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Investigation of the oxidation behavior of diesel particulate matter

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Abstract

In this work, an attempt was made to identify and decouple several effects contributing to the complexity of kinetics of diesel particulate matter oxidation by oxygen. Adsorbed hydrocarbons provided limited contribution to the overall reactivity of the un-pretreated particulate matter. Even upon their thermal desorption, the first few percents of carbon in particulate matter were oxidized at an anomalously high rate. Further oxidation occurred at a lower rate with rather uniform kinetic characteristics. The high initial reactivity can be restored repeatedly by exposure of particulate matter to the ambient air for the prolonged periods of time (weeks) at room temperature. The experimental results suggest that these changes in reactivity of carbon are chemical, not morphological, in nature. The results are consistent with the hypothesis that prolonged ambient aging leads to formation of some highly reactive groups on the carbon surface, responsible for the subsequent relatively facile initial oxidation. A high density of these surface groups presumably cannot be obtained during the more vigorous oxidation process at higher temperatures.

Keywords: Diesel particulate matter; Carbon; Oxidation; Kinetics

1. Introduction

Emissions of particulate matter, soot, from diesel engines are a subject of increasingly stringent environmental regulations [1]. In recent decades, substantial understanding of the processes leading to diesel particulate matter formation and in-cylinder oxidation has been developed [2–5], which supported a dramatic improvement of engine-out emissions.

However, to satisfy new standards, including 2007 regulations for mobile diesel applications, further reduction of particulate matter is required. This can be achieved using diesel particulate filters (DPFs) installed in the exhaust stream. Unfortunately, under the majority of driving conditions, regeneration of the DPFs by oxidation of particulate matter is challenging. Knowledge about oxidation of diesel particulate matter under conditions found in diesel exhaust is less mature and still quite controversial, as summarized in an excellent recent review by Stanmore et al. [5]. The controversy applies not only to the quantitative data, but also to the qualitative trends. For example, contradicting accounts of the effect of water vapor on the reactivity of various particulate matter samples is given in the publications by Neft et al. [6] and in one of the earlier publications of our group [7]. Additional complication is related to the fact that reactivity and other properties of particulate matter samples are known to strongly depend on their origin [5,6,8–10].

This work represents part of an on-going project targeted at understanding the effect of various diesel exhaust conditions on the rate of oxidation of real diesel

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particulate matter, collected from various engines and duty cycles. The ultimate objective was to obtain the kinetic information, required for the development of robust and efficient DPF regeneration strategies.

2. Experimental

2.1. Particulate matter samples

Two samples of diesel particulate matter, herein referred to as "A" and "B", were used in this work. Sample A was generated by an engine running through repetitive low-load cycles; sample B by a different engine operated in a low-load steady-state mode. In both cases, ultra-low sulfur diesel fuel (<15 ppm) was used. The particulate matter samples were accumulated for many hours on cordierite DPFs (NGK C-558, 100 cpsi). Due to the relatively low exhaust temperatures, the rate of oxidation of the particulate matter during the collection process was very substantially lower than the rate of soot generation by the engines. At the end of the loading process, the DPFs were taken out of the exhaust system, and the diesel particulate was transferred into sample containers, which were sealed and stored under ambient conditions.

Samples A and B differed by ash content (14 and 6.5 wt.%, respectively) and volatile organic fraction (13 and 9 wt.%, respectively). Also, their reactivity was found to be significantly different, as reported in our earlier publication [10].

