Kinetics of Nascent Soot Oxidation in a Flow Reactor

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Oxidation kinetics of soot are typically measured with carbon black or well aged soot as substrates. The soot surface is also assumed to be graphitic in theoretical soot oxidation rate calculations. However, recent experimental and theoretical studies show that nascent soot can have structures and surface composition drastically different from mature, graphitized soot. In this study, oxidation of nascent soot by O$_2$ was observed at $T= 950$ and 1000 K for oxygen concentrations ranging from 1000 to 7800 ppm in a laminar aerosol flow reactor at ambient pressure. Oxidation behavior of primary particles ($D_p = 11$ nm) of nascent soot from a premixed ethylene flame was observed by tracking the shift in the particle size distribution function (PSDF) under a given residence time. The measured rate of the surface reaction ranges from $1 \times 10^6$-$3 \times 10^6$ g/cm$^2$s for nascent soot. The rate of oxidation observed at the given conditions is an order of magnitude faster than predicted by the classical Nagle Strickland-Constable (NSC) correlations derived from graphite oxidation. Heterogeneous surface reaction rates are highly sensitive to the surface composition. Thus the faster rate of surface reaction by the nascent soot observed presently suggests that the surface composition of nascent soot is more reactive than the conventional graphite surface.

1. Introduction

Soot formation is crucial to a larger number of combustion processes. Critical gaps in the fundamental understanding of soot formation remain (Wang 2011). These gaps include the kinetics of soot oxidation. Recent studies on nascent soot morphology, particle size distribution function (PSDF) and composition have highlighted differences between nascent soot and mature, graphitized soot (Zhao et al. 2007, Abid et al. 2008, Cain et al. 2010, Cain et al. 2011). Specifically, it has been shown that nascent soot can contain a significant amount of aliphatic components (Cain et al. 2010, Cain et al. 2011, Wang 2011). Because the heterogeneous surface reaction kinetics and mechanism are expected to be highly sensitive to the surface composition, the oxidation kinetics of nascent soot surfaces is not expected to be the same as that of aged or graphitized carbon surfaces. In other words, the rate of nascent soot oxidation by e.g., molecular
oxygen, can be substantially different from what is described by the classical, empirical Nagle-Strickland Constable (NSC) equation (Walls and Strickland-Constable 1964), which was developed largely for graphite or carbon black oxidation.

Early studies of soot oxidation by $O_2$ typically used aged soot or carbon black as the reactant. A kinetic theory for reaction of oxygen with a carbon surface was first proposed by Eyring and coworkers (Blyholder et al. 1958) to describe observations of graphite oxidation. Two distinct reaction sites were introduced to explain the maxima that were observed in the oxidation rate above 1400 K. The two reaction sites were also adopted in the development of the NSC expression, derived from measurements of bulk pyrographite oxidation by $O_2$ (Walls and Strickland-Constable, 1964). The NSC expression has since been extended to describe high temperature carbon oxidation and used in models of soot formation and oxidation (see, e.g., Frenklach and Wang, 1991).

The understanding of soot oxidation has improved since the NSC expression was first proposed. The progress has been summarized by Stanmore, et al (2001) and Lall and Zachariah (2009). The oxidation rate of soot has been measured at temperatures above 1700 K by aerosolizing carbon black in a shock tube (Park and Appleton 1973, Brandt and Roth 1988, Brandt and Roth 1989, Cadman and Denning 1996). Shock tubes allow for the temperatures relevant to flames to be accessed but these studies could not utilize fresh nascent soot as the reactants. The kinetics of soot oxidation has also been studied in flame/dual flame environments or vitiated oxidizing flows in which the rates of soot oxidation may be followed at high temperatures (Lee et al. 1962, Fenimore and Jones 1967, Feugier 1972, Garo et al. 1990, Echavarria et al. 2011). However, flame gas usually contains a large number of reactive species (e.g., hydroxyl and other radicals), making the fundamental kinetic processes and mechanisms difficult to isolate and probe.

