Combustion Science and Technology

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MEASUREMENT OF SOOT SURFACE GROWTH KINETICS

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Surface growth is one of the major steps in the soot formation processes where most of the total mass is formed. Freshly generated soot from an ethylene diffusion flame was sampled and mixed with ethylene in a flow tube at elevated temperatures and using nitrogen as the carrier gas. The changes in the size of the soot particles after hydrocarbon addition were measured using a differential mobility analyzer. These measurements showed a significant mass increase of soot particles as a result of the hydrocarbon addition where the total number density remained the same. Soot surface growth kinetics were obtained from the changes in the size, surface area and volume distributions. The activation energy (E_a) for ethylene was obtained. Pure pyrolysis experiments for ethylene were also performed. The surface growth process yield was found to be higher than the yield of the pyrolysis process.

INTRODUCTION

Soot is a primary pollutant emitted from mobile and stationary power plants. Soot is considered as one of the important environmental risk factor affecting the global climate and human health. In a recent study (Pope et al., 2002) it was found that long-term exposure to combustion-related fine particulate air pollution is an important risk factor for cardiopulmonary and lung cancer mortality. Menon et al. (2002) recently reported that the presence of excessive amounts of soot in the atmosphere may cause changes in precipitation and ambient temperature histories that lead to cycles of increased floods and droughts. Change in the local climate due to the excessive amount of soot in the atmosphere is an important problem in the rapid growing countries like China. In addition to local climate changes, soot is found to be one of the important contributors to the global warming (as important as CO_2). Understanding soot formation in combustion processes is a very important (and daunting) task to control this unwanted pollutant emission.

Soot formation is a very complicated, multi-stage process which includes nucleation (also known as particle inception), surface growth, coagulation, agglomeration and aggregation and oxidation. At the initial nucleation stage, the first condensed phase materials form from the gas species originating from the pyrolysis or oxidation products of the fuel molecules such as acetylene and PAH. This process leads to very small particles with diameters up to 2 nm which have only a small fraction of the total particulate mass formed ultimately. The characteristic time for nucleation is 50 ms (Harris and Weinera, 1985). Most of the mass addition to these nucleated particles occurs in the surface growth stage.

Surface growth involves the attachment of the gas-phase growth species (one of them is acetylene). During the surface growth phase the mass increases however total number density remains mainly constant. After this significant mass increase which continues for tens of milliseconds comes the last stage which is called the chain formation by agglomeration and aggregation. At this last stage the mass does not increase but the number density drops due to agglomeration and aggregation of the particles. The characteristic time for this stage is 50 ms.

The main purpose of this work is to study the soot surface growth stage which is mainly responsible for most of the total soot mass formation. Ethylene was mixed with freshly generated soot from a diffusion flame in a flow tube at elevated temperatures using nitrogen as the carrier gas. Soot surface growth rate were obtained by measuring the growth rates using a differential mobility analyzer (DMA). The yield of the surface growth was also measured and compared with the yield related of the pyrolysis.

EXPERIMENTAL DESCRIPTION

The main purpose of these experiments is to measure the surface growth of freshly generated soot particles by adding hydrocarbon under elevated temperatures. It is important to use freshly generated soot particles to eliminate the reduction in the surface reactivity due to aging effects, such as surface oxidation. Since the addition of hydrocarbon growth precursors may undergo both homogeneous nucleation as well as surface growth, a major experimental challenge in studying surface growth is to ensure that one is suppressing homogenous nucleation, which will corrupt to make data interpretation difficult. Homogeneous nucleation, if unaccounted for, will eventually result in small cluster-soot interactions and an artificial surface growth.

The soot for our experiments was generated in a Santoro-type diffusion burner (Santoro et al., 1983). The soot was diluted such that for the residence time in our experimental system no particle-particle coagulation events should occur to perturb the size distribution. The diagram of the experimental apparatus is shown in Figure 1. Ethylene was used as the fuel at flow rate of $140 \, cm^3 \, min^{-1}$. Soot particles were collected from the flame by using a sampling probe with an inner diameter of 11 mm and a 1 mm orifice. Nitrogen at a flow rate of 20 slpm (standard liters per minute) was used to dilute and cool the soot particles which are then transferred to the quartz reactor tube placed inside the tube furnace.

