



FLAME SYNTHESIS OF COMPOSITE CARBON BLACK-FUMED SILICA NANOSTRUCTURED PARTICLES

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Abstract—Simultaneous synthesis of SiO₂/C nanostructured powders is investigated in a premixed flame aerosol reactor by combustion of acetylene and SiCl₄. The powders are found to be composed of SiO₂ either encapsulated in or partially covered by carbon black. The effect of fuel equivalence ratio (ϕ) on carbon black yield and specific surface area is presented. High ϕ means fuel-rich flames that result in finer fumed silica though the specific surface area of the composite powder remains virtually unchanged with ϕ . The presence of silica enhances the carbon black yield 2–3 times. Applying external electric fields across the flame allows synthesis of nanostructured powders with closely controlled specific surface area and composition. Making composite powders permits application of much higher electric fields than with pure carbon black before field breakdown. Increasing the electric field intensity decreases the specific surface area of the product powder in contrast to that of electrically assisted flame synthesis of pure silica and other oxides. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The nearly molecular scale of nanoparticles and their uniquely active surfaces provide a potential basis for the development of innovative engineering technology and consumer applications. As nanoparticle synthesis techniques improve, practical considerations of nanoparticle applications become increasingly important. For example, the simultaneous production of two different nanoparticle materials is a potential pathway for synthesis of nanocomposite particles with unique properties. This type of process could provide new engineering materials as well as eliminate difficult processing steps like powder mixing. Two representative nanostructured particle systems with such potential are also two of the largest volume particulate materials produced in flames by the chemical process industry: carbon black and fumed silica.

Formation of carbon black and fumed silica in flames has been studied in detail by Donnet *et al.* (1993) and Ulrich and Riehl (1982), respectively. In summary, carbon black is formed by nuclei inception and surface growth while fumed silica is formed by chemical reaction and coagulation. Fumed silica and carbon blacks are routinely made in flames on an industrial scale. Carbon black is used, among other applications, to increase the wear resistance of automobile tires. Silica particles also reinforce the structure of rubber, significantly increasing its strength by forming silica networks within the rubber structure (Hashim *et al.*, 1995; Mandal *et al.*, 1995). Silicas with high specific surface area result in stronger networks (Cochrane and Lin, 1993). The combination of carbon black and silica particles is more effective at reinforcing rubber than carbon black alone, although silica does not disperse as well as carbon black and some carbon black is required for static electricity dissipation (Bomal *et al.*, 1993; Waddell *et al.*, 1993). Carbon black and silica are also precursors for the production of silicon carbide (Murukawa *et al.*, 1987; Vlasova *et al.*, 1993) and opaque silica aerogels (Lee *et al.*, 1995).

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In flame processes, product particle characteristics are usually controlled by gas mixing, precursor concentration, process temperature, and cooling rates (Ulrich, 1984). Electric fields during flame synthesis of powders provide another means of controlling the characteristics of the product particles (Payne and Weinberg, 1959, Vemury and Pratsinis, 1995). Hardesty and Weinberg (1973) showed that the SiO₂ primary particle size decreased with increasing applied potential and attributed it to reduced particle residence time in the flame. Xiong *et al.* (1992) showed theoretically that charging could narrow the particle size distribution below that dictated by the self-preserving limit (Lai *et al.*, 1972). Vemury and Pratsinis (1996) and Vemury *et al.* (1997) made fumed silica particles with closely controlled aggregate and primary particle sizes by applying electric fields created by needle and plate electrodes across a premixed flame.

In the above applications, it is typical to mix commercial fumed silica with carbon black. However, since both fumed silica and carbon black are manufactured by flame aerosol processes, it may be more efficient to make these powders by a single process. This may eliminate the need for solid powder mixing and minimize possible segregation and non-homogeneity in the final product. Furthermore, these composites may have new applications beyond rubber reinforcement or materials manufacture such as combination adsorbent catalysts. Here flame aerosol synthesis of composite carbon black-fumed silica particles is investigated. The goal of this work is to characterize the effect of the fuel equivalence ratio (ϕ) and an applied electric field on the formation, growth, and properties of flame-made composite carbon black-fumed silica particles.

EXPERIMENTAL

Figure 1 shows the experimental setup which consists of: the flame reactor, the precursor/carrier gas delivery system, the electrode current measurement apparatus, and the powder collection assembly (Vemury and Pratsinis, 1996). The reactor is made of three concentric quartz tubes, where the center tube (17 mm i.d.) is a laminar premixed flat flame burner, the second tube is a spacer (8 mm wide), and inert N₂ gas flows through the outer tube (6 mm wide). The central tube is packed to half of its volume with glass beads ($d = 5$ mm) to facilitate mixing of the reactants. The end of the tube contains a 3.8 cm ceramic monolithic honeycomb with 62 openings cm⁻² to stabilize the flame (Vemury *et al.*, 1997).

Oxygen and acetylene are premixed, pass through a check valve to prevent flame flashback, are diluted with argon, and introduced into the burner. The flow rates of argon, acetylene, and nitrogen are held constant at 1400, 350, and 2000 cm³ min⁻¹, respectively, while 250 cm³ min⁻¹ of Ar are bubbled through a gas washing bottle containing SiCl₄. Assuming that SiCl₄ vapor is at equilibrium with argon, 100 cm³ min⁻¹ pass into the flame reactor, providing a SiCl₄:C₂H₂ molar ratio of 1:3.5. Evaporation experiments, however, indicated that the argon is 88% saturated with SiCl₄, giving a corrected SiCl₄:C₂H₂ molar ratio of 1:4 and all subsequent calculations account for this.

