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Ceria-catalyzed Soot Oxidation studied by Environmental Transmission Electron Microscopy

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Abstract

Environmental transmission electron microscopy (ETEM) was used to monitor *in situ* ceria-catalyzed oxidation of soot in relation to diesel engine emission control. From time-lapsed ETEM image series of soot particles in contact with CeO₂, or with Al₂O₃ as inert reference, mechanistic and kinetic insight was obtained into the catalytic and non-catalytic oxidation mechanisms. Specifically, the results indicated that the catalytic soot oxidation mechanism involves reaction centers at the CeO₂-soot interface and that the interface reaction kinetics was in good agreement with previous macroscopic measurements.

Keywords: Diesel exhausts emission control, soot oxidation, ceria-based catalysts, environmental transmission electron microscopy

1. Introduction

Gasification of carbonaceous matter plays an important role in diverse areas such as coal conversion and vehicle emission control. Currently, the awareness of soot abatement in the exhaust from diesel engines is increasing due to new environmental legislation regarding the exhaust specifications [1]. The soot removal is accomplished by the introduction of filters on diesel-driven vehicles [1], and one attractive approach to effectively regenerate the filters onboard is to functionalize the filters for catalytic oxidation of deposited soot [2]. Ceria-based materials are widely adopted for this purpose and have been subject to several investigations [3-5]. It is generally accepted that the redox properties of CeO₂ are of key importance for the catalytic effect, but the detailed reaction mechanism and the location of the catalytic active sites are being debated. For instance, it is proposed that the reaction occurs at the soot-CeO₂ interface [3] and that the reaction occurs through spill-over of active oxygen from CeO₂ to reaction centers distributed at the soot surfaces [2,3,6]. Averaging techniques, such as temperature-programmed

oxidation and thermo-gravimetric analysis [2-9], and TEM studies [10], were mainly used to study soot oxidation reaction. Although these studies provided significant insight, previous work on metal-catalyzed gasification of graphite emphasized that environmental transmission electron microscopy (ETEM) is a beneficial complement, because direct observations at the carbon-catalyst interface can be observed *in situ* during the gasification reaction [11-13].

In the present Communication, we apply ETEM to address the reactions occurring at the soot-ceria interface during exposure to oxidation conditions. Time-lapsed ETEM image series were obtained *in situ* of soot particles in contact with catalytic active CeO₂ or with catalytic inert Al₂O₃ as reference. The observations revealed that the catalytic oxidation occurred at the soot-CeO₂ interface, whereas non-catalytic combustion was independent of the oxide location. Furthermore, based on ETEM observations at different temperatures, the catalytic interface kinetics were determined and found to be in good agreement with previous findings.

2. Experimental

The experiments were performed in a CM300 FEG TEM (FEI Company) equipped with an environmental cell for *in situ* studies [14]. The system provides images and time-lapsed image series (movies) with a resolution better than 0.14nm of samples during exposure to reactive gases up to 10 mbar and elevated temperatures up to 900°C. To model soot deposited in a diesel particulate filter, a carbon black (CB) powder of particles with a diameter of about 30nm (Printex U, Degussa GmbH) was mechanically mixed with a CeO₂ catalyst powder (produced according to [15]) with a volume ratio 1:10. As reference, the CB was also mixed with α -Al₂O₃ powder in the same ratio. The differences in mass-thickness contrast and morphology facilitated the identification of the CB and oxide particles in the TEM images. Specimens for ETEM experiments were made by dispersing a CB-oxide powder in dry state over a stainless steel TEM grid which was subsequently mounted in the heating holder (Gatan model 628). After insertion into the TEM, the sample was exposed to 2mbar O₂ and heated at 50°C/min to a reaction temperature in the interval 300-600°C. Similar experiments were made as reference with 2mbar N₂. At a given reaction temperature, images and movies of the CB-oxide samples were recorded using a low-light and fast-scan CCD (Tietz Fastscan F-114). During imaging, 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 CB oxidation kinetics.

For comparison with the ETEM experiments, CB-oxide samples were oxidized *ex situ* in a separate reactor until approximately half of the CB was combusted. The samples were mortared to obtain tight physical contact between the CB and oxide material. They were oxidized in 2mbar O₂ in N₂ (1bar total pressure) in a plug flow reactor, where the progress of the reaction was followed by monitoring the CO and CO₂ levels. A relatively high temperature, T=600°C, was used for oxidation of the CB-Al₂O₃ mixture, which is characteristic for thermal soot combustion [8]. A relatively low temperature, T=350°C, was used for the CB-CeO₂ mixture, which is characteristic for the catalytic oxidation [8]. In both cases, the O₂ conversion was below 50% insuring that the whole sample was exposed to O₂. After the oxidation reaction, the samples were transferred for conventional transmission electron microscopy (CTEM) investigations in a CM300 FEG TEM from FEI Company.

