Studies on Synthesis of Single-Walled Carbon Nanotubes by Gas-Phase Chemical Vapour Deposition

Anna Moisala

Laboratory of Inorganic Chemistry
Department of Chemistry
University of Helsinki
Finland

Center for New Materials and
Department of Engineering Physics and Mathematics
Helsinki University of Technology
Espoo, Finland

Aerosol Technology Group
VTT Processes
Espoo, Finland

Academic Dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in the Auditorium A110 of Chemicum, A.I. Virtasen Aukio 1, on the 3rd of March, 2006 at 12 noon.
Supervisors

Professor Esko Kauppinen  
Centre for New Materials  
Helsinki University of Technology  
Finland

Professor Markku Leskelä  
Laboratory of Inorganic Chemistry  
Department of Chemistry  
University of Helsinki  
Finland

Reviewers

Professor Eleanor Campbell  
Atomic and Fundamental Molecular Physics  
Gothenburg University  
Sweden

Professor Päivi Törmä  
Nanoelectronics and Nanotechnology  
Department of Physics  
University of Jyväskylä  
Finland

Opponent

Professor Morinobu Endo  
Electrical & Electronic Engineering  
Faculty of Engineering  
Shinshu University  
Japan

© Anna Moisala  
ISBN 952-91-9966-X (print)  
ISBN 952-10-2948-X (PDF)  
http://ethesis.helsinki.fi
Abstract

This thesis introduces a new method for selective synthesis of single-walled carbon nanotubes (SWCNTs) by gas-phase chemical vapour deposition (CVD). This so-called hot wire generator method is based on the formation of catalyst nanoparticles having controlled particle size, via resistive heating of a metal wire (iron or nickel). The particle size varied from 1–3 nm to 1–15 nm in the in situ and ex situ set-ups, respectively. Subsequently, these particles were introduced to a laminar flow reactor where the growth conditions for SWCNTs were maintained. The SWCNTs were formed as a result of catalytic carbon source decomposition on the particle surface at 870–1460 °C. The applicability of carbon monoxide, ethanol and octanol as the carbon sources is presented. The SWCNTs produced by this method were generally less than 100 nm long and their diameters ranged from 0.6 to 2 nm. The SWCNT product was found to have high purity with respect to amorphous carbon. Furthermore, the SWCNT production efficiency was high, i.e. the ratio of number of catalyst particles to SWCNTs was close to unity.

Comparative studies on SWCNT synthesis were carried out with a conventional gas-phase CVD method, where the catalyst particles were formed by thermal decomposition of catalyst precursors, such as ferrocene and iron pentacarbonyl. The SWCNTs were produced with CO as the carbon source at 600-1150 °C. The diameters of the SWCNTs produced ranged from 1 to 3 nm under all experimental conditions. The length of SWCNTs depended on the residence time in the region of the reactor, where the temperature was preferable for the CO disproportionation, and varied from few nanometres to several micrometres. In situ sampling showed that SWCNTs were formed in a temperature range from 891 to 928 °C (at a set furnace temperature of 1000 °C) and the estimated growth rate exceeded 2 μm/s. The in situ sampling also revealed that the SWCNTs nucleated from individual catalyst particles, but subsequent aggregation was observed under all reactor conditions. However, many of the catalyst particles formed in situ did not catalyse the growth of SWCNTs.
Preface

The work presented in this thesis was mainly carried out at the Centre for New Materials at Helsinki University of Technology. I wish to thank my supervisor Professor Esko Kauppinen for his guidance and advice throughout the work. I also wish to give most sincere thanks to Professor Markku Leskelä for his support in finalising this thesis.

I am forever grateful to my co-supervisor Dr Albert Nasibulin for all his efforts throughout this work. You have endlessly discussed results and contributed in this work in numerous ways. I couldn’t have wished for better colleague to work with!

I wish to thank Professor Eleanor Campbell and Professor Päivi Törmä for their valuable work in pre-examining this thesis. I am also deeply honoured to have one of the leading researchers in the field of carbon nanotube synthesis, Professor Morinobu Endo, as my opponent.

I wish to acknowledge all of the co-authors for their input into this thesis. Especially the efforts of Dr Hua Jiang on excellent transmission electron microscopy are greatly appreciated. Also the theoretical approaches of Dr David Brown (computational modelling) and Dr Sergei Shandakov (mobility of cylindrical particles in an electric field) are noteworthy.

Million thanks go also to a dear friend and former Cambridge colleague, Dr. Jane Crawshaw, for removing most of the Finnish from the English.

Furthermore, I would like to thank all my colleagues at HUT and VTT for the fun place to come to every morning... Special thank you regarding this goes to the office mates, Tatti and Jouni! Also Anna and Paula & David deserve big hugs for being good friends as well as outstanding co-workers. And family and friends in Finland as well as abroad, thank you for sharing these exciting times with me!

Finally, funding from the Finnish Funding Agency for Technology and Innovation (TEKES), Academy of Finland, European Community and Neste Foundation is gratefully acknowledged.

Cambridge, January 2006
Anna Moisala
List of publications


Contents

Abstract.......................................................................................................................... 3
Preface............................................................................................................................. 4
List of publications ........................................................................................................ 5
List of symbols and acronyms ....................................................................................... 7
1 Introduction .................................................................................................................... 8
2 Literature review .......................................................................................................... 10
  2.1 Carbon nanotube structure, properties and applications ..................................... 10
  2.2 Catalytic synthesis of single-walled carbon nanotubes ....................................... 12
    2.2.1 Supported chemical vapour deposition ......................................................... 12
    2.2.2 Gas-phase chemical vapour deposition ......................................................... 14
    2.2.3 Formation mechanisms .................................................................................... 15
  2.3 On-line detection and analysis of single-walled carbon nanotubes ..................... 17
3 Experimental ............................................................................................................... 18
  3.1 Synthesis methods .................................................................................................. 18
  3.2 Characterisation methods ....................................................................................... 22
4 Results and discussion ................................................................................................ 24
  4.1 Synthesis with pre-made catalyst particles ......................................................... 24
  4.2 Synthesis with in situ produced catalyst particles ............................................... 26
  4.3 On-line detection of single-walled carbon nanotube formation .......................... 34
5 Summary ...................................................................................................................... 36
References ....................................................................................................................... 39

