Mechanistic investigations of single-walled carbon nanotube synthesis by ferrocene vapor decomposition in carbon monoxide

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The single-walled carbon nanotubes (SWCNTs) were synthesized by the carbon monoxide disproportionation reaction on Fe catalyst particles formed by ferrocene vapor decomposition in a laminar flow aerosol (floating catalyst) reactor. On the basis of in situ sampling of the product collected at different locations in the reactor, kinetics of the SWCNT growth and catalyst particle crystallinity were studied. Catalyst particles captured before SWCNT nucleation as well as inactive particles were determined to have cementite (Fe3C) phase, while particles with γ- and α-Fe phases were found to be embedded in the SCWNTs. The growth rate in the temperature range from 804 to 915 °C was respectively varied from 0.67 to 2.7 μm/s. The growth rate constant can be described by an Arrhenius dependence with an activation energy of $E_a = 1.39$ eV, which was attributed to the carbon diffusion in solid iron particles. CNT growth termination was explained by solid–liquid phase transition in the catalyst particles. A high temperature gradient in the reactor was found to not have any effect on the diameter during the SWCNT growth and as a result on the chirality of the growing SWCNTs.

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1. Introduction

Carbon monoxide (CO) disproportionation on Fe catalyst has been long known to yield filamentous carbon [1,2]. Such filaments having a tubular graphitic structure later came to be called carbon nanotubes (CNTs) [3,4]. Further developments in experimental and characterization techniques have allowed the synthesis and observation of multiwalled, few-walled, double-walled, and single-walled CNTs [5–7]. Unique and useful properties of SWCNTs have attracted tremendous scientific interest. There are currently only three common methods for the synthesis of this material in laboratory and industrial scales: arc discharge [4,5], laser vaporization [8,9], and chemical vapor deposition (CVD) [10–13]. Among these methods, the CVD process, especially the aerosol (catalyst floating) synthesis, has attracted much attention [14–20] because of potential for industrial scale production of high-purity SWCNTs at low cost.
Recently our group reported a technique for the production of high-purity SWCNTs based on ferrocene vapor decomposition in an atmosphere of CO [20]. This method allowed us to produce a novel material, nanobuds, consisting of fullerences covalently attached to SWCNTs [21]. Also, the phenomenon and mechanisms of spontaneous charging of SWCNTs in the gas phase have been thoroughly investigated [22]. This allowed us to develop a method for gas-phase separation of individual SWCNTs with their subsequent deposition onto a variety of substrates, an alternative method to time-consuming liquid separation method. SWCNTs produced by this method were successfully applied to transparent electronics, memory devices, field effect transistors and cold electron field emitters [21,23,24].

In spite of successful utilization of the CVD method, there are still many open questions related to the mechanism of the SWCNT formation in the aerosol method [25–27] particularly and in the CVD method in general [28,29]. In addition, the mechanisms of the CNT formation can vary from system to system depending on the synthesis method, experimental conditions and diversity of the reagents participating in the CNT formation processes. It is worth noting that the conventional CVD synthesis method requires substrates, which can significantly alter the formation and growth of CNTs. In the aerosol CVD synthesis the whole process takes place in the gas phase, i.e. at the surface of catalyst particles suspended in the gas. The conditions of the CNT formation and growth can be controlled by residence time and steepness of the temperature gradient in the reactor and by the composition of the gaseous reagents.

In this paper on the basis of in situ sampling experiments from different locations in the SWCNT reactor different aspects related to the growth mechanism were examined. It has been widely discussed that the active catalyst particle state resulting in the formation of SWCNTs is Fe, while cementite (Fe3C) is usually attributed to an inactive catalyst state [30–33]. However, recently Yoshida et al. [34] have reported the CNT growth from Fe3C phase. Here, the chemical state of active and inactive catalyst particles for the synthesis of CNTs was investigated. Another important issue is related to the growth rate of SWCNTs and activation energies of the limiting stage of the nanotube growth [33,35–37]. Only two experimental kinetic studies of the SWCNT growth at different temperatures have been reported [38,39]. The CNT growth rate and activation energy were measured mainly for the synthesis of multiwalled CNTs [40–45]. Another important issue has been recently raised by Yao et al. [37], whether the diameter and, therefore, the chirality of SWCNTs can be tuned during the SWCNT growth by changing the temperature during the synthesis process. The samples were examined by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques.