The oxidation behavior of soot at lower temperatures has been examined ex-situ. For example, oxidation kinetics has been studied gravimetrically for carbon black, flame soot and diesel soot in immobilized beds (Otto 1980, Ahlstrahm and Odenbrand 1989, Gilot et al. 1993, Neeft et al. 1997, Encinar et al. 2000, Lee et al. 2011). These studies developed the knowledge of the effects of temperature, oxygen concentration and the size of the particle on its oxidation kinetics. However, the collection and separation methods involved in preparing fixed bed reactors may alter the composition and reactivity of otherwise nascent soot. More recent studies have used spectroscopic techniques to examine soot oxidation but problems related to immobilizing the soot sample remain (Schmid et al. 2011, Schuster et al. 2011).
Electron microscopy techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have allowed for the soot morphology and size to be examined. The oxidation behavior of flame and diesel soot below 1000 K has also been followed under TEM by observing the change in size and morphology (Ishiguro et al. 1997, Vander Wal and Tomasek 2003, Vander Wal and Mueller 2006, Yehliu et al., 2012). The TEM method gives an unmatched resolution for measuring the size and morphology changes, but the technique requires that the soot sample be immobilized on a TEM grid. During TEM imaging, the low pressure may cause the soot sample to undergo some devolatilization and the high energy electron beam can cause sample damage (Lieb and Wang 2013). These difficulties obscure a reliable measurement of oxidation kinetics of nascent soot.

Measurements are ideally made with soot in the original aerosolized, flame state. The Tandem Differential Mobility Analyzer (TDMA) method has been introduced and used by Zachariah and coworkers to examine the oxidation behavior of soot at the tip of a coflow diffusion flame and from a diesel engine (Higgins et al. 2001, Higgins et al. 2003, Kim et al. 2005, Nienow et al. 2005, Jung et al. 2006). The TDMA method is capable of generating monodisperse soot particles to better examine the effect of particle size on soot oxidation the aerosolized state.

In the present work, the fundamental rate of nascent soot oxidation by molecular oxygen was examined at around 1000 K in an aerosol flow reactor. The various obstacles to measuring the oxidation kinetics of nascent soot were minimized by using fresh, freely suspended soot immediately extracted from flames as the reactant. Specifically, a particle sample was extracted continuously from premixed burner stabilized stagnation (BSS) flame and diluted immediately to reduce particle-particle coagulation. The particle sample was then introduced into the flow reactor.

As reported previously, BSS flames are in a pseudo 1-D configuration which allows for nascent soot be probed under well defined boundary conditions (Abid et al. 2009a). The stagnation probe allows for the residence time of soot particles to be controlled in the flame, allowing for soot at the different growth stages to be examined. Similar to Zachariah and coworkers, the electrical mobility was measured in the present study to determine the particle size distributions before and after oxidation occurs. Emphasis was placed on minimizing the transit time from the point where the soot was sampled to the flow reactor inlet. By using a short transit time and suspending the particles in an inert flow of cold nitrogen, the changes in the surface composition and morphology may be minimized. A main difference between our work and that of Zachariah and
coworkers is that the particles we examine are younger and have not undergone carbonization which may occur at the tip of their coflow diffusion flames.

2. Experimental Methodologies

A schematic summarizing the oxidation experiment is shown in Figure 1. Nascent soot was directly extracted at a distance of 0.8 cm from the burner surface of a 15.1 % ethylene-21.8 % oxygen-argon flame ($\phi = 2.07$, $T_f = 1850$ K) using a probe sampling technique similar to previous characterization of PSDFs in BSS flames (Abid et al. 2009a, Abid et al. 2009b, Camacho et al. 2013). The flat flame burner is water cooled and the burner diameter was 5 cm. The mass flow rates of oxygen, argon and nitrogen were controlled by critical orifices.

Nascent soot enters into the sampling probe orifice and was diluted and chilled in a carrier flow of nitrogen with the dilution ratio of approximately 100. The aerosol was carried to the flow reactor within a transmission time of 0.1 sec and mixed with a high-temperature stream of oxygen/nitrogen or nitrogen mixture. The high temperature stream is pre-heated to maintain an isothermal temperature profile in the flow reactor. The combined mixture enters into a tubular flow reactor which has 1.8 cm inner diameter. The residence time was 0.2 seconds in the flow reactor. In the present study, the diagnostic for nascent soot oxidation is the change in the PSDF, which was measured with a TSI Scanning Mobility Particle Sizer (Electrostatic Classifier 3085 and Condensation Particle Counter 3095). Sampling probes embedded at the inlet and the outlet of the aerosol reactor allowed for the PSDF to be measured before and after a given oxidation time.

