Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor

Anna Moisala, Albert G. Nasibulin, David P. Brown, Hua Jiang, Leonid Khriachtchev, Esko I. Kauppinen

Abstract

A gas-phase process of single-walled carbon nanotube (SWCNT) formation, based on thermal decomposition of iron pentacarbonyl or ferrocene in the presence of carbon monoxide (CO), was investigated in ambient pressure laminar flow reactors in the temperature range of 600–1300 °C. Ferrocene was found to be a better catalyst precursor in the studied conditions since iron pentacarbonyl decomposes at lower temperatures resulting in the excessive growth of catalyst particles. In situ sampling carried out at 1000 °C showed that the SWCNT growth occurred from individual metal particles in the heating section of the furnace in the temperature range of 891–928 °C, in which the growth rate was estimated to exceed 2 μm/s. FT-IR measurements of gaseous products revealed that the majority of the CO disproportionation took place on the reactor walls. Raman measurements confirmed the results of TEM observations, namely, the formation of very high purity SWCNT product. On-line aerosol number size distributions were measured to detect the conditions of SWCNT formation and the product morphology changes. Mechanism of SWCNT formation in the gas phase from ferrocene and CO is discussed.

1. Introduction

For over a decade carbon nanotubes (CNTs) have been the source of abundant theoretical and experimental research due to their extraordinary mechanical, electrical and optical properties. Since the properties of CNTs vary depending on their structure, synthesis method development has targeted selective formation of CNTs with controlled diameter, length and chirality, as well as the number of concentric graphite walls. Among the various production methods, supported (e.g. Cassell et al., 1999; Dai et al., 1996; Li et al., 2004a) and gas-phase (e.g. Bronikowski et al., 2001; Cheng et al., 1998a; Li et al., 2004b) chemical vapour deposition (CVD) has been found to be efficient and selective for either single-walled (SWCNT) or multi-walled carbon nanotube growth. Gas-phase CVD, in particular, has potential for large-scale SWCNT production since it is a continuous process involving both catalyst particle formation and SWCNT nucleation and growth. Direct product collection from the effluent and the absence of support material further reduce the amount of process steps in the gas-phase method. Since research on the gas-phase CVD has been mostly directed toward synthesis method development, basic understanding of the mechanism of SWCNT nucleation and growth has received very little attention despite its importance on the development of more efficient SWCNT synthesis methods. A few basic steps, however, are generally acknowledged to take place during CNT formation via CVD methods. These methods rely...
on decomposition of carbon containing compounds on the surface of nanometre-sized transition metal particles that serve two main functions. The particles act as catalysts for carbon source decomposition as well as CNT formation sites. Either metal–organic or organometallic compounds, such as ferrocene or iron pentacarbonyl, have been used to form catalyst nanoparticles by thermal decomposition in the gas-phase (e.g., Bladh et al., 2000; Bronikowski et al., 2001; Cheng et al., 1998b; Ci et al., 2001; Satishkumar et al., 1998; Sen et al., 1997). The size of the catalyst particles has been found to correlate with the diameter of the SWCNTs (Nasibulin et al., 2005a).

Ideally, the carbon source should decompose only at the surface of the catalyst nanoparticles thus liberating carbon atoms for CNT formation. However, most of the carbon sources, including hydrocarbons and alcohols, thermally self-decompose at high temperatures resulting in the formation of by-products such as amorphous carbon deposits and soot particles. This can be avoided by utilising carbon monoxide (CO), since the disproportionation reaction \(2\text{CO}(g) \leftrightarrow \text{C}(s) + \text{CO}_2(g)\) requires the presence of a catalyst surface. The SWCNT production based on CO disproportionation has been carried out either as atmospheric or high-pressure (HiPco) processes in the presence of iron nanoparticles from iron pentacarbonyl decomposition (Bladh et al., 2000; Bronikowski et al., 2001).

This work aims to promote the understanding of the basic mechanisms of SWCNT formation in the gas-phase CVD by investigating the conditions for CNT growth (temperature and location in the reactor), the factors affecting SWCNT length, and the sizes of catalyst particles, which subsequently determine the formation of the CNTs. The experiments were carried out in laminar flow reactors and emphasis was placed on controlling the residence time and temperature history in the reactors. The temperature and flow conditions within the aerosol reactor were characterised via computational fluid dynamics (CFD) calculations.

In this study SWCNTs were produced mainly via thermal decomposition of ferrocene in the presence of CO, which has not been reported previously. The results were compared to those with iron pentacarbonyl as the catalyst precursor. In contrast to the HiPco process, the present experiments were conducted at ambient pressure. In order to determine the temperature for SWCNT nucleation and the rate of the SWCNT growth, in situ sample collection method was developed. The catalyst precursor decomposition and CO disproportionation processes were also studied by Fourier transform infrared spectroscopy (FT-IR) and gas chromatography (GC). The mechanism of SWCNT formation is discussed on the basis of the experimental data and detailed transmission electron microscopy (TEM) investigations.

