Studies on Mechanism of Single-Walled Carbon Nanotube Formation

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We presented detailed studies of the formation of single-walled carbon nanotubes by an aerosol method based on the introduction of pre-formed catalyst particles into conditions leading to carbon nanotube synthesis. Carbon monoxide and iron nanoparticles were used as a carbon source and a catalyst, respectively. The vital role of etching agents such as CO₂ and H₂O in CNT formation was demonstrated on the basis of on-line Fourier-transform infrared spectroscopy measurements. Hydrogen was shown to participate in the reaction of carbon release and to prevent the oxidation of the catalyst particles and the hot wire. The addition of H₂ and small amounts of CO₂ and H₂O led to an increase in the carbon nanotube lengths. The catalyst particle evaporation process inside the reactor was found to become significant at temperatures higher than 1100 °C. The carbon nanotube growth was found to occur at a temperature of around 900 °C in the heating section of the reactor by in situ sampling and the growth rate was calculated to exceed 1.1 μm/s. A detailed analysis of possible processes during carbon nanotube formation revealed heptagon transformation as a limiting stage. A mechanism for carbon nanotube formation was proposed.

**Keywords:** Single-Walled CNT, Aerosol Synthesis, Etching, In Situ Sampling, FT-IR, Growth Rate, Heptagon Transformation, Mechanism.

1. INTRODUCTION

Carbon nanotubes (CNTs) have been the subject of great interest since their discovery due to their remarkable mechanical, optical, electrical, and thermal properties. Several applications have already been demonstrated for this extraordinary material. However, success in any applications strongly depends on the ability to synthesize coherent and defect-free nanotubes with controlled diameter, length, and wall structure. The development of production methods for CNT synthesis with specific qualities requires detail understanding of the mechanisms of CNT formation.

The known techniques for carbon nanotube fabrication can be divided into two classes, physical and chemical, according to the carbon atomization method in the initial production stage. Chemical production is based on the catalytic decomposition of carbon containing precursor materials. The obvious advantage of this method is the possibility of producing CNTs at relatively low temperatures. The chemical methods can be further divided into surface chemical vapor deposition (CVD) (e.g., see Refs. [2–4]) and aerosol (floating catalyst) synthesis (e.g., see Refs. [5–8]). In the CVD process, the carbon precursor decomposition and CNT formation take place on the surface of catalyst particles that are supported on a substrate. In aerosol synthesis the whole process takes place in the gas-phase or on the surface of catalyst particles suspended in the gas.

The mechanisms of CNT growth have been widely investigated, especially for the CVD method (e.g., see Refs. [9–14]). Understanding has improved significantly due to advancement in in situ TEM observations of the CNT growth. Nevertheless, the mechanisms of the CNT formation can vary between systems depending on...
the production method, experimental conditions, and diversity of the components participating in the CNT formation processes (e.g., see Refs. [17, 18]). It is worth noting that, in the CVD synthesis, the presence of the substrate can significantly alter the mechanism of the CNT formation. However, investigations of the mechanisms of CNT growth using aerosol methods are seldom found in the literature.19-21

The present paper studies the formation of single-walled CNTs in the gas phase (i.e., without the influence of the substrate on the processes of CNT nucleation and growth) and discusses the effect of the experimental conditions. The CNTs were synthesized by a novel aerosol method5,22 based on the introduction of pre-formed iron catalyst particles into conditions leading to CNT formation. In our process, the possibility of further catalyst particle growth after CNT nucleation is excluded in contrast to the methods reported in Refs. [23, 24] and discussed in Ref. [21]. This can help to correlate the resultant CNT dimensions to those of the introduced catalyst particles. Furthermore, clear advantages of the method are the continuity in the CNT production process and the ease in controlling the experimental conditions (temperature, residence time, and gaseous composition). On the basis of theoretical calculations, FT-IR measurements, in situ sample collection, and detail investigations of the influence of the experimental parameters on the properties of the products, the mechanisms for CNT formation are proposed.

2. EXPERIMENTAL DETAILS

2.1. Experimental Setup

The experimental investigations of CNT formation were carried out in a laminar flow aerosol reactor described elsewhere.8 The device consisted of a hot wire generator (HWG) and a heated vertical tubular reactor 44 cm in length (Fig. 1). A stainless steel (or ceramic) tube, with 22 mm internal diameter inserted inside a furnace (Entech) has been used as the reactor. The HWG, which is a resistively heated thin iron wire (0.25 mm in diameter), was placed inside a ceramic tube (with external and internal diameters of 13 and 9 mm) inserted inside the reactor to maintain inert conditions for catalyst particle formation. The particles produced in the HWG tube were typically carried in a H2/N2 mixture (with mole component ratio of 7/93) at a flow rate of 400 cm3/min and mixed with outer CO flow (typically QCO = 400 cm3/min) inside the reactor. Downstream of the reactor a porous tube dilutor (12 L/min) was used to prevent the product deposition on the walls via thermophoresis and diffusion. Inside the stainless steel reactor, known temperature profiles have been maintained at measured maximum wall temperatures of 924, 1019, 1067, and 1114 °C. The stainless steel tube used in the experiments was composed of Fe (53), Ni (20), Cr (25), Mn (1.6), Si (0.5), C (0.05 weight%).

![Fig. 1. Schematic presentation of the experimental setup, temperature profile, and position and temperatures inside the reactor used for in situ sampling of the product.](image)

The ceramic tube was made of Al2O3 (≈99%). The reactor was operated at ambient pressure. The average residence time inside the reactor was about 2–3 s.