2. Experimental

The experimental setup used for the mechanistic investigation of SWCNT growth is shown in Fig. 1. The SWCNT growth process is based on ferrocene vapor decomposition in a CO atmosphere. The catalyst precursor was vaporized by passing ambient temperature CO (with a flow rate of 300 cm3/min) through a cartridge filled with a ferrocene powder [20]. The flow containing ferrocene vapor was then introduced directly into the high temperature zone of a ceramic tube reactor (with an internal diameter of 22 mm) through a water-cooled probe inserted 6.5 cm deep in the reactor. Additional CO flow of 100 cm3/min was introduced from outside the water-cooled probe. The partial vapor pressure of ferrocene fed to the reactor was maintained at 0.7 Pa. In order to preserve the conditions of SWCNT formation, a 105 ppm flow of H2O vapor was added [46]. The experiments were performed using two different temperature profiles. The low temperature profile (at the set temperature of 800 °C) had a maximum temperature of 862 °C, while a maximum temperature of 1054 °C corresponded to the high temperature profile (at the set temperature of 1000 °C). The temperature profiles were measured by positioning a K-type thermocouple (SAB Bröckskes GmbH and Co., KG, Germany) at various locations in the reactor and shown in Fig. 1.

The products were collected from the gas phase on TEM grids (Lacey Carbon 400 Mesh Cu, Agar Scientific Ltd., UK) either in situ by means of thermophoretic forces or downstream of the reactor using an electrostatic precipitator. It is worth noting that TEM observation of the product collected ex situ revealed bundles of SWCNTs. In order to in situ sample the product, a stainless steel sampling rod with a TEM grid attached to the top was rapidly inserted into the reactor and
held in a steady position for 30 s. The product was collected due to the thermophoretic forces between the hot atmosphere in the reactor and the cold sampling rod. Samples of aerosol product were taken from different positions inside the reactor.

For XRD measurements, macroscopic amount of SWCNTs was collected by filtering the flow downstream of the reactor through 2.45 cm diameter nitrocellulose disk filters (Millipore Corp., USA). The XRD patterns were recorded in transmission mode on a planar imaging plate under vacuum in order to minimize air scattering. Wide angle X-ray scattering experiments were made using a rotating anode with Mo Kα radiation (0.711 Å). The morphology and crystallinity of the products were investigated with a field emission gun transmission electron microscope (Philips CM200 FEG) at an accelerating voltage of 200 kV and with a transmission electron microscope equipped with an imaging Cs-corrector (FEI Titan 80-300) at an accelerating voltage of 300 kV.

3. Results

3.1. In situ sampling experiments

At the low temperature profile, the product collected from the sampling point corresponding to a temperature of 816 °C (17 cm from the top of the reactor) did not reveal the presence of SWCNTs. Rather only inactive catalyst particles were seen during the TEM observation. This position corresponds to the pre-nucleation SWCNT condition. SWCNTs were detected in the product collected downstream at the sampling points corresponding to the following temperatures: 857 °C (22 cm from the top of the reactor), 853 °C (27 cm), 845 °C (32 cm) and 763 °C (39.5 cm). Multiple measurements made from TEM images allowed the determination of the average length of SWCNTs at these different locations. The statistic sample was about 50 CNTs for each position. The length of individual SWCNTs collected at the temperature of 857 °C was 388 nm (Fig. 2a). At the temperatures of 845 and 763 °C the average SWCNT lengths were 1225 and 1622 nm, respectively (Fig. 2b and c), as summarized in Table 1.

Similar experiments were performed at the high temperature profile. It was found that the product collected from different areas of the reactor consisted of SWCNTs, except one sample, which was collected at the temperature of 885 °C (13 cm).

The latter revealed the presence of particles only and apparently corresponded to the conditions of the SWCNT pre-nucleation. Surprisingly, the length of SWCNTs collected from different locations at the high temperature profile was 290 nm and did not depend on the position. The reason for the termination of the SWCNT growth will be discussed in the next section.

On the basis of the SWCNT length, temperature and residence time in the reactor the average growth rate of SWCNTs can be calculated. Computational fluid dynamics calculations (CFD) calculations [20] showed laminar flow behavior in the reactor and thereby the residence time could be calculated taking into account a Poiseuille velocity distribution (the flow rate in the centerline is two times higher than the total rate).

Fig. 2 – TEM images of the product collected at different temperatures (positions from the top): (a) 816 °C (13 cm); (b) 857 °C (22 cm) and (c) 845 °C (32 cm).
The growth temperature was assigned to the middle point between two sampling positions. The calculations showed that at the low temperature profile for temperature ranges of 816–857, 857–845 and 845–763 °C the average growth rates were 1.01, 1.11 and 0.67 μm/s, respectively. At the high temperature profile, the average growth rate of 290 nm long tubes in the temperature range from 885 to 945 °C was calculated to be 2.7 μm/s.

