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Direct observations of CeO₂-catalyzed soot oxidation at the nano-scale using environmental transmission electron microscopy

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ABSTRACT

Environmental transmission electron microscopy (ETEM) was used to study *in situ* the kinetics and dynamics of CeO₂-catalyzed soot oxidation at the nano-scale. From time-lapsed ETEM image series, direct insight was obtained into structural changes of soot particles in contact with CeO₂ during exposure to oxidizing conditions. Based on the insight, it was shown that catalytic soot oxidation was governed by reactions at the CeO₂-soot interface and that this finding was consistent with previous findings.

INTRODUCTION

Particulate matter (PM) from diesel exhaust contains soot particles carrying toxic compounds [1] which are suspected to cause various health problems [2]. For this reason, legislation will in the coming years demand further reduction in diesel PM. To meet the requirements, manufacturers have announced a future use of catalyzed diesel particulate filter (DPF) systems on their vehicles [2]. Efficient DPFs are today available [3,4] and currently the major technological challenge is related to the regeneration of these filters [4]. Catalytic soot oxidation is a beneficial strategy for filter regeneration [1-3,5], and producing DPFs with a catalyst coating is the preferred strategy in most diesel exhaust PM reduction projects [1].

Ceria-based materials are known to catalyze soot oxidation [6-8]. It is generally accepted that redox properties of CeO₂ is of key importance for the reaction mechanism, but the location of the catalytic active site is being debated [3,4,7]. This is in part related to the fact that in most cases, averaging techniques have been applied, which do not directly provide information about the reaction-induced changes in the individual soot particles. On the other hand, transmission electron microscopy (TEM) techniques provide versatile tools for directly studying the individual nanostructures at length-scales down to the atomic level. Advances of environmental transmission electron microscopy (ETEM)

[9-12] further allow direct observations to be obtained of solid catalysts *in situ* during exposure to reactive gas environments, providing important insight into the relationship between nanostructures and catalytic reaction mechanisms.

In this contribution, we present the first ETEM results that directly visualized *in situ* soot oxidation catalyzed by CeO₂ [13]. Based on time-resolved ETEM image series (movies), we show that CeO₂ catalyzed soot oxidation through soot-CeO₂ interface-related processes.

EXPERIMENTAL DETAILS

To model soot deposited in a DPF, a carbon black powder (Printex U, Degussa GmbH) was mechanically mixed with a CeO₂ catalyst powder. As reference, the carbon black was also mixed with catalytically inert Al₂O₃ powder.

For temperature programmed oxidation (TPO) experiments, the mixed carbon black-oxide powder was mortared to obtain tight physical contact. To secure an optimal gas flow through the sample, the mixture was pressed into a tablet which was subsequently crushed into grains. The TPO experiments were conducted by heating a sample in 0.2% O₂ in N₂ at a pressure of 1 atm and flow of 100 ml/min with a constant rate of 2°C/min until a maximum temperature was reached corresponding to T_{max}=350°C for the CeO₂ mixture and T_{max}=600°C for the Al₂O₃ mixture, respectively. As 50% of the carbon black was oxidized, as determined by mass spectrometry, the samples were cooled to room temperature and subsequently analyzed by conventional transmission electron microscopy (CM300 FEG TEM from FEI Company).

The ETEM experiments were performed using a CM300 FEG TEM (FEI Company) equipped with an environmental cell for *in situ* studies [12]. This instrument provides images and time-lapsed image series (movies) with a resolution better than 0.14nm of samples during

exposure to reactive gases and elevated temperatures. For the ETEM experiments, samples were prepared by distributing carbon black-oxide powder on a stainless steel grid which was subsequently mounted in a specimen holder with heating capabilities. After insertion in the environmental cell, the sample was exposed to 200Pa O₂ and heated to a reaction temperature in the interval 300-600°C. After reaching the reaction temperature, images or movies were recorded using a low-light and fast-scan CCD (Tietz Fastscan F-114). In all experiments, the beam current density was kept below 0.16A/cm² which was found to be sufficient to avoid influence of the electron beam on the oxidation kinetics.

RESULTS AND DISCUSSION

First we focus on powder samples that have been exposed to oxidation conditions in TPO experiments.