The product was collected from the gas phase by an electrostatic precipitator (Combination electrostatic precipitator, InTox Products) on a Lacey carbon coated copper grid (Agar Scientific Ltd.) In order to detect the location and temperature where CNTs start to grow in situ sampling from the centerline of the reactor was carried out. For this purpose, a stainless steel rod with an attached silica thin film coated nickel TEM grid (Structure Probe Inc.) was rapidly inserted into the reactor and held in position for 1 min. The product was collected due to the thermophoretic forces between the hot ambient atmosphere in the reactor and the cold sampling rod. The temperatures at the in situ sampling locations were measured by thermocouples after the collection (Fig. 1). On-line measurements of the gaseous composition after the reactor were carried out by a Gasmet Fourier-transform infrared spectroscopy (FT-IR) gas analyser. The morphology and the crystallinity of the as-obtained product were investigated with a field emission transmission electron microscope (TEM, Philips CM200 FEG). For qualitative elemental analysis of CNTs, an electron energy-loss spectrometer (EELS, GIF200) coupled with the TEM was used. The number size distributions of the aerosol product in the range from 2 to 200 nm were measured by a differential mobility analyser (DMA) system consisting of a charger, a classifier (Vienna type modified Hauke, classifier length 11 cm), and a condensation particle counter (CPC, TSI 3027).

2.2. Experimental Results

Initial experimental investigations revealed unstable CNT production with the described set-up. Analysis of the experimental data showed that these difficulties were associated with the reactor wall conditions. It was found that, in order to provide the stable CNT synthesis, the walls needed to be saturated by the catalyst material. Practically, this could be achieved either by deposition of the catalyst material on the reactor walls or simply by using a reactor tube made of the catalyst material. The effect of the wall conditions will be further investigated in this paper.

Figures 2(a–b) shows an example of bundles of single-walled CNTs produced in a stainless steel tube reactor. The product was synthesized at a furnace temperature of $T_{furn} = 924 \, ^\circ C$ with an outer flow rate of $Q_{CO} = 400$ and an internal flow rate of $Q_{H_2/N_2} = 400 \, cm^3/min$. In general, it was observed that only single-walled CNTs were produced, most of the catalyst particles initiated the growth of CNTs, and the produced CNTs contained only a small amount of other carbon deposits.

The conditions for CNT formation can be determined by DMA measurements. Since, when CNTs are formed, there is a visible shift in the size distribution towards much larger mobility diameter and lower aerosol concentration. As an example, the number size distributions of the aerosol product synthesized at different temperatures are shown in Figure 3. Iron nanoparticles were produced using pure nitrogen as the outer flow. Replacing it by CO resulted in the formation of CNTs. The DMA detection of CNTs corresponded to a mean mobility diameter larger than 10 nm.

Thus, the CNT production conditions could be easily determined without having to resort to time-consuming TEM observations. However, the DMA measurements were always confirmed by TEM.

In order to study the mechanism of the CNT formation, the effect of hydrogen and the addition of small amounts of methane, water vapor, and carbon monoxide on the product will be further investigated. Also, the results of the in situ sampling experiments to detect the temperature of CNT formation and the FT-IR measurements to study the chemistry of the processes occurring inside the reactor will be presented.

2.2.1. CO Disproportionation Kinetics

In order to find the preferable conditions for CO disproportionation reaction

$$\text{CO}_{(g)} + \text{CO}_{(g)} \leftrightarrow \text{C}_{(s)} + \text{CO}_2(g), \quad \Delta H = -169 \, kJ/mol$$

kinetic investigations were carried out. The experiments were performed in a horizontal quartz tube at a heating rate of 5 °C/min from room temperature to 1000 °C. A silica substrate with deposited 15 nm sized iron particles was placed inside the tube. The CO flow rate through the tube was maintained at 8.3 cm³/min. The concentration of the gaseous product (CO₂) was monitored on-line by IR-measurement techniques. Investigations using 15 nm sized iron particles (Fig. 4) show appreciable reaction rates in the temperature interval from 470 to 820 °C with a maximum rate at 625 °C. This reaction occurs also even at lower temperatures (down to 325 °C) and temperatures up to 900 °C however at very low rates. At temperatures lower than 325 °C the reaction is limited kinetically. At temperatures higher than 900 °C it is limited thermodynamically as can be seen from the values of Gibb's free energy, $\Delta G$.

Note that all thermodynamic data and equations for calculating the constants of gaseous reactions were
derived using the data bank of thermodynamic parameters presented in the commercial F*A*C*T software.\textsuperscript{25} The enthalpies, $\Delta H$, of different reactions are given for a temperature of 900 °C.

2.2.2. Effect of Hydrogen

In order to assess the effect of hydrogen on the product, 5 different carrier gases, i.e., two mixtures of H$_2$/N$_2$ with volumetric ratios of 7/93 and 0.07/99.93 and high purity H$_2$, N$_2$, and Ar (99.999 vol%), were introduced into the HWG tube. The presence of hydrogen was found to be essential for the process of CNT formation, since no CNTs were produced when the reactor was operated without hydrogen (in pure N$_2$ and Ar atmospheres through the HWG). Figures 2(c–d) shows TEM images of the product synthesized using argon as a carrier gas. Inactive conditions for CNT growth result in particles covered with amorphous carbon. It was also found that the heating wire began oxidizing even in a high purity nitrogen (AGA, 99.999 vol%) atmosphere with low oxygen traces ($\leq$3 ppm). Similarly, the oxidation of the nanosized catalyst particles can also take place. Rapidly changing the gas source from H$_2$/N$_2$ (at the conditions of CNT production) to pure N$_2$ immediately led to the disappearance of CNTs from the products as measured by DMA and confirmed by TEM. Recently, Moisala et al.\textsuperscript{26} thermodynamically showed that only non-oxide metal particles behave as catalysts in the CNT formation. In this sense, metal oxide particles must be reduced.