APPENDICES

Papers I-VI
List of symbols and acronyms

CO carbon monoxide
CO$_2$ carbon dioxide
H$_2$ hydrogen
L length
N$_2$ nitrogen
N$_2$/H$_2$ mixture of nitrogen and hydrogen in mole component ratio N$_2$:H$_2$ = 93:7
$p$ partial pressure
$T$ temperature
$t_{RES}$ residence time
$Q$ flow rate (gas compound indicated as a subscript)
$\sigma$ geometric standard deviation

CFD computational fluid dynamics
CNT carbon nanotube
CVD chemical vapour deposition
CPC condensation particle counter
DMA differential mobility analyser
ESP electrostatic precipitator
HR-TEM high resolution transmission electron microscopy
HWG hot wire generator
MWCNT multiwalled carbon nanotube
NSD number size distribution
RBM radial breathing mode
SWCNT single-walled carbon nanotube
TEM transmission electron microscopy/transmission electron microscope
1 Introduction

Since their first report in 1991, carbon nanotubes (CNTs) have inspired enormous interest among both experimentalists and theoreticians [1]. Their extraordinary mechanical, electrical and optical properties have suggested many potential technological innovations [2,3]. Due to the high carbon–carbon bond strength, CNTs are one of the strongest materials known in nature and this is why they are used as reinforcing filler in composite materials. Depending on their structure, CNTs are either metallic or semiconducting leading to a wide variety of electronic applications. As a result of their high aspect ratio, i.e. ratio of length to diameter, CNTs have also been considered as one-dimensional systems for fundamental physical studies.

In order to fully exploit their technological potential, CNTs should ideally be synthesised in bulk quantities or with pre-selected properties. The most common CNT synthesis methods are arc-discharge, laser ablation, and chemical vapour deposition (CVD). Arc-discharge and laser ablation methods are based on vaporisation of solid carbon targets at high temperatures. The benefit of these methods is the high crystallinity of the CNT product, i.e. the number of defects in the CNT wall structure is low [4,5]. However, these methods generally produce a complex mixture of carbonaceous materials, including SWCNTs or multiwalled CNTs (MWCNTs), carbon particles, and amorphous carbon, making product purification an unavoidable process step.

The CVD method involves catalytic decomposition of carbon containing precursor molecules on the surface of catalyst particles at moderate temperatures of approximately 600–1200ºC. Conventionally the CVD method is performed in the presence of transition metal catalyst particles supported on a substrate. The CVD method enables the selective production of MWCNTs or SWCNTs, depending on the reaction chemistry and process parameters, such as temperature. Furthermore, pre-determined CNT structures can be formed via catalyst patterning on the substrate [e.g. 6–8].
Alternatively, the catalytic CNT synthesis can be performed in the gas phase without support material [9,10]. The gas-phase CVD method, also called the aerosol or floating catalyst method, also enables selective production of SWCNTs, and the lack of support material reduces the need for product purification. The continuous gas-phase CVD method is a promising route for large-scale production of SWCNTs.

The structure, properties and potential applications of the CNTs have been extensively studied. However, the synthesis methods and, more importantly, the CNT formation mechanisms have not been fully addressed, even though a better understanding would be likely to lead to better control of the CNT product properties and higher CNT production efficiency. Questions that remain to be answered with respect to gas-phase CVD synthesis of SWCNTs include the size of the catalyst particles during SWCNT nucleation and the evolution of the catalyst particle size during SWCNT growth. The information about the SWCNTs’ nucleation temperature and location and growth rate is also still missing as well as what determines the SWCNT length. Furthermore, the cause of aggregation, i.e. bundling, of SWCNTs during the gas-phase synthesis method has not been resolved.

This thesis introduces a novel gas-phase synthesis method for continuous and selective SWCNT synthesis. The method enables careful control of the catalyst particle size at the conditions of the CNT nucleation by introducing pre-made catalyst particles into the reactor where the SWCNTs form. Comparative studies were made with a gas-phase CVD method, where the catalyst particles were obtained by thermal decomposition of catalyst precursors such as ferrocene and iron pentacarbonyl. Both methods were used to study SWCNT formation mechanisms.
This thesis is based on publications I–VI, which are attached as appendices. The novel method for SWCNT formation has been introduced in Paper III and its applicability with various carbon sources is demonstrated in Paper IV. The systematic studies of SWCNT formation in the gas-phase CVD method are presented mainly in Paper VI. The use of nickel acetylacetonate as the catalyst precursor for SWCNT synthesis has been shown for the first time in Paper I. Additionally, this thesis introduces a novel method for the on-line detection of SWCNT formation by a differential electrical mobility analyser (DMA) technique (Paper V). The role of metal nanoparticles in the catalytic synthesis of SWCNTs, based on theoretical calculations of the properties of metal nanoparticles, as well as on a literature survey of the effects of the catalyst particles on the SWCNT synthesis is discussed in Paper II.

2 Literature review

2.1 Carbon nanotube structure, properties and applications

A carbon nanotube can be thought of as a graphene sheet rolled up to form a cylinder, ideally with a hemispherical cap at one end [2,3]. They may be found either as individual cylinders, i.e. SWCNTs, or as two or more concentric cylinders, i.e. MWCNTs, shown schematically in Figure 1. The dimensions of CNTs vary over a wide range. The diameters of SWCNT are usually 0.4–3 nm, and the lengths from few tens of nanometres to several centimetres. Diameters of the MWCNTs can reach tens of nanometres depending on the number of concentric walls. The distance between the concentric walls in MWCNTs is ideally equal to the interlayer distance in graphite (approximately 3.4 Å).
Depending on the manner in which the graphene sheet is rolled up, the arrangement of carbon atoms along the cylinder circumference can be “arm-chair”, “zig-zag” or several different intermediate chiral structures. The arrangement of the carbon atoms in the cylinder is referred to as the chirality and is defined in terms of indices \((n,m)\) illustrated in Figure 2. The chirality of the graphene sheet determines the electrical conductivity of the SWCNT, giving rise to a wide variety of electronic applications. Metallic SWCNTs have equal \(n\) and \(m\). When \(n - m\) is a multiple of three, the SWCNT is a small band gap semiconductor, while all other combinations result in a large band gap semiconductor SWCNTs [11].

