Growth of Carbon Nanotubes on Controlled Sized Metal Nanoparticles by Manipulation of Supersaturation

A thesis presented for the degree of Doctor of Philosophy

by

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Declaration

The work presented in this thesis is, to the best of my knowledge and belief, original except as acknowledged in the text. I hereby declare that I have not submitted this material, either in full or in part, for a degree at this or any other institution.

Phillip Newman

5/11/2013
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<th>Definition</th>
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<tbody>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>$C_h$</td>
<td>Chiral Vector</td>
</tr>
<tr>
<td>$d_t$</td>
<td>Carbon Nanotube Diameter</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>$E$</td>
<td>Transition Energy in the Density of States</td>
</tr>
<tr>
<td>$a_{C-C}$</td>
<td>Nearest Neighbour Carbon-Carbon Distance</td>
</tr>
<tr>
<td>$\gamma_o$</td>
<td>Nearest Neighbour Carbon-Carbon Interaction Energy</td>
</tr>
<tr>
<td>$Y$</td>
<td>Young’s Modulus</td>
</tr>
<tr>
<td>$B$</td>
<td>Bulk Modulus</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transformed Infra-Red</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectroscopy</td>
</tr>
<tr>
<td>FT-Raman</td>
<td>Fourier Transformed Raman</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas Constant</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
<tr>
<td>$dm/dt$</td>
<td>Rate of Mass Loss</td>
</tr>
<tr>
<td>$a$</td>
<td>Unit Area</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass Loss</td>
</tr>
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</table>
\( k_{\text{evap}} \)  
Reaction Rate of Evaporation

\( k \)  
Reaction Rate

\( \kappa_{\text{trans}} \)  
Dimensionless Transmission Coefficient

\( A \)  
Energy Barrier to Nucleation

\( W \)  
Concentration of Possible Growth Sites

\( \Delta G^\# \)  
Energy Barrier

\( \Delta S^\# \)  
Activation Entropy

\( \Delta H^\# \)  
Activation Enthalpy

DCM  
Dichloromethane

MFC  
Mass Flow Controller

\( r_{\text{crit}} \)  
Critical Radius

\( \Delta \mu \)  
Supersaturation

\( \Delta \mu_o \)  
Supersaturation of a Crystal without Edge or Curvature Defects

\( d \)  
Diameter

\( \sigma \)  
Interfacial Energy

\( \alpha \)  
Specific Free Energy of the Whisker Surface

\( V_c \)  
Volume of the Atomic Species Forming the Structure

\( P \)  
Actual Pressure

\( P_s \)  
Saturated Vapour Pressure

\( k_B \)  
Boltzmann’s Constant

\( T \)  
Absolute Temperature

\( V \)  
Growth Rate of Whiskers

\( d_c \)  
Critical Minimum Particle Diameter

\( r \)  
Inner Radii

\( R \)  
Outer Radii

\( J \)  
Steady State Nucleation Rate

\( V_\infty \)  
Isotropic Growth Rate of Crystals
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_0$</td>
<td>Inter-atomic Distance Between Atoms in the Lattice</td>
<td></td>
</tr>
<tr>
<td>$T_{dep}$</td>
<td>Temperature that Defines the Deposition Rate from the Ambient Environment to the Tip Directly</td>
<td></td>
</tr>
<tr>
<td>$C_1$</td>
<td>Concentration of Atoms at the Tip</td>
<td></td>
</tr>
<tr>
<td>$C_{side}$</td>
<td>Concentration of Atoms at the Side</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>Plank’s Constant</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>Length of the Tube</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Average Length of Diffusion of Ad-atoms on the Sidewalls</td>
<td></td>
</tr>
<tr>
<td>$1D$</td>
<td>One-Dimensional</td>
<td></td>
</tr>
<tr>
<td>$2D$</td>
<td>Two-Dimensional</td>
<td></td>
</tr>
<tr>
<td>$\tau_{ind}$</td>
<td>Induction Time</td>
<td></td>
</tr>
<tr>
<td>$G-T$</td>
<td>Gibbs-Thompson</td>
<td></td>
</tr>
<tr>
<td>FAD</td>
<td>Filtered Arc Discharge</td>
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Publications

Abstract

Carbon nanotubes are unique materials that exhibit extraordinary electrical properties which are determined by their chirality and diameter. They have great potential for use in electronic and energy related applications; however, a major roadblock for their practical usage is the limitation in understanding of how synthesis parameters modulate the diameter, length, and the type of carbon nanotubes (SWCNTs or MWCNTs). These parameters can be outlined as the catalyst and support material, the type of carbon precursor, the carbon introduction rate, and growth temperature. Theoretically, the latter two modulate the supersaturation and thus the thermodynamics and kinetics of the nanocarbon nucleation and growth. However, their role on the formation of the nanotube product has never been reported in the literature. The investigation of the role of catalyst, substrate and the supersaturation on the nature of the nanocarbon product is the broad aim of this Thesis.

The first part of this study involved the investigation of metal particles deposited onto silicon surfaces. This was achieved by using various Si surfaces (i.e. smooth Si, smooth oxidised Si and porous Si) onto which metal nanoparticles (Fe and Co) were deposited using the respective metal acetates via a dip coating method. By doing this we have studied the solvent influence on the size of the metal nanoparticles produced. On smooth substrates, single-component solvents give rise to smaller catalyst nanoparticles with much narrower particle size distributions than mixed solvents did. Deposition of the nanoparticles on nano-porous substrates not only further improved the control over the particle sizes but also minimised the negative effects when mixed solvents were used.

Optimisation of the nanocatalyst deposition was then followed into examination of how the controlled nano-gram quantities per unit time of the hydrocarbon precursor material can be introduced in the nanotube growth chamber over a fixed period of time. In doing this we initially examined the evaporation kinetics of ethanol under dynamic gas conditions typically employed for carbon nanotube formation. This was achieved through the use of thermal gravimetric analysis in conjunction with gas IR spectroscopy analysis. The results showed as expected that as the temperature increased there was an increase in the rate of evaporation. In addition, it was
confirmed that the evaporation rate was greatly affected by the carrier gas type with nitrogen causing a higher evaporation rate than argon. The gas-IR analysis also showed that the molecular state of the ethanol changes when in the vapour state giving rise to the formation of monomers, small clusters and large clusters of ethanol.

Next it was important to examine how the ethanol pyrolysis was affected during isothermal decomposition at a series of temperatures > 500 °C i.e temperatures at which the decomposition of ethanol vapours would occur. This experiment was achieved through the use of a flow-through chemical vapour deposition system where the pyrolysis products were characterised by gas IR and by GC-MS analysis. For the first time, it was found that as the temperature increases there is a shift from non-aromatic products (e.g. ethylene) to smaller aromatics (e.g. benzene, toluene) to much larger fused aromatic structures (e.g. pyrene) under conditions typically employed for nanotube formation.

Finally, using the results obtained from the previous sections a series of carbon nanotube growth experiments were designed. This was done in order to examine the effect of carbon introduction rate, i.e supersaturation, on the nucleation and growth of carbon nanotubes and their rates in accordance with classical nucleation theory. Through this we have determined that supersaturation can have a large effect on the nucleation of carbon nanotubes with the nucleation rate increasing quickly as the carbon introduction rate increases. The results and discussion outlined in this Thesis are useful for further optimisation of the nanotube formation process by chemical vapour deposition.
Chapter 1

Introduction to Carbon Nanotubes
1.1 History

Before the major identification of CNTs by Iijima in 1991 \(^1\) it is possible that CNTs were noted as other forms of tubular carbon i.e. carbon whiskers, filaments or fibres. Carbon filaments and fibres were first observed in 1960 when Bacon grew, what he called, graphite whiskers \(^2\). This was followed in 1972 by Koyama who grew “scroll like” graphitic crystals from benzene \(^3\) and was also displayed in Oberlin’s work in 1976 on graphitized carbon fibres \(^4\). However, research into CNTs did not advance until 1991 when Iijima observed multi walled carbon nanotubes (MWCNTs) in the soot from the arc discharge production of fullerenes (Figure 1) \(^1\). These fullerene particles were discovered in 1985 by Kroto \textit{et al.} \(^5\) and were the first of the hollow large carbon clusters to exhibit special properties that had not been observed in other compounds. The half fullerene structure is also used as a representative structure for CNT end caps (See Figure 2 in Section 1.2).

![Figure 1. Left: Standard fullerene structure. Right: Standard MWCNT structure.](image)

By 1993 the synthesis of single walled carbon nanotubes (SWCNTs, Figure 2) on a transition metal catalyst had been achieved using arc discharge synthesis. This was done almost simultaneously by two separate groups, Iijima \textit{et al.} \(^6\) using iron and Bethune \textit{et al.} \(^7\) using cobalt as catalysts. The research and mathematical modelling quickly showed that there would be numerous applications for this new nanomaterial due to their unique mechanical and electrical properties. The CNTs were shown to have variable elasticity and stiffness allowing applications from composite reinforcement to lubrication \(^8\), while electrical properties of CNTs enabled them to...
act as either metallic or semi-conductors depending on their degree of helicity (chirality) \(^{8,9}\). These properties would allow CNTs to be used in a large variety of nano-scale electronic devices as well as electrode and sensor applications \(^{10}\).

### 1.2 Structure of Carbon Nanotubes

Ideally the structure of a CNT consists of a network of hexagonal carbon rings, commonly viewed as a graphene sheet or a honeycomb lattice \(^{11}\). This sheet is rolled forming long tubes capped with a half fullerene (Figure 2) \(^{12}\). Of the two types of CNTs the SWCNTs are the easiest to describe as one rolled-up graphene sheet with a diameter ranging from 1-3 nm and a length of several micrometers \(^{13}\). The second type of CNTs (MWCNTs) has a co-axial arrangement of multiple SWCNTs separated by an interlayer spacing of 0.34 nm as described by the Russian doll model (Figure 2) with diameters ranging from 2 to 20 nm and, like SWCNTs, several micrometers in length \(^{13}\). However, one of the evolving areas of CNT research is growing long CNTs and in 2007 researchers at the University of Cincinnati were able to grow an aligned CNT array of 18 mm in length \(^{14}\).

![Figure 2. Left: Russian doll model of a MWCNT showing the interlayer spacing and diameter approximations. Right: SWCNT structure displaying the half fullerene cap, diameter approximations as well as the length profile of the CNT.](image-url)
1.3 Carbon Nanotube Properties

1.3.1 Structural Properties

Not all CNTs are equal; fine change in the degree of helicity and the number of six
membered rings per turn can cause the conductivity of the CNT to vary between
metallic to semi-conducting. Based on the values of vectors $a_1$ and $a_2$ (Figure 3)
and the integers $n$ and $m$, the structure of CNTs can be broken up into 3 types:
armchair, zig-zag and chiral. When $n=m$ i.e. 10, 10 the structure is called armchair.
The armchair CNTs exhibit electrical properties similar to that of metals. When the
CNTs are characterised by integers of $n \neq m$ the structure is called chiral. Depending
on the values of $n$ and $m$ the electrical properties of chiral CNTs can vary from
metallic to semi-conductive. The third type is called zig-zag CNTs which are
characterised by integers of $n,0$ i.e. 10, 0 and generally have semi-conducting
properties.

![Figure 3. The unrolled honeycomb lattice of a nanotube. The vectors OA and OB define the chiral
vector ($C_h$) and the translational vector (T) of the CNT, respectively. The rectangle OAB'B defines
the unit cell for the CNT. When A is brought to O a CNT is formed. This figure shows an (n, m) = (4,
2) CNT 16. Also to the right of the image there are representations of the (10,0) Zig-zag, (10,5)
Chiral, and (10,10) Armchair CNTs showing how the rolling can affect the overall structure of the
CNT.](image-url)
In other words, the folding of the graphene sheet that determines each of these chiralities (Figure 3), when the folding is determined by the chirality vector, \( \mathbf{C}_h \), which is represented by:

\[
\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n,m) \quad \text{Eq 1}
\]

where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the vectors between zig-zag CNTs and armchair CNTs. The axis of a zig-zag CNTs correspond to a \( \theta = 0^\circ \), whereas the armchair CNT axis corresponds to \( \theta = 30^\circ \) with chiral CNTs being all values in-between i.e. \( 0 < \theta < 30^\circ \). By knowing the integers \( (n, m) \) of a CNT it is possible to determine its diameter, \( d_t \), through the use of:

\[
d_t = \frac{c_h}{\pi} = \sqrt{\frac{3a_{C-C}(m^2+mn+n^2)}{\pi}} \quad \text{Eq 2}
\]

when \( a_{C-C} \) is the nearest neighbour C-C distance (1.421 Å as in graphite), \( c_h \) is the length of the chiral vector and the chiral angle \( \theta \) is determined by:

\[
\theta = \tan^{-1}\left[ \sqrt{\frac{3m}{m+2n}} \right] \quad \text{Eq 3}
\]

This shows that a CNT can be specified by either its \( (n, m) \) indices or equivalently by \( d_t \) and \( \theta \).

1.3.2 Electronic Properties

The nanometre dimensions of SWCNTs together with the unique electronic structure of the graphene sheet they are made from allow SWCNTs to exhibit unique electronic properties. \(^{16}\) Early theoretical calculations \(^{17-19}\) showed that the electronic properties of SWCNTs are very sensitive to their geometrical structure, i.e. chirality. While it is well known that graphene is a zero-gap semiconductor, theory has shown
that SWCNTs have the possibility of being either metallic or semiconducting materials\textsuperscript{15}, depending upon their diameter and degree of helicity as defined by the following rules:

- (n, n) tubes are metals,
- (n, m) tubes with \( n - m = 3j \) (where \( j \) is a non-zero integer) are very tiny-gap (exact value not specified) semiconductors (very close to metallic conductors),
- SWCNTs with \( n - m = 3j + 1 \) are large gap semiconductors (~ 1.0 eV for \( d_{0.7 \text{ nm}} \))\textsuperscript{8}.

These phenomena are due to two main factors: The first being the unique band structure of graphene, which has electronic states that cross the Femi level at two inequivalent points in \( k \)-space\textsuperscript{8}. This occurs because an isolated sheet of graphite is a zero-gap semiconductor whose electronic structure near the Femi energy is given by an occupied \( \pi \) and an empty \( \pi^* \) band. These bands have linear dispersion and meet at the Femi level at the K point of the Brillouin zone\textsuperscript{8}. The second being the quantization of the electron wave vector along the circumferential direction\textsuperscript{8}.

Figure 4. Zone folding scheme representing all CNTs with \( n - m = 3j \) as metallic conducting CNTs and all others as semi-conducting CNTs.
If the zone folding scheme (Figure 4) was followed for all CNTs than anything where \( n - m = 3j \) would all be metallic conductors \(^{20}\), however, due to curvature effects, a tiny band gap opens up when \( j \neq 0 \) which is viewed as peaks in the density of states (DOS) diagram (Figure 5). This means that a more accurate way to describe the electronic properties of CNTs is to state they come in three varieties: large-gap, tiny-gap semi-conductors and zero-gap conductors. Armchair \((n, n)\) tubes are always metallic, independent of curvature, as a result of their symmetry. As the \( d_t \) of the large-gap and tiny-gap CNTs increases the band gap decreases with a \( 1/d_t \) and \( 1/d_t^2 \) dependence. Meaning that for most experimentally observed CNTs, the gap observed in the tiny-gap varieties would be so small that all the \( n - m = 3j \) CNTs could be considered metallic at room temperature. This is due to their thermal energy being sufficient to excite electrons from the valence to conduction band \(^{16,21}\).

![Figure 5](image-url)

Figure 5. Electronic densities of states (DOS) for \((5,5)\), \((7,1)\), and \((8,0)\) nanotubes showing van Hove singularities characteristic of one-dimensional systems. The \((5,5)\) (Bottom) armchair nanotube is metallic for symmetry reasons. The \((7,1)\) (Middle) chiral tube displays a tiny gap owing to curvature effects, but will display a metallic behaviour at room temperature. The \((8,0)\) (Top) zigzag tube is a large-gap semiconductor \(^8\).
The DOS diagrams shown in Figure 5 are representative of the semi conducting and the metallic conducting properties of the CNTs. Each peak in the DOS diagram is known as the van Hove singularities and is representative of where the electrons tend to exist in the orbitals. In the outer singularities of the semiconducting CNT there is a need to transition between peaks as opposed to the metallic tubes where electrons can move more readily. The band gaps (Figure 5) of CNTs can be estimated using:

$$E = \frac{ka_{C-C} - \gamma_o}{d}$$  \hspace{1cm} \text{Eq 4}$$

where $E$ is the transition energy, $a_{C-C}$ is the nearest neighbour C-C distance, $\gamma_o$ is the nearest neighbour C-C interaction energy (2.9 eV $^{22}$), $d$ is the SWCNT diameter and $k$ is an integer constant. The values of $k$ can be 2, 4 and 8 for the 1st, 2nd and 3rd van Hove singularities in semiconducting tubes and 6 and 12 for the 1st and 2nd van Hove transitions in metallic tubes respectively $^{23}$.

### 1.3.3 Mechanical Properties

Carbon nanotubes have been studied from both a theoretical and an experimental viewpoint (Table 1) since Iijima’s discovery in 1991. Early calculation focused predominantly on the theoretical approach. Due to their structure and the C=C bond strength the CNTs demonstrate exceptional mechanical properties $^{24}$. The classical theory of elasticity $^{25}$ defines a series of moduli (i.e. Young’s modulus, Bulk modulus) that characterize the response of a material when subjected to strain which causes its shape and/or volume to change from its equilibrium configuration $^{24}$. Young’s modulus, $Y$, defines the response of the system when strained along a particular axis, while Bulk modulus, $B$, and defines the amount that a material will compress under a given amount of external pressure (Figure 6). So far, most of the focus has been on the Young’s modulus of various CNTs as Bulk modulus experiments have proven problematic due to the way CNTs compress.
First theoretical studies by Robertson et al. \(^{26}\) of the elastic properties of SWCNTs date back to 1992. This group performed calculations on SWCNTs based on various empirical models, as described by Tersoff \(^{27}\) and Brenner \(^{28}\), also to check the reliability of the empirical model a selected subset of CNT calculations were performed by employing first-principles. This established that the strain energy (the energy difference, per atom, of a given CNT and an infinite graphene sheet) is inversely proportional to the squared radius of the CNT, which is consistent with the classical elastic theory \(^{29}\). Concerning Young’s modulus, calculations show that the stiffness of the tube corresponds to the \(C_{11}\) elastic constant of graphite single crystals in the direction of the layer planes (determined experimentally to be 1060 GPa \(^{30}\)).

One other interesting result of these early studies was that both models predicted that the Young’s modulus of the CNT should decrease for very narrow diameter (< 8 Å) CNTs due to the fact that the curvature strain increases (C-C bonds are weakened) as the diameter decreases \(^{24}\).
Table 1. Young’s modulus and Bulk modulus of SWCNTs and MWCNTs from both a theoretical and experimental viewpoint. Their moduli are compared with those of well-known materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (GPa) Experimental</th>
<th>Young’s Modulus (GPa) Theoretical</th>
<th>Bulk Modulus (GPa) Experimental</th>
<th>Bulk Modulus (GPa) Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>27-4150 *31-33</td>
<td>850-1160 *30-34</td>
<td>90 *35</td>
<td>100-350 *36</td>
</tr>
<tr>
<td>SWCNT</td>
<td>200-3000 *31,38</td>
<td>1000-5000 *30-39,40</td>
<td>1-60 **33</td>
<td>100-800 *36</td>
</tr>
<tr>
<td>Steel</td>
<td>186-214 *32</td>
<td>208 *33</td>
<td>160 *32</td>
<td>160 *44</td>
</tr>
<tr>
<td>Diamond</td>
<td>128-1050 *25,26</td>
<td>1050-1219 *47</td>
<td>442 *48</td>
<td>442 *49</td>
</tr>
</tbody>
</table>

*This is dependent upon the wall thickness chosen as some studies use 0.66 Å while others use 3.4 Å as the wall thickness depending upon the model chosen *39.*

**Such a low value was explained by crushing and flattening of the tube cross-section to elliptical one under hydrostatic pressure thus providing additional mechanisms for volume reduction and decrease of the tube elasticity.

Experimental mechanical evaluation of any type of CNT never occurred until 1996 through the work of Treacy *et al.* *31.* This group focused on determining the Young’s modulus of a series of anchored MWCNTs. Their technique employed transmission electron microscopy (TEM) to locate CNTs that were embedded in an amorphous material at one end with the other end exposed to free space. This made it possible to monitor the amplitude of thermally induced oscillations of the free standing tip as a function of the ambient temperature. Which allowed the Young’s modulus to be inferred as long as the CNTs were supposed to behave as hollow cylinders with a given wall thickness. This gave an average value 1800 GPa from 11 CNT samples was obtained with values ranging from 400 to 4150 GPa. The distribution of data is relatively large, reflecting experimental difficulties in obtaining amplitude of oscillations, internal and external CNT diameter, and CNT length. This was however the first evidence that carbon nanotubes possess remarkable elastic properties.

This method was further developed by Wong *et al.* *32* who showed that an Atomic Force microscope (AFM) could be used to bend the CNT laterally and simultaneously measure the restoring force exerted by the CNT on the AFM tip as a function if the CNT deflection (Figure 7). To perform this experiment the CNTs had to be pinned to a substrate, as the deformations inflicted on the CNTs were much
larger than what occur with the thermal oscillation measurements performed by Treacy et al. 31. The experimental approach was validated by first carrying out a test on SiC nanorods which have a known value for Y between 600-660 GPa. Once it was confirmed as a valid testing procedure the CNTs were tested and gave a value for Y of 1280 ± 600 GPa, which was insensitive to CNT diameter. This showed a good correlation with the theoretical work of Treacy et al. 31.

The above experiments proved that CNTs did have remarkable mechanical properties with the highest ever measured Young’s modulus (twice that of SiC nanorods). They were also shown to be remarkably flexible in experiments conducted by Falvo et al. 50 who used an AFM probe to bend MWCNTs laterally until they twisted over themselves and then recover their original configuration without any sign of failure, reinforcing that CNTs have extraordinary resilience, toughness and flexibility.