Another possible role of hydrogen in the production of CNTs is in providing additional carbon atoms for the CNT synthesis. It is well known that, at the studied furnace temperatures, another reaction (CO hydrogenation) leading to carbon liberation can occur: \textsuperscript{8}

$$ H_2(g) + CO(g) \leftrightarrow C(s) + H_2O(g), \quad \Delta H = -136 \text{ kJ/mol} \tag{2} $$

As will be discussed, reactions (1) and (2) have similar thermodynamic behavior.

If the role of hydrogen was limited to the prevention of catalyst oxidation, one could expect that a change in the hydrogen concentration would not modify the final product. To address this, statistical measurements of the sizes of CNTs synthesized at the same conditions (except for the hydrogen concentration through the HWG) were performed in a similar manner to Ref. [21]. For the measurements, three different concentrations of hydrogen were used: 0.07% and 7% in the mixture with nitrogen and 100%. The results of the statistical measurements performed on the basis of the high resolution TEM images are shown in Figure 5. As can be seen, the influence of hydrogen on the diameter of catalyst particles and CNTs is insignificant. On the contrary, H$_2$ has a strong effect on the CNT length, which varies from 50.9 via 60.0 up to 500 nm when increasing the hydrogen concentration. It is worth noting that the statistical measurement of CNT lengths in pure hydrogen was impossible to carry out since mainly bundled CNTs were formed at this condition and only a few individual CNT lengths could be measured. An example of the CNTs produced in pure hydrogen is shown in Figure 6.

2.2.3. On-Line FT-IR Measurements

The chemical analysis of the gaseous products was carried out by means of an on-line FT-IR technique downstream of the reactor at different experimental conditions. It was found that the effluent composition significantly depends on the state of the walls. At the conditions active for the CNT synthesis, the main gas phase products were CO$_2$ and H$_2$O with concentrations in the ranges of 60–200 and 20–70 ppm, respectively. The concentrations of these gaseous products drastically increase (up to some maximum value) after the CO introduction together with H$_2$/N$_2$ into the "clean" stainless steel reactor (baked over night in a hydrogen/nitrogen atmosphere) and significantly decrease (halved) after 1 hour. Relatively stable gaseous composition can be achieved only after 3–4 hours of continuous operation.

Figure 7 shows a comparison of FT-IR spectra obtained at the conditions of CNT synthesis (HWG on) and after switching the HWG off. The experiment was performed at $t_{\text{run}} = 924$ °C using a CO and H$_2$/N$_2$ (7/93) mixture as the carrier gases. A small amount (less than 2 ppm) of CH$_4$ was identified, though, it was close to the detection limit of the FT-IR device. Interestingly, the effluent composition did not depend on the operational status of the HWG: neither CO$_2$ nor H$_2$O concentration changed, again demonstrating an important role of the walls. The only difference observed was a significant decrease in HCN concentration (from 20 to 1.8 ppm), indicating the role of the high temperature of the wire in its synthesis. The presence of N-containing compounds among
the gaseous products allowed us to conjecture that the produced CNTs may be doped by nitrogen. Glerup et al.\textsuperscript{27} recently showed the possibility of growing single-walled nitrogen-doped CNTs in an arc-discharge process with a nitrogen concentration up to 1%, determined by using a very sensitive EELS spectrometer coupled with a dedicated STEM (VG HB501). However, nitrogen was not detected in our CNTs with a conventional EELS spectrometer (GIF200) and TEM.

To further understand the role of the reactor walls, on-line FT-IR measurements were also performed in the temperature range from 30 to 924 °C with a heating rate around 6–10 °C/min. Note that the HWG was not operating during this experiment. The maximum H\textsubscript{2}O and CO\textsubscript{2} concentrations in the gas product were detected in the temperature range from 500 to 750 °C, confirming the kinetic studies of CO disproportionation described previously. The highest CH\textsubscript{4} concentration was found between 450 and 700 °C with a maximum of 8 ppm. Methanol was detected below 200 °C at the level of detection limit of the FT-IR device.
2.2.4. Effect of CH₄, CO₂, and H₂O Additions

As was found previously (Fig. 5(c)), the CNTs produced using H₂/N₂ (7/93) mixture are rather short (about 60 nm). In an attempt to increase the length of the CNTs, small amounts of CH₄, H₂O, and CO₂ were introduced into the reactor.

For this purpose, additional carbon sources for the growth of the CNTs at temperatures higher than 900 °C, where the CO disproportionation reaction is thermodynamically prohibited, can be added. Methane is a promising candidate since its catalytic decomposition occurs at temperatures higher than 900 °C. The experiments were carried out at 924 and 971 °C by adding about 1000 ppm of CH₄. TEM observations of the products revealed that the CNT length did not significantly change. Since the CNTs were covered by some carbon deposits, it can be conjectured that the CH₄ decomposition occurred after the CNT formation ceased.

As has been shown, water vapor at a level of 20–70 ppm is always present among the effluent gases due to the catalytic CO hydrogenation reaction (2) on the reactor walls. It can be expected that the presence of H₂O is essential for the CNT growth as nanotubes were never formed under catalyst unsaturated wall conditions. An experiment was carried out at 924 °C by introducing 150 to 330 ppm of water vapor in addition to ‘native’ water formed on the reactor walls. An increase in the CNT length was observed especially at the lower added water concentration (150 ppm). The highest experimental water concentration resulted in fewer produced CNTs. Moreover, the CNTs were much weaker under the TEM beam, likely indicating a high level of defects in the produced tubes. Statistical measurements of the lengths of the CNTs can not be carried out due to the bundling effect, however, under careful TEM investigations individual CNTs up to 300 nm were found at the water concentration of 150 ppm.