![Figure 1. Schematic image of SWCNT (left) and MWCNT (right) (courtesy of Thomas Swan Ltd.).](image)

![Figure 2. Schematic representation of chirality with the \(n,m\) indices presented in parentheses. Metallic and small band gap semiconductor SWCNTs indicated with solid markers and large band gap semiconductor SWCNTs with hollow markers [12].](image)
The mechanical properties of CNTs are due to the high C–C bond strength. Young’s modulus of SWCNTs has been reported to be up to 1.8 TPa, while 1.0 TPa has been measured for MWCNTs [13,14]. The high tensile strength and ability to tolerate large strains make CNTs valuable reinforcement materials for polymer composites. Thermal conductivities of 1750–5800 and 3000 W/mK have been found for SWCNTs and MWCNTs, respectively [15,16]. The resistivity of CNTs is in the range of $10^{-4}$ to $10^{-3}$ Ωcm, while the current density reaches above $10^9$ A/cm$^2$ [17]. Reduction of brittleness combined with high electrical and thermal conductivity also make CNTs interesting additives in ceramic and metal composites [18–23].

Field emitter devices, like, for example, flat panel displays, and electrochemical devices, such as super capacitors and actuators, have been manufactured from arrays of CNTs and take advantage of their electrical properties and either high aspect ratio or large surface area [24–26]. Individual CNTs have been applied as field emission electron sources and tips in scanning probe microscopy [27–30]. Furthermore, nanometre-sized electronic devices, such as field effect transistors and switches, as well as nanotweezers and chemical sensors have been manufactured [31–34].

### 2.2 Catalytic synthesis of single-walled carbon nanotubes

#### 2.2.1 Supported chemical vapour deposition

Supported CVD synthesis of SWCNTs is based on the catalytic decomposition of carbon-containing molecules, i.e. carbon sources, on the surface of catalyst nanoparticles, supported on a substrate [6,8–10,35–40]. Typically, the CVD synthesis is carried out in a step-like fashion. The first step involves the introduction of the catalyst or catalyst precursor on the support. This can be realised, for example, by impregnating the substrate with metal-containing
precursor solution, by sputtering a thin metal layer or by dispersing metal-containing organic carriers on the substrate. The second step is a heat treatment, which results in the thermal decomposition of the metal-containing precursor compounds, fracturing the sputtered metal film, or removal of the organic carrier by combustion, yielding metal or metal oxide particles at the substrate surface. Subsequently, the CNT growth proceeds in the presence of the carbon source or, in the case of metal oxide particles, is preceded by reduction in a hydrogen (H₂) atmosphere.

Carbon-containing molecules, ranging from carbon monoxide (CO), alcohols and fullerenes to aliphatic and aromatic hydrocarbons, can be used as sources of carbon [6,36,41–46]. At low partial pressures of the carbon source, SWCNTs are formed, whereas higher vapour pressures lead to MWCNTs [47]. The use of oxygen-containing species, such as water or alcohol, has been shown to enable the synthesis of high-purity SWCNTs. This was proposed to improve the efficiency of SWCNT production as it prolongs the catalyst lifetime by removing amorphous carbon from the particle surface [8,44].

The method is a batch process, where the CNT growth continues for a set reaction time and the product is collected from a substrate or the reactor walls after cooling. The reaction times vary from minutes to hours and the reactor temperatures are commonly 600–1200 ºC. A list of synthesis conditions applied in the supported CVD method is given in the literature survey of Paper II. At present the supported CVD method enables the formation of ordered free-standing SWCNT mats with thickness up to 2.5 mm and individual SWCNTs as long as 4 cm, at growth rates of 250 and 66 μm/min, respectively [8,46].

The formation of SWCNTs generally takes place when the catalyst particle diameter is less than 5 nm [e.g. 6,47]. Nanoparticles of iron, nickel, cobalt or molybdenum, either alone or as mixtures, are most commonly used as catalysts in CNT production [6,47,48]. The suitability of transition metals as catalysts for CNT synthesis is due to their various physical and chemical properties, including melting
temperature, equilibrium vapour pressure and carbon diffusion rate in the metal, and on their ability to catalyse the carbon source decomposition reaction. The high solubility of carbon in transition metals is regarded as one of the most important factors enabling their use as catalysts in the production of CNTs. The higher yield of CNTs with bi-metallic catalysts has been attributed to particle melting point reduction, increase in the carbon solubility and the formation of well-dispersed metal clusters upon segregation during CNT formation [36,49].

In addition to providing support for the CNT growth, the substrate material, which is most commonly aluminium oxide or silicon dioxide, may be used to inhibit the catalyst particle growth during CVD. For this purpose, the substrates should be porous or interact strongly with the catalyst particles [50]. Two different CNT growth mechanisms have been observed, depending on the strength of catalyst–substrate interaction [51]. The root growth takes place when the interaction is strong and the particle stays pinned at the support surface during CNT growth. Whereas, weak interactions favour the tip growth mechanism, in which the catalyst particles are lifted from the substrate surface by the growing CNT.

2.2.2 Gas-phase chemical vapour deposition

In the gas-phase CVD synthesis both the catalyst particle and the SWCNT formation take place in the gas-phase and the product is ideally collected from the gas phase by aerosol particle collection methods, such as filters and cold collectors [e.g. 10]. The catalyst particles are most commonly formed by thermal decomposition of gaseous organometallic precursor compounds, such as ferrocene, cobaltocene and iron pentacarbonyl [e.g. 9,10]. Solid precursors are vaporised prior to transport into the reactor [41,52]. Liquid precursors can either be introduced as vapour, by way of saturating the carrier gas, or as droplets [9,53,54]. The catalyst precursor vapour thermally decomposes in the heated reactor and subsequently forms the catalyst nanoparticles via nucleation, condensation and
coagulation processes. Additionally, colloidal solutions of metal particles have been used as the catalysts by injecting them into the reactor [55]. Similarly to the supported CVD method, the gas-phase method uses nanometre-sized transition metal particles as catalysts, and the distribution of the SWCNT diameters correlates with the size distribution of the catalyst particles [56].