The first experimental study of the elastic properties of SWCNTs was conducted by Krishnan et al. 38 in 1998. They used the same method described by Treacy et al. 31 with a much larger number of CNTs (27 in total) giving a mean value of 1250 GPa (distribution of 200 – 3000 GPa) which is similar to the value of the C_{11} elastic constant of graphite. This work was continued by Salvetat et al. 33,37 who deposited SWCNTs bundles 37 and individual MWCNTs 33 on an ultrafiltration membrane with holes of approximately 0.4 µm in diameter. They searched for a CNT lying across one of the holes and then apply a load on the suspended length of the CNT using an AFM tip and measure the restoring force as a function of the deflection. Measurements were taken for MWCNTs produced by arc-discharge and Chemical Vapour Deposition (CVD). The arc-discharge MWCNTs gave an average Young’s
modulus of 870 GPa for as-grown CNTs and 755 GPa for CNTs annealed at 2773 K. Although the CVD method was still being developed for CNT synthesis the comparison was made with the arc-discharge CNTs giving an average Young’s modulus of 27 GPa. The measured values while lower than the values obtained by Treacy et al. 31 and Wong et al. 32 are still high compared to other materials except for in the case of the CVD grown MWCNTs which are much lower but have improved with the refinement of CVD systems (Table 1).

1.4 Carbon Nanotube Synthesis

1.4.1 Arc-Discharge

Until recently arc-discharge was the most widely used method for the formation of CNTs from graphite 51 and was the method used for the formation of CNTs by Iijima 1,52. The basic principle of arc-discharge involves the generation of an electric arc between two graphite electrodes in close proximity (< 1 mm apart). The two electrodes are kept in an inert atmosphere (helium or argon) 52,53 and low pressure (between 50 to 700 mbar) (Figure 8). A low-voltage (~ 20 V) direct current (100 A) is used to create a high temperature plasma (of the order of 4000 K) between the two electrodes, known as the inter-electrode plasma 54. This plasma causes the graphite electrodes to sublime and then cool rapidly causing the formation of a mixture of carbon-containing products such as soot, fullerenes and CNTs. This means that post synthesis the product requires separation of the CNTs from the soot and catalytic particles present.
There are two ways that CNTs can be formed in this system. The first is through the evaporation of pure graphite which forms two kinds of products: a deposit which grows on the cathode throughout the arc process and soot on the reactor walls. The deposit consists of a hard grey outer shell with a soft fibrous black core. The outer shell has been shown to consist of fused nanoparticles and MWCNTs while the core consist of one-third graphitic particles and two-thirds MWCNTs. The second way that CNTs can be formed is through the co-evaporation of graphite and a transition metal. This is achieved by drilling a hole in the centre of the anode and filling it with a mixture of metal catalyst and graphite powders or the anode can have the catalyst uniformly dispersed within the rod. This technique allowed the formation of the first SWCNTs. Many different types of metal particles, alloys, and non-metals have been examined for use in CNT synthesis by this method including: Co, Ni, Y, Fe, Lu, Mn, Li, Cr, Zn, Pd, Ag, W, Pt, Sn, Bi, Ge, Sb, Pb, Al, In, Cd, Gd, Hf and some non-metals B, Te, S, Se and Si. The use of different catalyst materials leads to the formation of amorphous carbon, metallic nanoparticles graphene sheets MWCNTs and SWCNTs of different confirmations. Many other factors can have an effect on the confirmation of the CNT including metal concentration, inert-gas pressure, type of gas used, the gas flow rate, and the geometry of the system.
Also diameter distributions of the CNTs are greatly affected by temperature, and the relative amount of metal added to the anode which affects the nucleation and growth of CNTs.

1.4.2 Laser Ablation

Historically, laser ablation was the first method used to form fullerene C60 in the gas phase. The premise behind the laser ablation system is fairly similar to that of arc discharge. Carbon is vaporised from the surface of a graphite disk into a carrier gas (helium or argon), using a focused pulsed laser. The graphite target is placed in the middle of a long quartz tube mounted in a tube furnace (Figure 9). This tube is sealed and heated to 1473 K when the tube is filled with the flowing inert gas and a scanning laser beam is focused on the graphite through circular lens. The laser beam scans across the graphitic surface causing a uniform face of vaporization, allowing carbon species to be picked up by the carrier gas towards a water-cooled Cu collector where CNTs and carbonaceous by-products are formed. This method was modified by Thess et al. by incorporating a second laser pulse to follow the first laser vaporization. This resulted in a more uniform vaporization of the graphite target and breaking up of the larger particles ablated by the first pulse allowing the CNT structure to grow more cleanly (form less soot), hence the purity of the CNT product was increased.

Figure 9. Schematic diagram of a laser ablation apparatus.
As with the arc-discharge method, this method can be controlled through the use of metal catalysts to form either MWCNTs or SWCNTs. In the early experiments conducted with this apparatus it was only possible to synthesis MWCNTs as pure graphite targets were used. The quality of the tubes formed could be varied through manipulation of the reaction parameters, such as type of gas and pressure (like in arc-discharge). SWCNTs were not synthesized until a small amount of transition metal was incorporated into the carbon target, however this method lead to the surface of the graphite target becoming metal rich, lowering the yield of CNTs. To overcome this problem Yudasaka et al. designed a system using two targets: one made of graphite powder the other an alloy of transition metals. The two targets were placed face to face and irradiated simultaneously. As with MWCNTs the yield of SWNTS improved at higher temperatures.

### 1.4.3 Advantages and Disadvantages of Arc-Discharge and Laser Ablation

Nanotubes synthesized by either the arc or laser methods historically have been the first methods through which SWCNTs were synthesized in relatively large (gram) amounts. This leads to most commercially available CNTs being synthesized by the arc-discharge technique for a compromise between cost and quality. However, the designs of these systems inherently lead to problems for large scale synthesis. One of the main issues is that vacuum conditions are required for the arc method which can be difficult and expensive to scale up. Also the graphite targets and electrodes need continuous replacement meaning neither system can run continuously. The main problem, however, is that the extremely high temperatures caused by the interelectrode plasma and the laser source cause these methods not to be viable for the use of CNTs in things such as electronic devices which use Si substrates and cannot withstand these extreme temperatures.
1.4.4 Catalytic Chemical Vapour Deposition

One method that has been developed in an attempt to overcome many of the problems that occur in arc-discharge and laser ablation is catalytic chemical vapour Deposition (CVD). This process makes it possible to synthesize various types of carbon filaments (generic name for elongated structures of diameters less than 100 nm) at temperatures ≤ 1273 K. For the formation of carbon filaments this process dates back to 1890 when French scientists observed carbon filaments growing during experiments which involved the passage of cyanogens over red hot porcelain.82 By the mid-twentieth century, CVD was an established method used for the production of carbon microfibers through the thermal decomposition of hydrocarbons in the presence of a metal catalyst.82 This method involves the decomposition of gaseous or volatile hydrocarbons, facilitated by a transition metal catalyst83,84, a process that has been known for more than 50 years29,85-88. In this context the word catalytic means that the metallic particle is acting as both a site for hydrocarbon decomposition and CNT nucleation89. The first recorded use for this method in the synthesis of CNTs was by Yacamàn et al.90 in 1993, whereby the decomposition of acetylene was done on an iron particle at 973 K. However there have been many early publications dating back as far as 1955 on the formation of multilayered tube like structures of carbon ranging from 10 to 200 nm91-94. This has led to the CVD system being the most widely used for CNT synthesis in modern research. A typical CVD setup involves a flow (tube) furnace which usually operates at atmospheric pressure90,95. Early experiments used a catalyst placed in a ceramic boat which was inserted into quartz-glass tubes and mixtures of acetylene (10 %) and nitrogen (90 %) were passed over the catalyst bed90, to synthesize CNTs at temperatures ranging from 773 to 1373 K. The process usually lasted for several hours. This leads to the formation of four different structural forms of carbon on the catalytic particles: amorphous carbon, filamentous amorphous carbon, graphite layers and MWCNTs (mostly covered with amorphous carbon).
The main advantage of the CVD system, in comparison to arc-discharge and laser ablation, is that it is a scalable technique for the synthesis of CNTs at low temperatures and ambient pressures. In terms of crystallinity (the ratio of defects present to graphitic like CNT) arc and laser grown CNTs have been shown to be superior to CVD grown CNTs (this is primarily true for the growth of MWCNTs but the synthesis of SWCNTs by CVD has crystallinity close to that of the arc and laser methods). However, for yield, purity and overall control of the structure of the CNT product CVD synthesis is superior to both the arc and laser method \(^{96,97}\). This is because the CVD method offers the possibility to harness hydrocarbons in any state (solid, liquid or gas \(^{82}\)), enables the use of many substrates, allows CNTs to be grown in various forms (aligned \(^{98}\), entangled \(^{99}\), straight \(^{100}\) and coiled \(^{101,102}\)) or on predefined sites to form patterns \(^{103,104}\). Also the growth parameters can be controlled, including: the carrier gas flow rate, temperatures of the furnaces and the nature of the metal catalyst. This does however lead to a problem, which is finding a balance between parameters to produce well crystalline CNTs with few defects. Along with this the nature of the support \(^{105,106}\) and the size of the active metal particles \(^{95}\) have a large effect on the CNTs that form. Through the variation of the above parameters different effects can occur in the CNTs. For example when long reaction times are used it is possible to form longer CNTs while if a different metal catalyst is used i.e. cobalt, iron or nickel, there can be an increase or decrease in the amount of amorphous carbon impurity. If different supports are used e.g. graphite or silicon, there can either be an extra build-up of graphitic particles as is the case of
graphite support or a well crystalline CNT could form on silicon substrates 53,101,107-
109.

Due to the many variables that can be manipulated in CVD systems there has been 
many derivatives designed to optimise the CNT synthesis. These include design 
optimisation: plasma enhanced CVD 110,111; laser assisted thermal CVD 112; thermal 
CVD 113; alcohol catalytic CVD 114; High pressure CO disproportionation process 
115,116. Also the mode of growth: vapour phase growth 117,118, aero gel-supported 
CVD 119,120, and the CoMoCat process 121.

In summary arc discharge, laser ablation, and CVD have been employed for the 
synthesis of SWCNTs. These methods originate from the same principle: a carbon-
containing (graphite, hydrocarbon, organometallics etc.) is atomised then quenched 
on a metal catalytic particle (Fe, Co, Ni, Mo etc, or alloys of these) from which 
CNTs grow. Atomisation of graphite requires temperatures of the order of 4000 K 
and hence arcing or laser methods are required. While the carbon compounds used in 
the CVD method can be carried out at much lower temperatures (~ 773 – 1273 K) 
which can be achieved at a much lower cost. However, the CVD tubes are relatively 
defective and have inferior properties compared to those produced by the arc and 
laser methods. Thus, most of the experiments that demonstrate outstanding electric 
and mechanical properties of CNTs have been carried out using non-CVD methods. 
This is not to say that current CVD methods do not have their place because the high 
temperatures used by arc and laser methods make them unsuitable for the deposition 
of CNTs on silicon or metal oxides, which are the basis of smart and functional 
materials.

1.5 Carbon Nanotube Growth Mechanism

So far there is no unified mechanism describing how CNT formation actually occurs. 
This is an area of much conjecture and many theories have been proposed in an 
trypt to solve the problem. Experiments have shown that the width and diameter 
distribution depend on the composition of the catalyst, growth temperature, as well
as hydrocarbon type, gas flow rate and nature of the support\textsuperscript{122-126}. To date the most widely accepted theory is based on the Vapour-Liquid-Solid (VLS) mechanism, which was employed in the sixties by Wagner and Ellis\textsuperscript{127} and later generalised by Givargizov\textsuperscript{128} to explain the formation of Si fibres. Soon after CNT discovery many similarities were noted in the way that CNT and silicon whiskers grew so this method was adopted for characterization of the growth of CNTs and other carbon filaments\textsuperscript{29,85,129-131}. The growth of carbon fibres on metal catalysts has been an area studied for over 30 years and during this time two major models for carbon filaments were developed. The first was the diffusion-limited growth model proposed by Baker \textit{et al.}\textsuperscript{83,129} and then expanded on by Rostrup-Nielsen and Trimm\textsuperscript{131}. This model explains the growth of carbon filaments in four stages:

1. Atoms collide with the surface of the metal and either adsorb or react.
2. Adatoms may be mobile on the surface.
3. Adatoms may either dissolve in the metal or cluster to form islands.
4. Islands may grow by the addition of other adatoms\textsuperscript{131}.

While this model does explain some of the factors about the growth of carbon filaments, it cannot be applied to growth when the metal particle is being transported with the growing carbon\textsuperscript{83,132}. Since this case happens frequently this model must be regarded as limited at best. The diffusion-limited growth model was followed by the development of the Adsorption-diffusion isotherm of the growth kinetics of vapour grown carbon fibres by Tibbetts \textit{et al.}\textsuperscript{85}. This study focused on two main issues: the phase of the catalytic particle and the origin of diffusion. This model suggests that the catalysts phase is austenitic iron. This is an iron carbide (Fe\textsubscript{3}C) phase formed when the system is between the temperature range 1073 K to 1673 K with approximately 0 to 2 % carbon present. Justification for this was reported by Baker \textit{et al.},\textsuperscript{133} who observed that Fe\textsubscript{3}C was not an active catalyst for filament growth. Also the low diffusivity of carbon in Fe\textsubscript{3}C, about $10^{-4}$ of Fe\textsuperscript{134} would limit the growth of carbon filaments to much less than that observed in many experiments\textsuperscript{85}. As Fe\textsubscript{3}C is the predominant phase surrounding austenite it is reasonable to conclude that austenite is the phase used for filament growth. As for the origin of diffusion there
are two possibilities for the driving force i.e. either a temperature or concentration gradient. Due to the fact that this system works with metallic particles in the nanometre range and the fact that, it is in the temperature ranges that filaments grow, carbon supersaturation would occur instantly and therefore it is unlikely that diffusion is driven by temperature. Hence it is logical to assume that the growth of filaments are driven by the carbon concentration gradient.

More recent studies using *in situ* growth under HRTEM have provided more information on the growth of CNTs and carbon filaments. A thorough study was undertaken by Krivoruchko and Zaikovskii which showed that at low temperatures (for CNT growth 873-973 K) Fe, Co and Ni were able to react with amorphous carbon forming a liquid state solution from which graphitic tracks precipitated. A similar study was carried out later by Ichihashi *et al.* and it was observed that, through the use of iron nano-particles, tubulisation of amorphous carbon occurred, however in this study it was stated that the catalyst was in a liquid like quasi solid state. According to the current literature, the mechanism for CNT deposition by CVD is explained by the Vapour-Liquid-Solid (VLS) theory developed to explain the growth of Si nanowires.

The VLS mechanism adapted for CNT growth is described in four steps;

1. diffusion of carbon into the vapour phase,
2. surface reaction at the vapour catalyst interface,
3. bulk diffusion through the catalyst particle, and
4. precipitation at the catalyst-carbon filament interface (Figure 11).

From this it is possible to determine that there are two major steps involved in the formation of CNTs Nucleation and growth.
Figure 11. Schematic illustration of the four recognized steps for CNTs’ growth, based on the VLS mechanism.

It is worth noting that the modified VLS model presumes that the metal particle is unhindered (i.e. not supported). This means that when supported catalyst materials are used a consideration needs to be made for the interaction between the catalyst and the support i.e. whether it’s weak or strong. When the catalyst-support interaction is weak (meaning that metal has an acute contact angle with the substrate) it is thought that the hydrocarbon decomposes at the top surface of the catalyst (Figure 12). The carbon then diffused down through the metal particle and CNTs precipitate out across the bottom of the particle which pushes the catalyst off the support. This reaction is thought to continue providing the top is open for the deposition of fresh hydrocarbon. Once the catalyst particle is completely covered with excess carbon the catalytic potential will cease and growth will stop. This mechanism for weak interaction is commonly known as the “tip-grow model” 82,88,129,139.
On the other hand when the catalyst-support interaction is strong (meaning the metal has an obtuse contact angle with the substrate) the hydrocarbon decomposition will, again, happen at the top surface of the catalyst (Figure 13). However, as the carbon diffusion takes place the precipitation will fail to push the catalyst off the substrate forcing the CNT to form at the apex of the catalyst (the point furthest from the substrate). Firstly, it is thought that the carbon crystallises out as a hemispherical dome (as this is the most stable confirmation of carbon-carbon networks on spherical particles). This then extends up as a seamless graphitic cylinder. Further hydrocarbon deposition takes place on the lower section of the catalyst (closer to the substrate), and the carbon diffuses upwards. This model for strong interaction is commonly known as the “root growth-model”. 

Based on these models it is possible to determine two main areas of conjecture. The first being that the VLS mechanism requires the catalyst to be in a liquid state while in a system that ranges from 873 to 1373 K, and the second the diffusion of the
carbon in the catalyst, and more specifically whether this is occurring via surface or bulk diffusion.

This adapted VLS mechanism, while it discusses many of the parameters of CNT growth correctly, does not explain all of the factors that affect the growth of CNTs. The VLS mechanism relies on the assumption that that the catalyst particle is in a liquid state which can be difficult for some particles as described in the next section. Also it struggles to explain the process by which the carbon diffuses and how the chemical state of the carbon can affect this process. However the main problem that this mechanism fails to address is what processes are involved in the precipitation stage also known as nucleation stage.

In summary, a liquid droplet of metal catalyst possibly a carbide serves as a preferential site for absorption of gas-phase reactant. When supersaturated, it then acts as a nucleation site for crystallization since excess carbon grows out from the saturated particle as a nanotube. This theory predicts that the size of the droplet defines the CNT diameter. There are problems with this concept. The melting points of bulk metals used as CNT catalysts are substantially higher than typical CNT growth temperatures. The latter can be as low as 773 K while the melting points of iron sub-group metal catalysts are > 1723 K. Dissolved carbon atoms can also decrease the melting temperature of the catalyst particle, and an iron carbide particle of 10 nm should theoretically melt at about 1173 K, which is significantly higher than the lowest reported synthetic temperature. Thus, the physical state of the catalyst particle during the synthesis is a subject to controversy as is the role and type of carbide phase.

1.6 Mode of Carbon Diffusion

As it is uncertain that the carbon is actually in a liquid phase during CNT synthesis it is important to know how the carbon diffuses, i.e. whether surface diffusion or bulk diffusion occurs. Early predictions on the mode of carbon diffusion on metal particles were made by Oberlin et al. stating that hollow fibres could only form
via surface diffusion. In 2004 these predictions were supported by Helveg et al., who used High-Resolution Transmission Electron Microscopy (HRTEM) to observe the carbon precipitation in situ during CNT growth. In 2007, these reports were verified by Hofmann et al. in a similar experiment. As these experiments were carried out it was also observed why smaller particles are required for SWCNT synthesis. It was found that small metal clusters (1-2 nm) have steep sharp edges giving them a high catalytic activity allowing them to form the more highly strained SWCNTs. As the cluster size increases the edge sharpness decreases thus reducing the catalytic activity. This means that bigger metal clusters (5-20 nm) tend to form more stable MWCNTs than SWCNTs and really big clusters (> 100 nm) have almost a spherical boundary and do not form CNTs. The in situ experiments that have been conducted show very minimal evidence to confirm that bulk diffusion occurs during CNT nucleation and growth. This led to the conclusion that it is most likely that surface diffusion is responsible for CNT formation. However, others suggested this may vary depending upon the physical state of the metal catalyst.

1.7 Carbon Nanotube Growth

While there is no direct experimental tool to observe how CNTs grow, the process seems to be much easier to understand than nucleation. Once stable CNT nuclei are formed, growth should proceed by the incorporation of the carbon at the root of the CNT. However this is not sufficient to account for the quantity of carbon contained in long bundles. This is due to the fact that the metal particle can only dissolve a relatively small amount of carbon meaning that a secondary source of carbon is required. It was proposed that extra carbon needed for CNT growth can be supplied by continued dissolution-precipitation through the metal particle. Alternatively, there is the possibility of direct insertion of carbon atoms at the nucleation site of the CNT. Finally, carbon can be directly attached to the growing CNT at the tip of the CNT when there is the presence of a catalyst atom. The study of Gavillet et al. determined that the catalyst atoms act as attraction sites for carbon ad-atoms rather than mobile atoms that stabilize the reactive dangling bonds, as previously suggested by Thess et al.
A mechanistic model of CNT growth can be represented in the extrusive-diffusive model (Figure 14). This model has been tested by measuring the relative weight gain of the CNTs (proportional to the average length) with respect to reaction time\textsuperscript{152,153}.

![Diagram of CNT growth](image)

Figure 14. Representation of the extrusive-diffusive model for CNT growth\textsuperscript{153}.

This model relies on a continuous feedstock of carbon atoms to be surrounding the growing CNT as a hot and dense gas, but allows the conclusion that growth occurs in a diffusive regime where the hot gas provides a viscous force which slows the growth of the CNT while the extruding force from the metal particle promotes CNT growth.
Chapter 2

Methods and Controls for Carbon Nanotube Growth
2.1 Optimisation of Carbon Nanotube Synthesis

2.1.1 Common Chemical Vapour Depositions Reactor

The CVD process is very sensitive to the operating conditions. Due to this the main factors involved in the synthesis of CNTs (i.e. hydrocarbon precursor, carrier gas flow rate, the nature, amount and size of the catalyst, the temperature and reaction time) have to be closely monitored to achieve optimal synthesis. Of these the choice and size of the catalyst is highly important as this has been shown to control the diameter distributions of the CNT product.

The CVD method of CNT synthesis has been used as either a single or dual furnace system. A typical dual furnace system involves a low temperature zone (usually < 573 K) where sublimation/evaporation of the catalyst containing precursor (e.g. Metallocenes) takes place and a high temperature zone where hydrocarbon pyrolysis and CNT formation occurs. The hydrocarbon and the catalyst-containing precursor are carried from the low-temperature zone into the high temperature zone by inert gas such as argon or sometimes argon-hydrogen mixtures. Andrews et al. described a similar dual furnace system, which is based on a continuous feed method involving the injection of a catalyst/carbon source solution into a heating chamber. The vaporised reagents in the low-temperature zone are directed by the flowing inert gas into the furnace where CNT nucleation and growth occurs in vapour phase, i.e. without support.
The single furnace system, similar to the continuous feed system described by Andrews et al.\textsuperscript{155} uses a catalyst/carbon source solution where ferrocene is dissolved in alcohol or other liquid hydrocarbon. Evaporation of the solution involves the solution being heated on a hot plate, which then allows the vapour to travel through the tube furnace with assistance from the inert gas flow\textsuperscript{154}. In these experiments there are a number of factors that can be controlled to optimise CNT formation. The carrier gas flow rate can be varied to control the amount of solution or catalyst being transferred into the high temperature zone of the tube furnace. The concentration of the catalyst dissolved in alcohol can also be varied\textsuperscript{156}. This in conjunction with the variation of carrier gas flow rate adds more control to the transfer of precursors into the high temperature reaction chamber. Varying the temperature allows control of the evaporation rates of the catalyst/alcohol solution which adds more control to the
above parameters. For further optimisation of CNT synthesis these parameters can be varied against temperatures set in the main reaction chamber.