Figure 1a-b presents conventional TEM images of an agglomerate of carbon black particles mixed with CeO₂ before and after a TPO experiment. The diameters of the carbon black particles in the catalytically oxidized sample (at 350°C with 50% conversion) were observed not to change. Figure 1c shows a carbon black mixed with Al₂O₃ after a TPO experiment. For this specimen, the non-catalytic oxidation at 600°C of 50% of the carbon black, the TEM images clearly show that the diameter of the carbon black particles did shrink in the TPO experiment. These results tentatively suggest that reaction centers could be highly localized in the catalyzed combustion (e.g. near the carbon black-CeO₂ interface) and more wide-spread distributed in the carbon black matrix in non-catalytic oxidation.

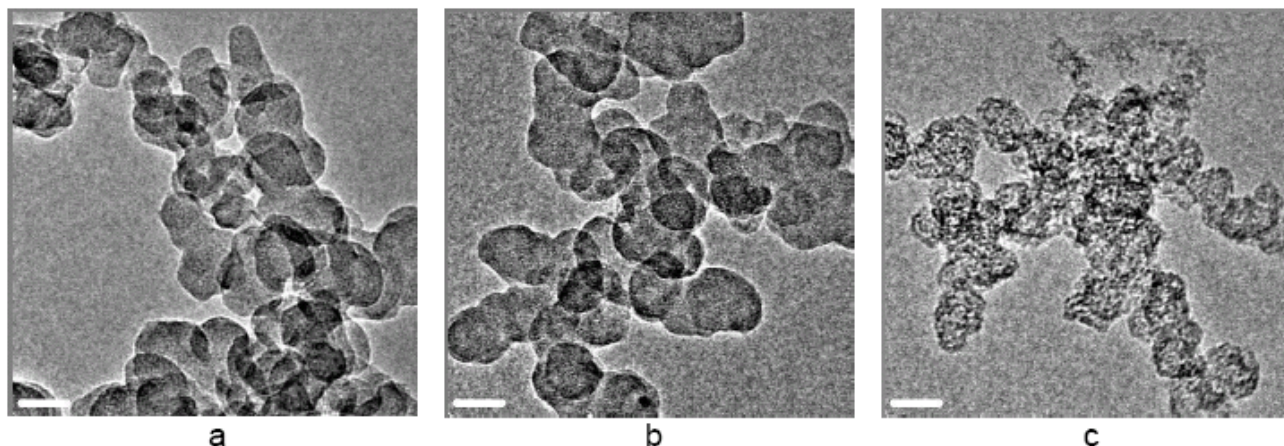


Fig. 1. TEM images of an agglomerate of carbon black particles (a) before oxidation, (b) after CeO₂-catalyzed oxidation at 350°C and (c) after non-catalytic oxidation mixed with Al₂O₃ at 600°C. Scale bars = 30nm.