The selection of appropriate carbon sources is similar for both the gas-phase and supported CVD methods, i.e. acetylene, CO, ethanol, benzene and toluene, etc. have been used [e.g. 10,53,54]. The addition of a sulphur-containing additive, thiophene, has been claimed to promote CNT growth due to a reduction in the melting temperature of the metal–sulphur particles, or modification of the catalyst particle surface [52,55].

One of the main differences between the supported and gas-phase CVD methods is the residence time, which in the gas-phase method is of the order of seconds. Laminar flow reactors are generally used. However, turbulent jets and water-cooling injectors have been used to enhance catalyst and carbon precursor mixing and in an attempt to control the catalyst particle size [10,53].

The gas-phase synthesis of SWCNTs has been coupled on a few occasions with product collection directly from the gas-phase, e.g. with filters and cold collectors [e.g. 9,55]. More commonly the product is collected from the reactor surfaces after cooling. This, however, allows catalyst nanoparticle and SWCNT nucleation and growth at the reactor surfaces in a manner similar to the supported CVD method.

### 2.2.3 Formation mechanisms

The SWCNT formation mechanism suggested by Dai et al. involves the catalytic decomposition of the carbon source on the metal particle surface, followed by the diffusion of the carbon atoms on the surface or through the bulk of the particle to an open edge of the growing CNT [6]. Subsequently, the carbon atoms become
incorporated in the graphene network. This, so called “Yarmulke mechanism”, proposes that in order to minimise the total surface energy, the excess carbon forms a graphene cap on the surface of the metal particle, since graphene sheet has 10–20 times smaller surface energy than most metals. Important features of this mechanism are the strong chemisorption of the graphene cap to the particle in a way that avoids any open graphene edges and the equal diameters of the catalyst particle and the CNT.

A statistical high-resolution transmission electron microscopy (HR-TEM) study, however, has recently revealed that the diameters of the catalyst particles are larger than those of the SWCNTs associated with them. A uniform diameter ratio of catalyst particle to SWCNT of approximately 1.6 was attributed to the geometric constraints of the continuous junction between the SWCNT cylinder and the graphene layer on the surface of the spherical catalyst particle [56]. Additionally, in situ TEM imaging has suggested that surface diffusion of carbon can alone account for the CNT growth and that bulk diffusion of carbon is not necessary [57].

Molecular dynamics simulations by Ding et al. have also shown that nucleation and growth of SWCNTs starts from carbon atoms forming a network at the catalyst particle surface within a temperature range of 600–1600 K [58,59]. Below 600 K, the available kinetic energy of the carbon atoms does not exceed the attraction between the carbon network and the catalyst particle, and SWCNT nucleation is not observed. Instead, the formation of encapsulated metal particles takes place. Above 1600 K, the overwhelming amount of defects in the carbon structure results in the formation of soot-like carbon particles. Maruyama et al. have predicted the formation of various graphene cap structures with diameters slightly smaller than those of the catalyst nanoparticles, depending on the catalyst particle diameter and temperature [60].

In the CVD methods the precipitation of the dissolved carbon cannot account for the centimetre and micrometre length SWCNTs observed, and a continuous feed of carbon atoms to the growing CNT structure
is necessary. According to molecular dynamics simulations, a concentration gradient of carbon in the metal particle works as the driving force for the diffusion of carbon in the metal and, correspondingly, for the continuation of CNT growth as long as a clean catalyst surface is present for the carbon source decomposition [58,59].

### 2.3 On-line detection and analysis of single-walled carbon nanotubes

Only a few measurement techniques have been introduced to study the CNT formation *in situ* during the CVD methods. Optical interference measurements and Raman scattering have been used for the *in situ* study of the CNT growth rate in the supported CVD method [61,62]. As mentioned earlier, the *in situ* TEM measurements gave a valuable insight to the understanding of the supported CVD growth of CNTs [57,63].

Optical emission spectroscopy alone, or coupled with mass spectroscopy, has been used to detect the chemical species involved in the CNT formation [*e.g.* 64,65]. Also gas chromatography coupled to mass spectrometry has been applied to the analysis of the chemical constituents of the effluent in order to study the chemical reactions during CNT growth [53]. Furthermore, thermogravimetric and differential scanning calorimetric measurements have been conducted while performing the CNT growth in the furnace of the thermal analyser [66]. The chemical state of the catalyst particles has been studied with X-ray photoelectron spectroscopy, while X-ray diffraction and UV-Raman spectroscopy have been applied to study the properties of the carbon deposit during supported CVD synthesis [50,67,68].
3 Experimental

3.1 Synthesis methods

Four experimental set-ups were used to synthesise SWCNTs and study their formation mechanisms (Papers I, III-VI). All experiments took place in laminar flow reactors consisting of vertical furnaces equipped with aluminium oxide tubes having inner diameters of 22 mm, and flow control and sample collection devices. The carrier gas flow rates were 300–980 cm³/min. The catalyst nanoparticles were produced either by evaporation and condensation of metal, or by thermal decomposition of catalyst precursors. CO, ethanol or octanol were used as carbon sources. Dilution of the aerosol at the outlet of the flow reactor with 12 l/min ambient temperature nitrogen (N₂) with a porous tube dilutor was applied in the experimental set-ups to avoid particle losses due to thermophoresis and diffusion and to cool the aerosol flow.

The novel method for SWCNT formation in the gas-phase is based on production of size-controlled catalyst nanoparticles via evaporation and condensation of metal vapour prior to their introduction to the furnace where SWCNT synthesis took place (Papers III, IV). In this method, iron or nickel wire was resistively heated to approximately 1400–1500 °C resulting in evaporation of metal from the wire surface. The surrounding temperature ranged from ambient temperature to approximately 400 °C, resulting in a large temperature gradient in the vicinity of the wire surface. Thus, supersaturation of metal vapour was reached rapidly and localised homogenous nucleation of metal clusters took place. Iron and nickel nanoparticles with highly controlled size were formed by this method and introduced to the laminar flow reactor where the conditions of SWCNT formation were maintained.

