Gas-phase synthesis of single-walled carbon nanotubes on catalysts producing high yield

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ABSTRACT
Composite catalysts are employed for high yield gas-phase synthesis of single-walled carbon nanotubes (SWCNTs). Specifically, silicon is investigated as an additive to iron catalysts for synthesis of SWCNTs in inverse diffusion flames. While silicon is often used as a substrate in supported-catalyst processes to promote nanotube growth, this study demonstrates that it can also be beneficial for gas-phase nanotube synthesis in diffusion flames. An oxy-fuel ethylene inverse diffusion flame is employed to provide a soot-free, carbon-rich environment for nanotube growth. Iron and silicon precursors are added to the fuel stream for nucleation of iron/silicon/oxygen catalyst particles, with the amount of particle oxidation determined by the amount of oxygen-enrichment and fuel dilution at a given temperature. Under optimum conditions, nearly 90% of the catalyst particles produce single-walled carbon nanotubes as compared to less than 10% when the catalyst consists of only iron and oxygen. The effect of silicon addition is investigated through variation of the iron/silicon ratio and measurement of nanotube growth rates. Silicon is shown to primarily affect SWCNT inception with minimal influence on growth rate.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) can be formed by placing catalyst particles less than 5 nm in diameter in the presence of a gas-phase carbon source (e.g. hydrocarbons or carbon monoxide) at elevated temperatures. The catalyst particles can either be supported on a substrate or suspended in the gas-phase. Currently, the most widely used technique to produce nanotubes is chemical vapor deposition [1-4], which employs a substrate. Substrate synthesis offers good control of diameter, length, and purity of the nanotubes. Consequently, this type of synthesis may lend itself well to applications such as nano-electronic devices. On the other hand, gas-phase synthesis techniques including, spray pyrolysis [5-8], the HiPCO process [9], and flame synthesis [10-17] offer the advantage of high growth rates and a continuous, volumetric process for larger-scale production of nanotubes. This type of synthesis may lend itself well to applications such as composite materials, which require large quantities of nanotubes.

Despite the advantages of gas-phase synthesis, these processes typically suffer from low catalyst yields [9,18-20]. Only a small fraction of catalyst particles produce nanotubes, and the remaining particles act as impurities on the walls of the nanotubes. To improve the viability of gas-phase synthesis for production of SWCNTs, catalyst yields must be increased to near that of substrate synthesis, which is often nearly 100%. Catalyst particles used in substrate synthesis are of uniform size and composition and thus, placing them in an environment that is uniform in temperature and species concentrations leads to high catalyst yield. Catalysts for gas-phase synthesis of SWCNTs are often formed from...
decomposition of a precursor, which provides metal atoms for nucleation of the catalyst particles. Although this method provides in situ particle formation, it leads to a size distribution of particles rather than particles that are monodisperse in size. The formation of single-walled carbon nanotubes is strongly dependent on particle size and thus many of the catalyst particles formed during gas-phase synthesis do not form nanotubes. Moreover, several studies have observed that many catalyst particles that appear to be of an appropriate size for producing SWCNTs are instead encapsulated in a carbonaceous shell [18–20].

This study investigates the use of iron/silicon composite catalyst particles to improve the catalyst yield for gas-phase synthesis of single-walled carbon nanotubes in diffusion flames. More specifically, an inverse ethylene diffusion flame is employed to provide heat and carbon for nanotube formation. Oxygen-enrichment of the oxidizer and dilution of the fuel is used to direct the pathway of carbon towards nanotube formation while minimizing formation of polycyclic aromatic hydrocarbons (PAHs) and soot [21–24]. In addition, it is used to optimize the oxidation state of the catalyst particles [25]. Precursors are added to the fuel side of the flame to provide iron and silicon atoms for the formation of iron/silicon/oxygen catalyst particles. Single-walled carbon nanotubes are shown to form on these catalysts on the fuel side of the flame at high growth rates and high yields.