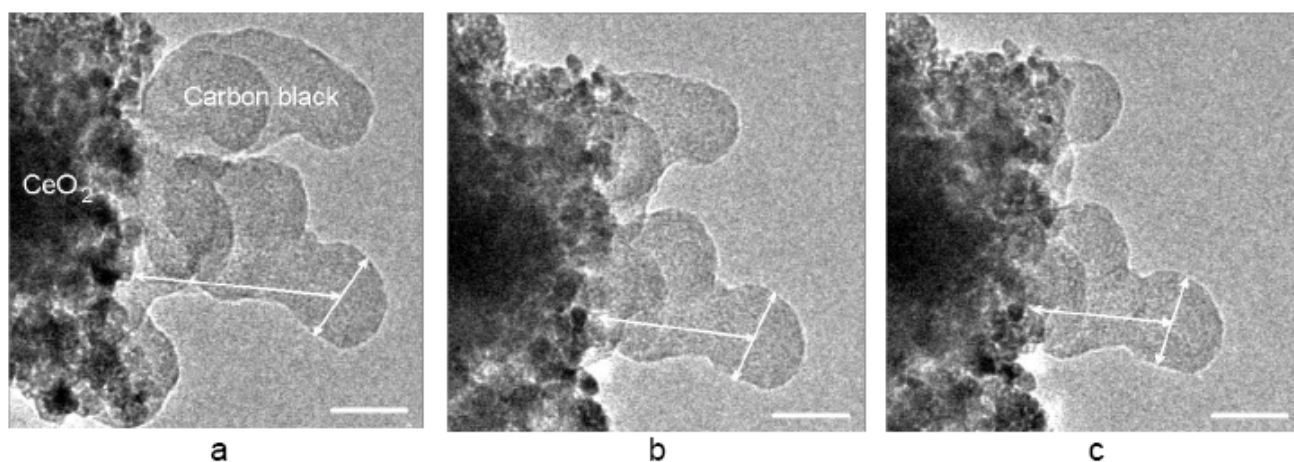


Fig. 2. ETEM images of an agglomerate of carbon black particles attached to CeO₂ during exposure to 200Pa O₂ at 475°C. Scale bars = 30nm. The time interval between the images is ~5min. The diameter of a carbon black particle and corresponding carbon black-CeO₂ distance is marked on each image.

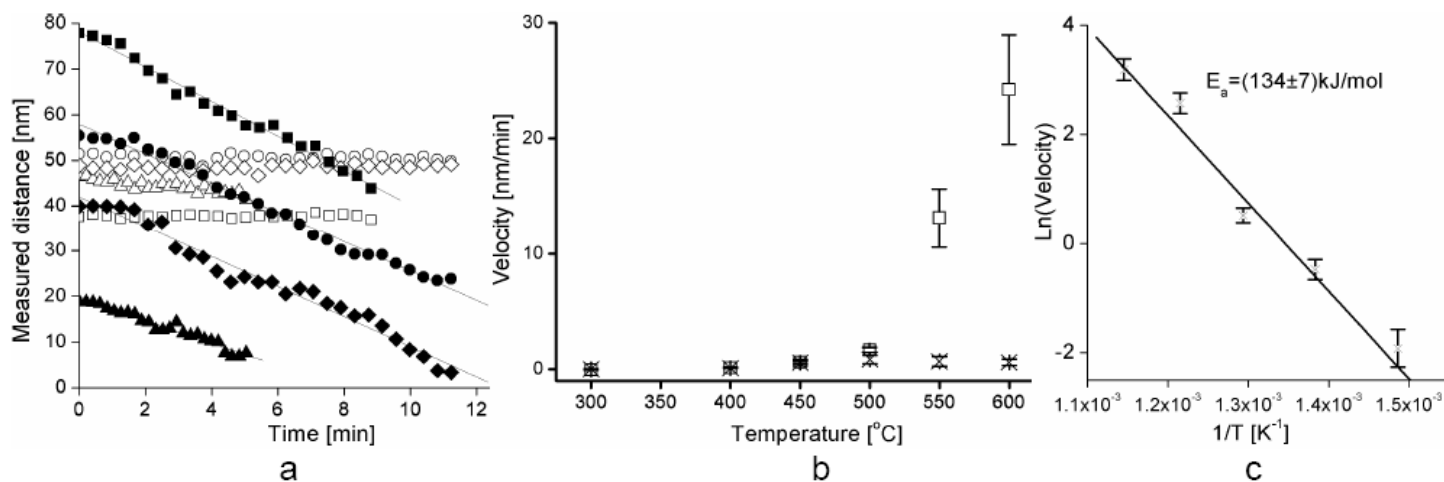


Figure 3: (a) Diameters of carbon black particles (open symbols) and distances from the carbon black particle center to the catalyst edge (filled symbols) as a function of time during exposure to 200Pa O₂ at 475°C. (b) The mean velocity of carbon black relative to CeO₂ (□) and Al₂O₃ (x) presented for different temperatures. The velocities are mean values of velocities of 10 particles at each temperature. (c) Arrhenius plot of the mean velocities between carbon black and CeO₂ from figure 3b.

To address this issue in more detail, ETEM experiments were carried out in which a carbon black-CeO₂ sample was monitored *in situ* during exposure to oxygen at 475°C. At this intermediate temperature, catalytic oxidation prevailed while non-catalytic oxidation was attenuated, which was confirmed by the TPO results. Figure 2 represents time-lapsed ETEM images of a carbon black agglomerate in physical contact with CeO₂. The distance between the centre of one of the carbon black particles and the CeO₂ was observed to shrink and the diameter of the carbon black particle was seen to remain constant in course of time. In comparison, carbon black-Al₂O₃ samples monitored by means of ETEM did not show any motion of the carbon black relative to the oxide under the same conditions.