The resistively heated metal wire was located inside a hot wire generator (HWG) in order to keep the wire in a protective gas environment (Papers III, IV). Two arrangements were used in the experiments. An in situ HWG consisted of the wire inside a small
ceramic tube with an internal diameter of 9 mm, positioned inside the flow reactor (Figure 3). This arrangement allowed adjustment of the location of metal particle introduction within the flow reactor, thus reducing the diffusion losses. Typically, the outlet of the HWG was positioned at a point at which the reactor wall temperature was approximately 400 ºC. An ex situ HWG device was kept outside the flow reactor at ambient temperature and the wire was protected by glass shielding.

Figure 3. Schematic presentation of the experimental set-up for SWCNT synthesis with pre-made catalyst particles, formed by in situ HWG arrangement, and CO as the carbon precursor.
A carrier gas was passed through the HWG for the transport of the metal vapour and, subsequently, the metal particles to the flow reactor. For this purpose either N₂ or mixture of N₂ and H₂ (N₂/H₂, mole component ratio 93/7 %) was used and the flow rate was typically 400 cm⁢³/min. In the flow reactor the metal particle-containing flow from the \textit{in situ} HWG was generally mixed with 400 cm⁢³/min of CO, which served as the carbon source (Paper III). In the \textit{ex situ} set-up the carbon source, which was CO, ethanol or octanol, and the metal particle-containing flow were mixed prior to the introduction to the flow reactor (Paper IV). Alcohols were introduced to the reactor either alone or with an additive, thiophene, by saturating a carrier gas with the corresponding vapours. The partial pressures of the alcohols varied from 9 to 7072 Pa during the experiments. Either SWCNTs or MWCNTs were formed when alcohols were used as the carbon sources. SWCNTs were produced at a reactor wall temperature range of 870–1460ºC and the residence time in the reactor was varied from approximately 4 to 6.5 s.

<table>
<thead>
<tr>
<th>Catalyst precursor Name</th>
<th>Formula</th>
<th>Decomposition temperature [ºC]</th>
<th>Precursor partial pressure [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel acetylacetonate</td>
<td>Ni(C₅H₇O₂)₂</td>
<td>250-300</td>
<td>7</td>
</tr>
<tr>
<td>Copper acetylacetonate</td>
<td>Cu(C₅H₇O₂)₂</td>
<td>286</td>
<td>0.27</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>Fe(C₅H₅)₂</td>
<td>465</td>
<td>0.8</td>
</tr>
<tr>
<td>Iron pentacarbonyl</td>
<td>Fe(CO)₅</td>
<td>350</td>
<td>4 or 0.3</td>
</tr>
</tbody>
</table>

For comparison, SWCNTs were also produced by a conventional gas-phase CVD method, in which catalyst precursor decomposes in the furnace simultaneously with SWCNT formation (Papers I, V, VI). Table 1 summarises the bulk decomposition temperatures and applied partial pressures of the catalyst precursors, which were ferrocene, iron pentacarbonyl, and nickel or copper acetylacetonate. In order to introduce the precursor compounds to the heated reactor, the carrier gas was saturated with the catalyst precursor vapour. The saturation was performed at ambient temperature in the case of ferrocene or iron pentacarbonyl (Paper VI) and at 100 ºC for copper and nickel acetylacetonates (Paper I). Water-cooling injector probes
were used in Paper VI to introduce the catalyst precursor vapours with a carrier gas into the heated gas flow in order to control the precursor vapour heating rate and residence time in the reactor.

As the carrier gases, either \( \text{N}_2 \) or CO, were used at flow rates \( (Q) \) between 300 and 440 cm\(^3\)/min. Additional gas flow of CO, \( \text{N}_2 \) or \( \text{N}_2/\text{H}_2 \) of up to 680 cm\(^3\)/min was added mainly for adjusting the residence time in the reactor. The residence time varied between 0.9 and 6.1 s. The experiments were carried out at reactor set temperatures of 600–1150 °C. Figure 4 presents the experimental set-up for CVD synthesis of SWCNTs from ferrocene and CO as the sources of catalyst particles and carbon, respectively.

![Figure 4. Schematic presentation of the experimental set-up for SWCNT synthesis with in situ formed catalyst particles, from ferrocene decomposition, and CO as the carbon source.](image)
3.2 Characterisation methods

The SWCNT product was collected directly from the gas-phase at the outlet of the reactor either on silver filters (Paper VI) or with an electrostatic precipitator (ESP) directly on carbon coated copper TEM grids (Papers I, III-VI). The morphology and crystallinity of the gas-phase product was determined by TEM and HR-TEM analyses (Papers I, III-VI). Furthermore, electron diffraction was used to study the catalyst nanoparticle crystallinity. Elemental analysis of the metal particles was carried out with an energy dispersive X-ray spectrometer (Paper I).

Additionally, in situ sample collection was performed on silica coated nickel TEM grids by attaching the grid to a stainless steel probe and introducing it to a selected location inside the reactor for 30 s (Paper VI). All of the samples were studied without additional sample preparation.

The aerosol number size distributions (NSDs, Papers I, III, V, VI) of the gas-phase product were measured continuously at the outlet of the reactors with a DMA system consisting of a charger, a classifier and a condensation particle counter (CPC). The DMA technique is based on size-classifying aerosol particles according to their electrical mobility and determining their number concentrations by optical measurements \[ \text{e.g. 69,70}. \] Two different measurement devices were used for NSD measurements in the size ranges of 9.8–400 nm (TSI Inc. DMA 3081 combined with TSI Inc. CPC 3022) and 3–200 nm (modified Hauke [71], combined with TSI Inc. Ultrafine CPC 3027). Since the electrical mobility size measurement is based on an assumption of a spherical particle shape, the NSD measurements of the high aspect ratio SWCNTs or their bundles were coupled with a theoretical approach to the mobility of cylindrical particles (Paper V).
Raman spectroscopy was carried out on samples collected on silver filters (Paper VI). The spectra were collected using two lasers, argon ion (wavelength 488 nm, Omnichrome 543-AP) and helium–neon (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\(^{-1}\).

Fourier transform infrared spectroscopy (FTIR) and gas chromatography (GC) were applied to study the decomposition reactions of the catalyst precursor and carbon source during the SWCNT synthesis (Paper VI). The FTIR measurements were mainly used to study the conversion of CO to carbon dioxide (CO\(_2\)). The FTIR instrument (GASMET DX4000, Temes Instruments) was fitted with a 1 dm\(^3\) flow-through cuvet and the measurement temperature was 150 °C. The GC measurements were conducted at 80 °C with a portable instrument (GC, Photovac VOYAGER, Perkin-Elmer) equipped with photo ionisation detector to study the thermal decomposition of ferrocene.