2. Functionally gradient fields and on-line diagnostics

A uniform environment for SWCNT synthesis is desirable so as to achieve a homogeneous product. From this perspective, a diffusion flame may not appear to be a desirable approach to nanotube synthesis due to the large gradients in temperature and species concentrations that naturally exist. Nonetheless, Unrau et al. [18,25] have shown that, if approached appropriately, these gradients create an unique environment capable of producing high quality nanotubes. Hydrocarbons typically form PAH and soot in high temperature environments but this can be avoided in diffusion flames by using oxygen-enrichment and fuel dilution [26], the extent of which can be characterized by the stoichiometric mixture fraction, $Z_{st}$, defined as

$$Z_{st} = (1 + \sigma Y_{F}/Y_{O})^{-1},$$

where $\sigma = W_{O}/v_{O} W_{F}/v_{F}$ Y is the mass fraction, W is the molecular mass, and $\sigma$ is the stoichiometric coefficient. Subscripts F and O refer to the fuel stream and oxidizer stream, respectively. By increasing $Z_{st}$ (accomplished by increasing oxygen concentration and/or decreasing fuel concentration), more oxidizing species are present in the high temperature zone relative to carbon-containing species. This leads to minimal PAH and soot formation [21,24]. Combining this concept with the inverse flame configuration (oxidizer streaming into a fuel environment) creates a high temperature, carbon-rich environment for nanotube formation that is free of PAH and soot. Carbon precursors for nanotube formation in the flame environment may include C$_2$H$_2$, C$_2$H$_4$, CH$_4$, and CO. $Z_{st}$ may also be used to control the oxidation state of the catalyst particles as increasing $Z_{st}$ leads to greater particle oxidation [18,25]. As noted above, an increase in $Z_{st}$ results in more oxygen-containing species in the high temperature zone. For particles forming on the fuel side of the flame, this also implies that more oxygen-containing species will be present in the particle formation region, leading to an increase in particle oxidation. By optimizing the catalyst particle composition and flame environment, single-walled carbon nanotubes that are largely free of PAH and soot have been shown to grow at rates of over 100 $\mu$m/s [25].

Using oxygen-enrichment and fuel dilution in a hydrocarbon diffusion flame leads to what can be described as functionally gradient temperature and species fields for synthesis of SWCNTs by directing the pathway of carbon away from soot formation towards carbon nanotube formation. On the other hand, nanotube formation is known to depend on the combination of temperature and local gas composition as well as catalyst composition. The effect of these variables on nanotube formation can be studied rapidly by employing a scanning mobility particle sizer (SMPS) to measure the size distribution in the flame (a near real-time measurement). An SMPS determines the size distribution of an aerosol by classifying particles according to their electrical mobility and subsequently counting them with a condensation particle counter. If both catalyst particles and nanotubes are present, their difference in electrical mobility will cause the size distribution to be bimodal with the smaller size mode corresponding to catalyst particles and the larger size mode corresponding to nanotubes [18,27–29]. Thus, the appearance of a second mode in the size distribution can indicate nanotube formation. In addition, a bimodal size distribution can provide estimates of nanotube purity and catalyst yield through a comparison of the two modes. For example, a larger first mode corresponds to more catalyst impurities and a lower catalyst yield [18]. With knowledge of the average diameter and charge of the nanotubes, an average length can also be estimated from the peak of the second mode [25,27]. This mode will shift to larger sizes as the nanotubes grow due to the increase in nanotube length. Thus, the growth region and growth rates (when combined with velocity measurements) can be determined. Consequently, the effect of a change in operating conditions can be quickly identified by monitoring the size distribution as obtained by an SMPS.

3. Experimental methods

A schematic of the experimental setup is shown in Fig. 1. Oxygen and nitrogen were introduced through the center tube of a coflow burner (14 mm in diameter). Ethylene and nitrogen were introduced through a concentric tube (51 mm diameter) so as to establish an inverse diffusion flame. Ferrocene and tetraethylorthosilicate (TEOS) were introduced with the fuel stream to provide iron and silicon atoms for catalyst particle formation. Ferrocene was introduced through sublimation by passing the fuel stream inert through a bubbler filled with ferrocene powder maintained at 23 °C. An additional inert stream was bubbled through liquid TEOS maintained at 23 °C and added to the fuel stream prior to introduction to the burner.
Many non-sooting flames were considered in this study but only two of these are presented as these represent critical flame conditions. The run conditions corresponding to these flames (A and B) are shown in Table 1. Flame A was used in a previous study for SWCNT formation on Fe:Si catalysts [18,25] and is used here as a basis for comparison. Flame B was chosen as it provides optimum conditions for SWCNT formation on Fe:Si catalysts. The molar Fe:Si ratio was varied from 1:1 to 9:1 by changing precursor flow rates such that the mean catalyst diameter remained an appropriate size for SWCNT formation. This corresponded to maintaining the total precursor flow rate at 0.1 cm³/min. Precursor flow rates were calibrated by condensing the vapor in a cold trap and measuring the weight gain over a given amount of time.