3.2. Inactive and active catalyst particles

In order to investigate the structure of inactive catalyst particles high-resolution TEM (HR-TEM) observations of products collected in the location before and after the SWCNT nucleation were carried out. For this purpose, the product was collected in situ at 885 °C (Fig. 3a), where no SWCNTs were detected, and inactive particles collected together with SWCNTs at 945 °C during the high temperature profile reactor conditions. This investigation revealed that in both cases inactive catalyst particles were in the form of Fe3C.

Active catalyst particles were investigated by means of HR-TEM imaging (Fig. 3b). For this purpose, catalyst particles embedded inside the SWCNTs synthesized at the high temperature profile were observed. The electron diffraction (ED) ring patterns obtained from the network of SWCNTs were indexed as γ-Fe. However, small amount of α-Fe phase can be also detected in the ED ring pattern. These results were confirmed by XRD of the bulk material collected downstream of the reactor. Fig. 4a shows a typical XRD pattern recorded on an imaging plate. γ-Fe peaks (referred to as 1,2,4,6,7) and α-Fe peaks (referred to as 1,3,5,7) can be identified by comparison with calculated diffraction profile. A comparison between the peak intensities indicates that the amount of α-Fe is 5–10 times smaller than that of γ-Fe. Characteristic peaks of Fe3C with the most intense (1 2 1) peak in the location marked by a star in Fig. 4b were not observed. This indicates that the amount of Fe3C was not greater than about a few wt.%.

3.3. Effect of temperature gradient on SWCNT diameter

As has been recently reported by Yao et al. [37], the diameter of CNTs can be tailored by changing the growth temperature (ΔT = 50 K). Since at the low temperature profile CNTs were grown in a high temperature gradient (from 816 via 857–763 °C), one can assume that the diameter of CNTs could vary during the growth. In order to study the temperature effect on the CNT diameter, ED measurements from long tubes produced in this high temperature gradient condition and collected downstream of the reactor were carried out. For this purpose, four individual SWCNTs were randomly selected and examined over distances of 3.6, 2.5, 1.3 and 0.6 μm. The chiral indices of the SWCNTs were calculated from ED patterns by intrinsic layer-line distance method [47]. An example of a TEM image of an individual SWCNT and its ED patterns taken at the distance of 2.5 μm are presented in Fig. 5. The calculations showed that the chirality of this SWCNT did not

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<th>Table 1 – Experimental conditions and results of the growth rate calculations on basis of in situ sampling measurements.</th>
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<td>Temperature range (°C)</td>
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Fig. 3 – (a) HR-TEM image taken from typical Fe3C nanoparticles, collected by in situ sampling in the CNT pre-nucleation zone at 885 °C; (b) HR-TEM image showing an example of inactive particles in a Fe3C phase and an active catalyst particle embedded in the SWCNT and (c) experimental and simulated electron diffraction ring patterns taken from a network of SWCNTs collected on TEM grid.
change over this length. The SWCNT was assigned to (13,8) chirality. Observations of the other tubes also did not reveal changes in the chirality. Obviously, the method for the CNT diameter alteration reported by Yao et al. [37] is not valid in the unsupported aerosol based system. The substrate can play a crucial role in the CNT diameter change in the experiments described by Yao et al. [37].

4. Discussion

Formally, the kinetics of the SWCNT growth can be described by a process considering the transformation of carbon deposited on the surface of a catalyst particle into the hexagonal SWCNT carbon network:

\[ \text{C}_{\text{at}} \rightarrow \text{C}_{\text{SWCNT}}. \]  

(1)

Then, the rate of this reaction, \( r \), is expressed through the carbon concentration \( [\text{C}] \) on the surface of the catalyst particle:

\[ r = k[C]^n = k_0[C]^n \exp \left( -\frac{E_a}{RT} \right). \]  

(2)

where \( k \) and \( k_0 \) are the rate constant and the pre-exponential coefficient, respectively; \( n \) is the reaction order; \( E_a \) is the activation energy of the SWCNT growth; \( R \) is the gas constant; \( T \) is an absolute temperature. It is worth noting that the concentration of carbon on the surface of catalyst particles does not determine the growth rate of CNTs. Otherwise, the highest growth rate would be observed at around 600–700 °C, where the Boudouard reaction has its maximum rate as discussed later [25]. Controversially, the maximum growth rate (915 °C) was observed at the conditions, where the disproportionation reaction rate was significantly suppressed thermodynamically. Therefore, the growth rate can be formally described as a zero order reaction. Plotting the kinetic data of the growth rate in the coordinates \( \ln \frac{r}{C_0} / T \) gives a linear dependence (Fig. 6), from which the pre-exponential coefficient and the activation energy were found to be \( k_0 = 1.99 \times 10^6 \text{ mol/s} \) and \( E_a = 133.8 \text{ kJ/mol} = 1.39 \text{ eV} \), respectively. This energy is close to the values reported in the literature for multiwalled CNTs [42,46,48,49] and SWCNTs [39] and can be attributed to the activation energy for diffusion of carbon atoms in bulk solid iron with concentrations of carbon from 0.1 to 1 mass% [50]. Thus, on the basis of our kinetic measurements one can conjecture that the limiting stage for the CNTs growth is carbon diffusion through the solid catalyst particles.