Computational fluid dynamics (CFD) calculations were performed to characterise the gas temperature and flow velocity profiles during the SWCNT synthesis (Papers I, III, VI). The conservation of mass, momentum and energy together with the buoyancy effects were considered in the axisymmetric calculations conducted with the Stream Wise CFD program \cite{72}. The flow rate and composition, pressure and the measured wall temperature profile were used as input data for the calculations. Furthermore, the mixing conditions of the gaseous species were calculated in Papers I and III, taking into account the transport properties of two gas-phase species and assuming inert wall boundary conditions.
4 Results and discussion

4.1 Synthesis with pre-made catalyst particles

As mentioned earlier, the novel method for SWCNT synthesis developed in this work involves the use of pre-made catalyst particles, which were formed by the resistive heating of a thin metal wire resulting in the evaporation of the metal from the wire surface (Papers III, IV). Due to the exponential dependence of the metal equilibrium vapour pressure on the temperature, the applied voltage and current had a large effect on the evaporation of metal and subsequently on metal particle formation. This method enabled the production of metal particles in the size range of 1–3 nm in the in situ HWG arrangement (Paper III). The metal particle sizes ranged from 1 to 15 nm in the ex situ HWG arrangement depending on the carrier gas flow rate over the heated metal wire (Paper IV). The higher flow rates resulted in larger temperature gradient and consequently in smaller average particle sizes.

The particles produced in the ex situ HWG were found to be non-crystalline, but crystallised after a heat treatment in the reactor (Paper IV). Oxidation of the metal wire as a result of trace oxygen in the carrier gas was observed when N₂ was used as the carrier gas through the HWG and SWCNT formation was inhibited. Thus, N₂/H₂ was used as the carrier gas to avoid particle and wire oxidation (Paper III).

The method was used to produce SWCNTs via the catalytic disproportionation of CO at reactor set temperatures of 870–1460 ºC (Figure 5). A small increase in the SWCNT yield was observed at increasing temperature and the product was typically in the form of agglomerates consisting of few SWCNTs (Papers III). The SWCNT diameters were from 0.6 to 2 nm when CO was the source of carbon, whereas ethanol yielded SWCNTs with diameters of 0.8–2.9 nm. The lengths of the SWCNTs ranged from 30–70 nm (Paper III) to 100–200 nm (Paper IV) with CO and ethanol as the source of carbon, respectively. SWCNTs were formed from ethanol at low partial
pressure \( p_{\text{Ethanol}} = 172.5 \) Pa), while high partial pressure \( p_{\text{Ethanol}} = 7072 \) Pa yielded MWCNTs (Paper IV). High product purity with respect to amorphous carbon was achieved when CO disproportionation was used as the source of carbon (Paper III). In the case of ethanol, the amount of amorphous carbon increased together with decreasing reactor temperature (Paper IV).

Figure 5. TEM (A) and HR-TEM (B) images of SWCNTs produced from CO with pre-made catalyst particles formed by in situ HWG arrangement.

Iron or nickel nanoparticles were produced by this method. The “active” catalyst nanoparticles associated with one end of the SWCNTs were generally below 3 nm in diameter, whereas larger catalyst particles were encapsulated by graphitic carbon. Correspondingly, the efficiency of the SWCNT formation was dependent on the mean catalyst particle diameter. The in situ HWG set-up allowed the best control over catalyst particle formation, i.e. the particle size ranged from 1 to 3 nm, and the ratio of the number of SWCNTs formed to the catalyst particles was close to unity (Papers III, IV). The effect of the particle size was exemplified in the ex situ experimental set-up, in which the catalyst particles from 1 to 15 nm in diameter could be used to form either SWCNTs or MWCNTs from alcohols as the carbon source depending on the synthesis conditions as presented in Figure 6 (Paper IV).
4.2 Synthesis with *in situ* produced catalyst particles

The individual SWCNTs produced by conventional gas-phase CVD ranged from 0.9 to 3 nm in diameter in all experimental set-ups. The lengths of the SWCNT bundles and individual SWCNTs, however, varied depending on the reactor temperature and residence time. When ferrocene was used as the catalyst precursor at $Q_{CO} = 410$ cm$^3$/min the SWCNT bundle lengths ranged from few hundreds of
nanometres at 1150 °C to several micrometres at 800 °C (Paper VI). Figure 7 presents TEM and HR-TEM images of the SWCNTs produced from ferrocene, iron pentacarbonyl or nickel acetylacetonate with CO as the source of carbon.

In the conventional gas-phase CVD, the catalyst particle formation takes place simultaneously with carbon source decomposition and SWCNT formation in the reactor. Ferrocene decomposition (465 °C) and CO disproportionation (preferably 400–900 °C) take place at similar temperatures, which prevents excessive catalyst particle
growth before the disproportionation takes place. The most efficient SWCNT formation from CO in the gas-phase CVD method was obtained with ferrocene as the catalyst precursor at 700–900 °C, i.e. at conditions corresponding to the smallest mean catalyst particle sizes, as described in more detail later, and most efficient CO disproportionation reaction. (Paper VI)

The other catalyst precursors, however, have notably lower decomposition temperatures as shown in Table 1 and the formation of SWCNTs was favoured at high reactor temperatures and flow rates, since in such conditions the catalyst particle growth was minimised. The highest amount of SWCNTs were formed at 1216 °C and $Q_{CO} = 420$ cm$^3$/min in the case of nickel acetylacetonate, while 1300 °C and $Q_{CO} = 910$ cm$^3$/min was found preferable for iron pentacarbonyl. However, increasing the temperature and flow rate simultaneously reduced the residence time in the reactor zone where the temperature is appropriate for CO disproportionation. The residence time was found to be an important parameter in determining the length of the SWCNTs and generally SWCNTs with lengths below 100 nm were formed. (Papers I, VI)