2. Experimental

The vertical laminar flow reactors used in the SWCNT production are presented in Fig. 1. The experimental set-ups included a precursor feed system, a furnace equipped with an alumina tube, and sampling and analysis devices. As carrier gases, nitrogen (N\(_2\), 99.999 vol%, AGA), nitrogen/hydrogen mixture (N\(_2\)/H\(_2\), 93/7 vol%, AGA) or carbon monoxide (CO, 99.97 vol%, AGA), which also served as the carbon precursor, were used. Filtering (Oxisorb, Messer) of CO was carried out prior to its introduction to the furnace.

Iron pentacarbonyl (Fe(CO)\(_5\), 99.999%, Sigma-Aldrich) vapour was introduced to the furnace by bubbling a carrier gas (N\(_2\)) through a reservoir of the liquid catalyst precursor at ambient temperature. Precursor vapour was introduced 16–30 cm from the furnace inlet at the flow rates between 310 and 407 cm\(^3\)/min. The precursor vapour pressure was 0.3 or 4 Pa based on equilibrium vapour pressure data (CRC Handbook of Chemistry and Physics, 2003) taking into account the dilution with N\(_2\) prior to the furnace. The experiments were conducted at furnace set temperatures between 1100°C and 1300°C with the flow direction upward.

To vaporise ferrocene (FeCp\(_2\), 99%, Strem Chemicals) a flow of carrier gas (300 cm\(^3\)/min) was continuously directed through a cartridge containing the precursor powder mixed with silicon dioxide powder (99.9%, Balzers Materials, weight ratio FeCp\(_2\)/SiO\(_2\) = 1: 4) at ambient temperature. A constant partial pressure of 0.8 Pa of FeCp\(_2\) vapour was introduced into the reactor. The experiments were conducted at set temperatures between 600°C and 1150°C with flow direction downward. The maximum temperatures in the reactor were about 20°C higher than the set ones.

Stainless steel water-cooled injector probes, held constantly at 22°C, were used to feed the precursors to the furnaces. The locations of the injector probes were varied in order to control the precursor vapour heating rate and residence time in the furnace. The temperature at which the precursor was introduced was determined by the furnace wall temperature and only slightly varied depending on the vertical location of the injector probe inside the furnace. For instance, the FeCp\(_2\) was introduced 7.5–20 cm from the furnace inlet corresponding to local wall temperatures between 770 and 790°C at the set temperature of 1150°C, respectively. In the reported experiments the FeCp\(_2\) vapour was introduced 7.5 cm from the furnace inlet unless otherwise specified.

Additional flow (up to 680 cm\(^3\)/min of either CO or N\(_2\)) was introduced in both experimental set-ups to adjust the residence time in the furnace. The total flow rate in the FeCp\(_2\) experiments was generally 410 cm\(^3\)/min and deviations from this standard condition are noted accordingly. After the furnace, the aerosol was diluted with 12 l/min of pure, ambient temperature N\(_2\) to reduce product losses to the reactor walls due to diffusion and thermophoresis and to decrease the product agglomeration. Moreover, the dilutor was used to reduce the gas product temperature after the reactor. Alternatively, the dilutor was removed and samples were collected via filtering on silver filters (Millipore, pore size 0.45 μm) at the outlet of the furnace at ambient temperature with a flow rate of 280 cm\(^3\)/min through the filter.

In situ sampling from the centerline of the reactor was carried out to detect the location and temperature of SWCNT growth. For this purpose, a silica coated nickel TEM grid was attached to a stainless steel rod and inserted into a selected location of the furnace for 30 s. The in situ investigations were...
Fig. 1. Set-ups for iron pentacarbonyl (A) and ferrocene (B) experiments, with the wall temperature profile and centerline location of the in situ sample collection shown for ferrocene experiments. Open circles represent sampling locations when CNTs were not observed, solid circles show the conditions of the CNT sampling.

performed at the set temperature of 1000°C with a CO flow rate of 400 cm$^3$/min at various sampling locations specified in Fig. 1B.

Samples were also collected from the gas phase by an electrostatic precipitator (InTox Products) on carbon coated copper grids. The morphology and the crystallinity of the product were investigated with scanning electron microscopy (SEM, Leo Gemini 982) and field emission transmission electron microscopy (TEM, Philips CM200 FEG). Raman spectra were measured for samples collected on silver filters. The spectra were recorded using two lasers (Ar$^+$ laser, 488 nm, Omnichrome 543-AP and He-Ne laser, 633 nm, Uniphase 1145P) and a single-stage spectrometer (Acton SpectraPro 500I) equipped with a CCD camera (Andor InstaSpec IV) providing resolution down to approximately 2 cm$^{-1}$.