Let us discuss the active catalyst particle state. Our results indicate that carbide is an inactive catalyst and likely can be a CNT pre-nucleation state. Apparently nucleation of SWCNTs occurs during or after the \( \text{Fe}_3\text{C} \) decomposition, when active phase for the CNT growth, \( \text{Fe} \) particles, is formed. The necessity of having \( \text{CO}_2 \) or water vapor in the reactor for the successful growth of SWCNTs is an additional indication of \( \text{Fe}_3\text{C} \) transformation according to the following reactions:
Fe₃C(s) + CO₂ $→$ 3Fe(s) + 2CO(g), \hspace{1cm} (3)
Fe₃C(s) + H₂O $→$ 3Fe(s) + CO(g) + H₂(g). \hspace{1cm} (4)

Literature data [30–33], wherein the growth of CNTs was terminated when the catalyst transformed into the Fe₃C phase, support our results. On the other hand, Yoshida et al. were able to synthesize CNTs from Fe₃C nanoparticles at 600 °C using C₆H₆ as a carbon source inside environmental TEM [34]. Even though Yoshida et al. provided the results of direct observation of the SWCNT growth, the effect of electron beam irradiation on the growth conditions remains unclear.

Fe exists in different thermodynamically stable forms: α-Fe (bcc phase) up to 912 °C and γ-Fe (fcc structure) at higher temperatures up to 1390 °C. The ED and XRD patterns obtained from the catalyst particles embedded inside SWCNTs found that the particles were mainly γ-Fe with a small fraction of α-Fe. The observation of the fcc phase at room temperature showed that Fe remained in its metastable phase. This can be explained by an encapsulation of Fe particles in SWCNT structure and confining the transition from γ- to α-phase, which is accompanied with 9% increase in the volume [51,52].

One can assume that since catalyst particles were examined at room temperature (not in situ), they can be subjected to significant chemical transformations during the cooling process. However, one can hope that such transformations do not occur during the in situ sampling experiments, since the collected product was quickly quenched by cooling from the reactor temperature to below 100 °C, at the moment of their deposition onto a cold TEM substrate. Neither this transformation could take place during the collection of CNT samples after the reactor, otherwise the thermodynamically metastable γ-Fe phase would not be observed. However, solidification of liquid particles certainly cannot be ruled out [53].

TEM observations allowed us to conclude that the length of SWCNTs depends on the reactor temperature profile. At the low temperature profile SWCNTs grew almost the whole way in the heated zone and their average length was found to be around 1622 nm. In contrast, at the high temperature profile the tubes were only 290 nm long and they grew only in a small temperature window between 885 and 945 °C in spite of appropriate conditions after this zone. In our previous paper [54], the reason for the initiation of CNT growth at around 900 °C was explained by CO₂ transport in the reactor. CFD showed that SWCNT starts to grow at the location, where CO₂, formed on the reactor walls, diffused to the centerline. CO₂ is known to be an essential reagent for the SWCNT growth [46,55] and its role was attributed to the etching effect (i.e. removing excess and/or catalyst “poisoning” carbon) and decomposition of Fe₃C particles. However, the reason for the SWCNT growth termination has not been discussed, yet.

Our in situ sampling experiments carried out in two different aerosol systems showed very similar results. Hot wire generator reactor based on the introduction of premade catalyst particles in CO atmosphere revealed that the growth of CNTs stops at a temperature of 908 °C. The method described in this paper based on the in situ produced catalyst particles revealed that the CNT growth was terminated at the temperature of 945 °C. Let us consider possible processes for the CNT growth cease.

CO disproportionation (Boudouard) reaction:

\[ 2CO \rightarrow CO₂ + C(s) \]  \hspace{1cm} (5)

has maximum rate at the temperature of about 625 °C. At temperatures below the maximum, the reaction rate is kinetically limited [25,55]. At higher temperatures the disproportionation reaction rate decreases, since this reaction is thermodynamically prohibited. One can suggest that the growth of CNTs was suppressed at temperatures about 945 °C, since the conversion of reaction (1) decreases with the temperature increase [54] and accumulated reaction product (CO₂) can turn reaction (1) in the inverse direction. However, the measured CO₂ concentration (1540 ppm) in the reactor [46] is almost 10 times lower than equilibrium concentration at 945 °C (14,600 ppm). Moreover, it is known that CNTs can be synthesized in the Fe–CO system by a substrate CVD method even at 1120 °C [54].