Carbon black is formed by incomplete oxidation of hydrocarbons followed by surface growth and oxidation. Fumed silica is formed by oxidation of SiCl₄, coagulation, and sintering. The oxidation conditions in the flame were characterized by a composite form of the equivalence ratio, ϕ , to account for simultaneous synthesis of carbon black and silica by accounting for the stoichiometric oxygen requirements for oxidation of SiCl₄:

$$\phi = \frac{(m_{C_2H_2}/(m_{O_2} - m_{SiCl_4}))_{actual}}{(m_{C_2H_2}/m_{O_2})_{stoichiometric}}, \quad (1)$$

where m_i is the number of moles of component i in the feed. The ϕ ranges from 3.3 to 4.5 as the oxygen flow rate varies from 350 to 282 cm³ min⁻¹, respectively. At higher ϕ the flame is no longer stable while it burns the honeycomb at smaller ϕ values.

Once particles form in the flame, they are collected on glass fiber filters (Gelman, $d = 142$ mm) placed 14.5 cm above the burner top. The open-faced filter is contained within

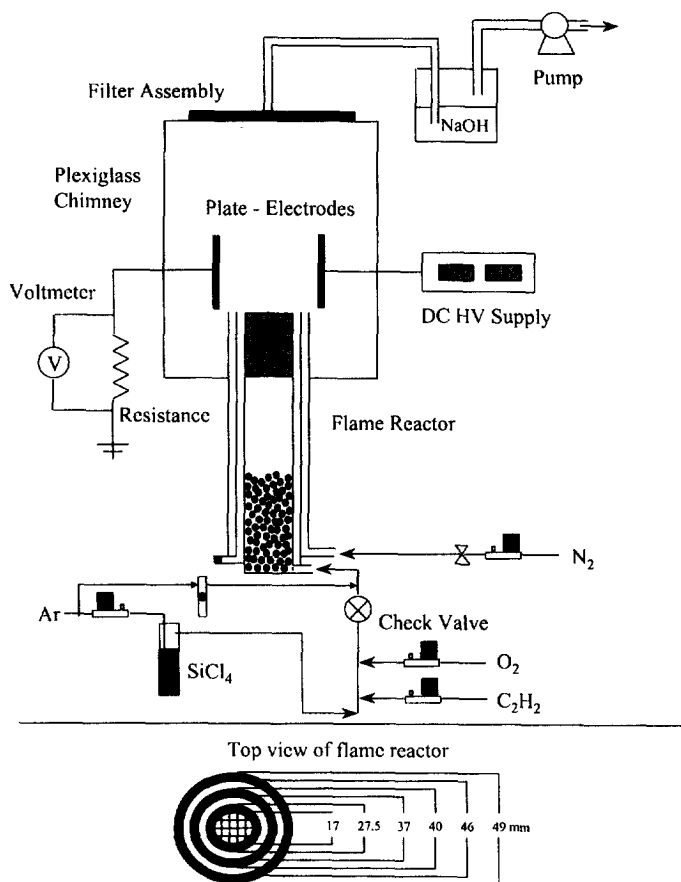


Fig. 1. Schematic of the experimental setup for synthesis of carbon black-fumed silica particles. The inset shows the burner cross section.

a cylindrical chimney to direct the flow into the filter assembly and minimize particle losses. The electric field is generated using stainless-steel plate electrodes positioned 5 cm apart at either side of the flame (Vemury and Pratsinis, 1996). The electrodes are 3.81 cm long, 2.54 cm wide, and 0.38 cm thick. One electrode is connected to a DC power supply (positive or negative) while the other one is grounded.

The specific surface area of the powders is measured by N_2 adsorption at 77 K (Gemini 2360, Micromeritics) using the BET equation. The fraction of carbon black in the collected powders is determined from the weight reduction after oxidizing the powders at high temperature in a furnace. The morphology of the powder is characterized by transmission electron microscopy (Philips EM 400 at 100 kV). Powder yields are determined from the weight of the collected powder and a theoretical stoichiometric calculation of the production of silica and carbon black. The temperature distribution along the flame height is determined by thermocouple measurements (S-type, Omega Engineering) after correction for radiation losses (Collis and Williams, 1959) though no correction was made for carbon black or silica deposits so the temperature measurements should be considered qualitative.

RESULTS AND DISCUSSION

Synthesis of carbon black-fumed silica particles

Figure 2 shows pictures of flames making pure carbon black (upper) and carbon black-fumed silica (bottom) particles at various ϕ . The pure carbon black flames are brighter than the carbon black-fumed silica flames possibly as a result of the higher temperatures of the former. A narrow gap is observed between the most luminous portion of

the pure carbon black flames and the burner top. This gap decreases as the ϕ decreases. For both pure carbon black and carbon black-fumed silica flames, increasing the oxygen flow rate (and thus decreasing the ϕ) produces a brighter, higher-temperature flame and decreases the amount of carbon black produced (Prado *et al.*, 1981).

