

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 using an infrared detector, 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.

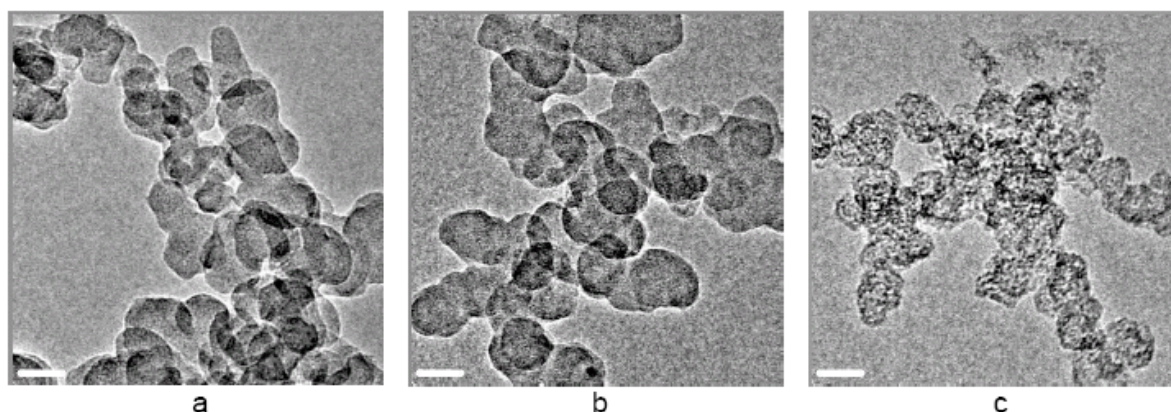


Fig. 1. TEM images of an agglomerate of carbon black particles (a) before oxidation, (b) after CeO₂-catalyzed oxidation at 350°C and (c) after non-catalytic oxidation mixed with Al₂O₃ at 600°C. Scale bars = 30nm.

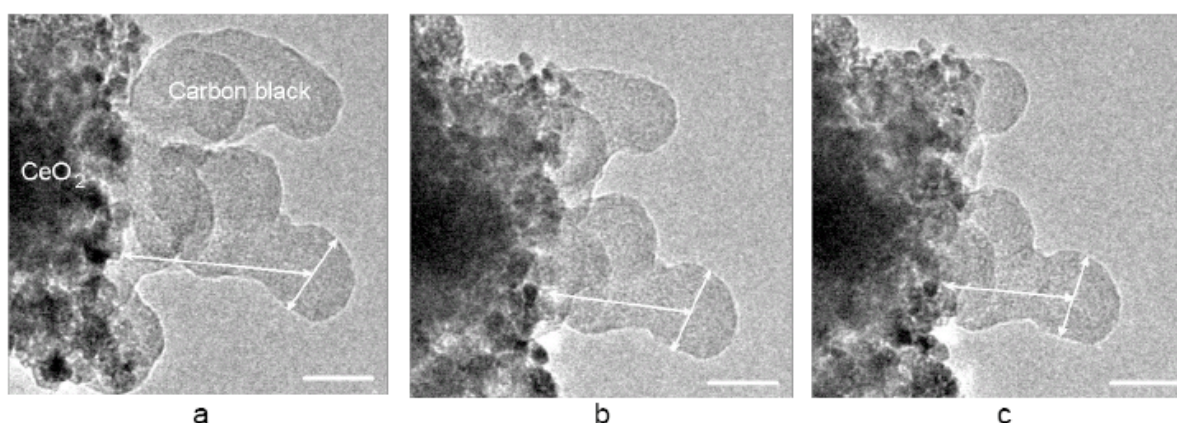


Fig. 2. ETEM images of an agglomerate of carbon black particles attached to CeO₂ during exposure to 200Pa O₂ at 475°C. Scale bars = 30nm. The time interval between the images is ~5min. The diameter of a carbon black particle and corresponding carbon black-CeO₂ distance is marked on each image.