The details of the burner and the sampling system were explained in detail in the previous work (Kim et al., 2005b; Higgins et al., 2003). The burner was operated for at least 30 minutes to reach steady state, and the size distributions from the flame was continuously monitored using a Differential Mobility Analyzer (DMA) coupled to a condensation particle counter (CPC). The variations in the size distribution of
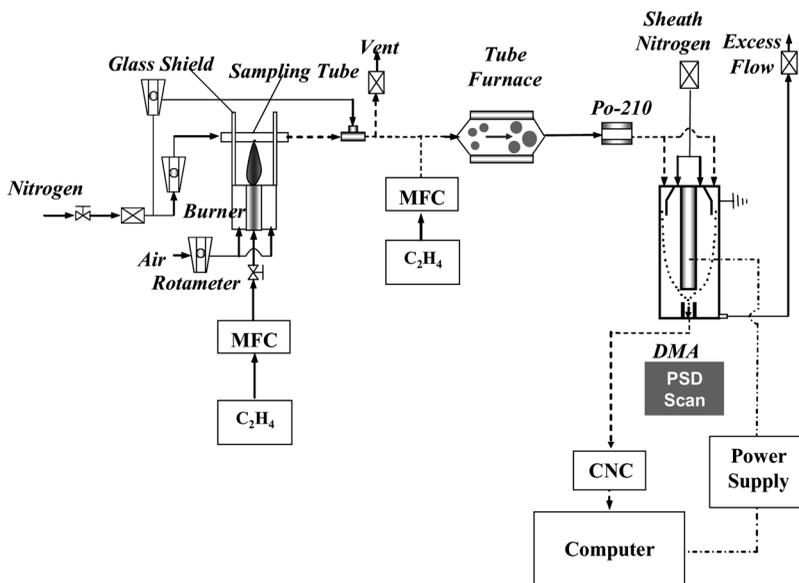
Figure 1 Schematic diagram of the experimental apparatus.

the soot particles sampled from the burner were minimal after the initial 30 minutes warm up period. Mixing with the hydrocarbon precursors occurred right before the soot particles enter the quartz reactor tube. Ethylene was used as the surface growth additive and was metered using a mass flow controller.

When the precursor is mixed with the soot aerosol and subsequently heated, the size distribution should change due to surface growth. The gas stream containing the soot particles are passed through a 210 Po bipolar diffusion charge (neutralizer) to establish a known equilibrium charge distribution. The DMA combined with condensation nucleation counter (CNC) is used to determine the rate of growth by measuring the size distribution of the soot particles with and without hydro-carbon addition. More details of the size distribution measurement may be found in previous studies (Kim et al., 2005a, b; Higgins et al., 2003).

In addition to the surface growth measurements, we have also performed direct pyrolyis experiment for soot formation from ethylene. The flame soot source was replaced by the nitrogen flow at 0.5 slpm. The precursor was introduced right before the flow enters the quarts tube placed in the tube furnace. The integrated size distri-butions were used to obtain the soot yield, which can be compared with the surface growth experiments. These pyrolysis experiments were necessary as they provided guidelines for the soot surface growth experiments, by establishing the threshold conditions for homogeneous nucleation.