Figure 3 shows the temperature of carbon black-fumed silica flames along the axis of the burner at $\phi = 3.9$ and 4.5. The maximum temperature is slightly above the burner top in the most luminous region and is shifted upward by an increase in the ϕ . Consistent with the observations in Figs 2 and 3 increasing the ϕ decreases the flame temperature. Furthermore, the gap between the flame and the burner is much smaller (virtually non-existent) than that in the absence of SiCl_4 .

Figure 4 shows a typical TEM micrograph of carbon black-silica nanostructured particles at $\phi = 4.5$. The relative composition of the carbon black-fumed silica particles produced in the flame was determined by oxidizing the samples at 800°C in a furnace. This allows a determination of the carbon black mass lost by oxidation. The mass loss was found to level off after 20 min for all samples indicating that all oxidizable material (carbon black) had been removed. Figure 5 shows the mass fraction of carbon black in the composite particles as a function of the employed ϕ . Decreasing ϕ corresponds to an increased oxygen flow rate and, thus, an increased oxidation of carbon black precursors and carbon black particles (Prado *et al.*, 1981). For a ϕ of 4.5 the carbon black mass is about 32% of the composite mass while it decreases to as little as 7% for a ϕ of 3.3. Visual observations of the samples indicated that the particles change in color from black to gray as the ϕ is decreased. After carbon black oxidation and removal in the furnace, the particles are rather white so virtually no carbon black remained indicating that carbon black was not encapsulated by silica particles.

Figure 6 shows the specific surface area (SSA) of the powder as a function of the flame ϕ before (filled squares) and after (open squares) the carbon black has been oxidized in the furnace, i.e. for carbon black-fumed silica and pure silica particles, respectively. Increasing the oxygen flow rate from 282 to 350 $\text{cm}^3 \text{min}^{-1}$ decreases the ϕ from 4.5 to 3.3 and marginally decreases the composite carbon black-fumed silica particle SSA from 185 to 125 $\text{m}^2 \text{g}^{-1}$, corresponding to an average primary particle size of 13.5–18.5 nm, respectively. From Fig. 6 it appears that the carbon black particles limit the contribution of the small silica primary particles to the SSA. Burning the carbon black off leaves behind the aggregates of fine silica primary particles, thus increasing the SSA. From the results in Figure 6 and from visual observation of the samples, it appears that carbon black particles encapsulate and/or form as separate particles than the nanostructured silica aggregates. Encapsulation may result from rapid formation of silica nuclei and subsequent growth by carbon black surface growth reactions on the silica surface. The surface coating of carbon black could also aid the dispersion of these composite powders in a polymer-like tire rubber (Bomal *et al.*, 1993).

As shown in Fig. 6 the SSA of the particles is decreased by decreasing the ϕ , while at the same time the mass fraction of carbon black is decreased (Fig. 5). Lower ϕ values result in higher-flame temperatures that enhance carbon black oxidation and sintering of silica, thus decreasing the SSA of silica and that of the composite particles. At low ϕ ($\phi < 3.7$), the SSA of the carbon black-silica aggregates before and after burn-off is quite similar. This is attributed to low soot yield and concentration and possible spotty coating of the silica aggregates. It should be noted that the reported SSA of the pure silica particles resulting after burn-off should be lower than that of pure silica made in the flame. Carbon black oxidation during burn-off and the heating process itself can contribute to additional silica sintering and reduction of its specific surface area. This may explain the fact that the SSA of pure silica at low ϕ is less than that of the SiO_2/C composite powders.

Effect of silica on carbon black yield

The yields of silica and carbon black were calculated stoichiometrically based on the amount of SiCl_4 and acetylene fed into the reactor. The silica yield remained constant