The carrier gas flow rates were determined by a flow meter (Gilian Gilibrator, Sensidyne). Nichrome–nickel thermocouples were used to measure the furnace wall temperature profiles. The gaseous components of the effluent with FeCp$_2$ as the catalyst precursor were studied by gas chromatography (GC) and Fourier-transform infrared spectroscopy (FT-IR). GC measurements were conducted at 80°C with a portable instrument (GC, Photovac VOYAGER, Perkin Elmer) equipped with a photo ionisation detector. The FT-IR (GASMET DX4000, Temes Instruments) was fitted with a 1-dm$^3$ flow-through cuvet and the measurement temperature was 150°C. The gas samples for GC and FT-IR measurements were collected in gas bags at a total CO flow rate of 410 cm$^3$/min.

The aerosol mobility number size distributions (NSDs) in the size range of 9.8–400 nm were measured by a differential electrical mobility particle sizer system, consisting of a differential mobility analyser (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3022). The DMA system allowed us to measure the electrical mobility of aerosol particles and thereby to distinguish catalyst particle aggregates from the bundles of CNTs (Moisala et al., 2005). Thus, the on-line NSD measurements were used to detect the conditions of SWCNT formation. Moreover, the on-line NSD measurements of the product were used to guarantee stable reactor conditions by ensuring unchanging NSDs.

3. Results

3.1. Computational fluid dynamics

Computational fluid dynamics (CFD) calculations were carried out with the StreamWise computer code (Brown et al., 2006). In addition to the conservation of mass, momentum and energy, buoyancy effects were considered in the two-dimensional, axisymmetric calculations. The temperature and flow velocity profiles were determined for the FeCp$_2$ set-up. The boundary conditions were the measured furnace wall temperature profiles at set temperatures of 800°C and 1150°C, the pressure (1 atm), the flow rates and compositions, the FeCp$_2$ vapour pressure (0.8 Pa) and the temperature at the precursor introduction location.

The calculations were performed for three different combinations of set temperature and temperature at FeCp$_2$ introduction, i.e., 800/509°C, 1150/770°C and 1150/790°C, the position of the injection probe being 7.5, 7.5 and 20 cm from the inlet of the furnace, respectively. The velocity vectors, temperature contours in the vicinity of the precursor introduction and
Fig. 2. CFD results for temperature profiles, velocity contours and selected streamlines for FeCp₂ set-up (the temperature colour scale is adjusted according to the set temperature).

Selected streamlines for each of the cases are shown in Fig. 2. Recirculation of the additional flow close to the injector probe outlet was observed in all cases. However, the flow containing the FeCp₂ vapour did not take part in the recirculation, and the total flow became fully developed and laminar as it moved towards the high temperature zone of the furnace, indicating laminar flow conditions for the catalyst particle formation and SWCNT growth. In the high temperature zone the gas flow heated up to the reactor wall temperature and was found radially uniform in temperature.

3.2. Iron pentacarbonyl vapour decomposition

Fe(CO)₅ vapour decomposition at 1100°C in both N₂ and CO atmospheres resulted in the formation of agglomerated iron particles when the precursor vapour pressure was 4 Pa (Table 1). At 1200–1300°C with a CO flow rate of 791 cm³/min, a few SWCNTs were observed. A lower precursor vapour pressure (0.3 Pa) resulted in a higher SWCNT yield when the CO flow rate was 660–910 cm³/min (Fig. 3A). The SWCNTs were tens of nanometres long. The mean metal particle size measured from high resolution TEM images was 5.1 nm with the geometric standard deviation of σ = 1.32 (Fig. 4). Lower CO flow rates resulted only in metal particle agglomerate formation.

Even though a slight increase in SWCNT yield was observed with increasing total flow rate and set temperature, the best experimental conditions (1300°C, QCO = 910 cm³/min) yielded mostly metal particle agglomerates and the SWCNT yield remained low. Changing the Fe(CO)₅ introduction location from 16 to 18 cm from the reactor inlet had no noticeable effect on the SWCNT yield, while introducing Fe(CO)₅ to 30 cm resulted mainly in metal particle formation.