As in our previous studies, a gas sampling probe coupled to an SMPS was employed to monitor the local size distribution of the particles in the flame. The probe was a fast-quench quartz dilution probe with a 0.5 mm inlet and was mounted above the flame to continuously sample the post-flame gases. The SMPS consisted of a Kr85 bipolar ion source, a TSI 3081 differential mobility analyzer (DMA), a TSI 3776 condensation particle counter (CPC), and a PC to run the software. Samples collected from the flame were observed using a JEOL 7001FIV scanning electron microscope (SEM) and a JEOL 2100F field emission transmission electron microscope (FE-TEM). These samples were collected using a thermophoretic sampler [30] which consisted of a TEM grid mounted on a vertically oriented thin metal plate which was rapidly injected and retracted, with a dwell time of approximately 75 ms. The large temperature gradient between the flame and the cold plate thermophoretically drives the particles to the grid in such a way that the sample is not size biased. Samples were also collected from the post-flame region on filters for X-ray fluorescence (XRF) analysis to determine the Fe:Si ratio. A type-B fine-wire thermocouple with a bead size of 150 ± 3 µm was used for temperature measurements. Temperatures were corrected for radiative losses using an energy balance equating the radiative heat loss of the thermocouple bead to the convective heat gain from the gas.

### 4. Results and discussion

In our previous studies, ferrocene was used as a precursor [18,25]. Upon decomposition, ferrocene provides iron atoms which nucleate to form iron particles. These particles form near the flame surface and oxidize to an extent that is dependent on temperature and the concentration of oxidizing species present in this region. For a given temperature, the concentration of oxidizing species is controlled by the oxidation state of the iron particles can be affected by changes in the Fe:Si ratio [24]. Higher oxidation state corresponds to greater oxidation and thus a lesser propensity for PAH and soot formation, as discussed above. Within the range of oxidation state where PAH and soot formation are minimal, it has been shown that the oxidation state of the iron particles can be affected by changes in the Fe:Si ratio [25]. The results suggest that when ferrocene alone is used as the precursor the optimum catalyst particle composition for SWCNT production is an iron sub-oxide. A typical size distribution resulting from this catalyst composition is shown in Fig. 2a. For spherical particles, such as the catalyst particles, the equivalent mobility diameter refers to the actual diameter of the particle. For nanotubes, the equivalent mobility diameter refers to the diameter of a spherical particle that would have the same electrical mobility as the nanotube [27]. The range of equivalent mobility diameters for the SMPS settings used in this study was 5–250 nm (assuming a charge of unity).

<table>
<thead>
<tr>
<th>Flame</th>
<th>( m_{\text{inner}} \pm 3% ) (mg/s)</th>
<th>( m_{\text{outer}} \pm 3% ) (mg/s)</th>
<th>( X_F )</th>
<th>( X_O )</th>
<th>( T_{\text{ad}} ) (K)</th>
<th>( Z_{st} )</th>
<th>( T_{\text{CNT}} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.2</td>
<td>146.5</td>
<td>0.06</td>
<td>0.75</td>
<td>1920</td>
<td>0.74</td>
<td>1200–1400</td>
</tr>
<tr>
<td>B</td>
<td>2.7</td>
<td>153.3</td>
<td>0.10</td>
<td>1.0</td>
<td>2500</td>
<td>0.75</td>
<td>~1300</td>
</tr>
</tbody>
</table>

- \( X_F \), mole fraction of fuel.
- \( X_O \), mole fraction of oxidizer.
- \( T_{\text{ad}} \), adiabatic flame temperature.
- \( Z_{st} \), stoichiometric mixture fraction.
- \( T_{\text{CNT}} \), temperature in nanotube growth region.
The left-most mode of the size distribution in Fig. 2a corresponds to catalyst particles that have not produced nanotubes. The size of these particles appears to be larger than the optimum size associated with SWCNT synthesis, which is typically less than 5 nm in diameter. TEM analysis (Fig. 2b) reveals, however, that the catalyst particles are of an appropriate size for SWCNT formation but they are encapsulated in amorphous carbon and thus, appear at a larger size in the measured size distribution. The second mode in Fig. 2a corresponds to SWCNTs. No MWCNTs were observed by TEM. The average length of the SWCNTs corresponding to the peak of the second mode was calculated to be about 1 μm and TEM studies support this conclusion [18,25]. The particles shown in Fig. 2b are representative of the smaller mode of the size distribution in Fig. 2a with many inactive catalysts surrounding a single nanotube. Fig. 2c is a photograph of flame A. Note the absence of yellow luminescence which would indicate the presence of soot. The size distribution shown in Fig. 2a was for a sample collected directly above the flame, however, nanotubes were only observed to form in the vicinity of the flame tip as indicated in Fig. 2c.