In a similar way, several carbon black particles in different agglomerates were monitored and their diameters and distances to the catalyst were mapped out under the same conditions (fig. 3a). Interestingly, this figure shows that all particles had constant diameters and moved towards CeO₂ with a constant velocity, irrespective of their initial distance to the catalyst. These findings explain the observed constant diameters of the carbon black particles oxidized catalytically in the TPO experiment. Furthermore, the dynamic observations suggest that the oxidation reaction was localized in the close proximity of the carbon black-catalyst interface and that the catalyst apparently was able to generate mobility of the carbon black particles towards the catalyst surface to reestablish the carbon black-catalyst interface. For ETEM experiments carried out at different temperatures in the interval 450-525°C, a dynamic behavior of the carbon black particles was observed to be similar to that shown in figure 2.

To address the question whether the interfacial reaction mechanism is consistent with previous observations, we probed the reaction kinetics using ETEM for experiments carried out in the interval 300-600°C. In these experiments, the velocity of the carbon black particles

towards the CeO₂ surface was determined from the carbon positions in just two images. In the intervening time interval, the electron beam was switched off to ensure that the effect of the beam was negligible. For each temperature, the mean velocity of 10 carbon black agglomerates relative to CeO₂ and to Al₂O₃ was evaluated (fig. 3b) and presented in an Arrhenius plot (fig. 3c). Assuming that the velocity of the agglomerates towards the ceria surfaces is proportional to the oxidation rate, the slope in the Arrhenius plot represents the apparent activation energy barrier. From figure 3c, we obtained an apparent barrier of 134kJ/mol, which is in good agreement with previously reported values [3,6-8]. It is well-known that the apparent activation energy barrier can depend on the degree of physical contact between soot particles and catalyst in such a way that macroscopic samples with tight contact usually result in lower values for apparent activation energy than loose contact mixtures [8,14]. Our value for apparent activation energy measured using ETEM agrees better with the tight contact-values than with loose contact-values for in the literature. This was expected because our ETEM experiments only considered carbon black agglomerates in direct physical contact with catalyst particles.

Our direct observations suggest that the catalytic effect is related to interface processes and show that the carbon-CeO₂ interface apparently can be re-established in the course of the reaction. This is interesting because it has also been noticed that the activity of catalytic soot oxidation decreases in time and that this is explained as loss in contact area between soot and catalyst [15]. This could seem in contrast with the present findings. However, we can add that in samples where the distribution of soot and catalyst is different than in the samples that were prepared for the ETEM studies, the situation could be that the soot agglomerates are parts of a larger network, e.g. a soot cake in a particulate filter. In such a situation there may be a competition between maintaining the soot-catalyst interface and avoiding removing the agglomerate from the soot network. Hence

breaking up the soot-catalyst interface could be possible and soot transport to the catalyst may be rate determining for oxidizing all the soot.

The finding that the soot moved toward the catalyst during catalytic oxidation also gives a hint to understand the mechanism in catalytic soot oxidation. One may speculate that the oxidation leaved empty sites at the solid-solid interface. In this case, attractive van der Waal forces between soot and CeO₂ could be responsible for re-establishing the interface. However, it is also possible that the oxidation reaction proceeded without creating empty interface sites. Such a process could be mediated by surface transport and restructuring of soot or ceria, comparable to the reaction dynamics revealed for catalytic graphene growth [16]. Based on kinetic arguments, a mechanism with spill-over of activated oxygen from the catalyst to the soot followed by diffusion over the soot surface and finally soot oxidation at an active site on the soot particle has also recently been suggested [7]. This mechanism could be consistent with the ETEM results, as long as the active sites on the soot particles are located within a few nanometers to the soot-catalyst interface,

CONCLUSION

Environmental transmission electron microscopy was used to obtain the first *in situ* observations of CeO₂-catalyzed soot oxidation at the nano-scale. The results provided insight into the reaction mechanism. Specifically, it was found that the catalytic oxidation reaction involved processes confined to the soot-CeO₂ interface region and that the catalytic reaction resulted in motion of soot agglomerates towards the catalyst surface that acted to re-establish the soot-CeO₂ interface in the course of the oxidation process. The observed reaction dynamics were found to consistently explain observations from TPO experiments and were in quantitative good agreement with previous kinetic results.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

PM: Particulate Matter

DPF: Diesel Particulate Filter

TPO: Temperature Programmed Oxidation

TEM: Transmission Electron Microscopy

ETEM: Environmental Transmission Electron Microscopy