RESULTS AND DISCUSSION

Pyrolysis Experiments

Size distribution results of the ethylene pyrolysis are plotted in Figures 2a–c. The temperature in the quartz flow tube was varied between 850℃ to 1050℃ and
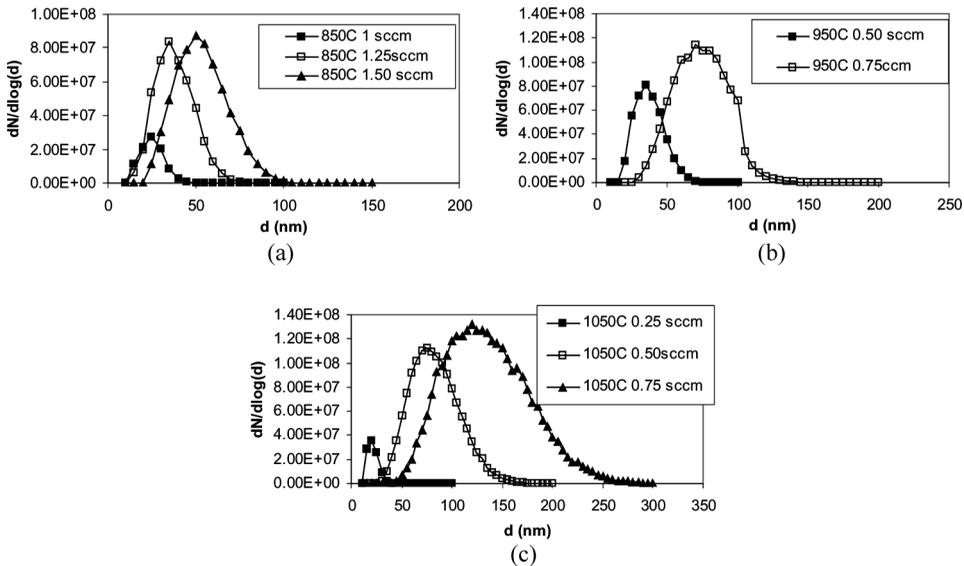
Figures 2a–c Ethylene pyrolysis experiments at various temperatures.

the precursor concentration was varied at each temperature. The minimum precursor concentration for each temperature represents the values below which no particles can be detected by the DMA/CNC system. At constant temperature, the total number density and the peak particle diameter increase with the precursor concentration. For example at 850°C the peak particle diameter increases from 25 nm to 50 nm as the precursor flow rate increases from 1 sccm to 1.5 sccm (1996 ppm ethylene to 2991 ppm ethylene). Similar behavior was observed at temperatures 950°C and 1050°C. Temperature also has a similar influence on the number density and peak particle diameter. For 1500 ppm ethylene in nitrogen, the peak particle diameter increases from 70 nm at 950°C to 120 nm at 1050°C

As mentioned earlier, precursor concentration in the surface growth experiments is very critical because even at relatively low temperatures the added precursor acts as a source of nucleation, and the particles grow further and coagulate with the flame soot. This is an unwanted condition for obtaining the surface growth kinetics. These pyrolysis experiments provide the guidelines to establish the experimental conditions where we can monitor soot surface growth in the absence of new particle formation. However it is important to keep in mind that the characteristics of the homogeneous nucleation in the presence of particles are expected to be different from the homogeneous nucleation alone.

The soot yield for the pyrolysis experiments is defined as the percent ratio of the total mass of the soot particles to the mass of the precursor added to the main flow (0.5 slpm nitrogen). The total soot mass produced is calculated by integrating the volume distribution (obtained from the corrected DMA measurements by converting the number density to the volume density) and multiplying by the soot density reported in the literature ($\rho = 1.8\,\text{g/cm}^3$). As can be seen from Table 1, the maximum yield was obtained as 1.2% at the highest temperature of 1050°C.

Table 1 Soot yield as a function of temperature and precursor concentration for ethylene

| Temperature (°C)	Concentration (ppm)	Yield (%)
850	1,996	0.01
850	2,494	0.05
850	2,991	0.12
950	999	0.12
950	1,498	0.81
1050	500	0.02
1050	999	1.23
1050	1,498	1.21

Soot Surface Growth Experiments

The experiments in this study differ from the previous studies (Kim et al., 2005a; Higgins et al., 2002) where the soot oxidation experiments were performed on the size-selected soot particles. A tandem DMA system was used in these experiments where two DMA's are set up in series. Monodisperse particles were selected from a polydisperse aerosol input stream and these monodisperse particles are then subjected to chemical processing (oxidation using air at elevated temperature). Our initial thought was to use a similar approach to study surface growth using monodisperse DMA selected particles. However we found that the small surface area of soot coming from the DMA meant that it was very hard to find a stable operating condition where we could see surface growth, and simultaneously operate without any homogeneous nucleation. This observation just reinforces the highly non-linear nature of homogeneous nucleation.