3.3. Ferrocene vapour decomposition

Iron particle formation was found to occur in a N₂ atmosphere at set temperatures above 500°C according to the aerosol NSD measurements (Table 2). However, set temperatures higher than 700°C were necessary for obtaining uniform NSDs with geometric mean mobility diameters of 39–44 nm and total particle concentrations of 2.4 × 10⁷–2.6 × 10⁸ #/cm³. The incomplete precursor vapour decomposition below 700°C was confirmed by the GC measurements, i.e., only 87% of the FeCp₂ vapour decomposed at 600°C, while at 1000°C and above more than 95% of the precursor decomposed (Table 3).

| Table 1 Experimental conditions and the corresponding product in the Fe(CO)₅ set-up |
|---|---|---|---|---|---|
| T_F (°C) | Fe(CO)₅ introduction (cm) | p (Pa) | Q_SAT + Q_ADD flow composition/ rate (cm³/min) | t_RES (s) | SWCNT (Y/N) |
| 1100 | 16 | 4 | N₂/407 + N₂/384 | 2.7 | N |
| 1100 | 16 | 4 | CO/407 + CO/384 | 2.7 | N |
| 1200–1300 | 16–18 | 4 | CO/407 + CO/384 | 2.5–2.3 | Y |
| 1100–1300 | 18–30 | 0.3 | CO/310 – 440 + CO/350 – 470 | 2.5–2.0 | Y |
| 1100–1300 | 30 | 0.3 | CO/310 | 4.8–4.2 | N |

T_F equals the set temperature, p is the partial vapour pressure of Fe(CO)₅, Q_SAT and Q_ADD are the saturation and additional flow rates and t_RES is the total residence time in the furnace.

A location of the injector probe outlet from the inlet of the furnace.

Based on TEM imaging.
Fig. 3. Overview and high-resolution TEM images (inset) of the CNT product. (A) Fe(CO)$_5$ ($T_F = 1300^\circ$C, $x = 18$ cm, $Q_{TOT,CO} = 910$ cm$^3$/min, $p_{Fe(CO)_5} = 0.3$ Pa). (B) FeCp$_2$ ($T_F = 800^\circ$C, $x = 7.5$ cm, $Q_{TOT,CO} = 410$ cm$^3$/min).

Fig. 4. Catalyst particle number size distributions (normalised frequency versus particle diameter) measured from TEM images.

The aerosol NSD measurement in the CO atmosphere generally resulted in larger mobility particle size and smaller concentration as compared to the N$_2$ atmosphere. For example, at $1150^\circ$C the mean electrical mobility size changed from 40 to 100 nm and the number concentration from $2.5 \times 10^7$ to $1.5 \times 10^7$ #cm$^{-3}$ when the carrier gas composition was changed from N$_2$ to CO. Fig. 5 shows how increasing the flow rate typically decreased the mobility particle size. Also an increase in the concentration was observed as a result of reduced product agglomeration.

FT-IR gas composition measurements revealed that less than 0.69% of the CO decomposed in the process (Table 3). The highest conversion of CO to carbon dioxide (CO$_2$) was measured at 800$^\circ$C. Only a slight increase in the CO$_2$ concentration was detected after introducing FeCp$_2$ vapour in the reactor, i.e., at 1150$^\circ$C the CO$_2$ concentration without FeCp$_2$ was 820 ppm, compared to 853 ppm in the presence of the precursor vapour. This indicates that the reactor walls have a very important role in the process, i.e., the disproportionation reaction mainly takes place on the iron covered reactor surfaces. Furthermore, in order to provide reproducible SWCNT synthesis conditions the reactor walls had to be saturated with iron. This was achieved by introducing FeCp$_2$ to the heated furnace with N$_2$ as the carrier gas prior to the introduction of CO.

An overview TEM image of the sample produced at 800$^\circ$C is presented in Fig. 3B. The sample contains SWCNT bundles with diameters below 20 nm and lengths up to several micrometers. Most abundant SWCNT formation took place at 700–800$^\circ$C. SWCNTs formed also at set temperatures between 900$^\circ$C and 1150$^\circ$C as well as at 600$^\circ$C, but their amount was lower. Changing the carrier gas composition from pure CO to a mixture of CO and N$_2$ (vol. ratio 2.7:1) resulted in a decrease in SWCNT yield at 1150$^\circ$C. Introducing N$_2$/H$_2$ to the reactor yielded only metal particle agglomerates with primary metal particle sizes above 10 nm. The formation of SWCNTs based on TEM imaging in the various experimental conditions is summarised in Table 2.

Based on the high resolution TEM imaging the metal particles associated with the SWCNT ends, considered as the active catalysts, were generally 3 nm and below in diameter, while the inactive particles were larger and encapsulated by carbon. Inactive metal particles were found in all experimental conditions and their amount increased with increasing set temperature. The mean metal particle diameter measured from TEM images varied from 4.0 at 800$^\circ$C to 6.5 nm at 1150$^\circ$C, with geometric standard deviations of 1.6 and 1.4, respectively (Fig. 4).