2.2. Experimental setup

2.2.1. Reaction system

A simplified diagram of the reaction system used to collect the bulk of the results in this work is shown in Fig. 1. Bottled gases (UHP grade, supplied by Inweld Corp.) were blended using the mass-flow controllers (MKS). Particulate matter samples were diluted with a large excess of pre-washed irregularly shaped fused silica chips (40–60 mesh) and loaded into a custom-designed fixed-bed fused silica reactor, which is described elsewhere [7]. Unless otherwise noted, the following conditions were used: sample—50 mg of un-pretreated particulate matter; total gas flow rate—400 scm^3/min; gas composition—10 vol.% O_2, balance He. The nominal residence time of the reaction gas in the soot/quartz chips sample bed was $\sim 2 \times 10^{-4}$ h. The experimental setup minimized the impact of gas-phase mass-transfer, ensuring adequate exposure of the soot particles to the O_2. We believe this is equivalent to close contact between particulate matter and exhaust gas flowing through the soot layer in the DPFs.

We have equipped the reaction system with a downstream reactor containing an oxidation catalyst, in order to achieve complete oxidation of CO and thus account for the overall amount of oxidation products in the form of CO_2. Furthermore, during the temperature-programmed desorption (TPD) experiments performed under a flow of He, auxiliary flow of O_2 was introduced upstream of the oxidation reactor, in order to oxidize the desorption products to CO_2. This arrangement has enhanced the detection limit and overall accuracy of the carbon balance, due to the measurement of a singe product. The efficiency of the oxidation catalyst was previously characterized using diluted CO gas (5000 ppm/He), and complete oxidation was observed below 200 °C. In all the reported experiments, the temperature of this secondary reactor was maintained at 350 °C.

The partial pressure of CO_2 in the effluent gas was measured using a quadrupole mass-spectrometer

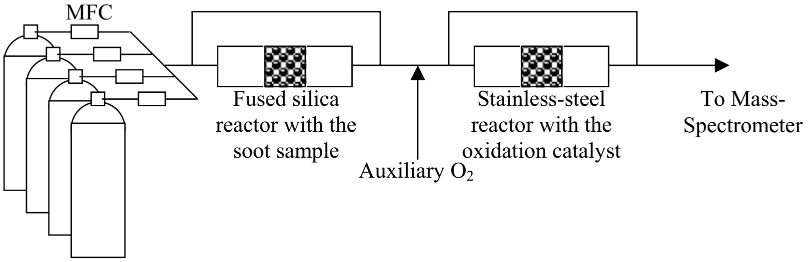

Fig. 1. Simplified schematics of the bench reaction system.

(Dycor) equipped with a custom-made capillary inlet system [11]. The CO_2 signal ($m/z = 44$) was normalized to the signal of the carrier gas He ($m/z = 4$), and absolute values were derived from daily calibrations against five different mixtures with known partial pressures of CO_2. The partial pressure of O_2 ($m/z = 32$) in the effluent gas was also continuously monitored to track its consumption by the oxidation reaction. Only the data within the differential O_2 consumption region were used for the kinetic analysis.

2.2.2. Thermo-gravimetric analysis (TGA)

In this work we used a thermo-gravimetric analysis (TGA; Perkin-Elmer TGA 7) primarily to confirm observations obtained using the bench reaction system. Due to the known mass-transfer limitation of the conventional TGA instruments for the particulate matter oxidation studies [5,12,13], the TGA data were only used for qualitative comparisons. Several milligrams of particulate matter were poured into the TGA pan without packing to minimize restrictions to the gas diffusion through the bed. The samples were then tested by the temperature-programmed oxidation (TPO) protocol described below using a 20/80 vol.% O_2/N_2 mixture.

In our experiments at temperatures below 550–600 °C, the problems of mass-transfer through the sample bed and poor dissipation of the reaction heat were found to be inconsequential, due to low rates of reaction. In this temperature range, excellent repeatability of the TGA results was observed, even between the experiments where the initial amount of particulate matter varied from less than 3.0 to over 4.5 mg. Also, we have consistently observed good agreement between the lower-temperature results obtained using TGA and the bench reaction system.

2.3. Experimental procedures

Several complementary experimental techniques were used in this work.