As a result of the above mentioned constrain, we performed the growth experiments on the total aerosol sample. Experiments have been performed where the freshly generated soot particles from the diffusion flame are mixed with the precursor (ethylene). Initially, with the precursor flow turned off we obtain a particle size distribution of the soot sampled from the flame, over several scans to ensure that the size distribution has reached steady state. A controlled amount of precursor is then added, to the soot aerosol flow and the resulting size distribution is measured after the system reaches steady state (10–15 minutes). Several back to back particle size distribution scans are performed to obtain the influence of the precursor addition on the size distribution of the flame soot.

Figures 3a–c show the soot size distributions (number, surface area and volume) before and after mixing with ethylene. The initial flame soot size distribution is the closed symbols while the open symbols represents the final size distribution resulting from mixing with the precursor. As can be seen in Figures 3a–c, the number density does not change significantly as a result of precursor addition indicating that homogeneous nucleation is not taking place. The size distribution was integrated to obtain changes in total number concentration, total surface area and total volume, and are summarized in Table 2 for three different temperature cases. As can be seen from Table 2, the total number concentration did not change as a result of precursor addition.

The peak particle diameter shifts from 60 nm for the original flame soot to 90 nm after mixing with ethylene. When we look at the surface area
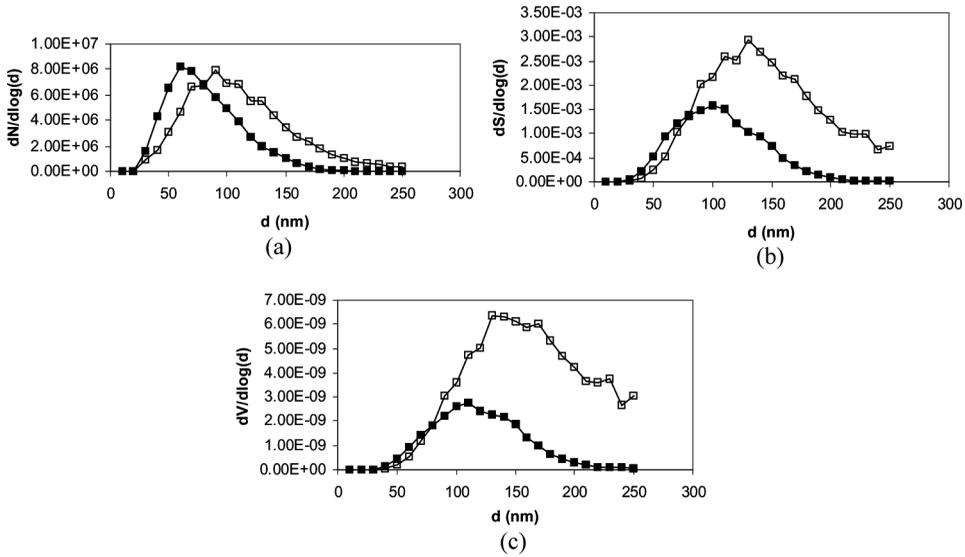
Figures 3a–c Size distributions (number, surface area and volume) showing the soot surface growth as a result of 0.2 sccm ethylene addition to flame generated soot at 950°C.

and volume distribution, a significant increase was observed for both the total surface area (54% increase) and total particle volume (100%). Given that the total number concentration did not change, the changes in the total surface area and the total volume are attributed to surface growth by addition of hydrocarbon precursors. The temperature for this experiment was 850°C which is relatively low when compared to the temperatures observed in the surface growth region in a diffusion flame. However, surface growth can occur at lower temperatures than the temperature at which the initial soot particles are generated (Haynes and Wagner, 1981). The high reactivity of the soot surface is such that