It was mentioned above that the wall conditions were very important for the synthesis of CNTs. CO₂ is the main gaseous product component in the reactor and plays an important role during the CNT synthesis. In order to test this, experiments were carried out in a “clean” wall reactor (ceramic tube baked overnight at 1200 °C), i.e. without the catalyst material on the walls. It was found that no CNTs were produced when pure CO was a carbon source. The introduction of a mixture of CO/CO₂ with a concentration of carbon dioxide of 1000 ppm led to the synthesis of CNTs up to 300 nm long. Figure 8 demonstrates the product synthesized at the temperature of 1000 °C. Thus, it can be deduced that CO₂ is essential for the synthesis of CNTs in general and its concentration has a significant effect on the length of the CNTs in particular.

2.2.5. In Situ Sampling of the Product

In order to detect the location and thereby the temperature, where the CNT growth starts, an in situ sample collection was carried out in the stainless steel reactor. The investigations were performed at \( T_{\text{in}} = 924 \) °C with outer \( Q_{\text{CO}} = 400 \) and inner \( Q_{\text{H₂/N₂}} = 400 \) cm³/min flows. The results of the samplings are shown in Figure 1. TEM observations revealed the presence of CNTs on the TEM grid introduced to a temperature of 908 °C and higher. At sampling temperatures of 894 °C lower only catalyst particles and no CNTs were found. The distance of the “growth window” between the 894 °C and 908 °C locations was 1.5 cm. Thus, one can interpolate that the CNT growth occurs at about 900 °C. This temperature coincides with the results reported in Ref. [8], where the growth of CNTs in a ceramic tube was observed to start from the set reactor temperature of 870 °C, which corresponds to a maximum wall reactor temperature of 890 °C.

It is worth noting that the average length of CNTs collected at 908 °C was the same as collected after the reactor (about 60 nm). On the basis of the in situ sampling experiments, the CNT growth rate can also be estimated. The residence time in the “growth window” taking into account the Poiseuille velocity distribution is calculated to be 0.054 s. Then, the CNT growth rate is estimated to exceed 1.1 μm/s. The obtained growth rate is the minimum possible value. For higher resolution (less than 1.5 cm) in situ sampling, a more precise and higher growth rate would be calculated.

3. DISCUSSION

3.1. Properties of Small Particles

It is known that the properties of small particles significantly differ from those of the bulk material. The melting temperature \( T_m \) for a given particle of radius \( r \) can be estimated on the basis of the Kelvin equation as

\[
T_m = T_0 \exp \left( -\frac{2\gamma r V}{r \Delta H_{\text{fus}}} \right)
\]

(3)
where \( T_0 \) is the bulk melting temperature; \( \Delta H_{\text{fus}} \) is the latent heat of fusion; \( V \) is the volume of a metal molecule; \( \sigma \) is the surface tension between liquid and solid. The results of the calculations are plotted in Figure 9. For a comparison, the results obtained by means of molecular dynamic studies carried out by Ding et al.\(^{29} \) are presented. As can be seen from Figure 9, these methods give similar results. In the reactor catalyst particles below 4 nm in diameter are expected to be in liquid state according to both methods.

The weight solubility of carbon in liquid bulk iron can be estimated as \([C]_w = 1.34 + 2.53 \times 10^{-3} T\).\(^{30} \) At the bulk iron melting temperature (1535 °C), it predicts a carbon solubility of 22.7 atomic%. Figure 9 also shows the dependences of solubility and equilibrium vapor pressure on the diameter of iron particles calculated on the basis of the Kelvin equations:

\[
\Omega^*_{\text{eq}} = \Omega^0_{\text{eq}} \exp \left( \frac{2\alpha V}{r k_B T} \right)
\]

\[
P^*_{\text{eq}} = P^0_{\text{eq}} \exp \left( \frac{2\alpha V}{r k_B T} \right)
\]

where \( \Omega^*_{\text{eq}} \) and \( \Omega^0_{\text{eq}} \) are solubilities in a particle and bulk material, respectively, defined as the ratio of the amounts of a solute and a solvent;\(^{26} \) \( P^*_{\text{eq}} \) and \( P^0_{\text{eq}} \) are equilibrium vapor pressures over curved and flat surfaces; \( \alpha \) is the surface tension; \( T \) is the absolute temperature; \( k_B \) is Boltzmann’s constant. As it is evident from Figure 9, both carbon solubility and equilibrium vapor pressure significantly depend on size below 10 nm.

Since produced CNTs are rather short, one can conjecture that the CNTs were grown by one-step segregation of carbon from saturated particles. On the basis of the calculations, the carbon solubility in iron taking into account the Kelvin effect can be as high as 65% (at.), which corresponds to a ratio between carbon and iron atoms of 1.9. It is worth noting that estimated carbon solubility of 50% (at.) and above has been already discussed in literature.\(^{31,32} \) The required carbon solubility to grow CNTs of given length assuming that all carbon initially dissolved in its corresponding catalyst particle can be also calculated. Based on the statistical measurements of the diameters of catalyst particles and CNTs (Fig. 5), the required carbon solubility would be very high, about 95.8 atomic%, which corresponds to a C/Fe atomic ratio of about 20. Such a large amount of carbon is highly unlikely to be dissolved at once in a particle even taking into account the Kelvin solubility increase. Thus, it can be concluded that carbon was continuously released due to CO disproportionation (1) and CO hydrogenation (2) during the CNT growth.