2.3.1. Temperature-programmed oxidation (TPO)

The sample of particulate matter was heated to 150 °C under a flow of He, then exposed to the gas flow of desired composition, and heated at a 5 °C/min rate to 700 °C. Complete oxidation of particulate matter was achieved by the end of the experiment in order to close the carbon balance. The results of TPO experiments are typically reported in the temperature range from ∼250–330 °C to ∼600 °C, which translated into the range of integral particulate matter conversions from <1 to ∼60–85%. The lower temperature boundary, related to the detection ability of our analytical system, was controlled by the reactivity of particulate matter samples. Very high oxidation rates at higher temperatures lead to experimental problems, such as poor dissipation of the heat of reaction, external mass-transfer limitations and conversion of O_2 beyond the differential regime. Thus, based on previous experience, the upper temperature boundary was chosen to minimize the impact of these factors.

2.3.2. Temperature-programmed desorption (TPD)

The sample was heated under a flow of He (300 sccm) at a rate of 5 °C/min to the target temperature (550 °C or 750 °C, as indicated in the text). Typically, the sample was held at the target temperature for 2 h and then cooled down under He and left under He flow until the subsequent oxidation experiment.

2.3.3. Sequential TPO experiments

The sample of particulate matter was pretreated using TPD to 550 °C, then cooled down to 150 °C, exposed to the desired gas flow and linearly heated up at a rate of 5 °C/min. Heating was stopped at 475 °C and the oxidation process was quenched by immediately switching to inert gas (He). The temperature limit for these experiments was chosen such that temperature range was broad enough for kinetic analysis, but also to limit particulate matter conversion to 10–15% of the total carbon amount. The sample was then cooled down to 150 °C in the inert environment and the oxidation step was repeated. In the final oxidation step, heating was continued to 700 °C in order to achieve complete oxidation of the particulate matter to obtain a carbon balance.

2.3.4. Isothermal experiments

The particulate matter sample was heated to 150 °C in a flow of He, subjected to the desired gas flow, heated at a rate of 5 °C/min to 375 °C and held at this temperature typically for 4–6 h, and then cooled down under the same gas composition. For the sake of simplicity, in the text these experiments are referred to as “isothermal”, although they included both heating and cooling steps.

3. Results

3.1. Temperature-programmed oxidation experiments

The results of the TPO experiments for samples A and B are shown in Fig. 2A and B. Excellent qualitative agreement was observed between the bench reactor and TGA results. In order to account for the progressive loss of soot due to the oxidation, the instantaneous reaction rate values were normalized to the amount of remaining carbon in the reactor. This is equivalent to a first order reaction in carbon, as reflected in the units of the rate constant ([μmol carbon oxidized/min]/[μmol carbon still present] $= \text{min}^{-1}$) in Fig. 2. It should be mentioned that the characteristic shape is retained even if a different reasonable assumption about the reaction order in carbon is made—from 0.67 to 1 [5–7,10,14]. Also, we have observed similar behavior of diesel particulate matter samples under a different set of experimental conditions, such as oxidation by O_2 in the presence of 5–15 vol.% H_2O vapor, and using a step–response oxidation technique [7].