3. Results and discussion

First we focussed on the samples oxidized *ex situ*. Figure 1a-b shows CTEM images of an agglomerate of CB particles from the CB-CeO₂ sample before and after oxidation *ex situ*. Apparently, the diameters of the CB particles did not seem to change although 50% of the CB was gasified catalytically. In contrast, the non-catalytic oxidized CB-Al₂O₃ sample contained CB particles with significantly reduced diameters (Fig. 1c). The qualitative observations were corroborated by CB particle size distributions measured from CTEM images (Fig. 1d). These results tentatively suggest that reaction centers could be highly localized for the catalyzed oxidation in the CB-CeO₂ sample and more widespread distributed in the CB agglomerates for thermal combustion in the CB-Al₂O₃ sample. **This suggestion is further supported by the observation that the image contrast of CB particles remained unaltered in the CB-CeO₂ sample but changed to become more granulated for the CB particles in the CB-Al₂O₃ sample (Figs. 1b-c).**

To address the role of the CeO₂ catalyst, ETEM experiments were performed to monitor agglomerates of CB particles attached to CeO₂ particles *in situ* during exposure to oxygen at an elevated temperature. The time-lapsed series of ETEM images show the main findings (Fig. 2). The images reveal that an agglomerate of CB particles moves towards the CeO₂ and vanishes in the course of time (Figs. 2a-

c), whereas agglomerates of CB particles are never observed to protrude and move away from the edges of the CeO₂ particles. These findings suggest that the motion is not related to only migration of CB along on the CeO₂ surface but must be related to the oxidizing reaction conditions. This point is further consistent with similar experiments using N₂ instead of O₂. In such experiments, ETEM image series reveal that CB particle agglomerates remain stable. Moreover, monitoring the CB-Al₂O₃ samples by ETEM during exposure to the oxidizing conditions (Fig. 2d-f) showed that agglomerates of CB particles were stable over the same temperature and period of time. The observations therefore indicate that the CeO₂ catalyzes oxidation of the CB agglomerates and concurrently generates motion of the agglomerate towards the catalyst surface.

In an analysis of the ETEM observations, CB particle diameters and positions relative to CeO₂ were mapped out in consecutive images (outlined in Fig. 3a-b [See also, supplementary material]). Figure 3c shows the results of two CB particles during oxidation at 500°C. Clearly, the relative distances in the images between CB particles and CeO₂ are seen to shrink linearly with time and so, because the periphery of the agglomerate also remained constant in time, the CB particles must move at constant velocity towards CeO₂. Furthermore, in the corresponding time interval in which the CB particles moved over projected distances comparable to their diameter, the CB particle diameter remained constant. These findings indicate that carbon is only oxidized by the ceria catalyst when carbon is situated in close proximity of the CB-CeO₂ interface and that the catalytic reaction mechanism therefore involves reaction centers near the CB-CeO₂ interface. Based on the observations we were able to pinpoint the reactive interface down to only a few nanometers due to the projection geometry (overlap of CeO₂ and CB) in the images and the roughness of the CeO₂ surface. The findings showing that the catalytic effect was localized at the CB-CeO₂ interface are further consistent with the observation that the CB particle size distribution was unaltered by *ex situ* catalytic oxidation. Moreover, many CB agglomerates were observed with a constant periphery in the projected ETEM images reflecting a constant linear motion towards CeO₂. However, agglomerates were also observed with the periphery changing in time. A change in periphery can be explained by a rotation with respect to an axis in the image plane and we therefore attributed such observations to CB agglomerates that moved towards and concurrently rotated around the CeO₂ to which the agglomerates were attached. The present analysis only included agglomerates that apparently moved linearly toward the ceria.

Next, we addressed the question if the interface reaction was sufficient to explain the catalytic role of CeO_2 by considering the kinetics associated with the CB- CeO_2 interface reaction. To probe the reaction kinetics, ETEM experiments were carried out at different reaction temperatures in the interval 300-600°C. The ETEM image series at different temperatures showed qualitatively the same behavior as in Fig. 2. In these experiments, the projected velocity of CB agglomerates towards the CeO_2 surface was determined from the difference in CB position relative to the CeO_2 in two consecutive images recorded with the electron beam switched off in the intervening time interval to further ensure that the effect of the beam was negligible. At each reaction temperature, an average velocity of the CB agglomerates was determined from ten different agglomerates. The average velocity was found to increase with temperature as shown in Fig. 3d. Assuming that the interface reaction rate is proportional to the projected velocity of the CB agglomerates, an apparent activation energy barrier for the CeO_2 -catalyzed CB oxidation can be obtained from an Arrhenius analysis of the data in Fig. 3d. From the analysis, an activation energy barrier of $E_a = (134 \pm 7)$ kJ/mol was obtained, which agreed with previously reported values [3-5]. In the previous investigations using averaging techniques, the determination of the activation energy is often found to depend on the degree of physical contact between soot particles and catalyst in such a way that “tight” contact mixtures usually result in lower activation energy barriers than “loose” contact mixtures [7]. The ETEM-based value for the apparent activation energy agrees better with the previously reported values for “tight” mixtures. This was expected because the ETEM only monitored CB agglomerates in direct physical contact with catalyst particles.

