differences among the various carbon materials.

The TPD technique appears an effective tool for the study of the mechanism of carbon particulate catalyzed oxidation. The strong increase of the rate of carbon oxidation in the presence of catalyst could be associated to the strong increase of carbon dioxide formation, due to the reduction of the catalyst.

An improved kinetic model for the catalyzed combustion of carbon particulate, taking into account the different effectiveness of carbon–catalyst contact, gives a good correlation with the experimental results.

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