While these methods have been proven to be useful for CNT synthesis they do have a major disadvantage which is that they have simultaneous pyrolysis of the hydrocarbon/catalyst vapours and nucleation of CNTs. Literature has shown that the type of pyrolysis products depend upon the pyrolysis temperature which is also true for the CNT product. Due to this, neither of the above set-ups are capable of independent control of hydrocarbon pyrolysis and CNT formation making the two processes mutually dependant.

2.1.2 University of Western Sydney Two-Stage Chemical Vapour Deposition System

To separate the pyrolysis of the hydrocarbon source from the nucleation and growth stages of CNT formation, a novel two-zone CVD system was designed and commissioned at the University of Western Sydney in 2009, in collaboration with the Institute of Physical Chemistry (Bulgaria). Unlike the existing two-zone CVD systems, where the first zone is used to evaporate organometallic compounds, at relatively low temperatures (< 573 K), and the second for the pyrolysis and CNT growth, the new CVD system uses the first zone only for pyrolysis of the hydrocarbon precursor (from 1073 to 1373 K). Prior to each experiment, the catalyst particles are placed in the second zone, on a suitable substrate, and reduced under a hydrogen-argon atmosphere. This setup allows for independent control over the hydrocarbon pyrolysis and CNT nucleation and growth stages. In addition, it has been designed for fast and precise manipulation of supersaturation through variation of either the temperature or concentration of the carbon species during the nucleation and growth stages (Figure 16).

This reactor uses quartz-glass tubes with a 2.5 cm internal diameter and two tube furnaces. The two independent temperature zones can be monitored with individual temperature controllers. Before the entrance of the quartz tube a glass container was
connected to introduce hydrocarbon vapour (Figure 16). The hydrocarbon vapours (usually ethanol vapours) are produced externally by two possible methods:

1. In a heated glass container which is fully immersed in a beaker filled with oil. The temperature of the oil was controlled by a hot stage with a thermocouple.
2. Through the use of a syringe pump which accurately injects precise quantities of ethanol into the system.

In either method the evolving ethanol vapours are carried into the first zone of the CVD by the flowing inert gas (usually argon). At the exit of the system there is an oil trap allowing the system to be sealed. This system can be manipulated to either act as a single or dual furnace system meaning synthesis of CNTs can either occur in the 1st or 2nd stage. Usually, pyrolysis of the ethanol occurs in the first stage which is at high temperatures and CNT synthesis occurs in the second zone where the metal nanoparticles are deposited on Si substrates. During experiments the system can be continuously purged with argon (> 99.999 % purity) or with a 95 % argon 5 % hydrogen mixture. In this case the hydrogen mixed gas was used in order to stop any oxidation of the metal catalyst. The setup has a gas flow control that reads in percentages of gas flow rather than cm³/min and is calibrated for argon, however, a conversion for other gases can be easily made.

Figure 16. Schematic representation of the two-stage CNT reactor.
2.2 The Effect of Reaction Parameters on Carbon Nanotube Synthesis

As mentioned previously many parameters effect the manner in which CNTs grow. These include; nature of the catalyst and support material, carbon source, synthesis temperature, carrier gas flow rate, pressure and reaction time. Also the introduction of heteroatoms, i.e. oxygen, can assist in the cleaning of the catalyst.

2.2.1 Nature of the Catalyst

For the synthesis of CNTs usually nanometre sized metal particles are required to enable the decomposition of hydrocarbons at a lower temperature than their usual decomposition temperature \(^{159}\). The use of transition metals has proven to be useful for CVD as well as arc-discharge and laser ablation giving rise to the thought that there is a similar growth mechanism involved in each of the methods. The most common catalysts are Fe, Co and Ni for two reasons 1) they have a high solubility of carbon at high temperatures and 2) they have high carbon diffusion rates. Also they have high melting temperatures and a low equilibrium vapour pressure which offers a wide range of temperatures for CVD synthesis allowing many different carbon precursors to be used \(^{82}\). Recent work by Ding et al. \(^{160}\) determined that Fe, Co and Ni have larger adhesion strengths to SWCNTs than metals such as Cu, Pd and Au which allows them to be more efficient in forming high curvature CNTs like SWCNTs.

Solid organometallocenes such as ferrocene, cobaltocene, and nickelocene, have also been used to catalyse CNT growth. This is due to their ability to liberate metal nanoparticles \textit{in-situ} and is thought to catalyse the hydrocarbon decomposition more efficiently \(^{139}\). Generally it is thought that the size of the catalyst particle controls the CNT diameter which has led to people attempting to control the catalyst size using methods such as the reverse micelle method (which allow uniform particle size to be synthesised) \(^{161}\). This approach has some limitations due to the heating of the particles in the CNT synthesis, as the temperature increases that particles tend to
aggregate which means there is no longer a uniform particle diameter is maintained 159. Attempts have been made to solve this problem by using porous materials to control the particle diameter 162-166 which will be discussed in the next section.

2.2.2 Nature of the Support Material

In the synthesis of CNTs a variety of catalyst supports have been used such as porous and non-porous substrates. Pores can come in many shapes (cylindrical, spherical, curved, straight etc.) and sizes (micropores < 2 nm, mesopores from 2 to 50 nm and macropores > 50 nm) 167. Many different substrates are used in the synthesis of CNTs including: alumina-silicates (zeolites) 168-171, silica templates 166,172, silicon 173-177, alumina 164,178 quartz 155,179, silicon carbide 180,181, CaCO3 182, and magnesium oxide 183,184. While the support is considered inert in terms of CNT nucleation it has been proven that each catalyst behaves differently according to its interactions with the support (for example if the metal were to form chemical bonds with the support its catalytic potential would cease). This means that for efficient CNT synthesis the interaction between the catalyst and support must be investigated.

It has been reported that some factors about the support material affect the quality of the resulting CNTs. These include; the substrate material itself, the surface morphology, textural properties, chemical state and structure. For example, the fact that zeolite supports with catalysts in their nanaopores have demonstrated high yields of CNTs with narrow size distribution due to the narrow pore distribution within the zeolite structure 171. Alumina supports have been reported to have stronger catalyst support interaction than catalyst-silica interactions. This is thought to allow high metal dispersion with limited aggregation of the metal particles (as aggregation can cause the formation of defective MWCNTs) 185,186. Latest considerations are that the chemistry of the oxide substrates may be playing some role in the growth of the CNTs and may be more important than the metal catalyst, however its full effect is still unknown 187.
2.2.3 Carbon Source and Temperature

A variety of carbon precursor materials have been used for the synthesis of MWCNTs by CVD. These include: ethylene\textsuperscript{175,188}, acetylene\textsuperscript{90,109}, methane\textsuperscript{108,189}, benzene\textsuperscript{190,191}, xylene\textsuperscript{192}, and carbon monoxide\textsuperscript{115} as some of the first precursors for MWCNTs synthesis. Lately MWCNTs were also produced using cyclohexane\textsuperscript{193,194} and fullerenes\textsuperscript{195,196}. The synthesis of SWCNTs by CVD was first reported by Dai \textit{et al.}\textsuperscript{79} in 1996, when they employed the disproportionation of carbon monoxide to carbon and carbon dioxide at 1473 K on a molybdenum catalyst. This work was followed by the synthesis of SWCNTs using the same carbon precursors as MWCNTs, i.e. benzene\textsuperscript{197}, acetylene\textsuperscript{198}, ethylene\textsuperscript{97}, methane\textsuperscript{189}, cyclohexane\textsuperscript{199}, fullerene\textsuperscript{200} etc., on various metal catalysts.

One of the main discoveries for the synthesis of SWCNTs came in 2002 when Maruyama \textit{et al.}\textsuperscript{114} demonstrated that alcohol could be used to synthesise high purity SWCNTs at relatively low temperatures (973 to 1073 K). Ethanol is one of the most popular CNT precursors used in CVD synthesis\textsuperscript{201,202}. It has been observed that when ethanol is used to synthesise CNTs there is a large reduction in the amount of amorphous carbon on the CNT product. This affect has been attributed to the etching of OH radicals\textsuperscript{203} (the ability of the OH radicals to react with amorphous carbon to form carbon monoxide and carbon dioxide). In a subsequent publications, Maruyama \textit{et al.}\textsuperscript{204} showed that intermittent addition acetylene in ethanol CVD assisted the ethanol in preserving the catalyst’s activity and enhance the CNT growth rate.

An important aspect of the carbon precursor is its molecular structure as this can change the morphology of the CNT\textsuperscript{195}. For example, the linear hydrocarbons such as methane, ethylene, acetylene etc., at high temperature under inert atmosphere decompose into atomic carbon or linear dimers/trimers of carbon and in general produce straight CNTs. The cyclic hydrocarbons such as benzene, xylene, cyclohexane, and fullerene tend to give rise to relatively curved/hunched CNTs with bonds between the walls\textsuperscript{195,196}. 

Synthesis temperature is also important. Experiments have shown that low temperature (873 to 1173 K) CVD synthesis of CNTs tends to yield MWCNTs while higher temperatures (1173 to 1473 K) tend to favour SWCNTs formation. This indicates that SWCNTs have a higher energy of formation (most likely due to the small diameters of SWCNTs as high curvature causes high strain energy). This is the main reason why the MWCNTs are easier to grow from most sources of carbon, while SWCNTs grow from selected carbon sources (like carbon monoxide, methane, ethanol etc. which have reasonable stabilities between 1173 to 1473 K). The common carbon sources for MWCNT growth (acetylene, benzene, cyclohexane etc.) tend to be unstable at higher temperatures and can lead to the deposition of large amounts of other carbonaceous compounds that are not CNTs.

2.3 Summary

Based on the above literature study we devolved four key areas that we believe required further analysis. This include: 1) controlling the deposition of metal nanoparticles on Si wafer (Chapter 3), 2) the evaporation of hydrocarbons, this is because our current CVD system can be used through evaporation (Chapter 4), 3) the pyrolysis of hydrocarbons in CVD systems (Chapter 5), and 4) examination of how varied carbon concentrations effects the growth of CNTs. In order to provide some focus in this we have limited our carbon source to only ethanol and this is the only one presented in Chapters 4 and 5.
Chapter 3

Effect of Solvent and Silicon Substrate Surface on the Formation of Metallic Nano Particles
3.1 Introduction

It has been reported that the diameter of the nanotubes is proportional to the diameter of the catalyst nanoparticles (such as iron, cobalt or other transition metals)\textsuperscript{205}. Therefore, to expand the applications of the CNTs in new areas such as semiconductor materials and applications where precise diameter of the CNTs is required, an improved control over the catalyst dimension is necessary\textsuperscript{206,207}.

Coating of substrates by dissolved metal acetates followed by conversion of the acetates to metal nanoparticles is a common method to prepare catalysts for CNT nucleation and growth\textsuperscript{208}. Despite a large amount of work being conducted into the area of nanocatalysts preparation from acetates, on single crystal Si wafer, the control over the particle sizes and their distributions have only been achieved to a limited extent\textsuperscript{209}.

The principal aim of this chapter is to investigate the role of the solvent type and substrate surface on the size uniformity of the nanoparticles produced. In order to achieve narrower particle-size distribution and particle uniformity, we carried out a systematic study into the effect of solvent composition and the Si-wafer substrate porosity on the sizes and size distributions of metal (Fe and Co) nanoparticles. The role of the solvent composition on particle distribution is also investigated and discussed.

3.2 Method

3.2.1 Solution Preparation

Metal acetate solutions were prepared by dissolving anhydrous iron acetate \((\text{CH}_3\text{COO})_2\text{Fe}\) (Aldrich, purity \(\geq 99.99\%\)) or cobalt acetate tetrahydrate \((\text{CH}_3\text{COO})_2\text{Co.4H}_2\text{O}\) (Aldrich, purity \(\geq 98.0\%\)) into both de-ionised water and ethanol or their mixtures. Five stock solutions were produced; two containing pure ethanol or pure water and three ethanol-water mixtures with ethanol: water volume ratios of 3:1, 1:1 and 1:3 with corresponding ethanol: water molar ratios of
approximately 1:1, 1:3 and 1:10 respectively. The metal concentration in the five solutions was kept at a constant of 0.01 wt% metal (the mol percentages for each of these values can be viewed in Table 2). These solutions were allowed to dissolve overnight, after which they were sonicated prior to use, following the procedure previously described \(^{203}\).

Table 2. Respective Mole Percentages of Metals in each Solution

<table>
<thead>
<tr>
<th>Ethanol: Water ratio</th>
<th>Fe (mol %)</th>
<th>Co (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Ethanol</td>
<td>0.00825</td>
<td>0.00782</td>
</tr>
<tr>
<td>E3:1W</td>
<td>0.00699</td>
<td>0.00663</td>
</tr>
<tr>
<td>E1:1W</td>
<td>0.00574</td>
<td>0.00544</td>
</tr>
<tr>
<td>E1:3W</td>
<td>0.00448</td>
<td>0.00425</td>
</tr>
<tr>
<td>100% Water</td>
<td>0.00322</td>
<td>0.00306</td>
</tr>
</tbody>
</table>

### 3.2.2 Preparation of Substrates

Three different substrates were used for coating. These include:

1. p-doped Si (100) wafer single-side polished (Aldrich),
2. p-doped Si (100) wafer single-side polished that had been thermally oxidized at 800 °C in air for 6 h, and
3. mesoporous silicon substrates as supplied by Dr Phil Martin of CSIRO Lindfield, NSW (three different substrates were employed with pore sizes ranging from 3-10 nm), preparation method described elsewhere \(^{210}\).

### 3.2.3 Coating of Substrates

These substrates were submerged, with the polished side up in each of the metal acetate solutions for a period of 10 min. The substrates were then removed from the solution and allowed to air dry for 30 min and then placed in an oven at 70 °C to
complete the drying process. Immediately after drying, the substrates were placed in a furnace at 400 °C in air, for 30 min, to decompose the acetate as well as any other organic residues left. Following these steps, the substrates were placed into a quartz tube furnace and put under a flow of argon and hydrogen mixture at 95 and 5% Ar and H₂ respectively at a flow rate of 350 cm³/min. After purging for 5 min at ambient temperature, the temperature was increased at a rate of 10 °C/ min up to 800 °C. Once temperature was reached the substrates were allowed to anneal for 30 min and then cooled down to ambient temperature while maintaining the reducing atmosphere.

### 3.2.4 Characterisation Techniques

The morphology of coated substrates was examined using a hot field emission gun scanning electron microscope (FEGSEM JEOL JSM 7001FA), with accelerating voltage varied due to differing properties of the samples. Size distribution for metal-containing coatings, after the 800 °C treatment, were determined through the measurement of 15 individual metal particles on each substrate, with error bars being calculated on the basis of standard deviation function:

$$\sigma = \sqrt{\frac{\sum(x-x̅)^2}{n-1}}$$  \hspace{1cm} \text{Eq 5}

where x is the diameter of the individual particle, \(\bar{x}\) is the average particle diameter, and n is the number of measurements.

The interactions between the water and ethanol in solutions with and without metal acetates were analysed by liquid FT-IR and FT-Raman spectroscopy using a Bruker Vertex 70 infrared spectrometer equipped with a FT-Raman attachment and 1064 nm excitation laser. Solutions were placed into a well through which attenuated total reflectance (ATR) FT-IR analysis was performed. For Raman analysis, the liquids were placed in vertical quartz glass cuvettes with rectangular cross sections and coated with a reflective layer at the back of the cuvettes. The vibrational
spectroscopy analysis was done through the collection of 64 scans with a spectral resolution of 2 cm$^{-1}$ (IR) and 4 cm$^{-1}$ (Raman). The interactions between the water and ethanol in solutions were also analysed by Nuclear Magnetic Resonance (NMR) spectroscopy. Samples were prepared by placing the solution into the NMR tube after which a lock solvent consisting of mixed D$_2$O and ethanol, with ethanol being used as an external reference for both the $^1$H and $^{13}$C peak, was placed in the NMR tube using a co-axial insert. The $^1$H and $^{13}$C NMR spectra were acquired using a Bruker 300 MHz spectrometer operating at 300 MHz ($^1$H) and 75 MHz ($^{13}$C). The $^1$H and $^{13}$C NMR spectra were obtained using 32 and 264 scans, respectively.

### 3.3 Results and Discussion

#### 3.3.1 Formation of Metal (Co and Fe) Nanoparticles on Smooth Si Substrates

##### 3.3.1.1 Unoxidised Substrates

For all experiments undertaken with the various Si substrates, the deposition of Fe and Co were carried out using the method described in section 3.2.3.

The oxidative decomposition of the dried acetates at 400 °C produces a continuous metal oxide film on the smooth substrate surfaces. Due to this being a featureless film the images are not shown here. Figure 17 a-e shows SEM images of the Fe nanoparticles, whereas Figure 17 f-j shows the respective Co nanoparticles, formed on smooth p-doped Si (100) wafer after heating at 800 °C in Ar/H$_2$ mixture. It needs to be emphasised that the representative images shown in Figure 17 are not of these metal particles; rather they represent the oxidized metal particles since the oxidation in air cannot be avoided prior to inserting the samples in the SEM examination chamber. The images distinctly show that in all cases the Si surfaces are covered by many clusters of particles rather than a film. This is not surprising as the metal atoms have a much stronger interaction with themselves, than they do with the Si substrate, therefore the metal particle formation occurs by the formation of islands followed by coalescence of metal atoms towards those islands $^{211}$. In other words, during heating at 800 °C in the reducing atmosphere, the featureless oxide film breaks apart, reduces
to the respective metal and the metal atoms agglomerate into clusters containing metal nanoparticles.

Figure 17. Typical SEM images of metal nanoparticles formed according to the method described in section 3.2.3 (Fe from a-e, Co from f-j) using varied ethanol–water volume ratios deposited on non-porous unoxidised Si substrates, a) pure ethanol solutions, b) ethanol-water solution with a 3:1 ratio, c) ethanol-water solution with a 1:1 ratio, d) ethanol-water solution with a 1:3 ratio, e) pure water solutions, f) pure ethanol solutions, g) ethanol-water solution with a 3:1 ratio, h) ethanol-water solution with a 1:1 ratio, i) ethanol-water solution with a 1:3 ratio, j) pure water solutions*. *note the sample measurements for j were taken from the smaller particles that are surrounded by the larger particles. The white scale bar represents 100 nm.
The microscopic examination of the nanoparticles produced by decomposition of acetates dissolved in pure water, ethanol and their mixtures demonstrate that the solvent composition has a major effect on the nanoparticles sizes and their distributions. Fifteen SEM images were collected from different regions of each sample surfaces. All were acquired under the same magnification of 50,000x which were then used for determination of the particle sizes and their size distributions using statistical analysis. The results are summarized in Figure 18.

Figure 18. (a) Average Fe particle sizes and distributions as observed on smooth unoxidised Si substrates, (b) average Co particle sizes and distributions as observed on smooth unoxidised Si substrates.

It can be seen from Figure 18 (a) that Fe particles deposited from pure ethanol have a similar distribution and average particle size to Fe particles deposited from pure water, while the Fe particles derived from the solvent mixtures exhibit not only a wider distribution of the particles sizes but also larger particle sizes. When ethanol is added to water the average Fe particle size increases reaching a maximum at a volume ethanol: water ratio of 75% to 25% is used. The average Fe particle produced
after the oxidation and reduction steps demonstrate both the largest particle sizes and the broadest particle size distributions which range from 106 to 172 nm. However, when pure ethanol is used as a solvent the average particle size decreases to about the size as that observed for pure water solvent (~ 35 to 40 nm). The same trend is observed for the Co particles, although their average sizes are smaller (with particle sizes ranging from 13 to 116 nm) and the respective distributions narrower than those of the Fe particles as seen in Figure 18 (b). Therefore, when smaller metal particles with similar dimensions are needed, it is vital to use pure solvents to dissolve the metal for the coating purposes.

### 3.3.1.2 Oxidised Substrates

Nanoparticles deposited on oxidised Si wafer, prepared using the method in section 3.2.3, displays similar features to those formed on the smooth unoxidised Si. For both the Fe and Co particles derived from their respective acetate in 100 % water solution once again exhibits the smallest average particle size and the narrowest distribution.
A notable difference between particles formed on the smooth unoxidised and oxidised Si wafers is that Co particles display an overall shift to a lower average particle size when particles are formed on oxidised Si wafer. However, within the range of these error values the same cannot be said for the Fe particles on the oxidised Si surface. This trend could likely be attributed to the adhesion of the metal particles to the substrate surface. If the adhesion of the metal particles to the oxidised Si was greater than it was to the unoxidised Si then the coalescence of the metal particles due to heating would be limited, which would lead to the formation of a smaller average particle size and the narrower distribution.\textsuperscript{212}

According to Arcos \textit{et al.}\textsuperscript{213} particles sizes depend on two factors 1) the interaction between the metal and the Si surface, 2) interaction between the metal and the solvent molecules. The results reported here demonstrate that the interactions between molecules of the pure solvents play more important role for the formation of smaller, uniform metallic clusters on smooth Si-substrate surface than the metal-Si

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Figure 19. (a) Average Fe particle sizes and distributions as observed on smooth oxidised Si substrates, (b) average Co particle sizes and distributions as observed on smooth oxidised Si substrates.
interactions. However, the metal-Si interactions seem to provide better control when mixed solvent systems are employed.