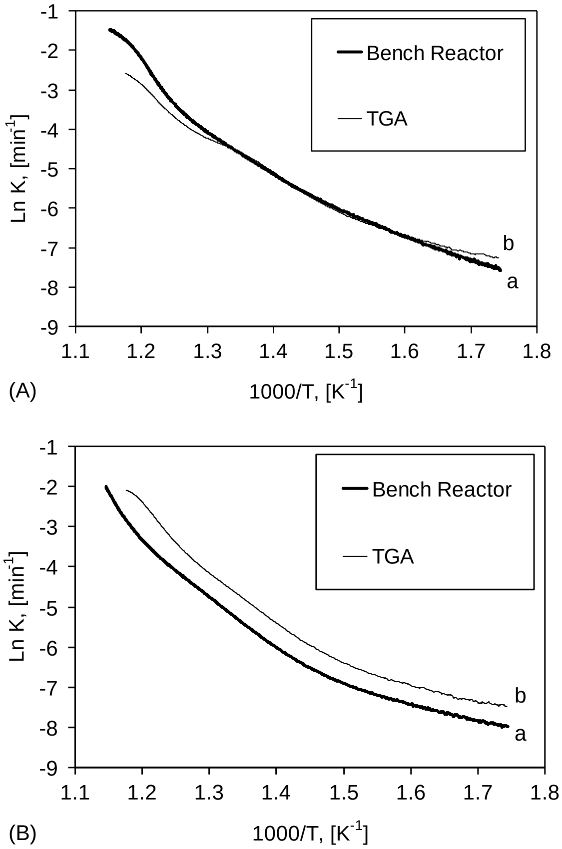

Fig. 2. (A) Results of the TPO experiment for sample A obtained using: (a) bench reaction system; (b) TGA. (B) Results of the TPO experiment for sample B obtained using: (a) bench reaction system; (b) TGA.

The results reported in Fig. 2 show that the apparent kinetic parameters were changing substantially during the course of the experiment. In particular, the concave shape of the curves implies that both the apparent activation energy and the frequency factor were increasing in the process of oxidation. The subsequent experiments were designed to determine if these changes were related to temperature or to changes in particulate matter properties during the process of oxidation.

3.2. TPD–TPO experiment

To evaluate the possible impact of the adsorbed hydrocarbons (often referred to as soluble organic fraction [SOF]), one of the particulate matter samples was pretreated using TPD. Sample B was heated under the flow of He to 550 °C and left at this temperature for 2 h. According to our data, this was sufficient to remove the adsorbed species from this sample of particulate matter. Then, the sample was cooled down before the standard TPO experiment.

The integral amount of CO_2 produced by oxidation of the TPD products was found to be only ∼2.5% of the total carbon balance. As one can see from Fig. 3, the TPD pre-treatment induced limited but measurable changes to the subsequent TPO results, but did not change the overall characteristic shape of the Arrhenius curve.

3.3. Sequential TPO experiments

Sequential TPO experiments were used to determine if the observed kinetic changes were related to the temperature regime. The approach was to quench temperature-programmed oxidation such as to limit

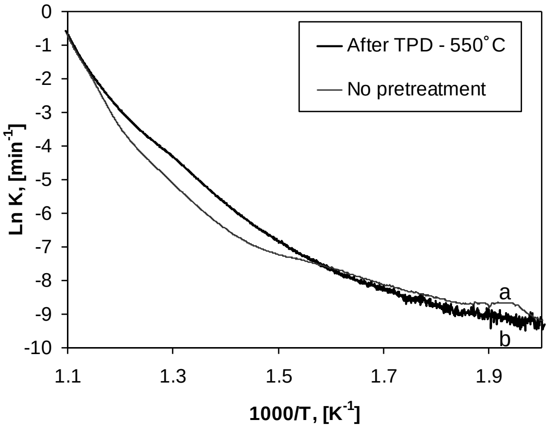

Fig. 3. Results of the TPO experiment for sample B obtained with the gas composition of 5 vol.% O_2/balance He: (a) without pre-treatment; (b) with the TPD pretreatment to 550 °C.

particulate matter conversion to 5–15%, cool the sample down under the flow of He, and then repeat TPO several times. For the final TPO step, heating was continued to 700 °C in order to achieve complete particulate matter oxidation and close the carbon balance.

We expected that if the kinetic changes reported in the Section 3.1 were primarily due to the temperature regime of oxidation, then every subsequent TPO should closely reproduce the results of the previous TPO, as the instantaneous reactions rates were normalized to the amount of remaining carbon. However, if the changes were induced by progressive oxidation, then subsequent TPO steps should produce progressively different results.