Table 2 The influence of ethylene addition to the flame soot on the total number concentration, total surface area, total volume and total mass at 3 different temperatures (a) 850°C; (b) 950°C; (c) 1050°C

| @ 850°C	N (1/cc)	Area (cm^2/cc)	V (cm^3/cc)	M (g/cc)
Flame Soot	8.92E + 06	5.74E − 04	5.16E − 10	9.29E − 10
Flame Soot + Precursor	8.62E + 06	8.81E − 04	1.03E − 09	1.86E − 09
% increase	− 3.4	53.5	99.6	99.6
@ 950°C	N (1/cc)	Area (cm^2/cc)	V (cm^3/cc)	M (g/cc)
Flame Soot	3.69E + 06	6.59E − 04	1.03E − 9	1.86E − 9
Flame Soot + Precursor	3.58E + 06	1.15E − 03	2.43E − 09	4.38E − 09
% increase	− 3	75	135	135
@ 1050°C	N (1/cc)	Area (cm^2/cc)	Volume (cm^3/cc)	Mass (g/cc)
Flame Soot	3.06E + 06	2.54E − 04	2.72E − 10	4.90E − 10
Flame Soot + Precursor	3.57E + 06	1.10E − 03	2.21E − 09	3.98E − 09
% increase	17	333	713	713
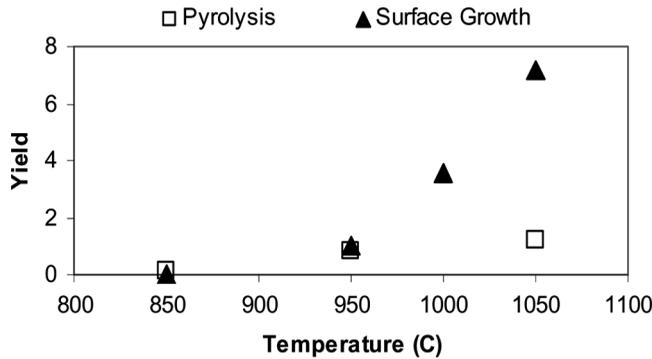
Figure 4 Comparison of the yield for pyrolysis and surface growth of ethylene.

the presence of soot can accelerate the decomposition of benzene and acetylene (which are generally accepted as the main species attached to the soot surface) in pyrolysis.

As expected, these surface growth reactions are sensitive to both temperature and growth species concentration where both need to be carefully adjusted to prevent unwanted nucleation. As the temperature is increased, the increase in the total surface area and total volume becomes more pronounced. For example at 1050°C, addition of 400 ppm ethylene in nitrogen results in an insignificant increase in the total number density (the change is within the experimental uncertainty), with a 333% increase in the total surface area, and 713% increase in the total volume (hence mass ,assuming that the soot density does not change, increases significantly).

The yield was also defined and calculated for the surface growth experiments and compared with the yield from the pyrolysis experiments. Surface growth yield is defined as percent ratio of difference in the total mass of flame soot (before and after precursor addition) divided by the total mass of precursor. The soot surface growth yield is compared with the pyrolysis yield for the precursor used in this study. Figure 4 shows that surface growth yield is higher than the yield of the pyrolysis process. Therefore the conversion efficiency of the precursor to soot by addition to the existing soot particles is higher than the conversion by pyrolysis alone.