Individual SWCNT diameters varied from 0.9 to 3 in all conditions. Their lengths, however, depended on the set temperature and residence time. At 1150$^\circ$C the SWCNT bundles were a few hundreds of nanometres long, while set temperature of 800$^\circ$C yielded several micrometers long bundles of SWCNTs. The SWCNT bundle length was reduced when the total flow rate was increased from 410 (Fig. 6A) to 600 cm$^3$/min.
Table 2
Experimental conditions, results from aerosol NSD measurements, and the corresponding product in the FeCp$_2$ set-up

<table>
<thead>
<tr>
<th>$T_F$ (°C)</th>
<th>FeCp$_2$ introduction$^a$ (cm)</th>
<th>$Q_{TOT}$$^b$ flow composition/rate (cm$^3$/min)</th>
<th>$t_{RES}$ (s)</th>
<th>$D_G$ (nm)</th>
<th>$C_{TOT}$ (#/cm$^3$)</th>
<th>$\sigma$</th>
<th>SWCNT (Y/N)$^c$</th>
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<tr>
<td>1150–700</td>
<td>7.5</td>
<td>N$_2$/410</td>
<td>3.7–5.4</td>
<td>44–39</td>
<td>$2.6 \times 10^7$–$2.4 \times 10^7$</td>
<td>1.6</td>
<td>N</td>
</tr>
<tr>
<td>600</td>
<td>7.5</td>
<td>N$_2$/410</td>
<td>6.1</td>
<td>32</td>
<td>$2.3 \times 10^7$</td>
<td>1.6</td>
<td>N</td>
</tr>
<tr>
<td>550</td>
<td>7.5</td>
<td>N$_2$/410</td>
<td>6.4</td>
<td>14</td>
<td>$4.4 \times 10^6$</td>
<td>1.6</td>
<td>N</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>N$_2$/300</td>
<td>5.1</td>
<td>27</td>
<td>$1.7 \times 10^7$</td>
<td>1.5</td>
<td>N</td>
</tr>
<tr>
<td>1150</td>
<td>12.5</td>
<td>N$_2$/410</td>
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<td>40</td>
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<td>N</td>
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<tr>
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<td>1.6</td>
<td>N</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>CO/410</td>
<td>3.7</td>
<td>100</td>
<td>$1.5 \times 10^7$</td>
<td>1.6</td>
<td>Y</td>
</tr>
<tr>
<td>1000</td>
<td>7.5</td>
<td>CO/410</td>
<td>4.2</td>
<td>94</td>
<td>$3.7 \times 10^6$</td>
<td>1.6</td>
<td>Y</td>
</tr>
<tr>
<td>900</td>
<td>7.5</td>
<td>CO/410</td>
<td>4.5</td>
<td>62</td>
<td>$2.5 \times 10^6$</td>
<td>1.6</td>
<td>Y</td>
</tr>
<tr>
<td>800</td>
<td>7.5</td>
<td>CO/410</td>
<td>4.9</td>
<td>44</td>
<td>$1.5 \times 10^5$</td>
<td>1.8</td>
<td>Y</td>
</tr>
<tr>
<td>700</td>
<td>7.5</td>
<td>CO/410</td>
<td>5.4</td>
<td>48</td>
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<td>1.8</td>
<td>Y</td>
</tr>
<tr>
<td>600</td>
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<td>CO/410</td>
<td>6.1</td>
<td>43</td>
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<td>12.5</td>
<td>CO/410</td>
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<td>Y</td>
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<tr>
<td>1150</td>
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<td>CO/410</td>
<td>2.3</td>
<td>31</td>
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<td>Y</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>CO/300</td>
<td>5.1</td>
<td>68</td>
<td>$4.9 \times 10^6$</td>
<td>1.8</td>
<td>Y</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>CO/600</td>
<td>2.5</td>
<td>42</td>
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<td>1.5</td>
<td>Y</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>CO/980</td>
<td>1.6</td>
<td>16</td>
<td>$2.5 \times 10^8$</td>
<td>1.2</td>
<td>N</td>
</tr>
<tr>
<td>1150</td>
<td>7.5</td>
<td>$Q_{SAT,CO/300}$</td>
<td>3.7</td>
<td>24</td>
<td>$2.7 \times 10^7$</td>
<td>1.5</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_{ADD,N_2/H_2/110}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$Q_{SAT,N_2/H_2/300}$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$Q_{ADD,CO/110}$</td>
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$T_F$ equal the set temperature, $Q_{TOT}$ is the total flow rate, $t_{RES}$ is the total residence time in the furnace, $D_G$ is the geometric mean mobility diameter of aggregates, $C_{TOT}$ is the total particle concentration, $\sigma$ is the geometric standard deviation of the number size distribution.

$^a$Location of the injector probe outlet from the inlet of the furnace.

$^b$ $Q_{SAT} = 300$ cm$^3$/min.

$^c$Based on TEM imaging.

