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Priority Communication

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 CeO_2, or with Al_2O_3 as inert reference, mechanistic and kinetic insight into the catalytic and noncatalytic oxidation mechanisms was obtained. Specifically, the results indicate that the catalytic soot oxidation mechanism involves reaction centers at the soot–CeO_2 interface and that the interface reaction kinetic properties are in good agreement with previous macroscopic, averaging measurements.

Keywords: Diesel exhausts emission control; Soot oxidation; Ceria-based catalysts; Environmental transmission electron microscopy

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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 for exhaust specifications [1]. Soot removal is accomplished by the introduction of filters on diesel-driven vehicles [1]. An attractive approach to effectively regenerate the filters onboard is to functionalize the filters for catalytic oxidation of the deposited soot [2]. Ceria-based materials are widely adopted for this purpose and have been the subject of several investigations [3–5]. It is generally accepted that the redox properties of CeO_2 are crucial to the catalytic effect, but the detailed reaction mechanism and the location of the catalytic active sites remain matters of debate. For instance, it was proposed that the reaction occurs at the soot–CeO_2 interface [3] and that the reaction occurs through spillover of active oxygen from CeO_2 to reaction centers distributed at the soot surfaces [2,3,6]. Averaging techniques, such as temperature-programmed oxidation and thermogravimetric analysis [2–9], and TEM studies [10], have mainly been used to study the soot oxidation reaction. Although these studies have provided significant insight, previous work on metal-catalyzed gasification of carbonaceous matter emphasized that environmental transmission electron microscopy (ETEM) could be a beneficial complement, due to its capability of providing direct observations at the carbon–catalyst interface *in situ* during the gasification reaction [11–13].

In the present work, ETEM was applied 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 CeO_2 or with catalytic inert Al_2O_3 as a reference. The observations reveal that the catalytic oxidation occurred at the soot–CeO_2 interface, whereas noncatalytic combustion was independent of the oxide location. Furthermore, based on ETEM observations at different temperatures, the catalytic interface kinetics was determined and found to be in good agreement with previous findings.

2. Experimental

The experiments were performed on a CM300 FEG TEM (FEI Company) equipped with an environmental cell for *in*

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situ studies [14]. Images and time-lapsed image series (movies) with a resolution of about 0.14 nm of samples during exposure to reactive gases and elevated temperatures can be recorded with this system. To model soot deposited in a diesel particulate filter, a carbon black (CB) powder of particles with a diameter of about 30 nm (Printex U, Degussa GmbH) was mechanically mixed with a CeO_2 catalyst powder, produced as described previously [15], with a volume ratio 1:10. To serve as a reference, the CB was also mixed with α-Al_2O_3 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 prepared by dispersing a CB-oxide powder over stainless steel TEM grids, which were mounted in the heating holder (Gatan model 628). After being inserted into the TEM instrument, a specimen was exposed to 2 mbar O_2 and heated at 50 °C/min to a reaction temperature in the interval 300–600 °C. Similar experiments were conducted with 2 mbar N_2 as a reference. 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 0.16 A/cm^2, which was sufficiently low to avoid influence of the electron beam on the CB particles.

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 crushed to obtain tight physical contact between the CB and oxide material. They were oxidized in 2 mbar O_2 in N_2 (1 bar total pressure) in a plug-flow reactor. The progress of the reaction was followed by monitoring the CO and CO_2 levels. A relatively high temperature (600 °C), characteristic for the thermal soot combustion [8], was used for oxidation of the CB–Al_2O_3 mixture. A relatively low temperature (350 °C), characteristic for the catalytic oxidation [8], was used for the CB–CeO_2 mixture. In both cases, the O_2 conversion was below 50%, ensuring that the entire sample was exposed to O_2. After the oxidation reaction, the samples were transferred for conventional TEM (CTEM) investigations on a CM300 FEG microscope (FEI Company).