The results of the sequential TPO experiments for samples A and B are reported in Table 1. The kinetic values were obtained using first order reaction formalism described in Section 3.1. For both samples, the kinetic parameters were progressively changing in the course of the first two TPO steps. It is interesting to point out that for sample A the kinetic parameters before quenching the first TPO and at the beginning of the second TPO step were very close. Poorer quantitative match was obtained for the less reactive sample B. This may be due to the lower intensity of its signal, which is reflected in the low correlation coefficient at lower temperatures.

It appears that by the end of the second TPO step, the kinetic changes were mostly complete. The final segment of the second TPO step produced parameters close to the third TPO step. Essentially, the entire third TPO experiment can be described by a single set of kinetic parameters with high correlation coefficients over the temperature range of 330–610 °C and up to the integral conversion of >80%. The final values of the activation energies (126 and 146 kJ/mol for the samples A and B, respectively) fall into the lower end of the frequently quoted literature values [5].

Thus, kinetic changes reported in Sections 3.1 and 3.2 could be attributed primarily to certain changes in particulate matter properties as it was progressively oxidized, i.e. to the integral conversion and not to the temperature regime. This implies that even after pre-treatment by the TPD, the studied particulate matter samples initially had higher reactivity, which was gradually lost during the oxidation. The changes appear to be completed after oxidation of approximately 10–25% of carbon. Further oxidation occurred fairly homogeneously.

3.4. Isothermal experiments

In order to better understand the relationship between particulate matter integral conversion and the changes in its reactivity, an additional set of isothermal

Table 1
Summary of the kinetic results of the sequential TPO experiments for samples A and B

Step/temperature range (°C)	Segment/ temperature (°C)	Sample A E_a (kJ/mol)	L_n (frequency factor)	R^2	Sample B E_a (kJ/mol)	L_n (frequency factor)	R^2
First TPO up to 475	Initial/250–290	76	7.6	0.914	49	2.0	0.865
	Final/435–475	107	12.9	0.998	111	13.0	0.998
Second TPO up to 475	Initial/250–290	106	12.5	0.910	71	5.1	0.878
	Final/435–475	126	16.0	1.000	135	16.7	0.997
Third TPO up to 700	330–610	126	15.9	0.999	146	18.4	0.997

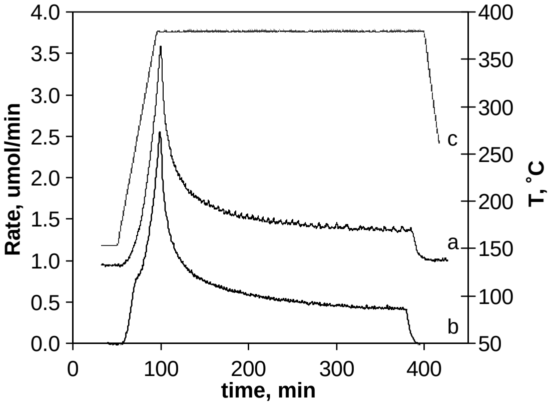

Fig. 4. Results of the isothermal experiments with sample B: (a) pretreated by TPD to 750 °C (offset); (b) fresh sample; (c) temperature trace (secondary ordinate scale).

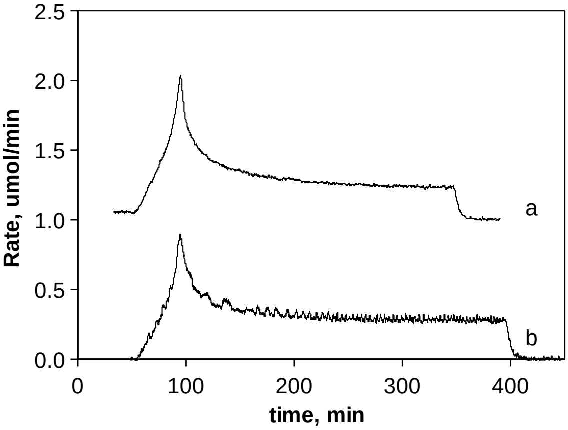

Fig. 5. Results of the isothermal experiments with sample B: (a) after 3 months of aging in air (offset); (b) after additional 2 months of aging in air.

experiments was performed with sample B. A relatively low temperature (375 °C) was chosen to achieve a low oxidation rate and thus better resolve the activity changes with time.

