

Real-time observation of soot aggregate oxidation in an Environmental Transmission Electron Microscope

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Received 1 December 2015; accepted 12 July 2016

Available online 22 October 2016

Abstract

The oxidation of soot, obtained from 1-decene and ethylene flames, in a mixture of ionized and molecular O₂, was observed in real time by environmental transmission electron microscopy for the first time. The oxidation mode (surface vs. internal), and rate, was measured for individual primary particles, demonstrating that mature primary particles primarily oxidize through surface reactions. Further experiments with less mature soot particles showed oxygen permeation into the core of the primary particles, causing internal oxidation, as well as surface reactions, demonstrating a link between soot ageing and the oxidation mode. Aggregate structural changes and fragmentation throughout oxidation were also characterized; with surface reactions weakening the bridges between primary particles until the aggregate breaks up. In the last stages of aggregate oxidation, the primary particles were seen to lose their graphitic shell and spherical nature, with the remaining disordered carbon reforming into large amorphous masses before burning away. The role of ionized oxygen species on oxidation rates is also discussed, and showed a strong dependence on electron beam voltage.

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Keywords: Soot; Environmental TEM; In situ; Oxidation; Fragmentation

1. Introduction

Soot released into the atmosphere from combustion has adverse effects on the environment, human health [1], and engine performance and

efficiency. These major detrimental effects of soot underscore the importance of understanding its formation and oxidation mechanisms, and mitigating its emission. Soot oxidation is specifically an area of interest, as it reduces soot release and competes with mass growth of the particles. Characterizing the effect of temperature, fuel composition and different gaseous species on aggregate structure is key to creating cleaner burning processes and improving soot removal methods.

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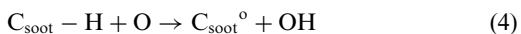
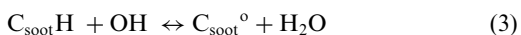
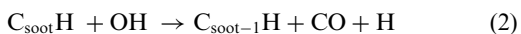
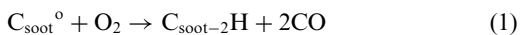
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The present work aims to analyze and understand the different oxidation processes and mechanisms by *in situ* experiments inside of an Environmental Transmission Electron Microscope (ETEM). The ETEM instrument provides a unique and novel opportunity to track individual soot aggregates in real time, and visualize their internal/surface oxidation, structural changes, and fragmentation.

2. Background

Mature soot consists of aggregates of individual primary particles, which are spherical in shape and range from 15–50 nm in diameter. The primary particles are composed of an amorphous carbon core surrounded by a graphitic shell [2]. Soot formation in flames is hypothesized to begin with the dimerization of polycyclic aromatic hydrocarbons (PAHs), which then grow further through surface reactions, gas phase PAH condensation, and coagulation, followed by coalescence and aggregate formation [3]. Oxidation and aggregate formation happen concurrently with the growth process. The particles then travel through the flame and either burn completely or escape through the flame front. The reactivity of the soot particles depends on many factors (e.g., maturity, composition, shape, etc.), all of which change the number of active sites on the surface of the particle [4]. These reaction sites allow for soot growth through surface chemical reactions, such as those described by the HACA (Hydrogen Abstraction, Carbon Addition) mechanism, or oxidation with O_2 and OH .

In soot oxidation, the particles are consumed by reactions with O_2 , O , and OH . For fuel rich conditions, the primary contributor is OH [5,6], while at fuel lean conditions, molecular oxygen plays a much larger role due to the abundance of O_2 . Some of the major reactions that contribute to oxidation are shown in Eqs. (1)–(4) [7].



It is hypothesized that the reactions with molecular O_2 primarily occur with active or dehydrogenated sites on the soot (i.e., C_{soot}^o). OH reactions do not require active sites; therefore, reaction rates depend both on gas concentrations as well as the availability of these active sites.

Apart from surface reactions, it also has been found that certain soot particles oxidize “internally” due to oxygen permeating into the particles [8–10]. High resolution transmission electron microscopy (HRTEM) studies [11] suggest that the burning mode depends on the particle nanostructure and oxidation conditions. Surface oxidation

was observed to result in a constantly decreasing primary particle diameter (d_p), while internal burning results in hollowing out of the particles, and the d_p remaining constant until the particle collapses. These modes of oxidation have a significant effect on the breakup or fragmentation behavior of the aggregate, and in turn, their emitted size; as internal oxidation would break up the aggregate as primary particles disintegrate, whereas surface oxidation weakens the “bridges” or connections between partially coalesced primary particles.

There have been numerous studies performed on the oxidation of soot from the combustion of various fuels (e.g., [12]); however, these have predominantly used experiments which track average and bulk soot properties [13]. The downside of such experiments is that, due to the inability to directly observe and track individual aggregates, they cannot answer many of the fundamental questions on how oxidation and its relevant processes occur. To measure the reactivity of soot particles, studies [14,15] have been carried out employing thermogravimetric analysis (TG). This method is based on a mass vs. time measurement of a bulk soot sample in a heated, controlled environment. Such analysis provides experimental data on apparent rate constants (k_c) and reactivity.

Another powerful imaging characterization tool is transmission electron microscopy (TEM). By collecting particles on thin amorphous carbon film supported on copper mesh grid, and imaging them inside of a high vacuum TEM, high resolution images can be obtained of aggregates, primary particles, and even the carbon plane spacing [16] in the primary particle shells. Such data also gives excellent validation for point by point comparison to numerical models.

The use of conventional TEM requires the sample be imaged while in high vacuum conditions (10^{-5} Pa). This atmosphere limits the instrument's function to imaging samples only pre or post reaction. *Ex situ* oxidation of the samples also proved difficult, with grids disintegrating quickly at temperatures higher than 500°C . Previous studies by Simonsen et al. [17] have managed to perform ETTEM studies on catalytic effects on soot burnup using conventional grids, with a maximum temperature of 600°C ; measuring reaction rates and soot's interactions with CeO_2 catalysts. No direct observation studies have been done, however, on soot aggregate oxidation behavior, fragmentation, internal oxidation, and the effects of oxygen species.

3. Method

An ETTEM was used for the current studies due to its high spatial resolution of 0.2 nm, as well as the ability to track individual particle reactions in real time, with heat, and in an oxygenated atmosphere. The small wavelength of high voltage

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