### 3.3.2 Formation of Metal (Co and Fe) Nanoparticles on Porous Si Substrates

The nanoporous Si substrates with an average pore size of about 10 nm were produced and supplied by Dr Phil Martin's research group at CSIRO Lindfield, NSW according to a methodology explained elsewhere. For comparison with the particles deposited on smooth Si substrates, the same solvent mixtures were used to dissolve the precursor salts and subjected to the method described in section 3.2.3. Figure 20 shows the effect of the nanoporous substrates on the metal particle size and their distributions. Unlike the nanoparticles deposited on smooth Si surfaces, both Fe and Co particles formed on the nanoporous substrate demonstrates sizes which are comparable with the pore sizes of the substrate with very narrow size distributions. From the magnified version of Figure 20a shown as Figure 20c we can see that the solvent type has much less of an effect on the particle sizes to what was observed on the smooth Si, with the particles are much smaller and demonstrate narrower distributions. The narrowest particle size distributions are observed when using Fe acetate dissolved in either pure ethanol or pure water. Also, as noted with smooth Si the broadest distribution was observed when there was a volume ratio of ethanol: water of 75% to 25% and this distribution gradually decreased as the water ratio was increased. The Co particles once again showed a much lower average particle size and size distribution than what was exhibited on the smooth Si as shown in Figure 20b. From Figure 20d it is evident that Co deposited onto the porous Si is less controlled by the water-ethanol mixtures. These samples show ethanol as the most suitable solvent for Co deposition on the porous or smooth Si wafer.
In summary, control over metal nanoparticles can be achieved either by manipulating the substrate porosity or by manipulating the solvent type. The substrate porosity has a greater effect on the particle sizes and their distributions than the solvent type. However, on smooth Si surfaces the solvent type and composition of the solvent mixture has a stronger effect on the particle sizes and their distribution.
3.3.3 Effect of Water-Ethanol Interactions on the Metal Particle Sizes

3.3.3.1 Water-Ethanol Interactions as a Function of their Volumetric Ratio

The results reported in the previous two sections indicate that the interactions between solvent molecules potentially influence the sizes of the metal particles. In order to understand this we initially analysed the mixed solutions without the influence of metal acetate, then analysed the introduction of Fe acetate in the following sections. The interactions between mixed solvents have been investigated previously by solution state infrared (IR) spectroscopy as shown by Falk \cite{215} and later by Mizuno et al. \cite{216} who employed the IR technique and Nuclear Magnetic Resonance (NMR) to study the changes in hydrogen bonds of water molecules during mixing with ethanol. In particular, the water H-O-H bending mode ($v_2$) was reported as useful for analysis because the $v_2$ band does not overlap with any other bands of ethanol. Unlike the reported studies, we also employed Raman spectroscopy to probe the symmetrical C-H stretches since the latter are far more intense in the Raman spectra than in the corresponding IR spectral data. Moreover, the use of Fourier Transform Raman Spectroscopy based on interferometer minimizes the uncertainty associated with external calibration methods when NMR spectroscopy alone is employed.

Here, we use the H-O-H bending mode and the symmetric C-H stretching mode determined by IR and Raman spectroscopy respectively as tools to investigate the interactions between the molecules in the mixed solvent systems. Figure 21 a shows that bending vibrational band of the H-O-H shifts to high wave numbers linearly from 1630 to 1655 cm$^{-1}$ with increasing ethanol concentration, which indicates an increasing hydrogen-bond strength between the water molecules in the mixture. That is, water molecules are getting closer to each other with the increase of the ethanol concentration. This trend (1645 to 1668 cm$^{-1}$) is consistent with the results reported by Mizuno et al. \cite{216} for ethanol: water mixtures in the absence of metal acetates.

The study of Mizuno et al. also reported significant shifts (up to about 10 cm$^{-1}$) in the C-O-H bending modes and C-O stretching modes of ethanol during mixing with water. While in the current study, the IR spectra for solvent mixtures in the presence of metal acetates show some wave number shifts associated with the C-O-H and C-O
modes, these are within 1-2 cm\(^{-1}\) range only and therefore makes the assignment of theses shifts to such interactions ambiguous. The same holds for the C-H stretching modes, which indicates that some peak shifts are likely but because their IR signatures were rather weak when large amounts of water was added it was difficult to determine their spectral positions unambiguously. This is why the shifts of the C-H stretching modes were determined by Raman spectroscopy.

![Graph showing spectral shifts on water-ethanol mixtures.](image)

**Figure 21.** Spectral shifts on water-ethanol mixtures. a) Infrared wavenumbers shift of the maximum of the water H-O-H bending mode upon addition of ethanol. b) Raman shift of the ethanol C-H symmetric stretches of the methyl group.
Figure 21b shows the Raman shift of the C-H symmetric stretches of the methyl group of ethanol molecules against volume fraction of ethanol in water. The plot shows that the methyl C-H symmetrical stretches shift to higher wavenumbers linearly with increasing water content which suggests an increase in C-H bond strength due to mixing with water. The other moieties (C-H of methylene, C-O stretches, and C-O-H bending modes) of the ethanol molecules do not demonstrate measurable wavenumber or Raman shifts upon mixing with water.

### 3.3.4 Effect of Water: Ethanol Ratio on the Proton NMR Spectra

The molecular water-ethanol interactions in the presence and absence of metal acetates were also investigated by $^1$H and $^{13}$C {H} NMR spectroscopy. The results of these investigations are presented and discussed in this section.

$^1$H NMR spectroscopic investigations for the CH$_2$ and CH$_3$ are summarised in Figure 22. Each of these was useful to provide additional information to the vibrational spectroscopy measurements on the water-ethanol interactions. The $^1$H NMR spectra in Figure 22a show the spectral position for the methyl protons of the CH$_3$ group of ethanol molecules, these demonstrate an up-field shift (from 1.546 to 1.123 ppm, i.e. 127 Hz) when water is added. The methylene protons in the CH$_2$ group shown in Figure 22b also display up-field shifts (from 3.966 to 3.573 ppm, i.e. 118 Hz). The up-field chemical shifts are indicative of progressively greater electron density around the CH$_3$ moieties and to a lesser extent around the CH$_2$ moieties with the addition of water. This gives some indication that self-aggregation of ethanol molecules may occur during mixing with water.
Figure 22. $^1$H NMR chemical shifts of ethanol water mixtures with and without acetate, (a) CH$_3$ range, (b) CH$_2$ range.
The hydroxyl region of the $^1$H NMR spectra as shown in Figure 23a demonstrates two distinct chemical shift regions associated with the two OH groups as observed in the pure solvents (one from ethanol at 5.761 ppm the other from water at 4.697 ppm). Upon mixing, i.e. the addition of water to ethanol, the solution containing 75% ethanol exhibits two peaks, one representative of ethanol the other of water (Figure 23a). However, by increasing the water content, i.e. the 50% ethanol sample, this dual peak collapses into one peak that appears closer to the OH peak of pure water.
Figure 23. Effect of water: ethanol ratios on the $^1$H NMR of the OH groups of ethanol and water with and without iron acetate in the range of 4.3 to 6.2 ppm with the mole ratio of ethanol: water displayed on the figure (a) OH shift without iron acetate, (a) the OH shift with iron acetate.
The most striking observation from the OH spectral region is that when the mixture contains 25 % ethanol in 75 % of water (which is close to 1:1 molar ratio) there are two distinctive OH environments. This suggests the formation of separate ethanol rich and water rich domains in the mixed solvent system. The other ethanol: water ratios exhibit just one peak with spectral position closer to that of the dominant component, water or ethanol respectively. The chemical shift of the hydroxyl proton of ethanol moves to high-field (i.e. proton is shielded) with increasing water concentration. The shielding of hydroxyl proton can be explained in terms of the reduction in the polarisation of the O-H bond and weakening of the hydrogen bonding strength with the addition of water. Also there is a noted downfield shift in the protons of the CH₂ and CH₃ of ethanol this has to be attributed to a shielding effect in these positions i.e. an increase in electron density.

3.3.5 Effect of Metal-Acetate on the Proton NMR Spectra on the Pure and Mixed Solvents

When iron acetate is added, the respective regions in the ¹H NMR spectra demonstrate non-linear shifts unlike the proton NMR spectra of the pure solvents or their mixtures. The spectral positions for the protons of the CH₃ group when mixed with iron acetate are shown in Figure 22a which demonstrates a lower magnitude of up-field shifts (from 1.504 to 1.195 ppm, i.e. 93 Hz) upon mixing with water. Likewise, the methylene protons of the CH₂ group demonstrate lesser up-field shifts (from 3.929 to 3.645 ppm, i.e. 85 Hz) upon mixing with water (Figure 22b). The main spectral difference between the pure solutions and the ones with iron acetate is observed in the solution containing 75 % ethanol and 25 % water (see Figure 22). When iron acetate is added, the methylene proton peaks of mixture containing 75 % ethanol demonstrate a significant deviation from the linear peak-position shift noted in the acetate-free solutions. While this does shift to lower ppm, meaning there is a shielding effect overall, it did not shift to the same extent as it does in the pure solutions. This means, in relative terms, there is a deshielding effect. The possible reasons for these effects will be discussed in the next section.
The OH chemical shifts shown in Figure 23b demonstrate an almost linear change of their spectral positions during mixing. The spectra also demonstrate a single peak only due to the OH moieties of water and ethanol. Interestingly, the peak widths decrease from pure ethanol to pure water, which suggests that pure ethanol-acetate mixture consists of various numbers of ethanol and acetate molecules in cluster where the hydrogen bond strength varies in much wider energy range than that in pure water-acetate liquid clusters. This is a remarkably different behaviour when compared to that in the absence of iron acetate and suggests the formation of more homogeneous chemical regions within the ethanol-water solutions when acetate is present in the mixture.

The $^{13}$C[\(\text{H}\)] spectra, not shown here but are summarised in Figure 24, further shows the results displayed in the $^1$H NMR of the CH$_3$ group of ethanol. The carbon of the pure solutions displays a linear shift (from 18.38 to 18.19 ppm) as the water content increases. In the presence of iron acetate the smaller; shift from 18.31 to 18.14 ppm is observed. This indicates that that addition of acetate negates the effect of mixing ethanol with water. It can also be noted that these two trends almost run in parallel with each other (as seen in the trend lines) (Figure 24). It should be noted that we did not observe any shift in the carbon of the CH$_2$ for $^{13}$C NMR which is consistent with the results of previous studies.$^{216}$.
Figure 24. Carbon-13 proton decoupled NMR spectra of ethanol water mixtures in the CH$_3$ group region of ethanol as a function of water content.

### 3.3.6 NMR and Vibrational Spectroscopy Correlations

The wave number position of the symmetric stretches of the C-H vibrational band of the CH$_3$ group determined by Raman spectroscopy is plotted against volume fraction of ethanol in Figure 21. The stretching band shifts by 6 cm$^{-1}$ to high wave numbers with increasing water content. This blue shift indicates an increase in the electron density of the C-H bond with the increase of the water, which leads us to conclude that partial electron transfer (opposite) occurs from the ethanol oxygen to methyl carbon and methyl hydrogen's. This is the same as what we obtained from the $^1$H NMR and $^{13}$C{H} data shown in Figures 22 and 24.

In the water rich domains, the 22 cm$^{-1}$ blue shift of the O-H bending modes determined by IR spectroscopy indicates that bond strength within the water molecules increases as well. In other words, the storage of the energy within the molecules in the separate domains is a more effective way to minimise the energy of the mixed solvent system than the increase hydrogen bond strength among all molecules in the mixed solvent system. These results support the aggregation of
ethanol molecules as characterised by IR and Raman spectroscopy, previously reported by Hu et al.\textsuperscript{217} as well as Mizuno et al.\textsuperscript{216}.

Our results indicate that in the mixed solvent there is a competitive effect between hydrogen bond formation and micelle formation by self-association. The segregation of the solvents into ethanol-rich and water-rich domains by self-association followed by reduction in the hydrogen bond strength in the water-rich domains seems to minimise the total energy of the system more effectively than the increased hydrogen bond strength in the water-ethanol mixtures as suggested by Mizuno et al. In the ethanol rich domains, the methyl groups are oriented towards each other as shown in Figure 25. As a result, the electron density around methyl and to lesser extent around methylene carbons is increased which leads to stiffening of the C-H\textsubscript{3} and C-H\textsubscript{2} bonds. This is supported by $^1$H and $^{13}$C\textsubscript{[H]} NMR data and by the 6 cm$^{-1}$ blue shift of the symmetric C-H stretched measured by the Raman spectroscopy shown in Figure 21.

![Representative model of the aggregation of ethanol molecules surrounded by water using the 1:1 mole ratio.](image)

Our results, rather surprisingly, demonstrate that the hydrogen bonding interaction between the water and between ethanol molecules weakens due to the formation of the self-associated ethanol aggregates in ethanol-water mixtures. At the same time,
the bond strength within individual molecules increases, though the effect is more pronounced in the water molecules than in the ethanol ones. While our data demonstrate similar trends as those reported by Muzino et al, our interpretation is different. According to them there is a cooperative effect of the hydrogen bonds within the aggregate and the hydrophobic interaction of the alkyl groups. Based on these results we conclude that overall hydrogen bond strength in water domains decreases, whereas the bond strength in the individual water molecules linearly increases with volume fraction of ethanol.

3.3.7 The Effect of Iron Acetate on Micelle Structures and Formation of Nanoparticles

It can be seen from Figures 22, 23 and 24 that the introduction of a small amount of iron acetate lessens the chemical shift due to mixing of water and ethanol. This could be due to three factors: 1) paramagnetic effects within the NMR, 2) a much lower electron density around the methyl and methylene groups, and 3) manipulation of the ethanol and/or water hydrogen bonds due to the iron acetate salt. It has also been found in both the NMR results and Raman spectroscopy results that there is an increase in the C-H bond strength (for both the methyl and methylene groups), an increase in electron density when water is added to ethanol. For the OH chemical shifts in the presence of acetate it can be concluded that the acetate acts as a surfactant giving rise to more homogeneous water: ethanol mixture. In the absence of acetate, the NMR data suggests that there are two distinctive regions; one rich in ethanol and the other rich in water. This allows us to propose a simple model where a possible hydrogen-bond interaction between the OH group of ethanol molecules and water molecules which give rise to a micelle-like structures in the mixed solvent system. When acetate salt is added, the metal ions and acetate ions are predominantly located at the ethanol: water interfaces, thus minimising the interface energy of the system. This model is supported by the observed broadening of the peaks in the OH shift region when metal acetate is added. The observed, up-field shifts in the methyl and methylene regions of the NMR spectra and the higher wavenumber shifts in the Raman spectra also indicate that the bond strength between the carbon and hydrogen atoms in the ethanol molecules increases. That is, the electron density around the
atoms in the ethanol molecules increases. However, the addition of the acetate metal minimises the up-field shifts, i.e., minimises the energy increase of the system due to mixing. This also means that there is a lower electron density surrounding the hydrogen when iron acetate is introduced possibly caused by less ethanol molecules being within the ethanol aggregation (i.e. a smaller micelle like structure) or components of the iron acetate incorporating into the ethanol aggregate causing the aggregate to spread.

Providing there is no or little influence from paramagnetic effects, which we have not been able to discount, these results would identify that there are two possible interactions being caused by the iron acetate: 1) that the iron acetate is interacting with the surface of the micelle like structure or, 2) components of the iron acetate are becoming a part of the micelle like structure without completely breaking the structure just causing it to spread more i.e. causing the electron density to delocalise. While option 2 is plausible in the 75% ethanol solutions it does not account for the linear shift to lower ppm with an increase in water which indicates the micelle structure still exists. Due to this scenario 1 seems more plausible and is confirmed in the OH region of the NMR when comparing the 75% ethanol solution with and without iron acetate. In this position it can be seen that without iron acetate there is a split peak shown indicating the presence of two different chemical species, however, when iron acetate is introduced these peaks merge into one meaning that the two different OH groups are effectively in the same chemical environment.

On the basis of these findings, we propose a simple mechanism for the mixing of water and ethanol when iron acetate is introduced. It is well-known that pure ethanol in water at the molecular level consists of large clusters of ethanol (Figure 25) having varying number of hydrogen bonded molecules. Upon mixing these clusters break apart into smaller self-associated domains: one rich in water and the other rich in ethanol. In the water rich domain, the hydrogen bonds of both the hydroxyl hydrogen and oxygen become stronger monotonically with increasing ethanol concentration. When metal acetate is added, it acts as a surfactant and minimizes the surface energy at the interfaces between the ethanol-rich and water-rich domains. This means the iron (Fe$^{2+}$) is attracted to the overall negative charge on the surface of the ethanol micelle (Figure 26) which caused some destabilisation of the micelle as the Fe$^{2+}$ withdraws electron density from the micelle. The results obtained show that the
hydrogen bonds of the water hydrogen's become stronger with increasing ethanol content of the mixtures. Of course, we have to assume that some of the acetate molecules are dissolved in the water-rich and ethanol rich domains.

![Diagram](image)

Figure 26. Representative model of the aggregation of ethanol molecules surrounded by water with the introduction of metal using the 1:1 mole ratio.

Based on the predicted model (Figure 26) combined with the molar ratios we can start to gain an understanding about how these aggregates may occur in the different ratios of ethanol-water. For the 100 % ethanol and water solutions there are no formal aggregations occurring, which means that when iron acetate is introduced it can easily spread throughout the solution leading to smaller particle sizes. The 75 % ethanol solution has a 1:1 molar ratio of ethanol: water; this means that for every ethanol molecule in an aggregate there has to be a water molecule interacting with it which will force clumping of the Fe around the surface of the micelle structure when they are deposited on the Si surface. The 50 % ethanol solution has a 1:3 molar ratio ethanol: water; which will allow the particles deposited to spread further as more of the Fe can disperse in the water. This trend is further noted in the 25 % ethanol sample, which has a 1:10 molar ratio of ethanol: water and exhibits smaller particle sizes when deposited onto Si.
3.4 Conclusion

In this chapter, the effect of the solvent type and the substrate porosity on the particle sizes and their distributions on atomically smooth and nanoporous Si substrates has been investigated.

1. The dissolution of the metal salts in pure solvents results in smaller particles and narrower particle distributions than the dissolution in mixed solvents. The narrower particle size distribution is achieved when water is used as a solvent of Fe acetate (particle sizes ranging from 25-41 nm).
2. The metal type also has an effect on particle size and size distribution, with Fe particles, overall, exhibiting a larger particle size and size distribution than the respective Co particle. For Co containing particles ethanol gives better control of the metal particle distribution range (ranging from 13 - 20nm)
3. The use of nano-porous Si provides the most effective way to control the deposition of metal nanoparticles. When nano-porous Si is used as a substrate the water solution containing Co-acetate an even narrower particle distribution (ranging from 8.0-14 nm).

We have also demonstrated that use of mixed solvent systems can have a greater negative effect on the size distribution of Fe and Co particles deposited onto Si wafer by employing a dip coating process.
Chapter 4

Rate of Thermal Evaporation of

Ethanol
4.1 Introduction

The evaporation of liquids is a phenomenon that is important in a wide range of physical and chemical processes. The evaporation of ethanol in a carrier gas is important in many chemical reactions and specifically of interest to us in preparing new forms of synthetic carbon such as nanotubes. Evaporation can be carried out in the absence of other gases or, in the presence of a carrier gas, the rate of flow of which can be varied. It is an activation process in that the molecules must gain energy to evaporate, and they must have a source of energy for this process. The amount of this energy may alter the nature of species in the evaporated state and thus the mechanism for the formation of synthetic nanocarbons.

The evaporation mechanism can be understood within the frameworks of transition state theory (TST), which is based on a quasi-equilibrium steady state process. The transition state (or activated complex) is an unstable transitory combination of reactant molecules that occurs at a saddle point on a multi-dimensional potential surface. The saddle point can be described as a maximum in only one dimension (along the reaction coordinate) and minimum in all the others. The reaction rate $k$ is defined as the rate at which the activated complex crosses the saddle point defined by $\Delta G^\ddagger$ in order to form products. The entropy $\Delta S^\ddagger$, and enthalpy $\Delta H^\ddagger$, of activation can also be determined to elucidate mechanism since the energy barrier, $\Delta G^\ddagger$, reflects both enthalpic and entropic contributions. TST leads to the Eyring equation, Eq. 6, which relates the reaction rate, $k$, to temperature, $\Delta G^\ddagger$, $\Delta S^\ddagger$, and $\Delta H^\ddagger$.

$$k = \kappa_{trans} \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \kappa_{trans} \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$$

where $k_B$ is the Boltzmann constant and; $h$ Plank constant and $\kappa_{trans}$ is a dimensionless transmission coefficient (the probability that the activated complex will pass through the transition state to form product). The parameter $k_B T/h$ represents the “speed” of barrier crossing (barrier-crossing frequency).
During evaporation, the reaction rate of evaporation, $k_{\text{evap}}$, can be measured by thermo-gravimetry and should be of zero-order kinetics mechanism provided that the surface area of evaporation remains unchanged $^{224-226}$. However it is possible that the liquid ethanol temperature, nature of the carrier gas, and gas flow rate might affect $\Delta G^\circ$, $\Delta S^\circ$, and $\Delta H^\circ$ if the nature of the activation complex can be dependent on weak interactions of ethanol molecules with each other. In this work, the evaporation rates were measured directly from the weight loss in the linear region of the mass-loss profiles at a set of isothermal temperatures under regulated argon or nitrogen as carrier gases. These measurements were supplemented by spectroscopic analysis of the ethanol molecules in the vapour state and the results are interpreted in terms of collisions of ethanol vapours with carrier gas molecules.

### 4.2 Method

#### 4.2.1 Isothermal Mass-Loss Measurements

The apparatus used for evaporation rate measurement was a NETZSCH Jupiter 449C thermoanalyser equipped with a $10^{-7}$ g resolution balance. A round-bottom cylindrical Al$_2$O$_3$ crucible with a volume of ~ 3.5 ml and an internal diameter of 1.6 cm was used for the evaporation rate measurements. Argon with purity >99.999 % or nitrogen with purity >99,999 % were used as the carrier-gases and the gas flow rate was maintained within ±1 cm$^3$/min for all experiments. Buoyancy effect was minimized by collecting and subtracting the mass-changes of empty crucible under the same temperature, gas type and gas-flow conditions. The evaporation rate measurements of ethanol (sigma aldrich >99.9% purity) were carried out in the isothermal mode having the experimental temperatures of the liquid ethanol varied from 30 to 70 °C increased in 5 °C increments. The ethanol samples were heated from 25 °C to the selected temperature and then the sample was held at the respective temperature, gas type and gas flow rate for 60 min. The experiments were repeated at different gas flow rates, 25, 50, 100 and 200 cm$^3$/min, respectively. For each experiment, the initial mass of the ethanol sample was about 2.5g. The measurement conditions and the mass-losses are summarized in Table 2.
4.2.2 Data analysis

The mass-loss data were analysed in terms of weight, \( m \) plotted against time, \( t \) at constant temperature. The isothermal evaporation rate, \( k_{\text{evap}} \) was determined from the isothermal mass-loss data according to:

\[
k_{\text{evap}} = -\frac{1}{aM} \left( \frac{dm}{dt} \right)_T
\]

Eq 7

where \( dm/dt \) is the rate mass-loss (g sec\(^{-1}\)) with the time per unit area, \( a \) (cm\(^2\)), \( M \) is the molecular weight (g mol\(^{-1}\)). The isothermal molar evaporation rate \( k_{\text{evap}} \) (mol sec\(^{-1}\) cm\(^{-2}\)) for each temperature and gas flow rate was calculated by dividing the experimental mass loss of the sample by the molecular weight of ethanol, 46.068 g mol\(^{-1}\) (assumed to be a monomer).