The results for the fresh and TPD-pretreated sample B are reported in Fig. 4. For several hours after reaching the target temperature, the rate of oxidation was steadily decreasing, much faster than the carbon amount loss. Indeed, over 5 h of isothermal oxidation, less than 10% of carbon was consumed, while the oxidation rate decreased several times.

Little difference was observed between the results obtained from the fresh and TPD-pretreated samples, with the exception of the SOF desorption/oxidation peak around 250 °C when heating the fresh sample to the target temperature. Thus, both fresh and TPD-pretreated samples demonstrated initial high reactivity, consistent with the results of Section 3.3.

Importantly, we have found that this high reactivity, lost in the process of oxidation, can be largely restored by exposing particulate matter samples to ambient conditions for a prolonged period of time (weeks), as describe below.

First, a fresh portion of sample B was exposed to the isothermal experiment similar to the one described in Fig. 4b. After 5 h at 375 °C, the reactor was cooled down to room temperature, removed from the reaction system and left exposed to laboratory ambient conditions. After ∼3 months of such aging, the reactor was re-installed and the particulate matter sample was re-tested using the same isothermal protocol. The resulting activity profile (Fig. 5a) was similar to the one observed in the first isothermal experiment (Fig. 4b), although the initial reactivity did not reach the level observed in the first experiment. The sample was then exposed to another ambient aging for ∼2 more months and re-tested again (Fig. 5b). Virtually no difference was observed between the results obtained after the first and second air aging steps (Fig. 5a and b). We have also found that the activity restoration similar to the Fig. 5 may be achieved after ambient exposure times on the order of 10 days.

In a parallel experiment, another fresh portion of sample B was isothermally tested, exposed to ambient conditions for 3 months and isothermally tested again (Fig. 6a). Then, the sample was cooled down, left in the reaction system under a flow of He for different periods and re-tested again (Fig. 6b and c). Remarkably, no signs of the high activity restoration were observed after 8 days under the He flow. This sample was then additionally aged for 3 more months under ambient conditions. Before the next isothermal testing, it was exposed to the TPD treatment (750 °C) to exclude the possibility that activity restoration was due to the adsorption of hydrocarbons or other species present in the ambient air. Subsequent isothermal testing (Fig. 6d) revealed that high reactivity was indeed restored due to the air aging, however after the TPD even higher level of initial reactivity was attained. The

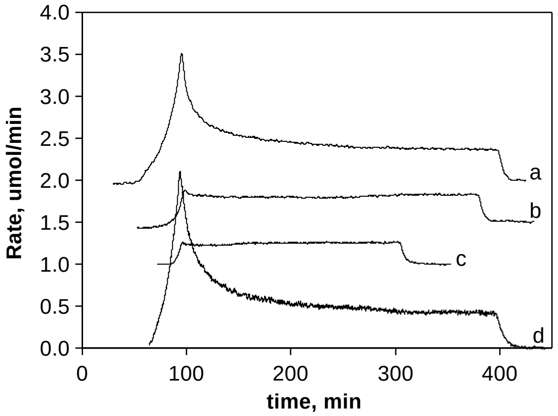

Fig. 6. Results of the isothermal experiments with sample B: (a) after 3 month aging in air (offset); (b) then after 1 day under He (offset); (c) then after 8 days under He (offset); (d) then after 3 more months in air and TPD to 750 °C.

quantitative changes after TPD were reproduced, but at present are not fully understood.