The size effect on the equilibrium vapor pressure should be also discussed. One can expect that the increase in the equilibrium pressure above catalyst particles might lead to their partial or complete vaporization in the reactor. Also, the fact that the reactor walls have to be saturated by catalyst material for a successful CNT synthesis affords ground for a suggestion that the vaporization of the catalyst from the reactor walls might lead to the prevention of the evaporation of the aerosol iron particles. Let us examine a change in the size of iron catalytic particles due to the vaporization and condensation inside the reactor. The mass vaporization rate, \( G \), can be estimated from the equality of the rates that molecule leave and stick to the surface of the gas phase:\(^{33} \)

\[
G = amn^0_{\text{eq}}(v)S/4
\]

where \( m \) is the iron atomic mass; \( \alpha \) is the accommodation coefficient; \( n^0_{\text{eq}} = P^0_{\text{eq}}/k_B T \) is an equilibrium concentration of iron vapor; \( v = \sqrt{8k_B T}/\pi m \) is an arithmetic mean velocity of iron atoms in the gas phase; \( S = 4\pi r^2 \) is the surface area of the particle.

At an iron partial vapor pressure of \( P \), the evaporation rate is determined only by the properties of the particle. In this case, the change in the particle mass, \( M \), over certain period of time, \( \tau \), due to the evaporation and condensation processes is determined by the following expression:

\[
dM/d\tau = -am(P^*_{\text{eq}} - P)(v)S/4k_B T
\]

or representing the mass of the spherical particles via its radius and density, the last expression taking into account the Kelvin equation for vapor pressure (5) can be rewritten in the form

\[
\frac{dr}{e^{r/r^*} - P/P^0_{\text{eq}}} = -\alpha \frac{P^0_{\text{eq}}}{\rho} \sqrt{\frac{m}{2\pi k_B T}} d\tau
\]

where \( r^* = 2\alpha V/k_B T \). At a constant temperature and partial vapor pressure, the time for the particle evaporation from an initial radius, \( r_1 \), to the final radius, \( r_2 \), can be estimated as:

\[
\tau = -\rho \frac{P^0_{\text{eq}}}{\alpha m} \sqrt{\frac{2\pi k_B T}{m}} \int_{r_1}^{r_2} \frac{dr}{e^{r/r^*} - P/P^0_{\text{eq}}}
\]
Fig. 10. Evaporation times of 2 nm sized iron particles at different saturation conditions.

Then, the time for the complete particle evaporation can be calculated by numeric integration of Eq. (9) from a given particle size \( r_i \) to the atomic iron radius \( r_f = 0.14 \) nm. The results of the calculations for the evaporation of iron particles assuming their liquid state at different iron vapor pressures and at \( \alpha = 0.716 \) (Ref. [34]) are shown in Figure 10. As one can see, the evaporation of iron particles becomes significant at temperatures higher than 1100 °C since the time for the complete evaporation of iron particles becomes comparable with the residence time in the hot part of the reactor (about 1 sec). As it is shown in Figure 10, there is only a very small difference between evaporation in unsaturated and saturated iron vapor conditions. Similar calculations for the solid particles showed the same trend, but with a slight increase in the evaporation time (about 2 times that of the liquid state). Thus, Figure 10 demonstrates that the effects of both the wall saturated conditions on the particle evaporation and the evaporation itself at temperatures lower than 1100 °C are insignificant.

3.2. Conditions for CNT Formation

3.2.1. Physical Aspects

In order to better understand the mechanism of CNT formation let us examine the processes that can limit the formation of the CNTs, i.e., carbon release due to chemical reactions; carbon transport through catalyst particles or on the surface of particles and CNTs; nucleation; and the growth of CNTs.

First of all, the process of a carbon delivery to the catalyst particles, i.e., reactions (1) and (2), should be considered. As was described earlier, appreciable reaction rates for CO disproportionation occurred in the temperature interval from 470 to 820 °C (Fig. 4). Taking into account that the kinetics of the CO hydrogenation reaction (2) is faster than that of CO disproportionation\(^{35,36}\), one can conclude that the carbon delivery process should be sufficient at temperatures of around 500 °C. Thus, if the reactions were the limiting stages, the CNTs would already grow at 500 °C. Certainly, there must be some other process limiting the CNT formation at low temperatures.

Let us consider the processes of carbon delivery due to volume diffusion in iron particle and surface diffusion on iron particles and CNTs. The volume diffusion of a carbon atom in α-Fe crystalline phase can be calculated as

\[
D_v = D_0 \exp(-E_{av}/k_B T)
\]

with a pre-exponential coefficient of \( D_0 = 7.9 \times 10^{-7} \) m/s and an activation energy of \( E_{av} = 0.79 \) eV.\(^{37}\) The diffusion of carbon atoms on the iron surface can be found on the basis of the following equation:

\[
D_s = a_0^2 \nu \exp(-E_{av}/k_B T)
\]

where the iron interatomic distance \( a_0 = 0.29 \) nm, the frequency of thermal vibrations \( \nu \approx 3 \times 10^{13} \) Hz and the activation energy of surface diffusion \( E_{as} = 0.35 \) eV.\(^{38}\) Let us estimate the characteristic time needed for a carbon atom to migrate across a 2 nm sized iron particle via volume diffusion (\( \lambda = 2 \) nm) and surface diffusion (\( \lambda = 3.1 \) nm) with a diffusion coefficient of \( D \) as

\[
\tau = \lambda^2 / (4D)
\]

Figure 11 presents the calculated characteristic times for the temperature dependent diffusivities. Both surface and volume diffusivities are quite high and so would not be expected to limit the processes of carbon delivery for CNT growth, even assuming that the iron particle is solid.