The \( k_{\text{evap}} \) data were used to estimate the enthalpies and entropies of activation in coordinates given by Eq 8, which relates the reaction rate, \( k \) to temperature \(^{219,220,227}\).

\[
R \left[ \ln \left( \frac{k_{\text{evap}}}{T} \right) - \ln \left( \frac{k_B}{h} \right) - \ln (\kappa_{\text{trans}}) \right] = \Delta S^\neq - \frac{\Delta H^\neq}{T}
\]

Eq 8

where \( \kappa_{\text{trans}} \) is a transmission coefficient usually assigned to unity, i.e. it is assumed that the transition state always proceeds to products and never reverts back to reactants; \( k_B \) is Boltzmann constant; \( h \) is Plank’s constant and \( R \) is the gas constant. Values of both entropic \( \Delta S^\neq \) and enthalpic \( \Delta H^\neq \) contributions to the activation barrier of evaporation, \( \Delta G^\neq \) were determined by linear regression of the left hand side of Eq 8 on \( 1/T \), which gives \( \Delta H^\neq \) from the slope and \( \Delta S^\neq \) as the ordinate intercept.
The determination of the entropy of activation by Eq 8 could be sometimes unreliable because it is calculated from the ordinate intercept by a large extrapolation to $1/T = 0$, i.e. $T = \infty^{228}$. Therefore, if the linear fit of {$[\ln \kappa_{trans} + \ln(k_B/T) + \Delta S^\circ/R]$ vs. $1/T$} is not very good, the error in $\Delta S^\circ$ can be quite large. We propose another linear form of Eq 8, which allows the determination of $\Delta S^\circ$ from the slope rather than from ordinate. It is derived simply by multiplying both sides of the Eq 8 by the temperature $T$:

$$RT \left[ \ln \left( \frac{k_{\text{evap}}}{T} \right) - \ln \left( \frac{k_B}{h} \right) - \ln(\kappa_{trans}) \right] = T \Delta S^\circ - \Delta H^\circ \quad \text{Eq 9}$$

, where the slope of the linear fit in coordinates {$RT[\ln(k/T) - \ln(k_B/T) - \ln(\kappa_{trans})]$ vs. $T$} gives $\Delta S^\circ$, and the ordinate intercept gives $\Delta H^\circ$ (Eq.9).

### 4.2.3 Infra Red (IR) Spectroscopy of Vapour Phase

To investigate the molecular state of the evolving vapours produced during the isothermal heating experiments the thermoanalyser was connected to a temperature-regulated IR gas cell (120 mm long with internal diameter of 8 mm) via 0.8 meter long, heated transfer line (maintained at the specific reaction temperature) with external diameter of ~ 3.5 cm and internal diameter of 2 mm. The IR spectra were collected by a Bruker Vertex 70 IR spectrometer through 1 mm aperture by a liquid nitrogen cooled IR detector. The spectral resolution was 2 cm$^{-1}$. To maintain constant temperature of the ethanol vapours during IR spectra collection, the temperature of the tubular crucible containing liquid ethanol was measured by a thermocouple attached to the bottom of the crucible. Also, the temperature of the vertical tube of the thermogravimeter was measured and manipulated with the help of another thermocouple. Three more thermocouples were used to monitor and regulate the temperature along the length of the gas transfer line and the IR gas cell. During each
of the isothermal heating step the evolving ethanol vapour were collected by the stream of the regulated gas and transferred to the IR gas cell. To stabilize the ethanol evaporation rate the samples were maintained at the respective temperature and gas flow rate for 20 min and then the IR spectra were collected. For example, when the evaporation was carried out at 30 °C, the temperature was maintained along the pathway of the evolved vapours; from the cylindrical crucible through the transfer line and during IR spectra acquisition. Similarly, when the evaporation temperature was 70 °C, the temperature along the pathway and in the IR gas cell was maintained at 70 °C.

4.3 Results and Discussion

4.3.1 Isothermal Evaporation Rates as a Function of Temperature, Gas Type and Carrier Gas Flow Rate

Table 2 shows the mass-loss data collected during isothermal heating at nine different temperatures ranging from 30 to 70 °C varied by 5 °C increments and four gas flow rates ranging from 25 cm³/min to 200 cm³/min and two carrier gases: nitrogen and argon. The isothermal measurements showed that after initial temperature and mass-loss fluctuations, which typically lasted less than 25 min, the sample temperature remained constant (±0.1 °C) and the weight of the sample decreased linearly at each temperature and gas flow rate. The linear mass-loss indicates that the evaporation of ethanol follows expected zero-order kinetics during the final stages (30 – 35 min) of the isothermal experiments. The temperature and gas-flow rate dependencies of the respective molar evaporation rates $k_{evap}$ in units (mol sec$^{-1}$ cm$^{-2}$), calculated according to Eq 7, are shown in Figure 27a and b.
Table 3. Total mass-losses during the last 30 min of 60 minute isothermal heating.

<table>
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<tr>
<th>Temp (°C)</th>
<th>Temp (K)</th>
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<th>50 cm³/min</th>
<th>100 cm³/min</th>
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<td></td>
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<td>N₂</td>
<td>Ar</td>
<td>N₂</td>
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</tbody>
</table>

Figure 27. Temperature and gas-flow rate dependence of the evaporation coefficient, \( k_{evap} \). (a) In argon. (b) In nitrogen.

As evident from Figure 27 and Table 3 the nature of the purging gas has a strong effect on the evaporation process. At 30 °C \( k_{evap} \) in nitrogen is approximately ten times higher than that in argon, but the difference decreases with the temperature and
at 70 °C the gas type has minimal effect on the evaporation rates (Table 3). Gas flow rate also modulates the evaporation process, though its effect is more significant for the evaporation in argon. Lower argon flow rates (25 cm³/min and 50 cm³/min) have little effect on the \( k_{\text{evap}} \) in the whole temperature interval, but increase of the gas flow rate to 200 cm³/min increases \( k_{\text{evap}} \) significantly. While similar tendency is observed for evaporation in nitrogen, the effect is much smaller compared to the evaporation dynamics in argon. This suggests that ethanol evaporation kinetics is modulated not only by the temperature and gas flow rate but also by the nature of the carrier gas.

4.3.2 Values of \( \Delta H^\# \) and \( \Delta S^\# \) from \( k_{\text{evap}} \)

The \( k_{\text{evap}} \) data were used to estimate the enthalpies and entropies of activation by linear regression in coordinates given by Eqs 8 and 9. The temperature/gas flow rate dependencies of the activation parameters are shown in Figure 28a–c and the results are summarized in Table 4. The comparison between the activation parameters derived according to these two equations demonstrates small differences between \( \Delta S^\# \) and \( \Delta H^\# \) values and therefore we conclude that the errors related to the determination of \( k_{\text{evap}} \) from the isothermal mass-loss data are small.
Figure 28. Determination of the activation parameters of evaporation as a function of temperature and gas flow rate in argon (a and b) and in nitrogen (c and d). a The $\Delta H^\circ$ was determined from the slope whereas $\Delta S^\circ$ from the Y-intercept according to Eq 8. b Activation entropy of evaporation, $\Delta S^\circ$ determined from the slope, whereas $\Delta H^\circ$ from the Y-intercept according to Eq 9. c Activation entropy of evaporation in nitrogen, $\Delta S^\circ$ determined from the slope, whereas $\Delta H^\circ$ from the Y-intercept according to Eq 8. d Activation entropy of evaporation in nitrogen, $\Delta S^\circ$ determined from the slope, whereas $\Delta H^\circ$ from the Y-intercept according to Eq 9.
Table 4. The activation parameters, $\Delta H^\ne$ and $\Delta S^\ne$, for the ethanol evaporation as function of the gas flow rate.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Gas flow rate cm$^3$/min</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ar</td>
<td>N$_2$</td>
<td>Ar</td>
<td>N$_2$</td>
</tr>
<tr>
<td>$\Delta H^\ne$ (kJ/mol)</td>
<td></td>
<td>81.7 ± 0.6</td>
<td>27.3 ± 1.0</td>
<td>74.3 ± 0.7</td>
<td>27.2 ± 0.8</td>
</tr>
<tr>
<td>$\Delta S^\ne$ (J/mol K)</td>
<td></td>
<td>-112.7 ± 2.0</td>
<td>-272 ± 3.5</td>
<td>-134.6 ± 2.0</td>
<td>-270 ± 2.5</td>
</tr>
</tbody>
</table>

According to Eq 8

The activation enthalpy of evaporation in argon values show that at 30 °C the increase of the gas flow rate from 25 cm$^3$/min to 200 cm$^3$/min decreases $\Delta H^\ne$ from ~82 kJ/mol to ~48 kJ/mol, respectively. Simultaneously, the $\Delta S^\ne$ at 25 cm$^3$/min gas flow rate is negative (-113 J/mol K,) and becomes more negative (-209 J/mol K) with the increase of the gas flow rate to 200 cm$^3$/min. Unlike in argon, the activation parameters of evaporation in nitrogen show no significant variations on the gas flow rate (Table 4 and Figure 28c and d). The enthalpy barrier to evaporation in nitrogen is much lower than that in argon and is ~27 kJ/mol, whereas $\Delta S^\ne$ is about -270 J/mol K. The three times lower activation enthalpy to evaporation, $\Delta H^\ne$ could explain the much higher rates of evaporation in nitrogen at 30 °C than in a dynamic argon atmosphere. The large negative entropies of activation, suggest a more ordered structure in transition state than in the ground state for both nitrogen and argon and also more so at high gas flow rates in argon. In other words, the system loses degrees of freedom with the increase of gas flow rate possibly due to restriction of the motion of the ethanol molecules in the transition state. This rather surprising result is
understandable if in the transition state, two or more molecules are strongly bound to each other via intermolecular interactions differently than in the liquid state.

4.3.3 Energy Barrier to Evaporation, $\Delta G^\#$

The free energies of activation, $\Delta G^\#$ in the temperature interval 30 – 70 °C were determined according to $\Delta G^\# = \Delta H^\# - T\Delta S^\#$. In nitrogen, the gas flow rate has a little effect on the energy barrier to evaporation (Figure 29 a). At 30 °C the increase of the nitrogen rate from 25 cm$^3$/min to 200 cm$^3$/min slightly decreases $\Delta G^\#$ from ~109.6 kJ/mol to ~ 108.6 kJ/mol. However, under the same conditions the argon purging rate modulates the energy barrier to evaporation significantly. At 30 °C, the decrease of the $\Delta H^\#$ (favourable) is almost fully compensated by the negative and decreasing $\Delta S^\#$ (unfavourable) for purging rates up to 100 cm$^3$/min (Figure 29 b). That is, the contribution of $\Delta S^\#$ to $\Delta G^\#$ effectively cancels out the energy benefit from the decreasing activation enthalpy. The increase of the argon gas flow rate to 200 cm$^3$/min, however, reduces $\Delta G^\#$ due to significant decrease of the $\Delta H^\#$, which offsets the increase of the barrier to evaporation due to the large negative $\Delta S^\#$. Thus, the height of the energy barrier to evaporation at 30 °C drops from ~116 kJ/mol at 25 cm$^3$/min to ~111 kJ/mol at 200 cm$^3$/min. Under these conditions the evaporation rate increases nearly six times; from 0.3724 mg/min to 2.1345 mg/min (Table 3). The effect of the gas flow rate on $\Delta G^\#$ diminishes with temperature and at 70 °C the increase of the argon gas flow rate from 25 to 200 cm$^3$/min increases the rate of evaporation by 50 percent; from 16.74 mg/min to 23.87 mg/min (Table 3). The same holds for evaporation in nitrogen, where the evaporation rate increases from 19.70 mg/min to 23.42 mg/min with the increase of the gas flow rate from 25 cm$^3$/min to 200 cm$^3$/min. Also at 70 °C the nature of the carrier gas and the gas flow rate have minor effect of energy barrier to evaporation; in argon $\Delta G^\#$ is ~ 120.4 kJ/mol whereas in nitrogen $\Delta G^\#$ is ~120.5 kJ/mol at 25 cm$^3$/min and ~119.7 kJ/mol and ~119.5 kJ/mol at 200 cm$^3$/min, respectively.
Figure 29. Free energy barrier to evaporation, $\Delta G^\circ$ as function of the gas flow rate (25 – 200 ml/min) and temperature (30 – 70 °C). (a) In nitrogen. (b) In argon.

4.3.4 Entropy-Enthalpy Compensation in Argon

Figure 30a shows an excellent linear correlation of $\Delta H^\circ$ on $\Delta S^\circ$ with the argon gas flow rate. Such linear correlations have been observed for many reactions and are referred to as the enthalpy–entropy compensation effect or iso-kinetic or iso-equilibrium relationships\textsuperscript{229,230}. However, these relationships need to be treated with
caution since it has been argued that this is an artefact of correlated errors in a measurement because these quantities are mutually dependent, both being derived from the same kinetic data. Indeed, many examples have been found to be statistical artefacts, but some are genuine signatures of the perturbations in molecular characteristics. Moreover, near ambient temperature enthalpy-entropy compensation are considered a typical feature of bimolecular associations arising from weak intermolecular interactions, particularly hydrogen bonding.

![Enthalpy-entropy compensation in argon](image)

**Figure 30.** Enthalpy-entropy compensation in argon. (a) Relationship between $\Delta H^\circ$ and $\Delta S^\circ$. Compensation temperature, $T_c$, determined from the slope is 0.5K. (b) Relationship between $\Delta H^\circ$ and $\Delta G^\circ$ at two temperatures and four argon gas flow rates.

*Krug et al.*, proposed two tests to determine whether statistical factors or thermodynamic factors are responsible for the entropy-enthalpy compensation effect.
They argued that; (i) if there is substantial difference between the mean experimental temperature and the correlation temperature $T_c$ determined from the $\Delta H$ on $\Delta S$ slope and (ii) if there is a linear relationship between $\Delta H$ on $\Delta G$ then the compensation effect has physical-chemical origin. Figure 30a shows that the first of these two criteria is met ($T_c = 0.5$ K and average experimental temperature 323 K). While the second (i.e. linear dependence of $\Delta H^\circ$ on $\Delta G^\circ$) is also met (Figure 30b), the changes in the slope indicate different compensation mechanisms as function of temperature and argon gas flow rate. It seems that the most probable basis for the decreasing $\Delta H^\circ$ and negative $\Delta S^\circ$ shown in Figure 30a is the formation of tightly bound transition state consisting of two or more ethanol molecules. However, there is a limit to the cost in entropy, which is reached when the bond strength in the transition state is large compared to thermal energies and at this point the slope of the $\Delta H^\circ$ versus $\Delta G^\circ$ should increase as the bond strength in the transition state increases, as it does (Figure 30b). This also suggests that most likely result of the lowering of the free energy barrier to evaporation in argon is due to changes in the transitional state configuration resulted because of interactions with argon molecules.

4.3.5 Molecular State of Ethanol Vapours

Gas-phase analysis of ethanol vapours by infrared spectroscopy (IR) is useful to characterize the interactions between the evolving ethanol molecules and the carrier gas molecules. While supersonic expansions could be a way of studying this here we use a thermogravimetric-evolving gas analysis method because we want to investigate the molecular state of the ethanol vapours under evaporation. Supersonic measurements would not give this information. The information is relevant in order to optimize conditions for CNT formation from ethanol whereas studies under supersonic conditions will provide information on possible aggregates present at conditions not applicable to CNT synthesis.

The IR gas cell, the transfer line, and the thermogravimeter output line were equipped with individual tubular heating elements and temperature controllers. This set-up allowed the entire path from the thermogravimeter to the spectrometer gas
cell, which is 0.8 m long, to be maintained at the same temperature at which the evaporation took place. Figure 31a-d shows the IR absorption spectra of evolving species in the wavenumber interval 3800 – 3100 cm\(^{-1}\) which is usually interpreted in terms of alcohol cluster size and isomerism. There are four main contributors appear in the hydroxyl stretching region of vapours produced at 30 °C; a narrow band centred at 3676 cm\(^{-1}\) consisting of multiple absorptions, a sharp weak band at ~3568 cm\(^{-1}\), broader bands at approximately 3474, 3402, 3253 and a shoulder at ~3225 cm\(^{-1}\) (Figure 31a). Comparison with investigations by supersonic jet expansion of noble gas-alcohol vapour mixtures allowed the assignment of these bands to ethanol monomers, and small-sized and large-sized ethanol clusters 243,245,246. By analogy, we assign the band centred at ~ 3670 cm\(^{-1}\) to conformation isomers. These conformers are designated trans- and two equal gauche-ethanol conformers distinguished by the orientation of the hydroxy group relative to the methylene group 247-249. The narrow band centred at 3568 cm\(^{-1}\) is assigned to hydrogen-bonded dimer, while the broad contours centred at about 3474, 3402, 3253 cm\(^{-1}\) to higher hydrogen-bonded linear aggregates, whereas broad shoulder at 3225 cm\(^{-1}\) to large ethanol aggregates consisting of cyclic tetramers. The increase of the gas flow rate from 25 cm\(^3\)/min to 200 cm\(^3\)/min has a strong influence on the intensity of the OH stretches. While the bands corresponding to ethanol monomers (centred at about 3670 cm\(^{-1}\)) are unchanged, the intensity and the area of the bands characteristic of the hydrogen-bonded species are significantly increased. In particular, the intensity of the vibrations centred at about 3253 cm\(^{-1}\) nearly triples when the gas flow rate is increased from 25 cm\(^3\)/min to 200 cm\(^3\)/min. With the increase of the temperature to 70 °C, however, the intensity of the broad contours attributed to the hydrogen-bonded aggregates significantly decrease but unlike the ethanol vapours produced at 30 °C, the change of the argon gas flow rate from 25 to 200 cm\(^3\)/min has no measurable effect on their intensities (Figure 31c).
Figure 31. Infrared spectra of the evolving ethanol vapours as function of gas type, gas flow rate and temperature. For comparison, the respective vibrational features of liquid ethanol are also shown. (a) OH stretches at 30 °C in argon. (b) OH stretches at 30 °C in nitrogen. (c) OH stretches at 70 °C in argon. (d) OH stretches at 70 °C in nitrogen.

The IR spectra of the ethanol species evaporated in flowing nitrogen at either 30 °C or 70 °C are dominated by the monomer species (Figure 31b and d). While some hydrogen-bonded aggregates are also present in the vapour phase, the increase of the gas flow rate or temperature cause no measurable change in the vibrations related to the aggregate species. In summary, the IR spectroscopy shows that at 30 °C not all evolving ethanol molecules in argon are monomers, some of them make new intermolecular bonds with other ethanol molecules and form various hydrogen-bonded aggregates. However, this is not the case during evaporation in nitrogen where the amount of hydrogen-bonded aggregates is small and does not depend on the gas flow rate. At 70 °C, neither the gas flow rate nor the nature of the carrier gas has a major effect on the molecular structure of the evaporated ethanol molecules.
4.3.6 Ethanol–Carrier Gas Interactions

The data reported here represents the energy barrier to the evaporation, $\Delta G^\circ$ of a system operating under gas flow conditions that is under conditions of kinetic control, not a classic thermodynamic equilibrium. Within the frameworks of TST there are three major factors that determine the rate of reaction; (i) the concentration of the activated complex (the species of the transition state), (ii) the rate at which the activated complex breaks apart and (iii) the way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products. The outcome depends on factors such as the relative kinetic energy, relative orientation and internal energy of the molecules.

From the kinetic and spectroscopic measurements we can deduce several characteristics of the transition state through which the ethanol molecules must pass. During evaporation in argon, both the gas-ethanol interactions and the temperature are evaporation rate determining. At 30 °C the negative $\Delta S^\circ$ (unfavourable) indicate a transition state that is more ordered than the reactants due to association of two or more ethanol molecules. In turn, the restriction of the relative motion of the molecules is accompanied with increased hydrogen bond strength, hence $\Delta H^\circ$ decreases (which is favourable). The stronger the intermolecular bonds that hold the activated complex together, the larger should be the restriction of overall motion. Thus, the two activation parameters, $\Delta H^\circ$ and $\Delta S^\circ$ can be traded off against each other because the strength of hydrogen bonds, near room temperature, is comparable to the thermal energies that oppose them. When the argon gas flow rate is increased from 25 cm$^3$/min to 200 cm$^3$/min the favourable decrease of the enthalpy brought about by structural tightening is only partially compensated for by the unfavourable entropy, with a net result of a more favourable free energy barrier to evaporation. It seems therefore that the argon-ethanol interactions stabilize the transition state and thus a significant amount of ethanol is evaporated as hydrogen-bonded ethanol aggregates. Clearly at 30 °C under nitrogen, energy from collisions can more readily be transferred than from argon and also that the activated complex in nitrogen more readily breaks apart to form the products. The latter is supported by the much higher evaporation rates at 30 °C in nitrogen and the fact that the ethanol vapours in
nitrogen consist of mostly single ethanol molecules. The enthalpy barrier to evaporation in nitrogen is also much lower than in argon which is supportive. However it would be speculative here to discuss whether this was due to the nature of the bonding in nitrogen but not in argon, due to collision geometry, or differences due to different transfer of vibrational, rotational or translational energy. In contrast, during evaporation at 70 °C the hydrogen bond strength is comparable to the thermal energy, i.e. the restraint is effectively opposed by the motion in both nitrogen and argon. At that temperature, the gas flow and the nature of the carrier gas have little effect on the energy barrier to evaporation.

One area where our results may be useful is in CNT synthesis where ethanol is used as the carbon source. Successful CNT synthesis requires optimization of catalyst, growth temperature, residence time in the reaction zone, and gas flow conditions. The latter is of particular interest, since a change of the evaporation conditions of ethanol may influence the amount of ethanol vapours and thus carbon flux during CNT formation and hence type of nanotubes. Therefore the results reported here may be useful for the optimization of pyrolysis conditions of ethanol vapours for CNT synthesis where similar conditions are used.

4. Conclusions

The activation parameters for ethanol evaporation in dynamic gas atmospheres, argon and nitrogen, as a function of the gas flow rate have been determined experimentally from the temperature dependence of the evaporation rate constants in the temperature interval 30 – 70 °C. At 30 °C the evaporation rate of ethanol in nitrogen is ten times higher than in argon independent of flow rate. At 70 °C the nature of the gas has no significant effect on the evaporation rates.