Effect of Equivalence Ratio on Flame Structure

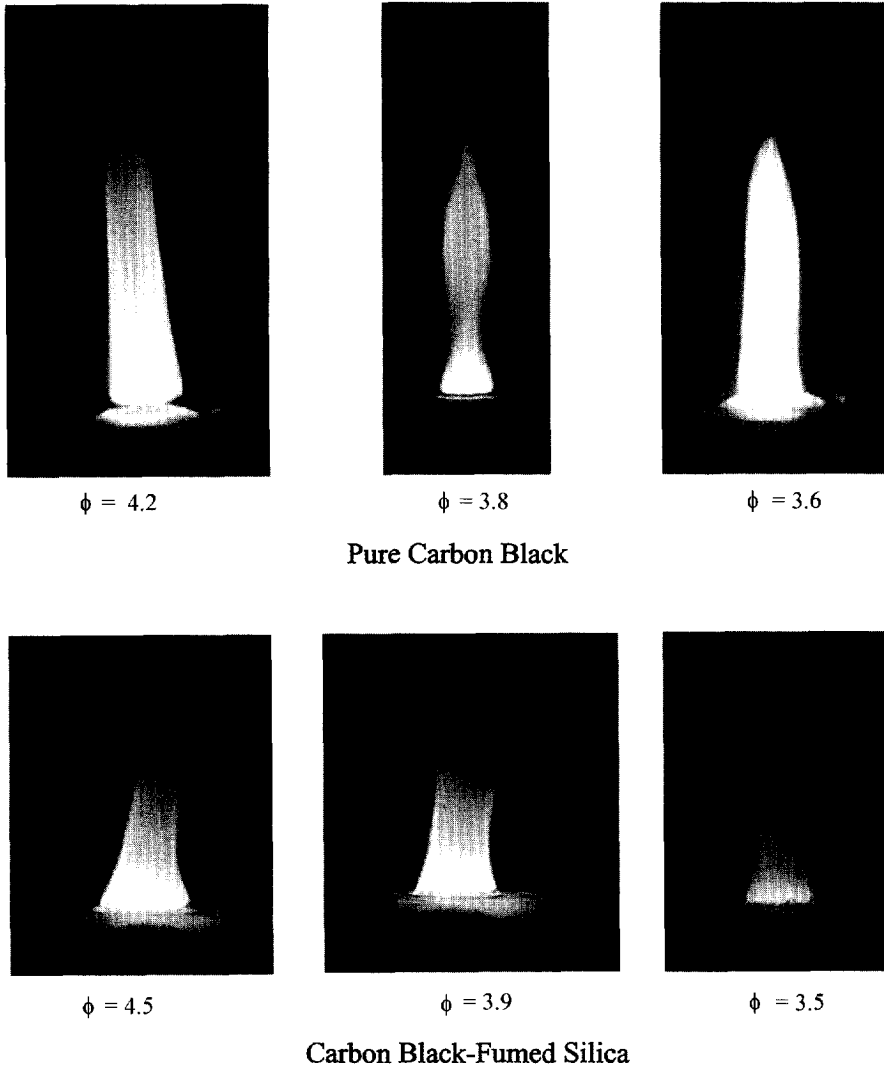


Fig. 2. Pure carbon black and carbon black-fumed silica flames at various fuel equivalence ratios. Decreasing the equivalence ratio increases the temperature of the flame, increasing its luminosity and decreasing the amount of carbon black produced.

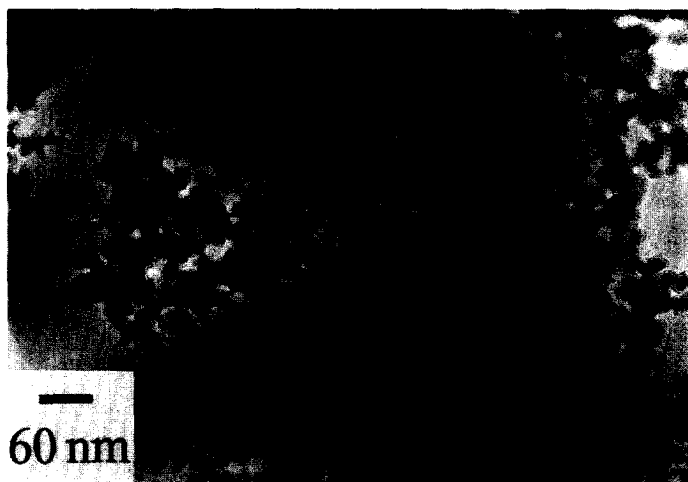


Fig. 4. TEM micrograph of carbon black-silica nanostructured particles at $\phi = 4.5$.

Effect of Applied Electric Field on Carbon Black-Fumed Silica Flame Structure

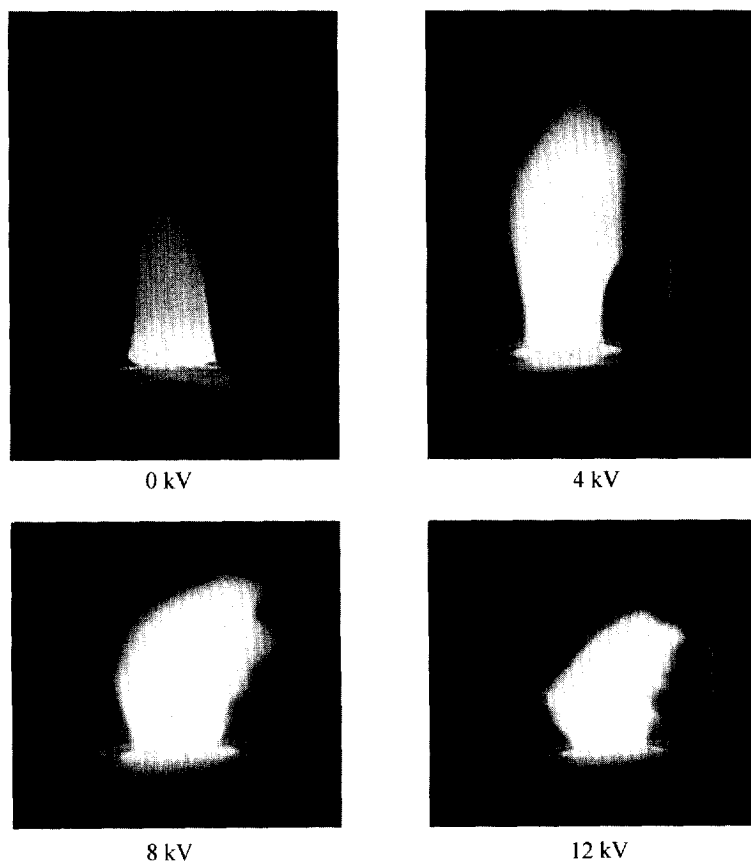


Fig. 8. The carbon black-fumed silica flame in the presence of an electric field. Increasing the applied potential spreads the flame open, reducing its height.