Catalyst yield (the number of catalysts producing nanotubes relative to the total number of catalysts) in the nanotube formation region can be estimated by comparing the number of particles associated with the second mode to the total number of particles. As seen in Fig. 2a, at best only about 1 in 10 particles produce a nanotube. As noted above, many of the catalyst particles in the SWCNT formation region were of appropriate size to produce SWCNTs but apparently did not. Similar results were obtained in other gas-phase synthesis studies in that many carbon-encapsulated particles were observed alongside SWCNTs despite appropriate catalyst diameters [19,20]. In an attempt to improve catalyst efficiency, and recognizing that iron particles supported on silica substrates have proven to be effective catalysts, silicon was added to the iron system. This was accomplished by introducing tetraethylorthosilicate (TEOS) as a silicon precursor in the fuel stream along with ferrocene. The decomposition of ferrocene and TEOS leads to the formation of silicon/iron/oxygen catalyst particles, with the amount of oxygen dependent upon Zst and temperature. Flame B (see Table 1) provided the optimum Zst and temperature distribution for catalyst oxidation while minimizing PAH and soot formation.

As silicon was added to flame B, a red emission appeared along the side of the flame, and was present for Fe:Si ratios between 9:1 and 1:1. The ratios of iron to silicon were determined by X-ray fluorescence to within ±5 mol%. The emission was most intense around a ratio of 2:1 and a photograph of flame B with this Fe:Si ratio is shown in the right half of Fig. 3a. Samples collected from this emission region were observed using SEM and TEM, which revealed that at a catalyst Fe:Si ratio of 2:1, the emission corresponded to the presence of SWCNTs. A typical size distribution collected from the red emission region of Fig. 3a is shown in Fig. 3b.

A comparison of Figs. 2a and 3b clearly shows that the number concentrations of the two modes (catalysts and
SWCNTs) have been significantly altered. With a catalyst Fe:Si ratio of 2:1, about 9 in 10 catalyst particles produce a nanotube in contrast to only about 1 in 10 when silicon is not present. The estimated lengths corresponding to several mobility diameters of the SWCNTs are also shown in this figure for illustration. These lengths were determined using the method of Unrau et al. [25,27]. Few particles are present below a size of 10 nm because most of them have produced nanotubes. Single-walled carbon nanotubes collected from the flame by thermophoretic sampling are shown in Fig. 4.

Fig. 4a is an SEM micrograph showing as-produced SWCNTs. The nanotubes are relatively straight with lengths of up to several microns and diameters that ranged from 1 to 2 nm. The TEM micrograph shown in Fig. 4b reveals a single, graphitic wall with an outer diameter of about 1.3 nm. Note that few catalyst particles are present on the nanotube surface, which is expected from the minimal catalyst particle mode in the size distribution (Fig. 3b). The results presented in Figs. 3 and 4 correspond to the optimum Fe:Si ratio (2:1) for the catalyst yield. Fig. 5 shows the variation of catalyst yield with the Fe:Si ratio. The catalyst yield increases almost linearly from ~25% to ~90% as the Fe:Si ratio is decreased from 9:1 to 2:1, where it reaches a maximum. Beyond this ratio, the yield decreases rapidly. The effect of the Fe:Si ratio on the average SWCNT length is also shown in Fig. 5. Average nanotube length was determined using the methods discussed in [27]. The trends in the variation of the average SWCNT length with the Fe:Si ratio is similar to that of the catalyst yield and reaches a maximum of 2.3 μm at a ratio of 2:1. Thus, the optimum Fe:Si ratio for catalyst yield and nanotube length appears to be 2:1.