The changes of the argon gas flow rate can manipulate the $\Delta G^\ddagger$ barrier to evaporation in terms of the relative contributions of the enthalpy and entropy of activation to $\Delta G^\ddagger$. In nitrogen, the changes of the gas flow rate have minimal effect of the energy barrier to evaporation.
In argon at different temperatures, the change in thermodynamic functions at different flow rates is attributed to different evaporation mechanisms due to interactions of ethanol with argon molecules. This is supported by simultaneous gas infra red spectroscopy, which demonstrated changes in concentrations of linear and cyclic hydrogen bonded ethanolic aggregates under the different evaporation conditions.
Chapter 5

Pyrolysis of Ethanol Vapours
Investigated by Gas FT-IR and GC-MS Techniques
5.1 Introduction

Ethanol is used widely in research and industry including: biofuels\(^{252}\), renewable energy\(^{253}\), and CNT synthesis\(^{254}\). In all of these areas it is important to investigate the pyrolysis and decomposition products of ethanol at elevated temperatures. Specifically, in CNT research using CVD synthesis, the carbon precursor that is introduced (e.g. ethanol) is expected to decompose on the surface of a catalyst particle\(^{254}\). While there have been extensive studies conducted on the influence of CVD parameters such as type of catalyst, temperature, and pressure\(^ {114,255-257}\), there has been evidence presented that alcohols can undergo decomposition before interaction with the catalyst (i.e. only under elevated temperature)\(^ {258}\). This means that in addition to the standard CVD parameters it is important to understand the products that are formed under thermal decomposition without the use of a catalyst. Generally decomposition products in these systems are analysed using FT-IR, GC-MS or a combination of the two. The previous GC-MS studies on the thermal decomposition of ethanol in an argon atmosphere have reported the formation of CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), C\(_2\)H\(_2\), H\(_2\) and soot\(^ {252}\). While FT-IR results have confirmed the presence of similar species\(^ {259}\).

Previous studies on the pyrolysis and decomposition of ethanol in argon have used a variety of techniques, primarily shock tube chambers\(^ {253}\) and flow through systems (e.g. CVD). While shock chambers have been used for the simulated decomposition of many hydrocarbons\(^ {253,260}\) the technique does not show a true representation of what could form under decomposition conditions associated with the synthesis of CNTs by CVD. This means that for a useful simulation of a CVD system the ethanol needs to be fed through a tube furnace at high temperatures and then the decomposed species to be analysed by extraction of the gasses downstream.

In this study, we will investigate the specific fragmentation and recombination reactions of ethanol molecules during pyrolysis in dynamic and isothermal heating using argon and argon/hydrogen atmospheres within the heated zone of the thermal decomposition of ethanol in the heated zone of a CVD system. The characterisation of the organic molecular species will be carried out using Fourier Transform infrared (FT-IR) and Gas Chromatography-Mass spectrometry (GC-MS) techniques in the absence of radical trappers (which are frequently used). This information will allow
us to develop a model for the different chemical products formed after the decomposition of ethanol under an argon and argon/hydrogen atmosphere, similar to conditions that will be used in CVD synthesis of CNTs.

5.2 Method

Experiments of ethanol pyrolysis were carried out in a single zone tube furnace (Lindberg) with a heated length of 30 cm and a quartz tube with length of 50 cm and diameter of 2.5 cm. The ethanol evaporation was carried out using a flask containing ethanol with the temperature of the solution controlled by a hotplate with thermocouple attachment (Figure 32). Ethanol vapours were produced by heating liquid ethanol at 70 ºC and purging it into the furnace by carrier gas at 25 cm$^3$/min. Two types of carrier gases have been used to purge ethanol into the furnace – Ar and Ar/H$_2$ mixture (5% H$_2$). Two types of experiments have been provided; the first is the dynamic experiment where a continuous supply of ethanol vapours have been decomposed in the furnace, heating from 40 to 1000 ºC at a heating rate of 10 ºC/min. The second set of experiments is the isothermal experiments at several different temperatures which have been performed to obtain more accurate results after the background ethanol vapours have been purged through the furnace which was maintained at a stable temperature.

5.2.1 Gas FT-IR Analysis

A FTIR spectrometer (Bruker Vertex 70 FT-IR equipped with heated IR gas cell) was connected to the furnace and used to identify the volatile products evolved during pyrolysis in the furnace (Figure 32). To achieve a stable IR spectrum the tube furnace was purged and analysed for 30 minutes. The experiments have been performed by setting up isothermal temperatures in the tube furnace from 400 to 1000 ºC with temperature intervals of 50 ºC.
5.2.2 GC-MS Analysis

GC-MS experiments utilised a split exhaust system whereby the system was first purged at the target temperature and 500 cm$^3$/min argon through the outer flow mass-flow-controller (MFC) and 500 cm$^3$/min through the injector. After 30 minutes the flow was adjusted to an overall flow of 1000 cm$^3$/min, 800 cm$^3$/min, 600 cm$^3$/min, 400 cm$^3$/min or 200 cm$^3$/min with ethanol injected at 100 µL.min$^{-1}$, 80 µL.min$^{-1}$, 60 µL.min$^{-1}$, 40 µL.min$^{-1}$ and 20 µL.min$^{-1}$ respectively and allowed to reach equilibrium over 10 minutes after which the exhaust flow re-directed to the capture line using a sacrificial 2mL GC vial to ensure that minimum air intrusion was allowed into the system. This process was carried out at temperatures of 700, 750, 800, 850, 900, 950 and 1000 °C, however only results for temperatures of 800 °C and above are shown here due to the low signal intensity below this temperature. For collection of the pyrolysis products, the sacrificial GC vial was replaced with a pre-weighed and vial which was immersed in an ice bath and the pyrolysis products were collected for 2 minutes. After weighing, 1 mL of dichloromethane (DCM) was added and the solution sonicated for 1 minute prior to mounting in the GC-MS auto-changer.
Gas-phase separation was performed using sample volumes of 0.1 µL which were injected via the cold-needle rapid injection technique with an injector temperature of 250 °C with no split applied. The mass spectrometer was tuned according to the manufacturer’s recommendations using a tris-(perfluorobutyamine) instrument standard. Gas chromatography was performed on an Agilent 7590A with an 18C column.

Helium flow was set at 1 cm³/min at 45 °C for 1 minute prior to ramping to 290 °C at a rate of 20°C per minute with the ion source initialised after a 2 minute delay. The final temperature of 290 °C was maintained for 15 minutes to ensure the elution of all material prior to subsequent injections. The system was then cooled to 45 °C and allowed to equilibrate for 5 minutes prior to the next injection.

Mass spectra were collected with a 3-300 m/z (mass/charge) range with species identification undertaken using Agilent instrument software package and the NIST 2008 mass spectrum library. The combined mass chromatograms were then exported and each identified species integrated via de-convolution using Origin Labs software. Phase plots were generated from the integration of each species after correction for the initial collected sample weight.

5.3 Results and Discussion

5.3.1 FT-IR Analysis of Gaseous Products Produced after Thermal Decomposition

5.3.1.1 Non-isothermal and Isothermal Pyrolysis of Ethanol

The results of the IR analysis of ethanol pyrolysis with dynamic heating at a ramp rate of 10 °C/min in an argon environment with temperatures range from 40 to 1000 °C are shown as an 3D FT-IR graph shown in Figure 33. This graph consists of many IR spectra collected every 15 – 20 seconds and then stacked together along the Z-axis (time). It provides a qualitative picture of the bond vibrations of the IR-active chemical species evolved during the dynamic heating period. In Figure 33 it can be seen that there are distinct transitions where the absorbance of peaks specific for
particular chemical species disappear (i.e. ethanol) and different chemical species start to form (i.e. ethylene)

![Graph](image)

**Figure 33.** Three dimensional gas IR spectra of the evolving species produced during the non-isothermal heating experiments in the temperature interval 40 – 1000 °C in dynamic Argon atmosphere. X-Axis – Wavenumber (cm$^{-1}$), Y-Axis – Absorbance (units), Z-Axis – Time (seconds).

Based on the dynamic pyrolysis experiments from 40 to 1000°C, several temperatures of interest were chosen; 400, 550, 750 and 900 °C at which there is a significant change in the IR spectrum, meaning that new chemical species are being formed. At these temperatures, isothermal pyrolysis of ethanol was undertaken for a period of 30 minutes during which time the IR spectra of the pyrolysis products were acquired. Figure 34 shows typical IR spectra of the gaseous species that were formed at these temperatures. Based in these results it was possible to determine the vibrational assignments of IR bands which are listed in Table 4.
Figure 34. FTIR spectra of the products of ethanol during isothermal pyrolysis at: a – 400 °C; b – 550 °C; c – 750 °C; d – 900 °C in an Ar atmosphere.

The spectrum at 400 °C has typical absorption bands corresponding to ethanol vapour (Figure 34a). The peak at 3670 cm\(^{-1}\) is attributed to OH stretching vibrations of the OH group of free alcohol with no hydrogen bonding. Peaks at 2981 and 2968 cm\(^{-1}\) are assigned to the asymmetric stretching modes C-H of the \(-\text{CH}_3\) and \(-\text{CH}_2-\) groups respectively. The peak at 2901 cm\(^{-1}\) is assigned to the combined symmetric stretches of the \(-\text{CH}_3\) and \(-\text{CH}_2-\) groups.

The vibrations centred at 1450, 1407, 1395 and 1393 cm\(^{-1}\) are attributed to the C-H bending modes. C-O stretching mode is apparent at 1249 cm\(^{-1}\) and a broad peak at 1240 cm\(^{-1}\) is attributable to OH in-plane bending. The out-of-plane and in-plane C-O stretching modes appear as broad peaks at 1065, 1057, 1027 cm\(^{-1}\) and 900, 879 and 865 cm\(^{-1}\) respectively.
Table 5. Assignment of bond vibrations for ethanol pyrolysis products.

<table>
<thead>
<tr>
<th>Assignment Mode</th>
<th>Peak position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethanol</td>
</tr>
<tr>
<td>OH stretching</td>
<td>3670</td>
</tr>
<tr>
<td>CH(_3) antisymmetric stretching</td>
<td>2981</td>
</tr>
<tr>
<td>CH(_4) antisymmetric stretching</td>
<td></td>
</tr>
<tr>
<td>CH(_2) antisymmetric stretching</td>
<td>2968</td>
</tr>
<tr>
<td>CH(_3) and CH(_2) symmetric stretching</td>
<td>2901</td>
</tr>
<tr>
<td>CH symmetric stretching</td>
<td></td>
</tr>
<tr>
<td>C=O stretching</td>
<td></td>
</tr>
<tr>
<td>C-H bending</td>
<td>1450; 1490; 1395; 1373</td>
</tr>
<tr>
<td>CH(_2) symmetric bending</td>
<td></td>
</tr>
<tr>
<td>CH(_4) antisymmetric bending</td>
<td></td>
</tr>
<tr>
<td>C-O stretching</td>
<td>1249</td>
</tr>
<tr>
<td>OH in-plane bending</td>
<td>1240</td>
</tr>
<tr>
<td>C-O out-of-plane stretching</td>
<td>1065; 1057; 1027</td>
</tr>
<tr>
<td>CH(_2) wagging</td>
<td>1341</td>
</tr>
<tr>
<td>C-O in-plane stretching</td>
<td>900; 879; 865</td>
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<tr>
<td>CH(_2) out of plane wagging</td>
<td></td>
</tr>
<tr>
<td>CH out of plane bending</td>
<td></td>
</tr>
</tbody>
</table>
Figure 35. NIST IR spectral standards for possible pyrolysis products summarised in Table 5; ethanol, methane, ethylene, acetylene, carbon monoxide, and ethanal. 

261.
Based on the IR assignments from the literature summarised in Table 5 it is possible to make conclusions on the structure of the gaseous products produced during pyrolysis in argon. During isothermal heating of ethanol vapours at 400 °C (Figure 34a) only ethanol is observed in the respective spectrum. By increasing temperature to 550°C, the intensity of the typical ethanol vibration peaks start to decrease (Figure 34b), which can be attributed to the beginning of the ethanol decomposition. A new sharp peak at 3016 cm\(^{-1}\) is attributed to methane antisymmetric stretching mode. The peaks at 1763, 1745 and 1732 cm\(^{-1}\) are assigned to the C=O stretching vibrations demonstrating the presence of aldehydes. Also the C-H band has been shifted to 2739 and 2702 cm\(^{-1}\) which is typical for aldehydes. The sharp peak at 949 cm\(^{-1}\) is attributed to out of plane wagging of CH\(_2\) group in ethylene. Also, the typical bending mode for ethylene CH\(_2\) is observed at 1360 cm\(^{-1}\). Further comparison of Figure 34b with the known spectra shown in Figure 35, confirms wavenumbers which indicate the presence of undecomposed ethanol together with traces of ethanal (determined by low intensity peaks at 2739, 1745 and 1763 cm\(^{-1}\)) . Other vibrations, the peak at 2348 cm\(^{-1}\) is a typical vibration for carbon dioxide, and a slitted peak at 2117 and 2121 cm\(^{-1}\) is attributed to the stretching and antisymmetric vibrations carbon monoxide. This means that some of the ethanol molecular fragments are being partially or completely oxidised (ethanal, CO, and CO\(_2\)), whereas others (ethylene) are reduced during the pyrolysis process in an inert atmosphere.

With the increase to 750°C, the typical vibrations of ethanol are not detected (Figure 34c). Also there is no appearance of the peaks attributed to the aldehydes. However, new peaks were observed at wavenumbers of 3314, 3225 and 730 cm\(^{-1}\) which were attributed to the stretching and antisymmetric vibrations of the C–H group of acetylene respectively. The symmetric and anti-symmetric bending vibrations of water vapours were also detected above 750 °C as multiple absorption lines around 3700 cm\(^{-1}\). Based on comparison with the characteristic spectra shown in Figure 35 and assignments in Table 5, the gas products may also contain acetylene along with the continued presence of ethylene, carbon monoxide, and carbon dioxide.

Further increase of the temperature to 1000 °C shows no change in the structures of the chemical species that are formed, there is, however, a decrease in the peak
intensities assigned for the CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}. Along with this there is also an increase in the peak intensities of the bands corresponding to the acetylene (Figure 34d).

In summary, the non-isothermal heating experiments of ethanol pyrolysis in argon atmosphere from 400 – 1000 °C demonstrate the formation of aldehydes, methane, ethylene, acetylene, carbon dioxide, carbon monoxide and water as possible products. However the isothermal experiments in argon atmosphere demonstrate that ethanol changes primarily to ethylene and ethanal during heating from 400 to 550 °C. It further changes to a mixture of ethylene and acetylene as the temperature rises to 750 °C and finally giving a much higher preference to acetylene at 1000 °C.

5.3.2 Relative Change in Concentration for Gaseous Products of Ethanol Decomposition with Increasing Temperature

Evolution of the main gas species produced during ethanol pyrolysis appears to be dependent on the temperature at which the decomposition is taking place (Figure 34). Carbon dioxide and water are not included as these species are commonly found in the atmosphere and IR spectra can be affected by the fluctuations in the atmospheric conditions in the laboratory.

As shown in Figure 33 ethanol pyrolysis does not commence at 400 °C and therefore the analysis of gaseous products did not commence until 500 °C. The Figure 36 shows the change in relative peak intensity, taken as there absorbance, for each of the IR active gas species. At 500 °C, gaseous products such as methane, carbon monoxide, ethanal, and ethylene are present along with ethanol (shown in Figure 36). Progression from 500 °C to 700 °C shows variation in the trend that occurs to each chemical species. In this temperature range, the ethanol concentration decreases gradually to zero with an increase in the levels of carbon monoxide, ethylene and methane. The maximum concentration of aldehydes is found at 550 °C and declined with temperature and disappeared at 750 °C.

The acetylene (C2H2) gas starts from 700 °C and appears to have a sharp increase in its relative concentration from 750 °C to 900 °C. This trend is followed by a gradual decrease in the concentrations of methane (CH4) and ethylene (C2H4) during which,
the carbon monoxide (CO) maintains a constant level. Finally, it is found that at 900 – 1000 ºC, acetylene is the main product of ethanol pyrolysis with minor products of carbon monoxide and methane, while ethylene proceeds to almost zero.

**Figure 36.** The evolution of gaseous species produced by ethanol pyrolysis in Ar atmosphere with increasing temperature.

### 5.3.2.1 Influence of the Introduction of Hydrogen to the Pyrolysis Atmosphere

The investigation of ethanol pyrolysis in an Ar/H₂ environment and characterisation of the volatile products by gas-IR spectroscopy was performed using similar procedures outlined for isothermal ethanol pyrolysis in pure Ar. Evolution of the gaseous species in Ar/H₂ are summarised and compared with those evolved in Ar (Figure 37).
As demonstrated in Figure 37a, the pyrolysis of ethanol vapour depends on the atmosphere. It can be seen that the ethanol vapours show an earlier drop in concentration when pyrolysed under an Ar/H₂ atmosphere, which is indicative of the ethanol pyrolysis commencing at a lower temperature. It is interesting to note that the final disappearance of the ethanol species occurs in the same manner, irrespective of any hydrogen present.

Similar to the pure Ar experiments, there are two notable regions of change; first during 500-750 °C and second during 750-1000 °C. In the first range there are prominent differences in the relative concentrations of the ethanal, methane, and
carbon monoxide chemical species. The aldehyde (ethanal), shown in Figure 37b, exhibits much lower relative concentrations during the Ar/H\textsubscript{2} pyrolysis experiments, which can be explained through comparison to Figure 37a. It is possible that hydrogen in the reaction chamber reacts with any aldehydes present and thereby reduces back to ethanol. This also explains why the ethanol decomposition finishes at the same point in both experiments but the Ar/H\textsubscript{2} commences at an earlier temperature. Similar to the aldehydes, the Figure 37c shows lower concentrations of methane over the temperature interval 500 to 750 °C when ethanol is pyrolysed in the presence of hydrogen gas. However, the evolution of carbon monoxide exhibits a significantly higher concentration (Figure 37f) when ethanol is pyrolysed in the presence of hydrogen gas.

In the second region from 750 to 1000 °C, only some of the chemical species methane, ethylene, acetylene, and carbon monoxide exhibit a change in concentrations when compared to those levels carried out in the absence of hydrogen. As seen in Figure 37f, in the first temperature region the carbon monoxide continues to stay at a higher concentration. The concentration of methane begins to drop in the second temperature range. However, it does not drop to the same extent that is noted in the pure Ar experiments. The most significant difference though is the onsets of evolution of ethylene and acetylene. In these though the relative concentration of acetylene is lower when compared to the pyrolysis in the absence of hydrogen, an overall higher concentration is maintained with an increasing trend during the second temperature range. It is interesting to note that the concentration of ethylene is fairly stable during the second temperature range and does not exhibit any drop in concentration.

In summary, it can be noted from this section that hydrogen gas has a significant effect on the concentrations of the chemical species that are produced during the pyrolysis of ethanol, however, the chemical profile if maintained the same. By changing the atmosphere to a mixture of Ar/H\textsubscript{2} causes various chemical processes to occur including reduction of ethanal and acetylene, thus increasing the concentrations of ethylene and carbon monoxide.
5.3.3 Qualitative Mechanism of Ethanol Pyrolysis

5.3.3.1 Ethanol Pyrolysis in Ar Atmosphere

Based on the gas-IR analysis, there are four main ways through which ethanol molecules are decomposed, which include breaking of: 1) C-C, 2) C-O, 3) O-H, and 4) C-H bonds. Generally it is assumed that this process would be governed by the respective bond strengths (347, 358, 464, and 413 kJ/mol). The comparison of the bond energies suggests that the C-C bond is the easiest to break. However, due to the large amount of thermal energy in the system, there may be several simultaneous bond cleaving reactions taking place. These could occur through the following pathways:

1) \[ CH_3 - CH_2 - OH \rightarrow \dot{C}H_3 + \dot{C}H_2 - OH \]

2) \[ CH_3 - CH_2 - OH \rightarrow \dot{C}H_2 - CH_3 + \dot{O}H \]

3) \[ CH_3 - CH_2 - OH \rightarrow C\bar{H}_3 - CH_2 - \dot{O} + \dot{H} \]

4) \[ CH_3 - CH_2 - OH \rightarrow CH_2 - CH_2 - OH \]

\[ \rightarrow CH_3 - \dot{C}H - OH \]

The radicals produced in pathways 1, 2, and 3 also have the potential to further decompose via hydrogen radical abstraction reactions (removal of hydrogen radicals) allowing the formation of aldehydes, i.e. formaldehyde and acetaldehyde, and ethylene through the following paths:

\[ \dot{C}H_2OH \rightarrow CH_2O + \dot{H} \] (Formaldehyde)

\[ \dot{C}H_2 - CH_3 \rightarrow C_2H_4 + \dot{H} \] (Ethylene)

\[ CH_3 - CH_2 - \dot{O} \rightarrow C_2H_4O + \dot{H} \] (Acetaldehyde)

There is also the possibility for ethylene to form through further decomposition of the radicals produced in pathway 4 as follows:
The termination of the radical structures generally occurs in one of two ways. These include: 1) the formation of a double bond or 2) the addition of hydrogen radicals to the structure. As many of the reactive chemical species formed during the pyrolysis of ethanol don’t have the capacity to form double bonds (CH₃, OH and H radicals) the termination will take place via the second method to form CH₄, H₂O, and H₂.

Based on these mechanisms it is possible to conclude that the formation of aldehydes can occur through pathways 1 and 3 while the formation of CH₄ only occurs through pathway 1. Comparing these mechanisms with the experimental results it can be noted that the highest concentration of the aldehydes occurs around 550 °C. At this temperature there is also CH₄ detected allowing the conclusion that the formation of aldehydes proceeds via pathway 1 which requires less energy than pathway 3.

In contrast, the formation of ethylene can occur through pathways 2 and 4. Through analysis of these pathways it is also possible that water can occur through pathway 4, however, water has only been detected in the IR analysis at temperatures above 750 °C. Therefore, it provides evidence to conclude that ethylene formed below 750 °C is following pathway 2, which is quite likely as pathway 2 requires less energy than pathway 4.

Once 750 °C is reached there is no longer detection of any aldehydes, which has gradually dropped off from 550 °C. This can be explained by the higher potential of aldehydes undergoing further decomposition forming H₂, CO, and CH₄. This also provides a better explanation as to why the amount of CH₄ and CO increases in the same temperature range. These decomposition pathways can be summarised as follows:

\[ CH_2O \rightarrow CO + H_2 \]

\[ C_2H_4O \rightarrow CH_4 + CO \]

Finally, at-the temperatures above 750 °C there is a decrease in the amount of ethylene and an increase in the amount of acetylene. This can be explained through the further decomposition of ethylene, are shown in the following reaction:

\[ C_2H_4 \rightarrow C_2H_2 + H_2 \]
5.3.3.2 Ethanol Pyrolysis in Ar/H₂ Atmosphere

The decomposition of ethanol in Ar/H₂ atmosphere has been found to reach completion faster when compared to the pyrolysis in pure Ar. Thus, the effect of hydrogen on initial stages of ethanol pyrolysis can be explained through protonation reaction of ethanol followed by cleavage of the C-O bond similar to pathway 2, as follows:

\[ CH₃ - CH₂ - O - H + H⁺ \rightarrow CH₃ - CH₂ - O⁺(H) \rightarrow CH₃ - C H₂ + H₂O \]

It is known that the electronegativity of oxygen is substantially greater than that of carbon and hydrogen. Consequently, the addition of H radicals to the ethanol leads to the formation of -O⁺H₂ intermediate structure, which then cleaves to give the CH₃CH₂ radical and water at lower temperatures. The protonation of hydroxyl group forms a precursor with a better leaving group (H₂O as opposed to HO⁻) and therefore lowers the energy required to cleave the C-O bond. However, if the temperature is increased, the decomposition of ethanol via removal of –OH group is possible as demonstrated above.