Another important carbon delivery process is carbon diffusion on the surface of CNTs. It is worth noting that calculations for diffusion on CNT surfaces with parameters reported by Louchev\(^{39}\) (\( a_0 = 0.14 \) nm, \( E_{as} = 0.13 \) eV) show even shorter characteristic times than for the diffusion on the surface of an iron particle. As was revealed by Krasheninnikov et al.,\(^{39}\) carbon atom adsorption and
migration strongly depend on the diameter and chirality of CNTs. We carried out calculations of the characteristic diffusion times for CNTs with various chiralities using the parameters reported in Ref. [39] \((d_0 = 0.246 \text{ nm, } \nu \approx 4 \cdot 10^{12} \text{ Hz, and } E_{\text{as}} = 1.0 \text{ eV for the largest residence time})\) and found a significant increase in the characteristic times for surface diffusion as shown in Figure 11. Even so, it can be concluded that the surface diffusion of carbon atoms is not a limiting stage.

Also nucleation cannot be a limiting stage. According to Maruyama et al.\(^{40}\) and Ding et al.\(^{41}\) calculations nucleation of CNTs occurs in a nanosecond time scale.

Based on the above consideration, we believe that the unknown limiting stage is the growth of CNTs. As was found on the basis of the statistical measurements of CNT dimensions, the ratio between the diameters of catalyst particles and CNTs does not significantly depend on the hydrogen concentration. One can calculate that the ratio is varying from 1.50 via 1.62 to 1.54 when the hydrogen concentration was increased from 0.07 via 7 to 100% (Fig. 5). This confirms our earlier finding of the correlation between the sizes of catalyst particles and CNTs produced at different conditions.\(^{21}\) In order to explain this phenomenon a geometric model of heptagon defect formation, which initiates and maintains the CNT growth, was proposed. It was suggested that the growth of CNTs occurs from the ordered (containing hexagons and pentagons) carbon layer on the surface of catalyst particles. We assumed that this layer continuously transforms into the CNT network at the metal-CNT interface via nucleation of negative curvature defects in the form of heptagonal rings.\(^{21}\) It was found that theoretical values for the diameter ratios between catalyst particles and CNTs are 1.34 and 1.81 for respectively 4 and 5 heptagons in the base of a CNT, while the experimentally observed ratio lies in between. According to the mechanism described in Ref. [21], the iron particle is covered with a carbon layer in the steady-state process of CNT formation. The CNT growth can be represented as a continuous carbon feed from the graphene layer (on a catalyst particle) to the cylindrical surface of a CNT via a defect junction. The junction is obtained through the creation of topological defects in the form of heptagons. Accordingly, the continuous generation of heptagons can be the limiting stage in the CNT growth.

The characteristic time for the heptagon formation can be estimated as

\[
\tau = \nu^{-1} \exp\left(E_{\text{th}}/k_B T\right)
\]

where \(E_{\text{th}}\) is an energetic barrier for the heptagon formation in the carbon network, reported to be 4.6–4.7 eV.\(^{42,43}\) For such a large energy, the characteristic time is estimated to be \(2 \cdot 10^6 \text{ s at } 900 \text{ °C. But this high energy may be significantly reduced if additional carbon atoms are present.}\(^{42}\) These extra carbon atoms can catalyze the bond switching in Stone-Wales (SW) defects\(^{42}\) and make so-called "handles" over hexagons to produce heptagons after relaxation.\(^{44}\) Figure 12 shows the schematic of this CNT growth mechanism. The additional atoms can be attached as handles (adatoms) to an already existed heptagon (Fig. 12a) and, by creating a bridge between atoms, make it generate an extra hexagon into the network in the wake of the heptagon (Figs. 12b, c). This makes the heptagon shift constantly with respect to the nanotube carbon network frame thus bringing the growth dynamics into the system. An important observation is that the extra atom in a heptagon decreases the total energy by 0.5 eV per handle due to the curvature effect.\(^{44}\) That means that the four or five heptagons in the stem of the growing nanotube, where curvature is large, act as generators of hexagons for the nanotube by attracting extra atoms for handles. On the other hand, the number of heptagons in the stem does not change because, as we showed in Ref. [21], it is determined by the overall geometry. Also the quartet/quintet of heptagons remains grouped in the stem while each heptagon is generating hexagons in its wake. Indeed, if one heptagon advances faster relatively to the nanotube frame then the local curvature will decrease and the rate of handle attachment, mediated by the local curvature, will also decrease. Correspondingly, the rate of hexagon generation in the wake of this heptagon would slow and would return the heptagon to the group because its relative velocity decreases. We propose that it is the "heptagon flow" rate that limits the nanotube growth rate. Certainly, many hexagons can be created independently of this "heptagon route" (e.g. by adding atoms to dangling bonds) but this process is as fast as the growth of the carbon layer over the iron particle and can not be a limiting stage in the CNT growth. Rough estimation supports the heptagon
route. Indeed, the characteristic velocity $V$ of a heptagon motion is

$$V = a_0 / \tau_h$$  (14)

where the shift $a_0 = 0.246$ nm is the size of the hexagon; $\tau_h$ is a time for the process of heptagon transformation shift, which can be found according to Eq. (13). Note, that $E_{th}$ can be estimated empirically (from the in situ sampling experiments). Taking into account Eqs. (14) and (15), for $V = 1.1$ µm/s (calculated for the growth time of 0.054 s) at a temperature of 900 °C:

$$E_{th} = k_B T \ln(a \cdot v / V)$$  (15)

one gets 2.8 eV, that can be compared to the energies predicted in Ref. [42] to be within the range 0.7–2.3 eV. It is worth noting that the energy value would not significantly change even if the growth time is decreased 10 times. Then the calculated energy is 2.6 eV.