Soot Surface Growth Kinetics

Several repeat experiments have been performed in order to extract the kinetic information of the soot surface growth. The effective global reaction rate constant (or sticking coefficient) is calculated by using Eq. (1) (Freidlander, 2005).

$$\alpha = \frac{dv}{dt}\frac{(2\pi mkT)^{1/2}}{p_1\pi d_p^2 v_m} \tag{1}$$
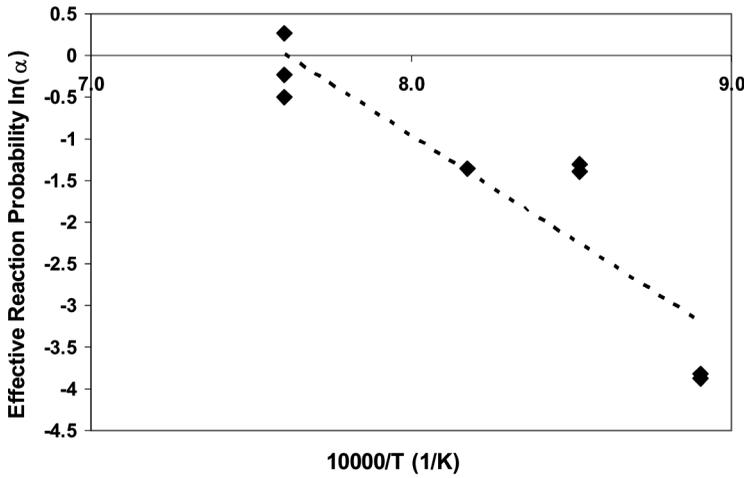
Figure 5 Arrhenius fit for surface growth reaction rate for ethylene addition ($E_a = 230\,kJ/kmole$).

where

dv/dt rate of conversion

   α the effective sticking coefficient

   p_1 partial pressure of the precursor

   πd_p^2 surface area

   v_m molecular volume of condensing species

   k Boltzmann constant

   m molecular mass

   T temperature

The rate of conversion represents the rate of the total particle volume increase in characteristic time (which is the residence time for our experiments).

Figure 5 shows the Arrhenius plot for decomposition of ethylene on soot particles from the diffusion flame. The activation energy (E_a) for ethylene was calculated as $230\,kJ/kmole$.

CONCLUSIONS

These experiments show the conditions under which the soot nano-structure (soot surface area) can be effectively modified by surface growth. The critical condition to prevent nucleation has been determined by pyrolysis experiments. It was also shown that the soot surface growth kinetics can be extracted from these type of experiments. By obtaining experimental data at a wide range of temperatures, the soot surface growth kinetics data can be extrapolated to be used in the practical systems. It has been shown that decomposition of the pyrolysis products of the precursors on the existing soot particles is much more efficient than the pyrolysis reactions alone.

REFERENCES

Freidlander, S.K. (2000) Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics, Oxford University Press, New York, Chap. 10, pp. 275–330.

Harris, J. and Weinera, M. (1985) Chemical kinetics of soot particle growth. *Rev. Phys. Chem.*, **36**, 31.

Haynes, B.S. and Wagner, H.G. (1981) Soot formation. *Prog. Energy Combust. Sci.*, **7**, 229.

Higgins, K., Jung, H., Kittelson, D.B., Roberts, J.T., and Zachariah, M.R. (2002) Size-selected nanoparticle chemistry: Kinetics of soot oxidation. *J. Phys. Chem. A.*, **106**(1), 96.

Higgins, K., Jung, H., Kittelson, D.B., Roberts, J.T., and Zachariah, M.R. (2003) Kinetics of diesel nanoparticle oxidation. *Environ. Sci. Technol.*, **39**(9), 1949.

Kim, S.H., Fletcher, R.W., and Zachariah, M.R. (2005a) Understanding the difference in oxidative properties between flame and diesel soot nanoparticles: the role of metals. *Environ. Sci. Technol.*, **39**, 4021.

Kim, S.H., Liu, Y.H., and Zachariah, M.R. (2005b) Method for measuring the charge and size distribution of nanoaerosols. *J. Coll. Interf. Sci.*, **282**(1), 46.

Menon, S., Hansen, J., Nazarenko, L., and Luo, Y. (2002) Climate effects of black carbon aerosols in China and India. *Science*, **297**, 2250.

Pope III, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., and Thurston, G.D. (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *JAMA*, **287**, 1132.

Santoro, R.J., Semerijan, H.G., and Dobbins, R.A. (1983) Soot particle measurements in diffusion flames. *Combust. Flame*, **51**, 203.