Therefore, the mechanism of pyrolysis of ethanol has been changed when the atmosphere is changed from Ar to Ar/H₂ mixture. Instead of C-C dissociation pathway, which was the main reaction pathway in Ar atmosphere, the ethanol pyrolysis via C-O bond dissociation is dominant when hydrogen is used. This change in ethanol pyrolysis mechanism can be used to explain the reduction in aldehydes concentration in Ar/H₂ atmosphere. In the presence of hydrogen, the ethanol dissociation via cleavage C-C bond requires more energy than the C-O cleavage, which means that the C-C cleavage is a minor pathway, hence leading to a reduction in concentration of aldehydes.

As noted in Figure 37f there is also an increase in the amount of CO produced in an Ar/H₂ atmosphere. This resembles pathway 1 which produces CH₄ which can further react with the water produced in the C-O cleavage at temperatures over 700°C through the following reaction:

\[ CH₄ + H₂O \rightarrow CO + 3H₂ \]
Thus, the concentration of methane will decrease, and concentration of carbon monoxide will increase as confirmed by the experimental data summarised in Figure 37. Concentration of ethylene was found to be constant at temperatures above 750ºC in the presence of hydrogen, while the concentration of acetylene starts to decrease in pure Ar in the same temperature range. The amount of acetylene produced is less in the hydrogen atmosphere, suggesting that hydrogen may inhibit the decomposition rate of ethylene via back reactions \(^{264}\) as follows:

\[
C_2H_2 + H_2 \rightarrow C_2H_4
\]

\[
C_2H_4 + H^* \rightarrow C_2H_5
\]

\[
C_3H_5 \rightarrow C_3H_4 + H^*
\]

In other words, during heating at temperatures above 500 ºC in an inert atmosphere, the gas IR spectra demonstrate that pyrolysis of ethanol involves the cleavage of bonds within the structure where some of the fragments are reduced to hydrocarbons while others are partially or completely oxidised, generally through multiple radical reactions. However, when the pyrolysis is carried out in reducing conditions then those favourable pathways (originally pathways 1 and 2) shift due to the protonation of the OH group and thus favouring the cleavage of C-O bond than the C-C bond. However, the overall process still follows a similar mechanism to what was observed in an Ar only atmosphere.

5.3.4 GC-MS Analysis of Gaseous Products Produced after Thermal Decomposition

5.3.4.1 Effect of Gas flow Rate and Temperature on Pyrolysis Products

Although the results from the FT-IR experiments are in accordance with the results of previous studies into the decomposition of ethanol \(^{252}\), they do not indicate a mechanism through which the recombination of ethanol pyrolysis products may occur. In order to examine this GC-MS analysis of gaseous products was undertaken without the introduction of radical skimmers (which prevent the recombination of
radicals that form). This was achieved through variation of the decomposition temperature and gas flow rate followed by collection of the vapours produced which were then introduced into the GC-MS. The analysis was carried out only in an argon atmosphere as we have already confirmed that the qualitative chemical profile remains the same during the changes in the pyrolysis atmospheres, Ar and Ar/H₂ mixture.

Analysis was carried out on an Agilent 7590A GC-MS equipped with an 18C column. Before measurements, the system was set to an initial temperature of 45 °C with a helium flow of 1 cm³/min for a 1 min hold time. The temperature was then ramped up to 290 °C at 20 °C per min with the ion source set for a 2 min delay. Once temperature was reached it was held for 15 min to allow for complete elution. Each sample was collected by attaching a sealed flask to a split exhaust system; this flask was initially purged using inert argon gas and placed into an ice bath for collection of the decomposition products. Once collected the samples were dissolved in 1 ml of dichloromethane (DCM) following which the samples were sonicated for 1 min and taken directly to the GC-MS auto-changer for analysis. Samples were subjected to temperatures from 800 to 1000 °C at 50 °C increments at in Ar with gas flow rates from 200 to 1000 cm³/min with 200 cm³/min increments. Samples were always collected for a time period of 2 min once ethanol injection had been equilibrated. Along with this the ethanol injection rates were modified, through the use of a syringe pump, at each gas flow rate in order to maintain a constant carbon concentration. It should be noted here that up until this point the evaporation process was being used, however, our experiments have shown that while evaporations has some control in a more ideal system, like a TGA, the control is difficult when using other heated stages that we needed in our CVD system. Due to this it was decided that we would switch to using a syringe pump system in order to get more quantifiable results for the CNT growth Chapter (Chapter 6).

The results of this analysis are shown as contour maps in Figure 38 which displays the intensity of the peaks observed through the variation of colours. Although it is not shown in these colour maps, one of the primary aromatic chemical species observed was the formation of benzene and toluene (which were impossible to accurately integrate due to solvent overlap), after which the formation of more substituted and higher order aromatics can be noted. The first step was the formation
of phynylethylene and styrene through the addition of either one carbon to toluene or two carbons to benzene. The next chemical species formed are indene and napthalene, which occurs by the addition of another one or two carbons followed by the ring closure (creating the five and six membered or two six membered rings). The intensities of these chemical species that evolve first are displayed in Figure 38a, b and c. It can be noted that, compared to the rest of the chemical species, they have very low amounts that which is likely due to the fact that they would transition quickly to the next forms of carbon.

The next step (as indicated by the GC-MS experiments) appears to be the formation of 1-methyl and 2-methyl naphthalene (caused by the addition of one more carbon to napthalene and is shown in Figure 38d and e to have higher concentrations around 900 °C). This process continues with the successive addition of one or two carbons with various rearrangements causing the formation of higher order aromatics. This progression continues from 1-methynaphthalene and goes to biphenyl (Figure 38f) which gets bridged further to create biphenylene (Figure 38g). During this transformation there is a side product that forms from 1-methyl naphthalene called acenaphthalene (Figure 38h), this material shows no further progression into larger structures.

From biphenylene additional carbons allow the formation fluorene (Figure 38i) then onto phenanthrene (Figure 38j). However, from fluoroene we have also noted the potential to form anthracene (Figure 38k) although further additions onto anthracene have only been observed as 1,8-diethynyl anthracene (Figure 38l) with no other notable structures being observed to propagate from either of these structures. Due to this, it must be assumed that any further additions much be occurring to phenanthrene. Based on this, it can be viewed that the next formation is 4H-cyclopenta [def] phenanthrene (Figure 38m) followed by pyrene (Figure 38n). Both of these structures show a continued trend (with the addition of one or two more carbons) that their formation requires slightly increased temperatures compared to the lower molecular weight structures. The final structure, which is predominantly formed at the higher temperatures, that was noted in this series of experiments has been viewed to be benzo [ghi] fluoranthrene (Figure 38o) which is created by the rearrangement of pyrene with the addition of a carbon.
Figure 38. Contour maps for the relative concentrations of the chemical species produced during ethanol decomposition, (a) phenylethylene and styrene, (b) indene, (c) naphthalene, (d) 1-methyl naphthalene, (e) 2-methyl naphthalene, (f) biphenyl, (g) biphenylene, (h)acenaphthene, (i) fluorene, (j) phenanthrene, (k) anthracene, (l) 1,8 diethynyl anthracene, (m) 4H-cyclopenta [def] phenanthrene, (n) pyrene, and (o) benzo [ghi] fluoranthrene.
Overall, it can be noted that there is a gradual increase in the molecular weight of the chemical species that are produced as the temperature increases. Also, as the molecular weight increases (i.e. increasing progressing from a to o in Figure 38) the maximum concentrations gradually shift to higher temperatures. This confirms that, in general, higher temperatures are required to cause the formation of higher molecular weight aromatics. Based on these results it is also important to note that many of the intermediate steps require the addition of one carbon while others require two. There are also stages that require both the addition of carbon in conjunction with a rearrangement of the aromatic structure. While this process could be used to explain the propagation from smaller to large structures it is also possible that the larger structures can be formed by the combination of two slightly smaller ones i.e. two benzene radicals to form biphenyl. It should also be noted that due to the acquisition that was undertaken in the GC-MS analysis there is no straight forward way to observe any of the single of two chain hydrocarbons. However, the existence of these structures has already been proven in conjunction with the use of FT-IR analysis as shown in the previous section.

Based on the knowledge we have gained it is possible to assume that decomposition the carbonaceous structures will form species that contain some type of radical conformation. This allows the shorter chain hydrocarbons to join into the higher molecular weight structures (the structures are shown in Figure 39).
Figure 39 summarises the key hydrocarbons detected during the pyrolysis of ethanol in Ar/H₂ determined by GC-MS. The main chemical species for propagation to higher molecular aromatics can be seen down the right hand side of Figure 39 in the rectangular box. These are being chosen as each of them only requires the addition of one or two radical carbons form their previous structures and have a shape that resembles the previous structure. The other products shown on the left hand side,
while they are produced by addition of the smaller hydrocarbons do not resemble the following structures.

Overall the GC-MS experiments have shown that temperature has a large effect on the type of ethanol recombination products that are formed. At the lower temperatures, primarily lower order aromatics are formed which gradually go to higher order aromatics as the temperature increases. It can also be noted that the changes in gas flow rate during pyrolysis of ethanol has only a very limited effect on the type of evolving species when compared to those evolved with changes in temperature.

5.4 Conclusion

In this Chapter the pyrolysis products of ethanol at temperatures ranging from 400 to 1000 °C, using both isothermal and non-isothermal experiments, are investigated by two gas-phase analysis techniques; gas-IR spectroscopy and GC-MS techniques. The gas-IR spectroscopy was useful in identifying the low molecular-weight species produced during pyrolysis in Ar. These include; ethanal, carbon monoxide, methane, ethene, and acetylene. Further examination into this process through the introduction of Ar/hydrogen into the decomposition chamber shows that the concentration of some decomposition products increase while many of the others decrease, mainly due to chemical reactions with hydrogen, for example, reduction of multiple bonded chemical species. It also shows that the fragmentation of the ethanol molecules under reducing atmosphere initiates at a lower temperature (~500 °C) compared to the Ar only atmosphere (~550 °C).

The GC-MS technique was more useful to characterise higher molecular-weight species produced during pyrolysis in Ar. This analysis allowed us to conclude that further recombination of the short chain hydrocarbons takes place gradually giving rise to higher order aromatics. This process is largely influenced by the temperature at which the ethanol pyrolysis occurs, with the lower molecular weight structures largely forming at slightly lower temperatures (below 850 °C) while the higher order aromatics required comparatively higher temperatures (above 850 °C).
In conclusion, this study into pyrolysis of ethanol confirms the importance of tuning the experimental parameters such as the furnace temperature, residence time and furnace chamber atmosphere in order to control the type and nature of the carbon source *en route* to CVD synthesis of nanocarbons. In particular, the Chapter 6 focuses on the systematic manipulation of these parameters on supersaturation during the CVD synthesis of CNTs in the presence of a metal catalyst and to determine the effects on the CNT morphology, composition, yield and the mechanism of their formation.
Chapter 6

Growth of Carbon Nanotubes by Manipulation of Supersaturation
6.1 Introduction

The nucleation and growth of CNTs are processes that have a major effect on the purity and the chirality of the CNTs produced during synthesis. These processes can be manipulated, according to classical nucleation theory, primarily through variation of the supersaturation within the system. For clarity, the theoretical grounds of classical nucleation theory are summarised in the subsequent sections taking into account the specific requirements of CNT synthesis. It will become apparent that two broad approaches can be used to manipulate the supersaturation; (1) temperature and (2) concentration of the carbon flux. We argue that for practical reasons the manipulation of concentration offers more convenient means of controlling the CNT nucleation and growth.

6.1.1 Classical Nucleation Theory

Because classical nucleation theory may provide some insight on how to optimise the CNT synthesis it is briefly summarised here and some important conclusions are drawn.

6.1.1.1 Nucleation

Nucleation is the process through which the formation of a new phase begins. Examples of this phenomenon include: condensation, evaporation, crystal growth, deposition of thin films and crystallisation. Original study into the kinetics of nucleation was carried out by Volmer and Weber in 1926, however, its theoretic thermodynamic grounds were established by Gibbs towards the end of the 19th century. Technically nucleation is a first order phase transition that occurs when phase boundaries are crossed, in order to achieve this; the system must be temporarily brought to a thermodynamically unstable state.
6.1.1.2 Driving Force

In general, the thermodynamic driving force for nucleation is a quantity, known as supersaturation (Δµ). In physical terms the supersaturation is the gain in free energy per molecule (or atom) associated with the phase transition. The difficulties in determination of Δµ arise from the incomplete knowledge on the exact values of the chemical potentials of molecules in the old phase (µ\text{old}) as well as the chemical potentials of molecules in the new phase (µ\text{new}) in relation to the experimentally controllable parameters. It is important that correct determination of Δµ is obtained for a reliable relationship between theory and experimental data to be established.

In order to gain an approximation for the Δµ differences the correct phase transitions has to be identified i.e. for condensation of vapours, condensation of solutes, boiling, evaporation and sublimation, dissolution, crystallization, melting, electrochemical deposition and electrochemical dissolution.

From the classical nucleation theory it is known that the nucleation and growth rates, will depend on the supersaturation (Δµ), in different ways. According to the nucleation theory the formation of a stable nucleus of a new phase is achieved when the size of a cluster equals a critical radius, (r_{crit})

\[ r_{crit} = \frac{2\sigma d_0^3}{\Delta \mu} \]  \hspace{1cm}  Eq 10

where (σ) is interfacial energy, and (d_0) is the mean intermolecular or interatomic distance and Δµ is determined by,

\[ \Delta \mu = \Delta \mu_0 - \frac{4v_c \alpha}{d} \]  \hspace{1cm}  Eq 11

where (Δµ_0) is the supersaturation of a single crystal without edge or curvature defects, (v_c) is the volume of the atomic species forming the structure, (α) is the specific free energy of the whisker surface and (d) is the diameter. The Δµ may also be represented as,

\[ \frac{\Delta \mu}{k_B T} = \ln \left( \frac{p}{p_s} \right) \]  \hspace{1cm}  Eq 12
where \( (p) \) is the actual pressure, \( (p_s) \) is the saturated vapour pressure at equilibrium, \( (k_B) \) is the Boltzmann constant and \( (T) \) is the absolute temperature. This can then be related to the growth rate of the whiskers \((V)\) through,

\[
V = b \left( \frac{\Delta \mu}{k_B T} \right)^n
\]

Eq 13

where \((b)\) is a representation of all factors that are related to growth which are not related to supersaturation and \((n)\) is used to correct for non-linearity of the expression. Through a combination of Eqns 11 and 13 it is possible to express the growth of whiskers as a factor of the whisker diameter.

\[
V = b \left( \frac{\Delta \mu_0}{k_B T} - \frac{4v_c a}{k_B T d} \right)^n
\]

Eq 14

This allows for a plot of \(\sqrt{V}\) against \(d\), determining the growth rates for particular supersaturation as a linear plot as seen in Gigargizov’s work in 1975. This work also showed that growth stops at a critical minimum particle diameter \((d_c)\) showing a relationship to supersaturation through:

\[
\frac{\Delta \mu_0}{kT} = \frac{4v_c a}{kT d_c}
\]

Eq 15

This Eq. 15 shows that any particles smaller than \(d_c\) cannot become supersaturated, meaning that growth will not occur. In specific relation to tubular structures the growth rate \((V)\) is related to the inner \((r)\) and outer radii \((R)\) by:

\[
V = V_{\infty} \left[ 1 - a \frac{d_0(1 + \frac{r}{R})}{R\left(1 - \frac{T}{T_{dep}}\right)} \right] \left[ 1 + 2 \frac{1}{\frac{1}{T_{dep}} - \frac{1}{T}} \right] \left( \frac{c_1}{c_{side}} \right) \frac{ht}{\lambda}
\]

Eq 16

where \(V_{\infty}\) is the isotropic growth rate of a large crystal, \(a\) is a dimensionless constant, \(d_0\) in the interatomic distance between the atoms in the lattice, \(T_{dep}\) is the temperature which defines the deposition rate from the ambient environment to the tip directly, \(c_1\) and \(c_{side}\) are the concentration of the atoms at the tip and the side walls respectively, h
is the enthalpy of the reaction, l is the length of the tube and λ in the average length of diffusion of the adatoms on the sidewalls. The use of Eq 16 was proved by Avramov in 2007 \(^{275}\) who provided a resultant fit to the experimental data of Dubrovskii \textit{et al.} \(^{276}\) on the relationship between diameter and length of GaAs whiskers, which showed that as R increased the amount of material required increased while λ remained constant. For CNTs this result could be different as GaAs whiskers are solid meaning r is set to 0 while CNTs are hollow.

For nucleation (formation of supercritical cluster) to occur there is energy of formation required, known as the barrier for nucleation, determined by:

$$A_{crit} = \frac{16}{3} \pi \frac{\sigma^3 d_0^6}{\Delta \mu}.$$  \hspace{1cm} \text{Eq 17}

This shows that the critical cluster and the barrier for nucleation are proportional to the surface energy, and inversely proportional to the supersaturation. The steady state nucleation rate, (\(J\)), is determined by,

$$J = \frac{\text{Const}}{\tau_{\text{ind.}}} \exp\left(\frac{-A_{crit}}{k_B T}\right).$$ \hspace{1cm} \text{Eq 18}

where \(\tau_{\text{ind.}}\) is a characteristic induction time. While the growth rate, \(V\), does depend on the supersaturation the effect is much weaker than it is for nucleation \(^{277}\).

$$V = W \frac{d_0}{\tau_D} \left[1 - \exp\left(-\frac{\Delta \mu}{k_B T}\right)\right].$$ \hspace{1cm} \text{Eq 19}

where \(\tau_D\) is determined by the diffusion coefficient and \(W\) is the concentration of possible growth sites.

\textbf{6.1.2 Effect of Substrate Surface}

The classical nucleation and growth theory was originally proposed Volmer in the 1930’s \(^{278}\) who studied the migration of adsorbed molecules on the surfaces of solids.
and was continued by Frank in the early 1950’s with his work on screw dislocations. Their studies eventually further evolved with the work of Sears in the mid 1950’s on the growth of various crystals, who formulated the conditions for 1D and two-dimensional (2D) crystal growth. Sears is probably the first to discuss the conditions for 2D (planar) vs. 1D (whisker) growth. According to him 1D growth of a whisker requires two factors: (1) a screw dislocation to be present, and (2) the process to be carried at low supersaturation.

The low supersaturation drastically decreases the rate of formation of two-dimensional nuclei on the whisker walls hence prevents its thickening. The screw dislocation provides a self-perpetuating source of kink positions, which at low supersaturation are the only possible growth sites so the whisker elongates via spiral growth mechanism.

6.1.3 Possible Ways of Manipulation of the CNT Nucleation and Growth

The supersaturation of the catalyst has been found to be a factor of its size, the temperature of the environment the carbon concentration. The supersaturation of the catalyst is a result of the decomposition of carbon-containing precursors and absorption of carbonaceous structures at the surface of the catalyst followed by dissolution of the carbon into the liquid metal phase. Therefore, the process should be carried out at temperatures which are low enough to minimise the catalyst-free formation of new carbon phases.

6.1.4 Precipitation of Carbon under Non-Equilibrium Conditions: Vapour-Liquid-Solid Mechanism

Under non-equilibrium conditions such as during cooling the solubility of the carbon decreases causing some carbon to segregate depending upon, the particular metal, its size, the temperature gradient, the pressure, and carbon concentration. This effect keeps escalating as the temperature decreases and the segregation force is at its
maximum close to the solidification point of the particle. Since carbon has a much lower surface energy when compared to transition metals like Co, Ni and Fe, segregation occurs via the carbon diffusing towards the surface of the particle. This causes the carbon to crystallise at the surface of the catalyst leading to, the formation of curved graphite sheets on the surface of the spherical metal particle, i.e. nucleation of CNTs. This is on the basis of the Vapour-Liquid-Solid (VLS) mechanism shown in Figure 40b and c.

![Figure 40](image)

Figure 40. Possible scenario derived from the VLS model for nucleation and growth of CNTs.

This leads to the conclusion that the intermediate is either a metallic particle surrounded by a graphitic shell or metal nuclei that has reached their carbon saturation level, whereby CNT formation can occur. When the carbon segregation velocity is low the carbon is progressively extruded from the metal particle and thus the carbon particles are able to undergo surface and bulk diffusion to form the most stable configuration (graphene sheet) shown in Figure 40d. However, if the segregation velocity is higher than the carbon flux to allow progressive incorporation of the carbon at the edges of the graphene layer, then it will cause surface instabilities (Figure 40e). This could be viewed as islands of carbon forming on the catalyst surface which would grow into CNTs (Figure 40f). However, the complete mechanism of this process is still under debate.
6.1.5 New Possible Ways to Manipulate the CNT Nucleation and Growth

The nucleation and growth rates plotted in Figure 41 show that in principle classical nucleation theory gives us some ideas on how to optimise the CNT nucleation and growth rates.

Figure 41. Graphical representation of the dependence of nucleation (J) and growth (V) rates on supersaturation.

Figure 41 compares the general dependencies of the nucleation rate (J) and of the growth rate (V) on $\Delta \mu$ at a given temperature. It is seen that there is a region (Zone 1) where $J$ is high so that very short exposures are sufficient to form nuclei. Since $V$ depends much less on $\Delta \mu$, large crystals cannot be produced for short exposures. There is another region where growth is possible but no new nuclei can be formed (Zone 2). At lower temperatures, both $V$ and $J$ quickly decrease because $\tau_{\text{ind}}$ increases (Eqns 18 and 19). It seems the very high CNT growth rates, demonstrated by all current synthetic methods, occur unintentionally at high $\Delta \mu$, where nucleation and growth are very rapid processes. Also, at high $\Delta \mu$, catalyst particles and CNT nuclei with different sizes are thermodynamically stable (Eq 10), thus CNTs with different diameters are formed. Further, during rapid growth (which consumes much larger
quantities of carbon than the nucleation) minor disturbances in the carbon flux would result in defect formation.