The effect of residence time on the SWCNT length was studied in the ferrocene set-up, either by increasing the flow rate or by varying the location of the injector probe. Increasing the flow rate reduced the SWCNT length as shown in Figure 8. Changing the location of the vapour introduction shortened the residence time before the maximum temperature was reached and altered the temperature gradient in the vicinity of the cooling probe. The heating rate at the point of vapour introduction varied from 12690 to 14040 °C/s at 7.5 and 20 cm, respectively, at 1150 °C [73]. TEM imaging revealed that introducing ferrocene vapour 7.5 cm from the inlet of the reactor at 1150 °C and constant flow rate of $Q_{CO} = 410$ cm$^3$/min resulted in the formation of micrometres long SWCNT bundles. Vapour introduction to 12.5 cm, resulting in a steeper temperature gradient, yielded bundles that were shorter than 100 nm in length. Eventually, only SWCNT nuclei were formed with vapour introduction to 20 cm (Paper VI).
Figure 8. TEM images of the gas-phase product showing the effect of residence time (flow rate) on the length of SWCNTs in the ferrocene set-up A) 3.7 s (Q_{CO} = 410 cm³/min), B) 2.5 s (Q_{CO} = 600 cm³/min), C) 0.9 s (Q_{CO} = 980 cm³/min).

The experiments carried out with ferrocene as the catalyst precursor showed that the SWCNT nucleation and growth had already taken place before the high temperature zone of the reactor was reached (Paper VI). Samples collected in situ in the reactor revealed that SWCNT nucleation took place in the vicinity of the point at which ferrocene was introduced into the reactor. At the set reactor temperature of 1000 °C the “growth window” for SWCNTs was found to range between 891 and 928 °C (Figure 9). The growth rate
of SWCNTs was estimated to be 2 μm/s based on the residence time estimated by CFD modelling and the SWCNT length obtained from TEM imaging.

![Figure 9. TEM images of samples collected in situ at 891 ºC (A) and 928 ºC (B) during conventional CVD synthesis of SWCNTs with ferrocene and CO at set reactor temperature of 1000 ºC.](image)

The in situ sampling also showed that SWCNTs initially grow from individual catalyst particles, but the gas-phase product is always collected as bundles. This is a result of the Brownian motion of the SWCNTs coupled with their large surface area and high number concentration resulting in a high probability of intertube collision (Paper VI). Upon collision SWCNTs probably adhere by van der Waals forces and find the most energetically favourable position of parallel SWCNTs in a bundle, which minimises the total free surface area.

The catalyst particle size depended on the reactor temperature as shown in Figure 10, which presents the catalyst particle size distributions measured from TEM images of SWCNT samples from ferrocene and iron pentacarbonyl set-ups. The decomposition of ferrocene at a constant flow rate of $Q_{CO} = 410$ cm$^3$/min yielded catalyst particles with mean particle diameters of 4.0 and 6.5 nm at 800 and 1150 ºC, respectively. Additionally the higher reactor temperature resulted in narrower particle size distribution, i.e. the
geometric standard deviation ($\sigma$) was 1.6 at 800 °C and 1.4 at 1150 °C. The changes in the particle size distributions together with GC measurements suggested that the decomposition of ferrocene, and correspondingly, the catalyst particle formation and growth, continued throughout the reactor space. On the contrary, iron pentacarbonyl decomposition was more localised to the point of vapour introduction in the reactor due to its lower decomposition temperature and faster decomposition reaction. At 1300 °C ($Q_{CO} = 910 \text{ cm}^3/\text{min}$) the mean catalyst particle size was 5.1 nm and the size distribution was narrow ($\sigma = 1.32$). The catalyst particle size depended also on the precursor partial pressure, the partial pressure of 0.3 Pa yielding smaller particles compared to 4.0 Pa. (Paper VI)

![Figure 10. Catalyst particle NSDs measured from HR-TEM images for conventional CVD with ferrocene or iron pentacarbonyl and CO at different temperatures.](image)

The morphology of the catalyst nanoparticles depended on the gas atmosphere in the reactor. The presence of $H_2$ during ferrocene decomposition resulted in the formation of catalyst particles with larger primary sizes (Paper VI). The particles formed via nickel acetylacetonate vapour decomposition at 1216 °C in a pure $N_2$ atmosphere were faceted with a particle size of 15–30 nm, while spherical particles with average particle size of 12 nm were formed with an equal molar ratio of $N_2$ and CO as shown in Figure 11 (Paper I). In a pure CO atmosphere the formation of particles with a mean
diameter of 4 nm was observed. The reduction in the particle size at an increasing mole fraction of CO was attributed to reduced particle sintering due to the metal particle surface passivation by carbon as a result of the disproportionation reaction at the particle surface.

![TEM images of nickel nanoparticles formed via conventional CVD with nickel acetylacetonate in N₂/CO (A) and N₂ (B) atmospheres at 1216 °C. Insert: ED pattern of the product and ring simulation for nickel.](image)

The amount of non-tubular carbon in the product was typically low, based on TEM imaging. The high sample purity was also clearly indicated by Raman spectroscopy of the product collected from the ferrocene set-up (Paper VI). In the spectra, a strong G-band, which is associated with graphitised carbon, is present, whereas practically no D-band, associated with disordered carbon, was observed (Figure 12). The radial breathing mode peaks were detected between 170 and 198.5 cm⁻¹, corresponding to SWCNT diameters ranging from 1.25 to 1.45 nm based on the expression: $D_{SWCNT} = \frac{248}{\nu}$ nm, where $\nu$ equals the Raman wave number shift [74].
Figure 12. Raman spectra measured at 488 and 633 nm laser wavelengths from filter samples collected during SWCNT synthesis by conventional CVD with ferrocene and CO.

The high sample purity was attributed to limiting the carbon release only to the catalytic CO disproportionation reaction either at the particle surfaces, where the carbon atoms were subsequently introduced to the growing SWCNTs, or at the metal coated reactor walls. The disproportionation reaction at the reactor walls was detected by the FTIR measurements as a background level of 820 ppm of CO$_2$ in the absence of catalyst nanoparticles. The CO$_2$ level in the presence of catalyst particles was approximately 850 ppm. The released CO$_2$ may take part in the removal of amorphous carbon via shifting the equilibrium of the disproportionation reaction toward CO (Paper VI).