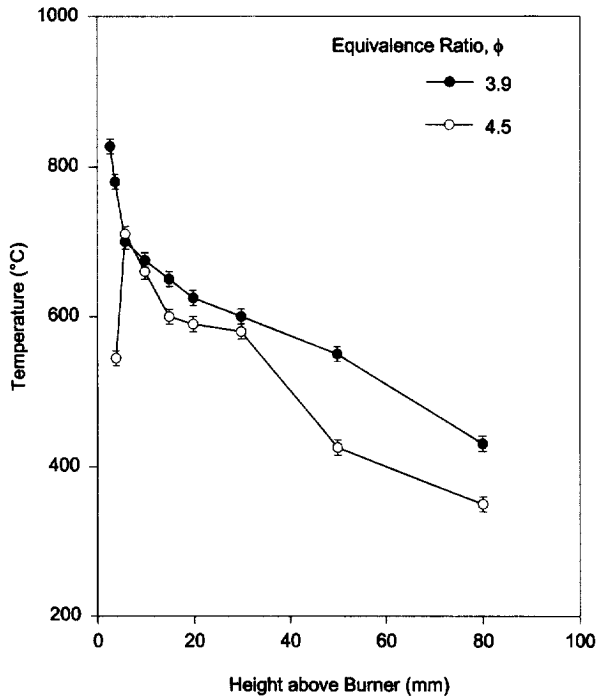


Fig. 3. Axial temperature profiles of the flame for $\phi = 3.9$ and 4.5. The maximum temperature decreases and moves further away from the burner with increasing equivalence ratio.

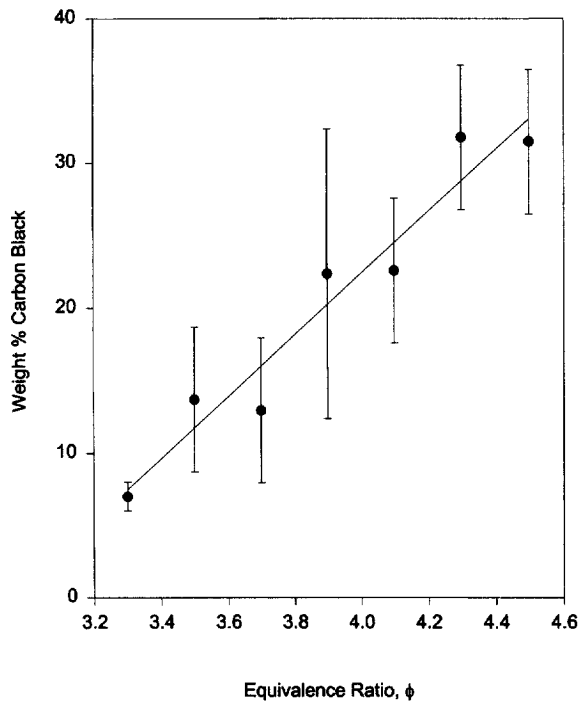


Fig. 5. Composition of the carbon black-fumed silica powders as a function of the ϕ . Increasing the ϕ increases the weight percent of carbon black and decreases the flame temperature.

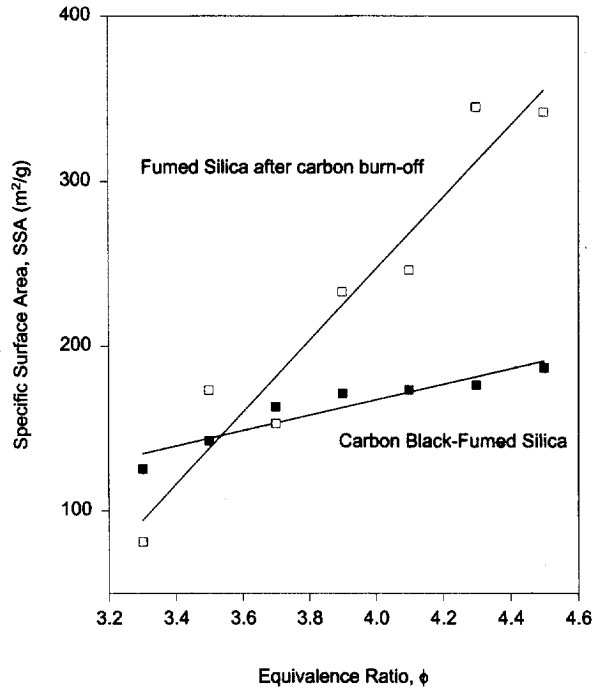


Fig. 6. Specific surface area (SSA) of the composite carbon black-fumed silica (filled squares) and the silica aggregates (open squares) remaining after the carbon black has been burned off. The large SSA of the silica is covered by the carbon black so that the surface area of the composite particles does not change appreciably with ϕ . The SSA of the silica particles increases significantly with ϕ as the flame temperature is decreased. The SSA after burn-off is at least that produced in the flame as sintering during burn-off can reduce the SSA.