Table 3
Amount of FeCp$_2$ and CO$_2$ in the effluent measured by GC and FT-IR, respectively

<table>
<thead>
<tr>
<th>$T_F$ (°C)</th>
<th>FeCp$_2$ (ppm)</th>
<th>CO$_2$ (ppm)</th>
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<tr>
<td>22</td>
<td>8</td>
<td>71</td>
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<tr>
<td>600</td>
<td>1.0</td>
<td>3652</td>
</tr>
<tr>
<td>800</td>
<td>0.9</td>
<td>6901</td>
</tr>
<tr>
<td>1000</td>
<td>0.4</td>
<td>1199</td>
</tr>
<tr>
<td>1150</td>
<td>0.3</td>
<td>853</td>
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(Fig. 6B), while at 980 cm$^3$/min only agglomerated metal particles were formed (Fig. 6C). Varying the injector probe location at 1150°C also changed the individual SWCNT and bundle length. Introduction of the precursor vapour 7.5 cm from the inlet of the furnace yielded up to a few micrometers long SWCNT bundles consisting of few hundreds of nanometres long individual SWCNTs (Fig. 7A). Introducing the FeCp$_2$ at 12.5 cm reduced the individual SWCNT and bundle lengths to below 100 nm (Fig. 7B), while the introduction at 20 cm yielded only SWCNT nuclei (Fig. 7C).

TEM observations of the samples collected in situ at set temperature of 1000°C revealed SWCNTs on TEM grids introduced to 928°C and above, and the length of the individual SWCNTs was found to be the same, approximately 150 nm, at all of these sampling locations (Fig. 8). Sampling at 891°C and below showed the presence of catalyst particles only. The residence time at the centerline in the “growth window” (from 891°C to 928°C) was 76 ms according to the CFD calculations, which resulted in a SWCNT growth rate of 2.0 μm/s.

The Raman spectra measured for a sample collected from the FeCp$_2$ set-up at 1150°C are shown in Fig. 9. Spectral
Fig. 6. TEM images showing the effect of the total CO flow rate (residence time) in FeCp$_2$ set-up on CNT and catalyst particle morphology at 1150 °C. (A) 410 cm$^3$/min (3.7 s). (B) 600 cm$^3$/min (2.5 s). (C) 980 cm$^3$/min (0.9 s).

Fig. 7. TEM images showing the effect of the location of FeCp$_2$ introduction on CNT and catalyst particle morphology at 1150 °C. (A) 7.5 cm. (B) 12.5 cm. (C) 20 cm.

Fig. 8. TEM images of the product collected at reactor set temperature of 1000 °C via in situ sampling at (A) 891 °C. (B) 928 °C.

features, i.e., the radial breathing mode (RBM) peaks between 170 and 198.5 cm$^{-1}$ and the strong G-band, in the collected Raman spectra indicated SWCNT formation. The SWCNT diameters ranged from 1.25 to 1.45 nm according to the expression: $D_{SWCNT} = 248/\nu$ nm, where $\nu$ equals the RBM Raman shift (Jorio et al., 2001). A notable feature of all of the collected spectra is the absence of a D-band, which is generally associated with disordered carbon, showing very high purity product with respect to amorphous carbon.
decomposition of FeCp2 takes place only at temperatures above the studied residence times (above 2.3 s) in the furnace, complete reaction rate constant for the precursor decomposition is sever-

eral orders of magnitude smaller in the case of FeCp2 compared to Fe(CO)5 (e.g. at 900 °C, \( k = 0.2 \) and \( 5.9 \times 10^3 \) s\(^{-1} \), respec-
tively) (Lewis and Smith, 1984; Krestinin et al., 1990). At the studied residence times (above 2.3 s) in the furnace, complete decomposition of FeCp2 takes place only at temperatures above approximately 1050 °C according to literature data. However, the GC measurements showed that, even at the highest studied set temperature of 1150 °C, all of the FeCp2 vapour did not decompose. This together with the larger geometric standard deviation of the particle size distribution suggests that the FeCp2 decomposition and growth processes continue throughout the reactor. It is also likely that the formed catalyst particles facilitate further decomposition of FeCp2 as observed earlier (Dyagileva et al., 1979; Nasibulin et al., 2005a). This results in a large number of active catalyst particles, which is benefi-
cial for SWCNT formation, but it also inevitably yields a wide distribution of metal particle sizes.

On the contrary, the Fe(CO)5 decomposition readily takes place at the studied set temperatures allowing more localised iron particle formation at the point of vapour introduction and yielding a narrow particle size distribution. However, the majority of the catalyst particles grow excessively before catalysing the carbon precursor decomposition and the SWCNT formation is prohibited due to the large metal particle size.

The highest efficiency of SWCNT formation was obtained when the mean metal particle size was the smallest and further optimisation of both set-ups toward smaller particle sizes and geometric standard deviations should result in a more effective usage of the catalyst material. The smaller average metal particle size in CO atmosphere compared to N\(_2\) reveals reduced particle sintering due to particle surface passivation by carbon (Nasibulin et al., 2003).