The addition of silicon to the catalyst particles clearly affects SWCNT inception but it could also affect SWCNT
growth. In order to investigate the role of silicon on nanotube growth, the average growth rate in flame B was determined using SMPS data and laser Doppler velocity measurements as described in [25]. Briefly, particle size distributions were measured along the trajectory of the nanotubes in the flame. As noted above, the second mode in the size distribution is indicative of nanotube formation and a shift of the second mode to larger sizes indicates nanotube growth. Thus, measurements of average length can be obtained from the peak of the second mode, and by combining these measurements with velocity data and distance, an average growth rate can be calculated. The emission present in Fig. 3a is an indicator of the trajectory of the nanotubes. Size distribution data collected along the emission region indicates that SWCNT formation and growth occurs from about 2–10 mm above the burner surface. Beyond 10 mm, growth is not observed (i.e. there is no shift in the second mode of the size distribution with distance). Note that the formation and growth region extends over more than half of the flame surface for flame B (Fig. 3a) as opposed to only occurring at the flame tip for flame A (Fig. 2b), where silicon was not added. Thus, adding silicon to the catalysts not only increases the catalyst efficiency at a given location in the flame but it also increases the area over which the catalyst is active towards SWCNT growth.

The average growth rate, as determined from SMPS data and velocity measurements, was estimated to be 150 µm/s. This growth rate was independent of the Fe:Si ratio within the range shown in Fig. 5 and is similar to the average growth rate of 125 m/s measured for SWCNT growth on FeO catalysts in flame A [25]. Temperatures were also measured for flame B and a false-color image of temperature contours is shown on the left side of Fig. 3a, along side a photograph of the flame. The black region on the left side of the figure indicates a region where the temperature was too hot to measure with the thermocouple without causing damage to it. Note that measuring the temperature in this region is not necessary since it is on the oxidizing side of the flame where nanotubes do not form. The red emission region in the photograph (e.g. the nanotube growth region) corresponds to a temperature of around 1300 K, which falls within the temperature range of the growth region for flame A (1200–1400 K) [25]. Since the temperatures and growth rates are similar for both flames A and B, the addition of silicon appears to have a minimal effect on the growth rate of SWCNTs in these diffusion flames.

The primary role of silicon appears to be related to SWCNT inception. This is evident from Fig. 5, which shows that catalyst yield can be dramatically increased with the addition of silicon. While further work is needed to understand the mechanism by which silicon enhances catalyst yield, one possible explanation is that the addition of silicon to the catalyst particles leads to a particle surface that allows for preferential formation of a graphitic cap on one side of the particle for nucleation of a nanotube. Molecular dynamics simulations have shown the when carbon atoms are deposited on a pure iron particle, the particle simply becomes encapsulated with carbon [31]. On the other hand, if one side of the particle is passivated with hydrogen atoms (representing a substrate), the carbon atoms diffuse along the surface to the opposite side of the particle and form a cap, which lifts off of the particle as more carbon is added to form the body of the nanotube. Similarly, pure iron or iron oxide particles in the gas phase probably do not provide a preferential location for nanotube nucleation on the particle surface since the surface of the particle is relatively uniform in composition. On the other hand, when silicon/iron/oxygen particles are formed in the gas phase, the binary homogenous nucleation process may lead to a particle surface on which the iron is not uniformly distributed. Iron-rich areas of the catalyst surface will readily decompose gas-phase carbon precursors (i.e. C₂H₂, C₂H₄, CO, and CH₄) while decomposition will occur to a lesser extent on silicon-rich areas. The higher density of carbon atoms on iron-rich area(s) of the particle surface may provide a preferential location for the formation of a graphitic cap and subsequent nanotube growth.

5. Conclusion

Heretofore, catalyst yields associated with gas-phase synthesis of single-walled carbon nanotubes have been low, rendering gas-phase synthesis somewhat ineffective. In this study, we have shown that single-walled carbon nanotube growth on iron-based catalysts in the gas phase can be dramatically influenced by the addition of silicon. When placed in a soot-free diffusion flame environment, silicon/iron/oxygen catalysts can reach yields of approximately 90% and the SWCNTs formed from these catalysts are relatively free of soot and catalyst impurities. The addition of silicon has a small effect on SWCNT length, increasing from about 1 µm for iron-based catalysts to over 2 µm for an Fe:Si ratio of 2:1. The primary role of silicon in the catalyst particles appears to be its influence on SWCNT inception as silicon addition had a negligible effect on growth rates. An Fe:Si catalyst may provide preferential diffusion of the carbon atoms on the catalyst surface for SWCNT cap formation due to the heterogeneous surface. This could lead to an increase in catalyst yield over iron catalysts since in the latter case the surface of these catalysts are homogeneous and thus do not provide preferential diffusion for SWCNT cap formation.

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**Fig. 5 – Variation of catalyst particle yield and SWCNT length with the Fe:Si ratio.**
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