($\cong 80\text{--}95\%$) and independent of ϕ for the conditions examined here as all SiCl_4 was oxidized. The balance reflects particles that were not collected on the filter as they escaped or were deposited on the chimney or filter casing. Figure 7 shows the carbon black yield for carbon black-fumed silica (open symbols) and pure carbon black particles (filled symbols) as a function of ϕ . The carbon black yield in the carbon black-fumed silica particles is 2–3 times greater than that of pure carbon black, with an increased enhancement at higher ϕ (Fig. 7). The enhanced carbon black formation may result from the presence of freshly formed silica particles that provide additional sites for carbon black formation by surface growth, possibly accelerating carbon black formation by increasing the number of active sites relative to those available during homogeneous nucleation of carbon black (Harris, 1988). This is supported by the results in Fig. 6 indicating that carbon black particles may encapsulate the silica particles. An additional explanation for the enhanced production of carbon black in the presence of silica is a possible reduction in flame temperature resulting from the presence of SiCl_4 in the flame and the formation of its chlorinated byproducts (Karra and Senkan, 1987; Allendorf *et al.*, 1989). Chlorine radicals tend to scavenge OH radicals, forming HCl and reducing the number of hydroxyl radicals that would contribute to hydrocarbon combustion and soot oxidation. The rate of carbon black oxidation is decreased at lower flame temperatures, thus increasing the carbon black yield versus that in the pure carbon black flame. These results indicate that simultaneous synthesis of carbon black-fumed silica powders may have a financial benefit versus manufacture of carbon black alone. Though this may be a small cost improvement, it can be a significant one given the volume of carbon black required by tire manufacturers.

Particle formation in the presence of electric fields

All experiments with an applied electric field were carried out at a $\phi = 3.9$ as this was the most stable flame. The maximum applied potential for either positive or negative polarities

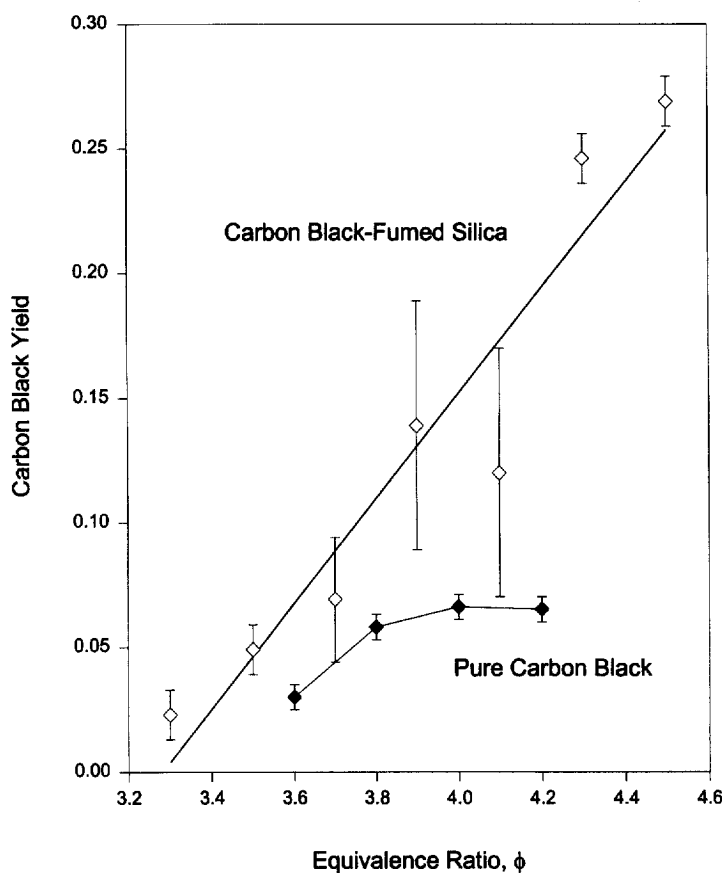


Fig. 7. Carbon black yield for synthesis of pure carbon black (filled diamonds) and carbon black-fumed silica (open diamonds) as a function of the fuel (acetylene) ϕ . In the presence of silica, the carbon black yield is increased up to three times versus that for pure carbon black formation as a result of decreased flame temperatures and the presence of silica particles acting as seed nuclei for carbon black surface growth.

was 12 kV. Figure 8 shows the flame structure at an applied electric field of 0, -4, -8, and -12 kV. For no applied potential, the flame is symmetric and conical. As the potential is increased, however, the flame structure increasingly spreads open (Vemury *et al.*, 1997). This is the result of the attraction of the positive and negative flame ions to the oppositely charged electrode. This effect intensifies as the electric potential between the plates is increased. A more significant inclination of the flame toward the negative (right) electrode is observed in Fig. 8 for all applied potentials. This results from the larger size of the positive ions in the flame and their greater relative drag on the gas molecules compared to that of negative ions (electrons and negatively charged gas molecules). The same number of positive and negative ions (electrons and negatively charged gas molecules) exist in the flame. However, the electrons have a smaller momentum. The momentum of positively and negatively charged gas molecules is roughly the same. Since the number of positive ions is equal to the number of electrons plus negatively charged gas molecules, the momentum of positive gas molecules is larger than that of the sum of electrons and negatively charged gas molecules. As the positive ions are drawn to the negative electrode, they drag neutral gas molecules in that direction, creating a net displacement toward the negative electrode (Payne and Weinberg, 1959; Vemury and Pratsinis, 1996).