3. Results and discussion

We first focus on the samples oxidized *ex situ*. Figs. 1a and 1b show CTEM images of an agglomerate of CB particles from the CB–CeO_2 sample before and after oxidation *ex situ*. Apparently, the diameters of the CB particles did not change, even though 50% of the CB was gasified catalytically. In contrast, the noncatalytic oxidized CB–Al_2O_3 sample contained CB particles of a significantly smaller diameter (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–CeO_2 sample and more widely distributed in the CB agglomerates for the thermal combustion in the CB–Al_2O_3 sample. This suggestion is further supported by the observation that the image contrast of CB particles was unaltered in the CB–CeO_2 sample but became more granulated for the CB particles in the CB–Al_2O_3 sample (Figs. 1a and 1c).

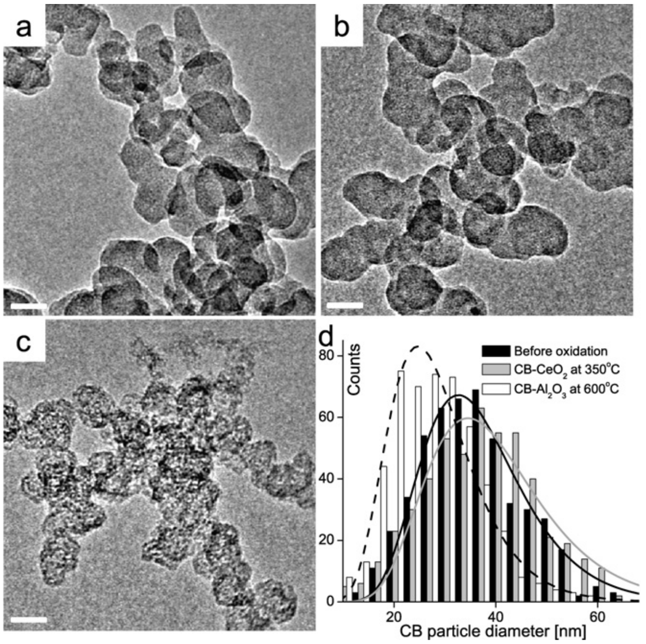

Fig. 1. CTEM images of agglomerates of CB particles. (a) A non-oxidized CB agglomerate (mixed with CeO_2). (b) A CB agglomerate (mixed with CeO_2) after catalytic oxidation *ex situ* at 350 °C. (c) A CB agglomerate (mixed with Al_2O_3) after noncatalytic oxidation *ex situ* at 600 °C. (a)–(c) Scale bars = 30 nm. (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.

To address the role of the CeO_2 catalyst, ETEM experiments were performed to monitor agglomerates of CB particles attached to CeO_2 particles *in situ* during exposure to oxygen at elevated temperatures. The time-lapsed series of ETEM images show the main findings (Fig. 2, see also supplementary material): The images reveal that agglomerates of CB particles moved toward the CeO_2 and vanished (Figs. 2a–2c), whereas agglomerates of CB particles did not protrude and move away from the edges of the CeO_2 particles. These findings suggest that the motion was related not only to the migration of CB along the CeO_2 surface, but also to the oxidizing reaction conditions. This finding is consistent with results of similar experiments using N_2 instead of O_2, in which ETEM image series showed that CB particle agglomerates remained stable. Moreover, monitoring the CB–Al_2O_3 samples by ETEM during exposure to the oxidizing conditions (Figs. 2d–2f) show that the agglomerates of CB particles were stable at the same temperature and over the same time period. Thus, the findings indicate that the CeO_2 catalyzed oxidation of the CB agglomerates and concurrently generated motion of the agglomerates toward the catalyst surface.

In an analysis of the ETEM observations, the CB particle diameters and positions relative to CeO_2 were mapped out in consecutive images as outlined in Figs. 3a and 3b. Fig. 3c shows the results for two CB particles during oxidation at 500 °C. Clearly, the relative projected distances in the images between the CB