Comparing the temperature dependence given by Eqs. (13) and (15) for the characteristic time of heptagon transformation with the characteristic times of diffusion processes discussed above (Fig. 11), it appears that Eq. (15) is indeed the limiting process of the growth.

3.2.2. Chemical Aspects

Let us discuss the most significant reactions that can take place in the reactor. As was previously mentioned, reactions (1) and (2) provide carbon for CNT formation. It is worth noting that the thermodynamic behavior of reactions (1) and (2) is very similar (Fig. 13). However, their inverse reactions are also very important as was revealed by FT-IR measurements and by CO$_2$ addition into a “clean” reactor, where CNTs were not formed by using pure CO. It can be concluded that the reverse (etching) reactions are of vital significance for the CNT synthesis. In the absence of etching agents (CO$_2$ and H$_2$O), released carbon likely passivates the catalyst particle surface, while at temperatures close to 900 °C, where the inverse reactions (1) and (2) are dominant, amorphous carbon can be easily removed. Removing carbon atoms involved in the hexagon-pentagon network requires higher energy than for amorphous carbon and thus etching agents are less likely to remove carbon already incorporated in the CNT structure.

The sum of reactions (1) and (2) can be presented as the well known water-shift reaction

$$CO + H_2O(g) \rightleftharpoons H_2 + CO_2(g), \quad \Delta H = -33 \text{ kJ/mol}$$  (16)

which determines the concentration of CO$_2$ and H$_2$O in the reactor. As it can be seen from Figure 13 that the direction of this reaction is determined by the temperature. At temperatures higher than 837 °C, the equilibrium is shifted towards the CO$_2$ formation, while at lower temperatures H$_2$O favored.

![Fig. 13. Temperature dependence of free Gibb’s energies of conjectured chemical reactions.](image)

On the basis of the FT-IR measurements, the catalytic reactions between hydrogen and carbon were shown to be insignificant for the formation of different types of organic compounds, like methane or methanol:

$$3H_2(g) + CO(g) \rightleftharpoons CH_4(g) + H_2O(g), \quad \Delta H = -227 \text{ kJ/mol}$$  (17)

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g), \quad \Delta H = -107 \text{ kJ/mol}$$  (18)

which can further decompose at high temperatures releasing atomic carbon. These reactions can be observed at low temperatures: reaction (17) lower than 650 °C; reaction (18) lower than 150 °C. Also, for their occurrence, a high H$_2$ concentration and high system pressure are needed.$^{45,46}$ Moreover, these reactions are very slow and to be significant require a large catalyst surface area, which likely was poisoned by carbon.$^{47}$ However, the reaction with carbon and hydrogen

$$2H_2(g) + C(g) \rightleftharpoons CH_4(g), \quad \Delta H = -91 \text{ kJ/mol}$$  (19)

can occur on the reactor walls, where carbon is deposited due to reactions (1) and (2). Indeed, by FT-IR measurements (Fig. 7), a small amount of CH$_4$ (below 8 ppm) was detected in the temperature range of 450–700 °C.

The presence of the high temperature resistively heated iron wire can lead to a partial decomposition of H$_2$ and N$_2$ flowing through the HWG. An equilibrium concentration of hydrogen and nitrogen atoms in the system can be calculated on the basis of the equilibrium constant $K$.
of reactions

\[ \text{H}_2(g) \leftrightarrow 2\text{H}_2(g), \quad \Delta H = 450 \text{ kJ/mol} \]  
(20)

\[ \text{N}_2(g) \leftrightarrow 2\text{N}_2(g), \quad \Delta H = 955 \text{ kJ/mol} \]  
(21)

where

\[ K = \frac{P^{2}_{\text{H}_2}}{P^2_{\text{N}_2}}; \quad \lg K = 11.04643 - 23287.583/T \]  
(22)

\[ K = \frac{P^{2}_{\text{N}_2}}{P^2_{\text{NC}}}; \quad \lg K = 11.76332 - 49791.667/T \]  
(23)

Let us note that the HWG was operated at a temperature close to the melting temperature of iron (1400–1500 °C). The estimated equilibrium partial pressure of hydrogen atoms in the reactor varies from 0.022 via 2.4 to 54 ppm at temperatures of 900, 1200, and 1500 °C, respectively, when a mixture of H\(_2\)/N\(_2\) (7/93) was used. The concentration of hydrogen atoms is significant thereby allowing the possibility of another reaction between hydrogen and carbon monoxide

\[ 2\text{H}(g) + \text{CO}(g) \leftrightarrow \text{C}(g) + \text{H}_2\text{O}(g), \quad \Delta H = -585 \text{ kJ/mol} \]  
(24)

important for the CNT growth, namely in the process of carbon release. This reaction has no thermodynamic limitations at high temperatures (Fig. 13) in contrast to reactions (1) and (2). The estimated equilibrium partial pressures of nitrogen atoms are 1.0 \times 10^{-12}, 2.2 \times 10^{-8}, and 1.6 \times 10^{-5} ppm at temperatures of 900, 1200, and 1500 °C, respectively, which is much lower compared to that of hydrogen. Thus, atomic nitrogen is seemed to be not important in the chemical processes occurring inside the reactor.

By FT-IR analysis it was found that HCN was mostly formed when the HWG was operating. It is worth noting that reaction between molecular species:

\[ 2\text{C}_2(g) + \text{H}_2 + \text{N}_2 \leftrightarrow 2\text{HCN}(g), \quad \Delta H = 192 \text{ kJ/mol} \]  
(25)

is prohibited thermodynamically at all considered temperatures (Fig. 13). However, when replacing H\(_2\) by atoms the reaction of hydrogen cyanide formation becomes thermodynamically possible. Here, we limit our consideration of HCN formation paths due to its insignificant role in the CNT formation process.