Figure 9 shows the measured current for positive (filled symbols) and negative (open symbols) potentials as a function of the applied potential for pure carbon black (circles) and carbon black-fumed silica flames (triangles). Increasing the potential increases the current across the flame. At the higher potentials (i.e. > 6 kV) a significant increase in the current

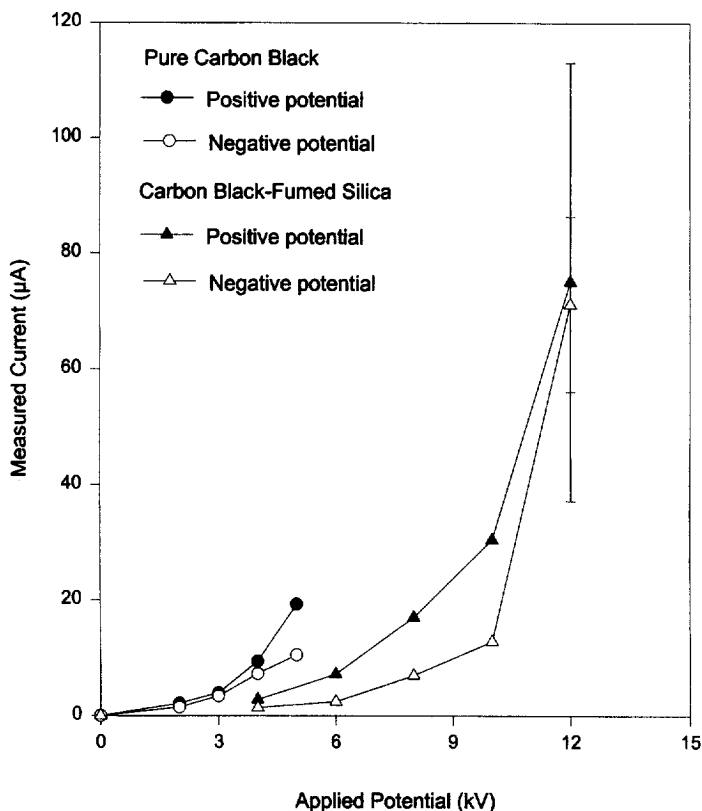


Fig. 9. Current measured across the flame for pure carbon black (circles) and carbon black-fumed silica (triangles) forming flames as a function of applied positive (filled symbols) and negative (open symbols) electric fields.

occurs with the potential as the shape of the carbon black-fumed silica flame begins to drastically change by the application of the electric field (Fig. 8). The carbon black particles emit ions, increasing the transport of current across the pure carbon black flame, resulting in the increased current relative to the carbon black-fumed silica flame. This results in a breakdown at smaller-field intensities across the pure carbon black flame from the strength of the "ionic wind" produced by the electrodes which acts to extinguish the flame just as a strong gust of air will. For this reason this flame can only be operated with applied fields set below 6 kV (Fig. 9). A lower current is measured for the carbon black-fumed silica flame versus the pure carbon black flame, possibly because the chlorine ions produced during SiCl_4 oxidation remove charged species present in the pure carbon black flame. Vemury and Pratsinis (1996) observed a similar reduction in current by the presence of SiCl_4 in premixed CH_4/O_2 flames. For both the pure carbon black flame and the carbon black-fumed silica flame the positive potential produces a larger current across the flame than for the negative potential.

The use of the electric field slightly reduces the powder collection efficiency of the filter. Some powder is deposited on the electrodes and on the plexiglass chimney surrounding the reactor, although this amount is small relative to that collected on the filter. At high potentials, however, the amount of powder collected here can approach that retained by the filter. Figure 10 shows the carbon black content of these powders as a function of the applied negative potential. There is a slight increase of the powder carbon black content with potential, probably as a result of the decreased residence time of the particles at high temperatures as the flame height is decreased by the electric field and the particles are attracted away from the high-temperature region of the flame (Hardesty and Weinberg, 1973). The amount of carbon black in the powder collected on the electrodes remains

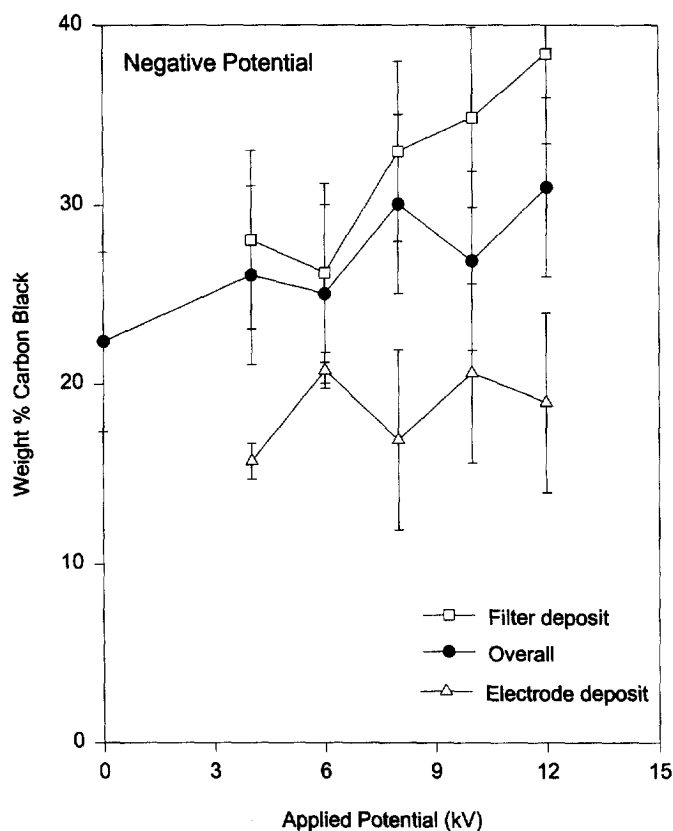


Fig. 10. Carbon black content of powders collected on the filter and the electrodes as a function of applied negative potential.