The above experimental observations prove that exposure to the ambient conditions for prolonged periods of time induced certain changes to the particulate matter properties. These changes resulted in its higher initial reactivity during the subsequent oxidation. Similar aging under an inert environment (He) did not lead to such changes.

4. Discussion

The process of oxidation of the diesel particulate matter was found to have a complex kinetic nature, which substantially complicated interpretation of the results. Without proper regard for this complexity erroneous conclusions can be attained. For example, simplified interpretation of the TPO results in the Sections 3.1 and 3.2 lead to a conclusion that the apparent activation energy was increasing with temperature, while opposite behavior is more common for similar heterogeneous processes. Indeed, at lower temperatures the process is usually limited by the high-activation energy steps (e.g. surface reaction), and at higher temperatures—by the lower activation energy steps (e.g. external diffusion). Subsequent investigation revealed that this effect was only apparent due to the superposition of several factors discussed below.

Adsorbed hydrocarbons could potentially provide the impact consistent with the described TPO results. In the process of TPO, the transition from the relatively facile oxidation of the hydrocarbons at the early stages to the oxidation of carbon at the later stages (higher temperatures), may produce the apparent increase in the activation energy. However, throughout this work we have observed that adsorbed hydrocarbons had limited impact on particulate matter oxidation. Comparisons of the results obtained for the fresh and TPD-pretreated sample B using TPO and isothermal techniques (Figs. 3 and 4) shows minor additional activity of the fresh sample at ∼250 °C. Also, in the sequential TPO experiments (Section 3.3), it was found that for samples A and B thermal desorption of adsorbed hydrocarbons did not affect the overall characteristic shape of the Arrhenius curves from the initial TPO steps. It is also possible that TPD treatment may lead to the desorption of hydrocarbons, as well as to certain modifications of particulate matter chemical or morphological properties, for example, to the loss of the oxygen containing groups on the carbon surface. This factor may be responsible for some additional quantitative differences observed after TPD, for example in the high-temperature part of the TPO experiment in the Fig. 3 and also in the results of the isothermal experiment in the Fig. 6.

Another factor, considered in this work, is the possible effect of temperature on the oxidation mechanism, since this offered some reasonable possibilities for the explanation of the observations from the Sections 3.1 and 3.2. However, the sequential TPO experiments (Section 3.3) revealed that upon the completion of certain initial changes in particulate matter properties over the first two TPO steps, a broad temperature sweep in the final TPO step was not accompanied by any appreciable change in the apparent kinetic parameters. Thus, kinetic changes observed in the TPO experiments were related to the progressive modification of the particulate matter properties, and not to the transition between different dominant reaction pathways in different temperature ranges.

High initial reactivity, rapidly lost in the process of oxidation, was observed in all types of experiments. This factor turned out to be a major contributor into the complexity of the TPO results and was also responsible for the progressive kinetic changes in the sequential TPO experiments. It was further unambiguously confirmed by the isothermal experiments. The sequential TPO experiments provided a tentative upper boundary for this process at the initial ~25% of carbon. The isothermal technique allowed us to narrow this range down to ~4–10%.

It is worth pointing out that we studied not model, but real diesel particulate matter samples, collected as described in the Section 2.1. Thus, it was quite surprising to find some anomalous “initial” properties, which were lost upon oxidation of the first several percent of carbon, since both samples have been previously exposed to mild oxidation conditions in the exhaust. This was suggestive, that perhaps the “initial” properties were acquired by the samples after collection, for example due to a prolonged contact with air at room temperature. The air aging experiments described in the Section 3.4 confirmed this hypothesis, as they have demonstrated that prolonged air aging resulted in the restoration of the anomalously high initial reactivity. This effect can be repeated for a given sample over and over again.