In comparison, similar ETEM measurements of the relative velocity of CB in contact with Al_2O_3 showed that the CB agglomerates did not move significantly relative to the Al_2O_3 even at the highest temperatures (Fig. 3d), emphasizing the importance of the interface reaction for the CeO_2 catalyst. It is noted that at the highest reaction temperature of 550-600°C, the CB particles tended to shrink in diameter suggesting that non-catalytic combustion of CB obtained a more significant reaction rate in this temperature range in accordance with previous studies [5,8] and with the particle size distributions after oxidation *ex situ* (Fig. 1c). The shrinkage rate was determined by monitoring CB particle diameters over time. The analysis showed that the CB shrinkage rate was less than 5% of the mean projected velocity of CB towards CeO_2 for all temperatures up to 600°C. Hence, motion of CB due to diameter shrinkage of CB particles located closer to the CeO_2 surface is of minor importance.

The direct observations suggest that the catalytic effect is related to interface processes and show that the CB-CeO₂ interface apparently can continuously be reestablished in the course of the reaction. This is interesting because it is noted that the activity of catalytic soot oxidation decreases in time and that this is explained as loss in contact area between soot and catalyst [8]. This scenario could seem in contrast with the present ETEM findings. However, it should be noted that **in particulate filters, the size and distribution of soot particles and catalyst may differ from the present model samples and the soot particles may be part of a larger network**, e.g. a soot cake. **In such configurations, other phenomena may play an additional role. For instance**, a competition may prevail between reestablishing the soot-catalyst interface and bonding the soot agglomerate to the soot network. Hence the soot-catalyst interface may breakup and soot transport to the catalyst surface will then be rate-determining.

Finally, we briefly turned to the origin of the reactions at CB-CeO₂ interface. The ETEM observations indicated that CB was removed from the interface. The removal of CB most likely happened through reaction with oxygen in the ceria surfaces in the form of CO₂ or CO. One may speculate that the oxidation leaves empty sites at the solid-solid interface. In this case, attractive van der Waal forces between CB and CeO₂ could be responsible for reestablishing the interface. However, the oxidation reaction may also proceed 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]. Recently, a catalytic reaction mechanism based on kinetic arguments was proposed to involve spill-over of adsorbed oxygen from the catalyst to the CB followed by diffusion over the CB surface, and finally CB oxidation at active sites at the CB particle [6]. This mechanism is also consistent with the present ETEM results as long as the active site at the CB particle is located within a few nanometers from the CB-CeO₂ interface. In present experiments, the apparent overlap with CB particles in the projected ETEM images hampered the interface processes to be resolved better than this limit. Further insight into the atomic-scale reaction mechanism in the ceria-catalyzed soot oxidation calls upon more detailed *in situ* investigations.

4. Conclusions

Environmental transmission electron microscopy (ETEM) was used to obtain *in situ* observations of CeO₂-catalyzed soot oxidation at the nano-scale. 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 reestablish the soot-CeO₂ interface in the course of the oxidation process. It was further demonstrated that the apparent activation energy of CeO₂-catalyzed soot oxidation could be measured with ETEM for a more well-defined tight physical contact situation. The observed reaction dynamics were found to consistently explain observations from *ex situ* oxidation experiments and were in quantitatively good agreement with previous kinetic investigations.

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Figure 1. CTEM images of agglomerates of CB particles. (a) An un-oxidized CB agglomerate (mixed with CeO₂). (b) A CB agglomerate (mixed with CeO₂) after catalytic oxidation ex situ at 350°C. (c) A CB agglomerate (mixed with Al₂O₃) after non-catalytic oxidation ex situ at 600°C. (a) –(c), scale bars = 30nm. (d) Particle size distributions of CB particles (including 500 counts each). **The particle size is determined as the diameter in a circular approximation to the projected area of the soot particles.** To guide the eye, a lognormal distribution function is fitted to each histogram.

Figure 2: Time-lapsed ETEM images of (a-c) CB-CeO₂ and (d-f) CB-Al₂O₃ recorded during exposure to 2mbar O₂ at 550°C. The time interval between each image is ~2min. Scale bars = 90nm.

Figure 3. (a-b) ETEM images of CB-CeO₂ during exposure to 2mbar O₂ at 500°C (extracted from the ETEM movie in supplementary material). Scale bars = 30nm. The time interval between the images is ~12min. The measured diameter (white line) and CB-CeO₂ distance (black line) is marked. **The estimated accuracy on diameter and distance is 0.5nm and 0.9nm, respectively.** (c) Diameters (open symbols) of CB particles and distances from the particle centre to the catalyst edge (filled symbols) as a function of time during exposure to 2mbar O₂ at 500°C. (d) Average speed of CB relative to CeO₂ (□) and Al₂O₃ (x) presented for different temperatures. **For each temperature, the average speed and the standard deviation thereof is obtained from observations of 10 particles in different agglomerates.** The insert presents an Arrhenius plot of the dataset.

Supplementary material: ETEM movie of CB-CeO₂ during exposure to 2mbar O₂ at 500°C. The frames are recorded consecutively with an intervening waiting time of 12.5sec, and the frame rate is 10frames/sec.