The presence of hydrogen has been previously reported to promote SWCNT formation by removing deposited carbon from the catalyst particle surface and by preventing metal particle oxidation (e.g. Li et al., 2004; Nasibulin et al., 2005b). In the present FeCp2 set-up the SWCNT formation was, however, completely prevented in the presence of hydrogen. Instead iron particles with larger primary sizes were formed, which likely originates from the accelerated particle formation processes due to the higher coefficient of diffusion and heat conductivity of H\(_2\) compared to other carrier gases. Additionally, the removal of amorphous carbon from the metal particle and reactor wall surfaces by H\(_2\) may also enhance metal particle sintering, as observed previously in SWCNT formation during supported CVD (Wong et al., 2005).

The formation of the SWCNTs was studied at different residence times by changing either the additional flow rate or the FeCp2 introduction location, which altered the residence time either in the whole reactor or only in the temperature region where disproportionation reaction was allowed, respectively. As described earlier, reduction of the SWCNT bundle length was observed when the flow rate was increased, which can be attributed to the reduced feed of carbon to the metal particles as a consequence of the lower residence time.

The introduction of the ambient temperature catalyst precursor vapour to the furnace resulted in a steep temperature gradient at the vicinity of the injector probe outlet (Fig. 2). This temperature gradient enabled SWCNT formation even when the injector probe outlet was located in the high temperature zone of the furnace, where the CO disproportionation is not allowed (the thermodynamically favourable temperature for the iron catalysed disproportionation reaction ranges only from approximately 400 °C to 900 °C (Nasibulin et al., 2006a)). As a result of this temperature gradient, metal particle formation, CO disproportionation and SWCNT growth took place before the upper temperature limit was reached. However, introduction of the precursor vapour deeper into the furnace resulted in a steeper temperature gradient (faster heating rate) resulting in

Fig. 9. Raman spectra at laser wave lengths of 488 and 633 nm measured for a SWCNT sample collected from FeCp2 set-up at 1150 °C.

4. Discussion

In the present experiments catalyst particles were produced via precursor vapour decomposition and the mean particle size was adjusted by catalyst precursor vapour concentration, carrier gas composition and set temperature. The large differences in the geometric standard deviations of the particle size distributions suggested differences in the metal particle formation processes between the two precursors. The standard deviation in the case of Fe(CO)5 was much smaller (\( \sigma = 1.3 \)) than that observed in the case of FeCp2 (\( \sigma = 1.6 \)).

The catalyst particle formation depends on the decomposition reaction kinetics of the precursor compound. The first-order reaction rate constant (\( k \)) for the precursor decomposition is several orders of magnitude smaller in the case of FeCp2 compared to Fe(CO)5 (e.g. at 900 °C, \( k = 0.2 \) and \( 5.9 \times 10^3 \) s\(^{-1} \), respectively) (Lewis and Smith, 1984; Krestinin et al., 1990). At the studied residence times (above 2.3 s) in the furnace, complete decomposition of FeCp2 takes place only at temperatures above approximately 1050 °C according to literature data. However, the GC measurements showed that, even at the highest studied set temperature of 1150 °C, all of the FeCp2 vapour did not decompose. This together with the larger geometric standard deviation of the particle size distribution suggests that the FeCp2 decomposition and growth processes continue throughout the reactor. It is also likely that the formed catalyst particles facilitate further decomposition of FeCp2 as observed earlier (Dyagileva et al., 1979; Nasibulin et al., 2005a). This results in a large number of active catalyst particles, which is beneficial for SWCNT formation, but it also inevitably yields a wide distribution of metal particle sizes.

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The highest efficiency of SWCNT formation was obtained when the mean metal particle size was the smallest and further optimisation of both set-ups toward smaller particle sizes and geometric standard deviations should result in a more effective usage of the catalyst material. The smaller average metal particle size in CO atmosphere compared to N\(_2\) reveals reduced particle sintering due to particle surface passivation by carbon (Nasibulin et al., 2003).

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The formation of the SWCNTs was studied at different residence times by changing either the additional flow rate or the FeCp2 introduction location, which altered the residence time either in the whole reactor or only in the temperature region where disproportionation reaction was allowed, respectively. As described earlier, reduction of the SWCNT bundle length was observed when the flow rate was increased, which can be attributed to the reduced feed of carbon to the metal particles as a consequence of the lower residence time.

The introduction of the ambient temperature catalyst precursor vapour to the furnace resulted in a steep temperature gradient at the vicinity of the injector probe outlet (Fig. 2). This temperature gradient enabled SWCNT formation even when the injector probe outlet was located in the high temperature zone of the furnace, where the CO disproportionation is not allowed (the thermodynamically favourable temperature for the iron catalysed disproportionation reaction ranges only from approximately 400 °C to 900 °C (Nasibulin et al., 2006a)). As a result of this temperature gradient, metal particle formation, CO disproportionation and SWCNT growth took place before the upper temperature limit was reached. However, introduction of the precursor vapour deeper into the furnace resulted in a steeper temperature gradient (faster heating rate) resulting in
shorter residence time in the disproportionation reaction temperature, and, correspondingly, in a reduction in the SWCNT length. In situ sampling confirmed that SWCNT growth started in the heating zone of the reactor.