Another possible mechanism restricting the SWCNT growth can be the appearance of physical obstacles during the bundling process. Formation of SWCNTs at very high concentrations in the gas phase leads to the increase in the inter-tube collision probability and as a result to the bundling process [22]. Consequently, a catalyst particle originally suspended in the gas and being grown a tube, after the bundling with other tube (or tubes), is physically confined from one side. Therefore, this disturbs continuous and uniform feed of carbon to the particle and destroys the steady state conditions for SWCNT growth [56]. Indeed, these speculations were confirmed by careful observations of the in situ collected SWCNTs: at the low temperature profile, SWCNTs were mainly individual, while the tubes collected at 945 °C (high temperature profile) were found mainly in the form of bundles. However, the bundling process is believed not to be the only and dominant reason for CNT growth termination.

The reason for the CNT growth termination can be attributed to the changes in the catalyst phase. Two different kinds of phase transitions are possible at this temperature range: from α-Fe to γ-Fe (912 °C) and from solid to liquid. The phase transition can result in the change of the catalyst properties (density, surface tension, carbon solubility) and therefore...
causes the interruption of steady state conditions for the CNT growth. It is worth noting that the difference between α-Fe and γ-Fe phases is as significant as the difference between solid and liquid Fe phases. In addition to substantial density difference, they have different carbon solubility: the maximum value in α-Fe is about 0.02 wt.% at 723 °C compared to 1.93% at 912 °C in γ-Fe [57]. In order to examine whether α-Fe to γ-Fe phase transition is responsible for the termination of the CNT growth, additional XRD experiments of samples produced at the temperatures around the phase transition point (890 and 960 °C) were carried out. However, the results did not reveal any significant difference in the XRD patterns and amount of iron phases compared to the results presented in Fig. 4a. This allowed us to conclude that the transition between two crystal phases likely did not play a crucial role in a CNT growth termination.

The transition from solid to liquid phase, which can occur in the heating zone of the reactor, most likely determines the conditions for the growth termination. It is known that the properties of small particles significantly differ from those of the bulk material. The melting temperature, Tm, for a given particle of radius, r, can be estimated on the basis of the Kelvin equation as [25].

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

where Ts is the bulk melting temperature (1535 °C); \( \Delta H_{fus} \) is the latent heat of fusion (13.8 kJ/mole); V is the volume of a metal molecule, which can be calculated from the density (7.87 × 10³ kg/m³); \( \sigma_r \) is the surface tension between liquid and solid (0.86 J/m²). The results of the calculations are shown in Fig. 7a. Melting temperatures of 900–950 °C correspond to 4.1–4.5 nm sized iron particles, which actually coincides with statistical TEM measurements [20], in which the mean particle diameters were varied from 4.0 nm (at low temperature profile) to 6.5 nm (at the set temperature of 1150 °C). Therefore, the size of the catalyst particles in the high temperature profile (set temperature of 1000 °C) lies between these diameters. Thus, Kelvin equation predicts the occurrence of catalyst melting during the growth of CNTs. However, the possibility of the CNT growth termination due to cementite decomposition can not be ruled out.

Fig. 7 – The effect of particle curvature on the melting temperature and carbon solubility in iron.

5. Conclusions

Experimental investigations of the SWCNT formation by an aerosol method based on CO disproportionation reaction on Fe catalyst particles formed by ferrocene vapor decomposition were presented. Kinetics of the SWCNT growth was studied on the basis of in situ sampling of the product at different locations in the reactor. It was found that the average growth rate constant complies with the Arrhenius dependence of \( k = k_0 \exp(-E_a/RT) \) with the pre-exponential coefficient \( k_0 = 1.99 \times 10^6 \mu m/s \) and the activation energy of \( E_a = 1.39 eV \). This allowed us to conclude that the limiting stage of the SWCNT growth is the diffusion of carbon atoms in solid iron catalyst.

HR-TEM observation of the product collected during in situ sampling experiments revealed that non-active catalysts were present in the form of Fe₃C. TEM and XRD investigations of the particles that initiated the growth of CNTs showed that these particles were mainly present in the form of γ-Fe with a small fraction of α-Fe. The examination of the diameters of SWCNTs grown in a high temperature gradient showed that the tubes remained their initial chirality.

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