Catalytic Soot Oxidation studied by ETEM

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Introduction

The awareness of soot abatement in the exhaust from diesel engines is currently increasing due to new environmental legislations for exhaust specifications. An attractive approach for effective soot removal includes the introduction of filters on the diesel-driven vehicles and the functionalization of the filters for catalytic soot oxidation (1,2). Ceria-based materials are widely adopted for this purpose. It is generally accepted that the redox properties of ceria are crucial to the catalytic effect, but the detailed reaction mechanism and the location of the catalytic active sites are still being debated. For instance, it has been proposed that the reaction occurs at the soot-ceria interface (3) and that the reaction occurs through spill-over of oxygen from ceria to reaction centers located at the soot surfaces (2-4).

Averaging techniques, such as temperature-programmed oxidation and thermo-gravimetric analysis, have mainly been used to study the soot oxidation reaction, e.g. (2-5). Although these studies provide significant insight, previous work on metal-catalyzed gasification of graphite suggests that environmental transmission electron microscopy (ETEM) may be a beneficial complement, because the technique allows direct observations at the carbon-catalyst interface to be obtained *in situ* during reaction (6).

In this contribution we present an ETEM study of the reaction mechanisms and kinetics involved in ceria-catalyzed soot oxidation related to diesel engine emission control (7).

Materials and Methods

ETEM has become a powerful tool in heterogeneous catalysis due to its ability to directly monitor catalysts *in situ* during exposure to reactive gases at elevated temperatures. The present experiments were performed using a CM300 FEG ETEM (8), or a Titan 80-300 image aberration-corrected ETEM, from FEI Company. 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 CeO_2 catalyst powder (or with an α-Al_2O_3 reference powder) with a volume ratio 1:10.

In the ETEM, the CB-oxide samples were exposed to ca. 2 mbar O_2 and a temperature in the interval 300-600°C. The samples were monitored by acquisition of time-lapsed ETEM image series (movies) using a low-light and fast-scan CCD camera. The electron beam current density was kept below 0.16A/cm^2, which was sufficiently low to avoid influence of the electron beam on the CB oxidation kinetics. A novel nanoreactor concept was also addressed for performing atomic-scale ETEM of catalysts under reaction conditions at gas pressures up to atmospheric pressures, i.e. ca. 1 bar (9).

Results and Discussion

The ETEM movies provide direct observations of soot particles in contact with catalytically active CeO_2 (or inert Al_2O_3) during exposure to an oxidizing gas environment. Specifically, the results show that the catalytic oxidation reaction involves processes, which are confined to the soot-CeO_2 interface region, and that the catalytic reaction surprisingly results in motion of soot agglomerates toward the catalyst surface (fig. 1), which acts to continuously re-establish the soot-CeO_2 interface in the course of the oxidation process.

The observed reaction dynamics is found to consistently explain observations from *ex situ* oxidation experiments. Moreover, a quantitative analysis of ETEM movies obtained at different reaction temperatures demonstrates that the apparent activation energy of CeO_2-catalyzed soot oxidation can be measured with ETEM for a more well-defined tight physical contact situation and is quantitatively in good agreement with previous kinetic studies, e.g. (3).

Significance

The first ETEM observations of the ceria-catalyzed soot oxidation reveal that the reaction mechanism involves reaction centers located near the soot-ceria interface.

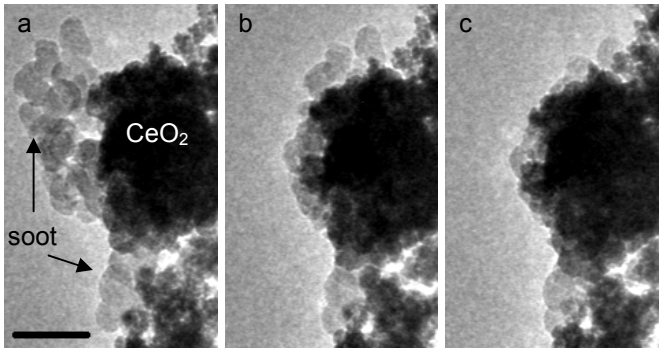

Figure 1. A time-lapsed ETEM image series of soot in contact with a CeO_2 catalyst acquired during the exposure to 2mbar O_2 at 550ºC. The time interval between the images is ~2min. Scale bar, 90nm. The figure is adapted from (7).

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