Considering the nature of this process, we would like to point out several remarkable features. First, restoration of the anomalous high activity occurred with exposure to ambient air, but not under an inert environment. Work is presently underway to identify which one, or combination of species in the air is responsible for this phenomenon. Second, it is hard to envision that major morphological changes of the carbon surface occur at ambient temperature, even over the course of several weeks or months. The possible scenario of the pores blocking due to volumetric condensation of, e.g. water vapor from air, can be excluded since high reactivity was retained even with the high temperature TPD treatment. In our opinion, a combination of the above factors favors a chemical, not morphological, explanation of the observed initial high reactivity. We propose, that during prolonged contacts with air at room temperature, some highly reactive groups, most likely involving oxygen and/or hydrogen atoms, are formed on the carbon surface. The groups are responsible for the relatively facile initial oxidation after ambient aging; however, they are removed at higher temperatures under oxidizing conditions resulting in the observed uniform lower activity. Tentative estimates show that the amount of the more reactive carbon in our experiments did not exceed the monoatomic layer for the dense particle, and is also in fair agreement with the data by De Soete quoted in [5], that oxygen groups occupy about $<5\%$ of the surface sites.

5. Conclusions

In this work, the kinetics of oxidation of diesel particulate matter was investigated by complementary experimental techniques. The results for the two studied samples can be summarized as follows:

1. The initial stages of oxidation are characterized by an anomalously high reaction rate, which is not related to adsorbed hydrocarbons (SOF).
2. Upon conversion of the first 4–10% carbon, reaction rates decreased several times. The subsequent oxidation appeared to occur quite uniformly, as it can be accurately described by a single set of kinetic parameters in the essentially entire experimental temperature range.
3. It was determined that high initial reactivity of particulate matter can be repeatedly restored by prolonged exposure to ambient conditions.
4. The experimental results suggest that these changes in the reactivity of carbon are chemical, not morphological, in nature. In particular, we propose that during prolonged ambient aging, some highly reactive groups are formed on the carbon surface. These groups are responsible for the subsequent relatively facile initial oxidation. Substantial density of these surface groups can probably not be obtained in more vigorous oxidation process at higher temperatures.

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References

[1] Control of Air Pollution From New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway

Diesel Fuel Sulfur Control Requirements, US EPA, 40 CFR Parts 69, 80 and 86.

[2] R.J. Santoro, Soot formation: a view of our current understanding, Chem. Phys. Proc. Combust., Fall Technical Meeting (1995) 37.

[3] I.M. Kennedy, Models of soot formation and oxidation, Prog. Energy Combust. Sci. 23 (1997) 95.

[4] H. Bockhorn, NATO Sci. Ser. C: Math. Phys. Sci. 547 (2000) 205.

[5] B.R. Stanmore, J.F. Brilhac, P. Gilot, Carbon 39 (2001) 2247.

[6] J.P.A. Neeft, T.X. Nijhuis, E. Smakman, M. Makkee, J.A. Moulijn, Fuel 76 (1997) 1129.

[7] A. Yezerets, N.W. Currier, H.A. Eadler, S. Popuri, A. Suresh, SAE Technical Paper 2002-01-1684.

[8] A.D.H. Clague, J.B. Donnet, T.K. Wang, J.C.M. Peng, Carbon 37 (1999) 1553.

[9] C. Li, T.C. Brown, Carbon 39 (2001) 725.

[10] A. Yezerets, N.W. Currier, H.A. Eadler, SAE Technical Paper 2003-01-0833.

[11] W.P. Partridge, J.M. Storey, R.A. Smithwick, G.L. Devault, M.J. Cunningham, N.W. Currier, T.M. Yonushonis, SAE Technical Paper 2000-01-2952.

[12] P. Gilot, F. Bonnefoy, F. Marcuccilli, G. Prado, Combust. Flame 95 (1993) 87.

[13] P. Gilot, A. Brillard, B.R. Stanmore, Combust. Flame 102 (1995) 471.

[14] G. Mul, W. Zhu, F. Kapteijn, J.A. Moulijn, Appl. Catal. B: Environ. 17 (1998) 205.