Fig. 10 shows our current understanding of the mechanism of CNT formation in the reactor at a set temperature of 1000°C. Decomposition of FeCp₂ vapour resulted in catalyst particle formation and likely in release of hydrocarbon fragments. The catalyst particles formed by collision processes. Also, the catalyst particle growth can continue as a result of the ferrocene vapour decomposition at the particle surfaces. Depending on the size of the catalyst particles, they either nucleated the growth of a SWCNT or became inactive by growing too large (usually above 3 nm in diameter). The GC and FT-IR measurements showed that all of the released hydrocarbon fragments decomposed in the reactor.

Some of the nanometer-sized catalyst particles were deposited on the reactor walls due to their high diffusivity. Also ferrocene vapour deposition took place releasing additional iron to the reactor walls. As mentioned earlier, stable SWCNT synthesis was dependent on the reactor wall conditions and reproducible results were obtained only after saturation of the reactor walls with iron. The importance of iron on the reactor walls can be explained by its catalytic activity in CO disproportionation that leads to the release of gaseous products (such as CO₂), which can play an important role in the CNT growth (Nasibulin et al., 2006b). This hypothesis is supported by the work of Hata et al. (2004), who have recently demonstrated the importance of water vapour in providing conditions for efficient growth of CNT forests from methane.

Both the iron particles in the gas phase and the iron coating at the furnace walls catalysed the CO disproportionation reaction yielding carbon and CO₂. The reaction at the surface of the catalyst particle in the gas-phase is the sole route to the SWCNT formation, while the CO₂ (the majority of which is released by the reaction at the reactor walls) is believed to contribute to the exceptional purity of the SWCNT product by shifting the equilibrium of the CO disproportionation reaction toward the formation of CO from CO₂ and amorphous carbon (Nasibulin et al., 2006b).

As discussed in Nasibulin et al. (2005a) the nucleation of SWCNTs is believed to occur from a graphitic layer on the catalyst particle surface. The SWCNTs grow further due to the addition of carbon from the CO disproportionation reaction to the particle surface. The role of CO₂ is expected to “etch” amorphous carbon from the catalyst particle surfaces at the CNT nucleation and growth stages. The etching effect prevents particle deactivation and maintains conditions for the Boudouard reaction as well as for CNT nucleation and growth.

The length of SWCNTs was found to be controlled by the residence time in the “growth window”. At temperatures higher than 928°C, the growth of CNTs stops due to the dominant role of the inverse Boudouard reaction. For the same reason, further CNT cleaning occurs at high temperatures, i.e., amorphous carbon is removed from the CNTs surface due to the presence of CO₂ in the gas phase. As was additionally confirmed by Raman measurements showing that the produced CNTs are very pure. Thus, the presence of etching agents such as CO₂, is important to dispose of amorphous carbon and to synthesize clean CNTs.

Agglomeration of the SWCNTs was observed in all experimental conditions. The SWCNTs are likely to move with random orientation following the gas flow. Their Brownian motion coupled with large surface area and high number concentration result in a high probability of intertube collision. Upon collision SWCNTs can adhere via van der Waals forces and bundle parallel to each other to minimise the total free surface. The in situ sampling proved that the SWCNTs were initially formed from individual catalyst particles and the bundling took place towards the outlet of the reactor after the SWCNT growth.

5. Conclusions

The formation of SWCNTs in the gas phase was studied. Catalyst nanoparticles were obtained from ferrocene (FeCp₂) and iron pentacarbonyl (Fe(CO)₅) vapour decomposition with CO as the carbon source to produce SWCNTs in ambient pressure laminar flow reactors. FeCp₂ was found to be a better precursor for production of catalyst nanoparticles in the studied conditions, in spite of the obtained wide catalyst particle size distribution. The decomposition of Fe(CO)₅ was more localised to the vicinity of the precursor introduction, but excessive
catalyst particle growth resulted in insignificant yield of SWCNTs even at the best conditions. In the FeCp2 set-up, SWCNTs were formed at 600–1150°C and the morphology of the product varied depending on the set temperature and residence time. The highest efficiency of SWCNTs formation per catalyst particle was detected between 700 and 900°C, corresponding to conditions of the smallest catalyst particle sizes and most efficient CO disproportionation reaction. The SWCNT length was controlled by the residence time in “growth window”, which, at the set furnace temperature of 1000°C, ranged from 891°C to 928°C. In situ sample collection confirmed the formation of SWCNTs in the heating zone of the furnace. A SWCNT growth rate of 2 μm/s was estimated in the “growth window”. The important effect of the CO2 in the process was discussed.

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