Another important role of hydrogen can be shown as its reaction with available oxygen in the carrier gas. O\(_2\) can participate in the reaction with released carbon:

\[ \text{C}(g) + \text{O}_2(g) \leftrightarrow \text{CO}_2(g), \quad \Delta H = -396 \text{ kJ/mol} \]  
(26)

\[ 2\text{C}(g) + \text{O}_2(g) \leftrightarrow 2\text{CO}(g), \quad \Delta H = -226 \text{ kJ/mol} \]  
(27)

thereby decreasing the amount of carbon available for CNT growth. Reactions (26) and (27) are thermodynamically favorable at all studied temperatures.

Let us discuss the effect of the etching agents and the existence of the growth window in light of well studied methods for CNT synthesis: HiPco process.\(^{21}\) One can conjecture that CNT formation in this method can also require CO\(_2\). Since the HiPco reactor is made of stainless steel with significant exposed surface area at temperatures favorable for CO disproportionation, one can expect the release of CO\(_2\) from the reactor walls in the same manner as proposed here for the HWG method. In fact, as was reported in Ref. [48], a high concentration of CO\(_2\) (on the order of 10,000 ppm) is known to exist at the reactor outlet under CNT synthesis conditions, though they have not reported CO\(_2\) concentrations in the absence of Fe(CO\(_3\)) \(_3\) precursor. Also concerning the HiPco method, at high pressures the equilibrium of CO disproportionation reaction (1) is shifted towards the formation of CO\(_2\) and C. Thus, the high CO pressure has effects on both the enhancement of the reaction rate due to an increase of the amount of reagent and also in widening of the CNT formation temperature range. In other words, the CO pressure increase can result in a “growth window” enlargement, so that the CNT growth at 30 bars occurs even up to 1200 °C.\(^{20}\) In this sense, ferrocene should be a better catalyst precursor due to its higher decomposition temperature, which can significantly decrease the “overgrowth” of catalyst particles.

3.3. Mechanism of CNT Formation

By examining the available experimental data presented in this paper and analyzing the conditions for CNT formation, a mechanism for CNT growth taking place in the present reactor can be proposed as is summarized in Figure 14. In the scheme, only the most important species taking part in subsequent stages and the relevant processes are indicated.

Catalyst particles are formed in the vicinity of the heated wire\(^{6}\) and further introduced into the reactor. Due to the high diffusivity of nanometer-sized particles, a portion of them is deposited on the reactor walls. Then, the deposited particles, together with already available catalyst (either in the form of previously deposited particles or as reactor wall material), catalyze CO disproportionation (1) and hydrogenation (2) reactions. As a result, CO\(_2\) and H\(_2\)O vapor are released into the gas phase and become available in the growth window.

Iron particles suspended in the gas phase also catalyse CO disproportionation and CO hydrogenation reactions resulting in atomic carbon release on the surface of the particles. Subsequently, carbon dissolves into iron particles. Eventually particles become saturated by carbon and conditions for carbon arrangement into a regular graphene sheet, including formation of hexagons and pentagons, are established. Once the particle is saturated by carbon, the next stage is nucleation of negative curvature (heptagonal) defects in the heptagon-pentagon network layer and the cap detachment (in the “growth window” at about 900 °C).
Fig. 14. Schematic representation of mechanism of CNT formation.

The further growth of CNTs occurs in a steady-state regime due to the presence of available carbon and additional carbon released from reactions (1) and (2) on the free (uncovered) surface of the catalyst particle. Both volume and surface diffusion are possible to deliver carbon atoms to the growing CNT network. At a temperature of about 908 °C, the growth of CNTs stops due to the dominant role of inverse reactions (1) and (2). For the

same reason at high temperatures CNT “cleaning” occurs, i.e., amorphous carbon precipitated on the surface of the CNTs is removed as a result of reaction with carbon dioxide or water, mainly produced on the reactor walls. Thus, the presence of etching agents such as CO$_2$ and H$_2$O is essential for the synthesis of the CNTs. 

4. CONCLUSION

Synthesis of single-walled carbon nanotubes (CNTs) by an aerosol method based on the introduction of pre-formed catalyst particles into conditions leading to CNT formation was carried out under different experimental conditions. Carbon monoxide and iron nanoparticles were used as a carbon source and a catalyst. A vital role of etching agents such as CO$_2$ and H$_2$O for CNT synthesis was demonstrated on the basis of on-line FT-IR measurements, theoretical calculations, and experimental observation. The effect of the addition of small amounts of CO$_2$ and H$_2$O also led to an increase in CNT length.

Hydrogen was shown to participate in the reaction of carbon release and to prevent the oxidation of the catalyst particles and the hot wire. The number size distributions of diameter and length of individual CNTs as well as the diameter of catalyst particles obtained from HR-TEM were presented. When hydrogen concentration was increased in the system, an increase of the length of CNTs was observed. The ratio of diameters of catalyst particles and produced CNTs was about 1.5–1.6 confirming our earlier finding introducing a geometric model of heptagon defect formation for nucleation and CNT growth.

A detailed analysis of possible processes during CNT formation revealed heptagon transformation as a limiting stage. The energy of this transformation was calculated to be up to 2.8 eV. On the basis of in situ sampling it was detected that the CNTs start to grow at a temperature of around 900 °C in the heating section of the reactor at the growth rate exceeding 1.1 μm/s. Mechanism for CNT formation was proposed.

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References and Notes


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