relatively constant ($\approx 20\%$) and less than that on the filter. The electrodes are closer to the flame and experience higher temperatures and thus more carbon black oxidation may take place there than at the filter. Similar results were obtained for a positive potential although the overall carbon black content decreased slightly with potential as more powders collected on the electrodes than for a negative potential.

The surface area of the powders collected on the electrode and the filter were also compared as a function of the applied potential (Fig. 11). For the negative potential, the SSA of the powder on the filter is reduced significantly once the flame structure changes sufficiently (i.e. potential > 6 kV), while the SSA of the powder on the electrode remains relatively constant. This is the result of the carbon black content of the particles in each location. An increased carbon black content was produced as the potential was increased (Fig. 10) and the flame height was reduced. This is also why no change was observed for the powder deposited on the electrode: the higher temperatures in this region oxidized the carbon black sufficiently to compensate for the increased carbon black formation in the flame. The SSA of the powders produced with a positive potential shows a trend similar to the negative potential, although compressed significantly by the increased amount of powders deposited on the electrodes. The yield of both carbon black and silica remained relatively constant as a function of the applied potential for both positive and negative potentials. It should be noted that this result with respect to SSA is in contrast to synthesis of pure fumed silica and other oxide nanostructured particles where increased field intensities always resulted in finer particles (Vemury *et al.*, 1997). The presence of silica enhances carbon black formation since lower temperatures are created by the presence of chlorine. However, electric fields enhance oxidation of soot (Payne and Weinberg, 1959; Artelt *et al.*, 1997) and as a result these two effects are balanced out, resulting in a constant carbon yield for the employed field range.

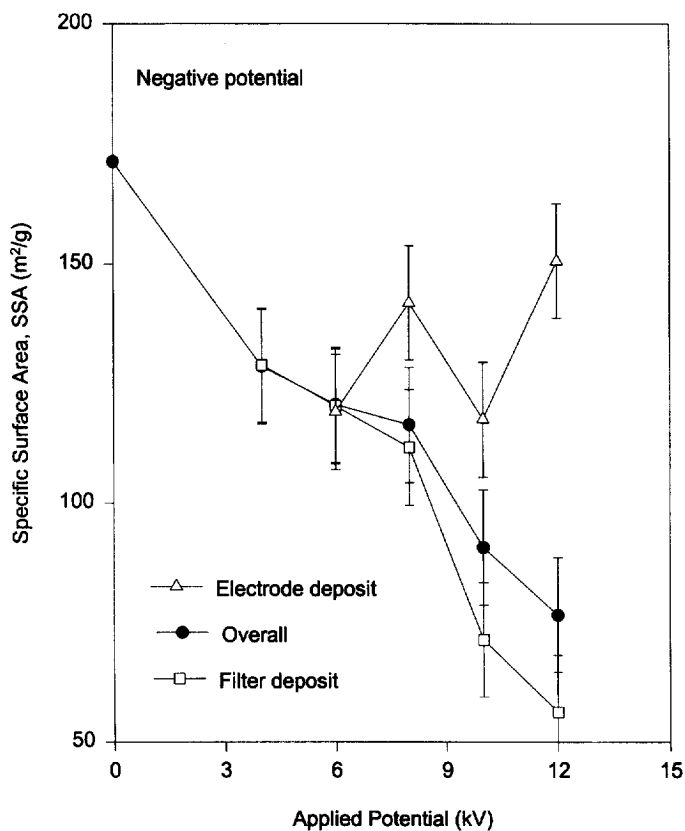


Fig. 11. Specific surface area of the powders collected on the filter and the electrode as a function of applied negative potential.

CONCLUSIONS

Composite carbon black and fumed-silica particles were produced in a premixed acetylene-oxygen flame. The dynamics of carbon black formation were determined by the effect of the fuel equivalence ratio (ϕ), the presence of precursor SiCl_4 , and the applied electric field on the flame temperature. The carbon black-fumed silica composite particles were composed of silica particles encapsulated in or partially covered by the carbon black. The yield of carbon black particles was enhanced up to 3 times by the reduction in flame temperature and enhanced surface growth brought about by the presence of silica in the flame. Increasing the ϕ increased the carbon black yield by decreasing the flame temperature while that of silica was not affected. Increasing the ϕ reduced the size of pure silica particles while the size of the carbon black-fumed silica particles was not significantly affected.

Plate electrodes were used to create unipolar electric fields at crossflow to the flame to further control the process. Increasing the applied potential altered the flame shape and reduced its height resulting in reduced particle residence times at high temperatures. As a result, the specific surface area of the composite particles was decreased and the carbon black yield was increased with increasing electric field intensity.

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