![Figure 1. Schematic of the coupled burner and flow reactor setup. Nascent soot is extracted from the BSS flame at 0.8 cm from the burner surface.](image-url)
3. Results and Discussion

Oxidation of nascent soot was observed at $T=950$ and 1000 K for oxygen concentrations ranging from 1000 to 7800 ppm. The total flow rate in the test section of the flow reactor was kept at 330 cm$^3$/s (STP) for every oxygen concentration. The results shown in Figure 2 are a comparison of the initial PSDF ($t=0$ sec) and the final PSDF ($t=0.2$ sec) in an inter nitrogen flow. Under inert conditions, there is no observable change in the normalized PSDF over the 0.2 sec flow time, indicating that particle-particle coagulation or particle thermal decomposition was suppressed. The suppression of these complicating factors enables a direct interpretation of the change expected for the particle size due to oxidation. The PSDF of nascent soot from the ethylene flame tested gives a median diameter of 10.9 nm. At this size, the particles are expected to be primary particles in the early stage of growth.

The PSDF under oxidation conditions was measured as a function of the oxygen concentrations at 950 and 1000 K, as shown in Figure 3. For each condition, the experiments were repeated at least three times to ensure the reproducibility of the experiment. The dilution ratio has not been calibrated thus the PSDF are reported on a normalized basis. Observable reduction in the particle diameter occurs for $>1000$ ppm O$_2$ for $T=950$ K. As expected the reduction in particle size increases with an increase in the O$_2$ concentration and temperature.

![Figure 2. Measured PSDFs (symbols) of nascent soot from the ethylene BSS flame, probed in the flow reactor in an inert nitrogen flow at the initial ($t=0$ sec, filled circles) and the final ($t=0.2$ sec, open squares: 950 K; open triangles: 1000 K) residence times.](image-url)
Figure 3. Measured PSDFs (symbols) of soot from the ethylene BSS flame as a function of the oxygen concentration ($t = 0.22$ sec). Left panel: 950 K; right panel: 1000 K. The lines are normal distributions which are fitted to the measured PSDF. The top plots show the PSDFs in inert nitrogen. Lines are log-normal fits to data.

The oxidation rate of nascent soot can be extracted from rate of PSDF reduction as long as the effective surface area undergoing oxidation is defined. Molecular oxygen may attack the soot particle in three distinct regimes depending on the degree of penetration. If the diffusion of
molecular oxygen into the particle is infinitely fast then all of the internal surface area of soot undergoes oxidation. The diffusion of oxygen may also be limited such that the inner area is only partially active. A third regime applies when all of the surface reactions occur on the outer surface.

In the present study, the outer surface area of the spherical particle is the only oxidation site considered. The observed median diameter is about 11 nm which suggests that the PSDF is composed of primary soot particles and that the mean free path of the gas is larger than the particle size. The penetration of oxygen into the primary particle is assumed to be unimportant. For a spherical particle with diameter, $D_p$, in the pseudo first order limit with respect to the molecular oxygen concentration, the mass disappearance rate on the basis of outer surface area consumption for a specific oxygen concentration is described by:

$$-\frac{dn}{dt} = \omega \left( \pi D_p^3 \right).$$

If the mass density of soot is a constant ($\rho_s = 1.5$ g/cm$^3$ taken from Zhao et al. (2007), we obtain

$$\omega = -\frac{\rho_s}{2} \frac{dD_p}{dt}.$$

The above equation shows that the time variation in $D_p$ is directly related to the surface oxidation rate of soot under this simplified analysis.

The measured oxidation rate of nascent soot is shown in Figure 4 as a function of oxygen concentration for all of the conditions tested. For comparison, the classical prediction of the oxidation rate by the NSC equation is also shown. Clearly, the NSC equation under predicts the oxidation rate of nascent soot by more than one order of magnitude. The reactivity of nascent soot towards oxidation by molecular oxygen is significantly higher than of graphite or carbonized soot.
Figure 4. Measured specific oxidation rate of nascent soot (symbols) compared to predictions by the NSC equation (solid lines). The dashed lines represent the NSC rates multiplied by a factor of 10.

4. Conclusions

Oxidation of nascent, uncarbonized soot by molecular oxygen was studied. Nascent soot was generated in an ethylene burner-stabilized stagnation flame. The rate of change in the median particle diameter was measured to range from −20 to −40 nm/s depending on the temperature and $O_2$ concentration. In terms of surface reaction, the measured rate ranges from $1$ to $3 \times 10^6$ g/cm$^2$/s. The observed rate of oxidation is much larger than that predicted by the classical NSC equation which suggests that the surface of nascent soot is more reactive than a traditional graphite or carbonized soot surface.
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6. References