The presence of iron and nickel nanoparticles resulted in SWCNT formation, but with copper nanoparticles, from copper acetylacetonate vapour decomposition, only concentric graphitic shells were produced. The properties of copper are different from
iron and nickel, *i.e.* the solubility of carbon in copper and copper melting temperature is lower and the equilibrium vapour pressure is higher. Empty, partially or completely metal filled carbon shells, *i.e.* carbon onion particles, were formed, possibly as a result of copper evaporation through the defects in the graphitic shells. The number of carbon onions increased with residence time and the amount of CO in the reactor. (Paper I)

### 4.3 On-line detection of single-walled carbon nanotube formation

On-line aerosol NSD measurements with the DMA method allowed an unambiguous identification of SWCNT formation. The NSD measurements were carried out continuously at the reactor outlet in all experimental set-ups in active conditions, where SWCNTs formed, as well as in inactive conditions where only catalyst nanoparticles were produced (Papers I, III-VI). Regardless of the SWCNT concentration and morphology, their formation could be detected by NSD measurement as an increase in the mean mobility diameter and as a decrease in the total particle concentration. As an example, the mobility diameter changed from 40 to 100 nm and the concentration decreased from $2.5 \times 10^7$ to $1.5 \times 10^7$ #/cm$^3$, when either catalyst particle agglomerates or SWCNT bundles, respectively, were formed in ferrocene decomposition experiments at 1150 ºC (Figure 13). Furthermore, the NSD measurements enabled the detection of changes in the morphology of the product, *i.e.* reduction of SWCNT and SWCNT bundle length at increasing flow rate and shorter residence time could be detected as a decrease in the mobility particle diameter (Paper VI).
A theoretical approach was developed for the electrical mobility of non-spherical objects to convert the NSD data, which is based on the spherical object shape, to the actual dimensions of the SWCNT product. This approach was tested for SWCNTs formed by the evaporation–condensation method. The geometric mean SWCNT bundle length of 52 nm measured from TEM images ($\sigma = 1.52$) was compared to the measured NSD data (mobility particle size 23 nm, $\sigma = 1.55$), which was converted to the effective sphere diameter. A good agreement ($D = 57$ nm) was found, when the SWCNT bundles were considered to have a perpendicular orientation in respect to the electric field during the measurement.

A mobility size-classified sample was collected at a selected voltage from ferrocene set-up. Also in this case the mobility size measured by DMA could be coupled with the product size observed by TEM. Furthermore, the mobility diameter ratio in active and inactive conditions could be used as a guide to the efficiency of SWCNT formation per catalyst particle. The highest ratio, i.e. the highest efficiency, was found for the in situ HWG set-up based on the DMA measurement. This result was confirmed by TEM imaging.
5 Summary

This thesis presents a new gas-phase synthesis method for the selective production of SWCNTs. The method involves resistive heating of a metal wire generating metal vapour from which nanoparticles nucleate. The nanoparticles were formed in a so-called hot wire generator, which was located either outside (ex situ) or inside (in situ) the flow reactor, in which the conditions of SWCNT formation were maintained. The method allowed the production of pre-formed metal particles with controlled particle size. The best control over the catalyst particle size was achieved by the in situ set-up, in which the catalyst particle size ranged from 1 to 3 nm. In contrast to the conventional CVD, this method yielded SWCNTs with high efficiency, i.e. practically all of the catalyst particles initiated the growth of SWCNTs. CO, ethanol or octanol were demonstrated as suitable carbon sources. The SWCNTs produced from CO ranged from 0.6 to 2 nm in diameter, were generally less than 100 nm long and the sample purity with respect to amorphous carbon was high.

For comparison, conventional CVD production of SWCNTs was carried out using ferrocene, iron pentacarbonyl or nickel acetylacetonate as the catalyst precursors and CO as the carbon source. The decomposition temperature of ferrocene coincides with that of CO and was, thus, found to be the preferred catalyst precursor for SWCNT production. Large differences in the decomposition temperatures led to excessive growth of catalyst particles and fast gas and vapour heating rates were required for SWCNT formation. The length of SWCNTs depended on this residence time and varied from few nanometres (SWCNT nuclei) to several micrometres (SWCNT bundles).

The in situ sampling carried out in the ferrocene set-up revealed that the nucleation of SWCNTs took place before the high temperature zone of the reactor, from individual catalyst nanoparticles. At a set reactor temperature of 1000 °C, the SWCNT nucleation and growth
took place at a temperature range from 891 to 928 ºC. Additionally, the SWCNTs growth rate exceeding 2 μm/s was estimated based on the in situ sampling. According to TEM imaging and Raman measurements the produced SWCNTs had high purity with respect to amorphous carbon.

In the conventional CVD process the catalyst particle formation took place either localised at the point of vapour introduction (iron pentacarbonyl) or gradually throughout the reactor length (ferrocene), and this affected the mean particle size and the width of the size distribution. The geometric mean catalyst particle size in ferrocene experiments in CO atmosphere varied from 4 to 6.5 nm at 800 and 1150 ºC, respectively. The catalyst particle size also depended on other parameters, such as gas atmosphere in the reactor, i.e. the catalyst particle size ranged from approximately 3 to 15–30 nm in CO and N₂ atmospheres, respectively, when nickel acetylacetonate was used as the catalyst precursor. In all experimental set-ups the metal particles above 3 nm in diameter were usually found inactive and encapsulated by carbon.

A schematic presentation in Figure 14 summarises the main gas-phase processes leading to SWCNT formation. We propose that in all experimental set-ups the SWCNT nucleation occurred in four steps: (i) the carbon atoms released by the decomposition of the carbon source diffused into and on to the metal particle surface; (ii) the particle became saturated with carbon; (iii) a graphitic layer formed on the particle surface and (iv) SWCNT nucleated.
Figure 14. A schematic presentation of the main gas-phase processes during SWCNT synthesis using pre-made and *in situ* produced catalyst particles and CO as carbon source.
Additionally, a tool for the on-line gas-phase detection of SWCNT formation, based on differential mobility analyser technology, has been introduced in this thesis. This technique was used in all studied SWCNT syntheses and the SWCNT formation was detected as an increase in the mean mobility particle diameter and as a decrease in the total particle concentration.

References


[12] Adapted from http://www.photon.t.u-tokyo.ac.jp


[73] Brown, D. P. Unpublished data.