We propose to control the CNT synthesis through the manipulation of $\Delta \mu$ during the nucleation and growth stages. Firstly, the CNT catalyst particles are exposed for a short time at $\Delta \mu$ where the CNT nucleation rate is relatively high but the growth rate is low (Zone 1). Then, they are exposed at low $\Delta \mu$ where the nucleation rate is negligible (Zone 2), but the super-critical nuclei can be developed by relatively slow growth. At the same time, due to the increased chemical potential the smallest nuclei, which were stable at higher supersaturation, would become unstable. This is because the critical nucleus size ($r_{\text{crit}}$) increases very fast at low supersaturation (Eq. 1) and therefore the smaller nuclei (i.e. the smallest catalyst particles and thinnest CNTs embryos) would become sub-critical and would decay (Gibbs-Thomson, G-T effect). This means that only the fraction of relatively thick nanotubes (for a given $\Delta \mu$) will grow. Thus, CNT with narrow diameter distribution should be obtained at the expense of longer growth times. This should allow for better control of (i) diameters, (ii) length (iii) defects.

In summary, there are several possible ways to control CNT synthesis:

(1) Manipulation of the supersaturation during the catalytic nucleation and growth stages,

(2) Manipulation of the surface energy at the catalyst/CNT interface,

(3) Growth from screw dislocations,

(4) Selecting the type of metal or alloy for catalyst.

Given the time limitations of the PhD project and the technical difficulties related to options two and three, only possibilities one and four are investigated.

### 6.2 Approach and Methodology

#### 6.2.1 Approach

Based on the discussion above a Two-stage Chemical Vapour Deposition (CVD) system has been designed and commissioned at UWS. The facility allows for the manipulation of the supersaturation by variation of temperature and carbon flux
The main advantage of the UWS two-stage CVD system is that it allows an independent control of the CNT nucleation and CNT growth stages by manipulating supersaturation, either by variation of the temperature in the second zone or more easily by manipulation of carbon flux (shown in Chapter 2 Figure 16). It is important to note that so far there are no reports in the literature where the CNT nucleation stage is separated from the CNT growth stage. Theoretically, such a separation has the advantage of a precise control over the CNT diameters, lengths and defects, and it is the main aim of this PhD project. Thus this project is focused on the manipulation of supersaturation during nucleation and growth stages as ways to control the CNT diameters, lengths, and stereochemistry. To the best of our knowledge the investigation of the effect of supersaturation on the carbon nanotube product is the first of this kind.

6.2.2. Methodology

6.2.2.1 Reactor

A major difference between the conventional CVD experiment (where the precursor pyrolysis and CNT nucleation and growth occur over the same catalyst) and the method proposed here is the separation of these processes in a two-temperature zone reactor. The first zone will operate at temperatures where pyrolysis and atomization of the precursor are promoted. The second zone is used for separate CNT nucleation and growth stages. This requires some modifications to the CVD apparatus available in our group. These include incorporating an injector control unit to the existing two-zone system (UWS). By changing the injection rate of the liquid alcohol and into the pyrolysis zone the carbon flux (i.e. $\Delta \mu$) is varied.

6.2.2.2 Catalyst and Support

The catalyst particles were obtained by deposition of metal salts (in this case iron acetate dissolved in water) on patterned silicon wafers, having a small number of cavities with known dimensions. The relatively large space between the cavities was used to guarantee easier determination of the CNT/catalyst nucleation and growth
rates. Substrates with different sized pores were used (i.e. 2-3, 5, and 10 nm). The metal salts were oxidized by heating in air, then prior to the CNT nucleation and growth experiments, the catalyst particles were produced *in situ* by reducing in Ar-H₂ gas mixture. Only, Fe will be used as the CNT nucleation catalyst in this study, but other catalysts such as Ni, Co, Mo and their alloys could be investigated in future studies. For each experiment iron acetate dissolved in water was deposited onto the 5 nm porous Si using the method outlined in Chapter 3 Section 3.2. This was selected as the coating procedure as it provided the most uniform particle sizes for the depositions of Fe, as shown in Chapter 3.

### 6.2.2.3 Porous Substrate

Substrates for the formation of vertically aligned CNT were prepared in collaboration with Dr Phil Martin (CSIRO Lindfield). Metallic particles will be deposited on flat atomically smooth mesoporous (2 – 10 nm) substrates. The size of the pores determined the size of the metallic particles. The preparation of mesoporous structures was carried out by phase separation of Al-Si during filtered arc deposition (FAD) process. The catalyst particles were obtained by deposition of metal salts (acetates dissolved in water) on patterned silicon wafers.

### 6.3 Results and Discussion

#### 6.3.1 Manipulation of Carbon Concentration and the Effect on Nanocarbon Growth

The focus here is to investigate the correlation between the nanocarbon products (CNTs and/or other forms of carbon) as a function of supersaturation, where \( \Delta \mu \) is manipulated by the carbon concentration through the ethanol injection rate. As we showed in section 6.1.1 in this chapter, supersaturation can be controlled by either temperature or concentration. However, the effect of temperature on the supersaturation at constant carbon concentration in not investigated, because the
theoretical melting point of carbon allotropes is above 4000 °C. This means that, in a typical CVD system where nanocarbons are synthesised between 500 and 1000 °C the supersaturation with respect to carbon would be huge. Therefore, the manipulation of the supersaturation by temperature variations in that temperature interval is unlikely to result in controllable effect on the nanocarbon nucleation and growths. This left the manipulation of carbon concentration through variation of carbon flux as the only viable means to gain control of the nanocarbon nucleation and growth rates as shown in Figure 41. Hence only the control of supersaturation by this means is investigated and discussed in this Chapter.

Two sets of experiments controlling the carbon concentration (i.e. supersaturation) were carried out in the dual zone tube furnace. For the first set of experiments, ethanol injection rates of 20000, 10000, 5000, 2500, 1250, 650, 330, and 270 nl/min for a period of 30 min were employed. However, at the very low insertion rates, i.e. 330 and 270 nl/min no growth of any sort of carbon was observed. It is worth noting that according to eqns 17 and 18 the induction time \( \tau_{\text{ind}} \) for the formation of a supercritical nuclei increases significantly with the decrease of the supersaturation. Simultaneously the growth rate, \( V \) of the supercritical nuclei decreases. For those reasons, for the second set of experiments the ethanol injection time was increased from 30 min to 120 min and the effect of even lower carbon supersaturation on the nanocarbon formation was investigated (300, 200, 100, 50, and 25 nl/min). When the time of the experiment was extended to 120 min the growth commenced but stopped again when the injection rate was decreased to 25 nl/min.

For each of these experiments the temperature of the ethanol pyrolysis furnace (the first zone) was maintained at 1000 °C, while the nanocarbon growth furnace (the second zone) was set to 700 °C. The ethanol injection was carried out using a syringe pump that was attached into the flow of the gas before the entrance to the furnace. The carrier gas used to purge ethanol into the furnace was limited to the Ar/H\(_2\) mixture (5% H\(_2\)) at a rate of 350 cm\(^3\)/min.

The formed carbon nanostructures and their dimensions were investigated by a scanning electron microscope equipped with a hot field emission gun (JEOL JSM 7001 FESEM). From fifteen random measurements the sizes of the nanostructures and the size deviations were calculated using the well-known formula:
where $x$ is the diameter of the individual particle, $\bar{x}$ is the average particle diameter, and $n$ is the number of measurements.

### 6.3.1.1 Determination of the Lower Limit of Supersaturation during the 30 Minute Experiments

For determining the lower limit of supersaturation for CNT growth experiments were carried out through gradual reduction of the rate that ethanol is introduced into the tube furnace. Figure 42 shows the electron micrographs of the nanocarbons formed on 5 nm porous Si substrates coated with Fe nanoparticles during a 30 min ethanol injection time. The comparison shows very little change in the CNT coverage across the surface when the ethanol injection rates were decreased from 20000, 10000, 5000, and 2500 nl/min (Figure 42a, b, c, and d respectively). Further reduction of the ethanol injection rate causes formation of fewer tubes and once the 1250 nl/min injection rate is employed the uncovered Si surface beneath the CNTs becomes visible (Figure 42e). This coverage continues to lessen with further reduction in the ethanol injection rate (Figure 42f and g respectively), until there is no detectable level of carbon on the Si and catalyst surfaces, as shown in the 270 nl/min ethanol injection rate experiments (Figure 42h). Additional experiments, not shown here, where even lower insertion rates were employed i.e. (150, 200, 250, and 300 nl/min) showed no carbon deposition. This suggests that under the employed conditions carbon growth can occur when ethanol injection rates are higher than ~ 300 nl/min.

These results indicate that in the 30-min time frame at the lower carbon concentrations (i.e. low supersaturation) that there is not enough carbon within the system to give rise to a large number of supercritical nuclei on Fe particles with average diameters of ~10 nm.
The classical nucleation theory suggests a possible explanation for these results. According to the theoretical approach summarised at the beginning of the Chapter 6 the supersaturation modulates both the energy barrier to nucleation, $A$ (i.e. critical nucleus size), given by Eq 17 and the nucleation rate $J$, given by Eq. 18 via the induction time $\tau_{\text{ind.}}$. These equations suggest two possible explanations for the absence of carbon deposition at very low ethanol injection rates under the employed conditions the carbon supersaturation is not sufficient to overcome either the energy barrier to nucleation, $A_{\text{crit}}$, or the $\tau_{\text{ind}}$ required to form a critical nucleus is longer than 30 minutes. For simplicity, we ignore the effect of supersaturation on the growth rate, $V$ given by Eq. 19 because the growth rate depends much less on the supersaturation than $A_{\text{crit}}$ and $J$ as it is discussed in the section 6.1.5 and graphically demonstrated by Figure 41.
Figure 42. SEM micrographs, collected at 50000x magnification, of the Fe catalysed carbon product formed on 5 nm porous Si substrates after 30 min reaction time at varied injection rates a) 20000 nl/min, b) 10000 nl/min, c) 5000 nl/min, d) 2500 nl/min, e) 1250 nl/min, f) 650 nl/min, g) 330 nl/min, and h) 270 nl/min. The white scale bar represents 100 nm.
Table 6. Observations of the nanocarbon formation on the 5 nm porous Si substrates during the 30 min reaction experiments with varied injection rates. Ethanol pyrolysis temperature was 1000°C whereas nanocarbon growth temperature was 700 °C.

<table>
<thead>
<tr>
<th>Ethanol Injection Rate (nl/min)</th>
<th>Types of Carbon Nanotubes Formed (Description of sample)</th>
<th>Average Tube Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20000</td>
<td>Well-formed tube like structures which have bent and are much thicker than the rest of the series. These have a very thick covering across the surface. No visible amorphous carbon (mostly tubes seen)</td>
<td>28.3</td>
</tr>
<tr>
<td>10000</td>
<td>Well-formed tube like structures which are straighter and thinner than what is observed for the 20000 experiment. These tubes have some separation without exposing the Si surface. Some amorphous carbon visible.</td>
<td>10.4</td>
</tr>
<tr>
<td>5000</td>
<td>Very similar to the ethanol injection rate 10000 nl/min experiment.</td>
<td>9.7</td>
</tr>
<tr>
<td>2500</td>
<td>Very similar to the ethanol injection rate 10000 and 5000 nl/min experiments.</td>
<td>9.4</td>
</tr>
<tr>
<td>1250</td>
<td>The best formed tube like structures which are very straight (not as many bends noticed) and are also the thinnest tubes made. The separation between the tubes has further increased and has started to expose the Si substrate. Very little amorphous carbon is noted.</td>
<td>6.8</td>
</tr>
<tr>
<td>650</td>
<td>Poorly formed tube like structures which have lots of bends and have increased diameters. There is a large amount of separation which means there is a lot of Si surface exposed. There is some amorphous carbon present but it is also spread. Looks like tubes have struggled to grow.</td>
<td>14.4</td>
</tr>
<tr>
<td>330</td>
<td>Very few tubes like structures observed, much of the carbon deposited could be presumed to be either amorphous or highly deformed tubes. There is a larger separation between the carbon structures to the point where nano-particles are noticeable. Tubes have become much thicker again.</td>
<td>27.3</td>
</tr>
<tr>
<td>270</td>
<td>Only catalyst nano-particles are observed.</td>
<td>No Tubes</td>
</tr>
</tbody>
</table>

In order to clarify if the induction time is not long enough for the formation of carbon products, a series of experiments were carried out at very low supersaturation (< 300 nl/min) but the exposure time was increased from 30 minutes to 120 min. These experiments are described in the next section.
6.3.1.2 Determination of the Lower Limit of the Supersaturation during 120 Minute Experiments

The carbon deposition products after the experiments carried out for 120 min are displayed in Figure 43. In a similar fashion to what was observed for the 30-min exposure time experiments, the 120-min experiments show minimal change in the tube coverage for the first 3 reductions in injection rate i.e. 300, 200, and 100 nl/min (Figure 43a, b, and c respectively). However, once the injection rate is reduced to 50 nl/min (Figure 43d) the CNT coverage drops dramatically and at 25 nl/min (Figure 43e) the growth has completely stopped. As with the 30-min set extra experiments were conducted around the point at which growth terminated under the employed conditions.

One of the primary differentiations that can be made between the 30 min and the 120 min exposure experiments is that at the maximum injection rate for each set shows the 120 min set to have wider, shorter and curlier tubes than the 30 min set. This is a trend that continues for both sets as the carbon injection rate is decreased.
Figure 43. SEM micrographs, at 50000x magnification, of the 120-min exposure experiments at varied injection rates a) 300 nl/min, b) 200 nl/min, c) 100 nl/min, d) 50 nl/min, e) 25 nl/min. The white scale bar represents 100 nm.
Table 7. Observations for the 120 min reaction experiments with varied injection rates. Ethanol pyrolysis temperature was 1000 °C whereas nanocarbon growth temperature was 700 °C.

<table>
<thead>
<tr>
<th>Ethanol Injection Rate (nl/min)</th>
<th>Types of Carbon Nanotubes Formed (Description of sample)</th>
<th>Average Tube Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>Poorly-formed tube like structures which are very bent and are very thick. These have a very thick covering across the surface so no Si surface is observed. It is difficult to distinguish between tubes and amorphous carbon</td>
<td>30.0</td>
</tr>
<tr>
<td>200</td>
<td>Better-formed tube like structures which are straighter and thinner than what is observed for the 300 experiment. These tubes have very little separation with no exposure of the Si surface. Some amorphous carbon visible. It is much easier to distinguish between tubes and amorphous carbon.</td>
<td>22.0</td>
</tr>
<tr>
<td>100</td>
<td>Very similar to the ethanol injection 200 nl/min experiment.</td>
<td>20.9</td>
</tr>
<tr>
<td>50</td>
<td>Poorly formed tube like structures which have lots of bends and have increased diameters and seem much longer (compared to the 200 and 100 experiments). There is a large amount of separation which means there is a lot of Si surface exposed. There is some amorphous carbon present but it is also spread. Looks like tubes have struggled to grow.</td>
<td>23.8</td>
</tr>
<tr>
<td>25</td>
<td>Only catalyst nano-particles are observed.</td>
<td>No Tubes</td>
</tr>
</tbody>
</table>

The comparison between the morphologies of the nanocarbons produced during the 30 min and the 120 min experiments indicate that the shorter time duration experiments but higher supersaturation conditions in general produce straighter and thinner tubes. Interestingly, the quality (i.e. how straight the tubes are) of the tubes tends to improve as the carbon injection rate decreases, i.e. the supersaturation decreases to a certain threshold (that in injection rates of 1250 nl/min for the 30 min experiments and 100 nl/min for the 120 min experiments). Below the respective threshold, fewer tubes with irregular diameters and lengths are observed across the substrate surface in comparison to the higher injection rate experiments. These results indicate that for any experiment series there is an optimum carbon introduction rate (i.e. supersaturation) which would allow for the straightest tubes to form.
Also based on these results it is possible to assume that at low carbon fluxes the system becomes very sensitive to any temperature and carrier gas flow fluctuations. Our interpretation is that when the growth step is carried out at very low supersaturation; even a small fluctuation in the carbon flux that reaches the growth site may cause a sudden drop in the growth rate $V$. This leads to the formation of an imperfect site (point defect) on the wall of the growing tube and thus may lead to change of the growth direction. As a result the tubes tend to become curlier.

### 6.3.2 Effect of 800 °C Ethanol Pyrolysis Temperature on Nanocarbon Growth

In Chapter 5 it is shown that in the pyrolysis temperature determines the nature of the decomposition products of ethanol (non aromatic, light aromatic and heavy aromatic). In general lower temperatures $< 800$ °C give rise to light non aromatic carboneous products whereas higher temperatures $> 900$ °C favour recombination of the light products to heavier aromatic species. In order to examine the influence of the nature of carbonaceous species (shown in Chapter 5 Section 5.3.4) on the nanocarbon product, a lower pyrolysis temperature of 800 °C instead of 1000 °C was chosen, while the nanocarbon growth temperature was kept the same (700 °C). All other parameters such as atmosphere, gas flow rate, catalyst nanoparticles deposition and nanocarbon growth temperature were kept the same as the experiments discussed in the previous two sections. Ethanol was once again introduced using a syringe pump with a needle that was inserted into the flow of the gas before the entrance to the furnace. Injection rates of 800, 700, 600, 500, 400, 300, 250, and 200 nl/min were employed during the experiments. Once growth was completed the samples were analysed using high resolution scanning electron microscopy, from which tube dimensions were determined on the basis of 15 measurements and the standard deviation is assigned for the error. Based on these results it is possible to gain information about the effect of predominantly non-aromatic pyrolysis products on CNT growth.

In Figure 44, the images show some well-formed but slightly curly tubes for the injection rates of 800, 700 and 600 nl/min (Figure 44a, b, and c respectively). As the
injection rates are reduced to 500, 400, 350, and 250 nl/min (Figure 44d, e, f, and g respectively) the majority of the CNT become much shorter and with many not progressing to a tube like structure. However, amongst these tubes are some much straighter and well-formed tubes. Finally the 200 nl/min exhibited no tubes (Figure 44h).
Figure 44. SEM micrographs, collected at 50000x magnification, of the Fe catalysed 800 °C ethanol decomposition temperature on 5 nm porous Si substrates at varied injection rates a) 800 nl/min, b) 700 nl/min, c) 600 nl/min, d) 500 nl/min, e) 400 nl/min, f) 300 nl/min, g) 250 nl/min, and h) 200 nl/min. The white scale bar represents 100 nm.
Table 8. Observations for the 800 °C pyrolysis temperature and 700 °C nanocarbon growth temperature experiments with varied injection rates

<table>
<thead>
<tr>
<th>Ethanol Injection Rate (nl/min)</th>
<th>Types of Carbon Nanotubes Formed (Description of sample)</th>
<th>Average Tube Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>Well-formed tube like structures which are bent and are thicker than the rest of the series. These have a very thick covering across the surface. There is some visible amorphous carbon (mostly tubes seen). They seem to have many defects.</td>
<td>21.4</td>
</tr>
<tr>
<td>700</td>
<td>The tube structures having a similar morphology but with fewer defects than the ethanol injection 800 nl/min experiment.</td>
<td>21.4</td>
</tr>
<tr>
<td>600</td>
<td>Well-formed tube like structures which are bent and are slightly thinner than the previous two. These have a very thick covering across the surface. There is some visible amorphous carbon (mostly tubes seen). These tubes, while diameters similar to the previously observed, but appear to be much shorter.</td>
<td>18.7</td>
</tr>
<tr>
<td>500</td>
<td>Poorly-form tube like structures which are bent and are generally thin. The covering across the surface has started to spread. There is some visible amorphous carbon (mostly tubes seen). They seem to have many defects. Overall the tubes are fairly short. Apart from the majority of the coating there are also some very thin long straight tubes.</td>
<td>12.7</td>
</tr>
<tr>
<td>400</td>
<td>Poorly-formed tube like structures which are bent and are generally thin. The covering across the surface is consistent. There is some visible amorphous carbon (mostly tubes seen). They seem to have many defects. The very thin long straight tubes are not observed in this sample.</td>
<td>12.2</td>
</tr>
<tr>
<td>300</td>
<td>Poorly-formed tube like structures which are bent and are generally thin. The covering across the surface has started to spread. There is some visible amorphous carbon (mostly tubes seen). They seem to have many defects. Apart from the majority of the coating there are also some very thin long straight tubes. The tubes are fairly short. Similar to the 500 sample.</td>
<td>10.1</td>
</tr>
<tr>
<td>250</td>
<td>Poorly-formed tube like structures which are bent and are generally thicker in comparison to the series. The covering across the surface has started to spread. There is some visible amorphous carbon (mostly tubes seen). They seem to have many defects. Overall the tubes are fairly short. Apart from the majority of the coating there are also some very thin long straight tubes.</td>
<td>17.4</td>
</tr>
<tr>
<td>200</td>
<td>Only catalyst nano-particles are observed.</td>
<td>No Tubes</td>
</tr>
</tbody>
</table>
From the results summarised in table 8 it is possible to conclude that, in general, the general, the tubes are less well formed when the pyrolysis temperature is 800 °C than the ones that were synthesised using the 1000 °C decomposition temperature. Overall the nano tube products lack uniformity, i.e. they tend to be very short though sometimes relatively longer tubes can be seen among the poorly formed ones. The differences in the formations of the CNTs could possibly be attributed to the different carbon species produced at 800 °C than that formed during pyrolysis of ethanol at 1000 °C.

From the gas FT-IR and GC-MS analyses of the ethanol pyrolysis outlined in Chapter 5 and the morphological examinations of the nanocarbon products described in this Chapter, it appears that there is a correlation between the nature of the pyrolysis species and the morphology of the nanocarbon product. The comparison between the morphologies of the nanocarbons produced at 700 °C from ethanol pyrolysis products generated either at 800 °C or at 1000 °C shows that the latter temperature gives rise to straighter tubes with visually fewer defects such as branches and diameter fluctuations. Assuming that no other factors contribute to the observed morphological changes, it seems logical to conclude that the nature of the pyrolysis products is responsible for the morphology differences between the two sets of samples. These results show that in order to obtain straighter CNTs with fewer defects pyrolysis products containing a significant proportion of aromatics in the gas phase are needed prior to their interaction with the transition metal nano catalyst.

### 6.4 Effects of Supersaturation on the Nucleation and Growth Rates of Carbon Nanotubes

As stated previously that from the classical nucleation theory summarised in section 6.1.1 to 6.1.5 it is known that the nucleation and growth processes and their rates both depend on the supersaturation, \( \Delta \mu \) but in different ways. Based on this for the model, the first process that needs to occur is the formation of a critical metal-carbon cluster. In the transition metal-carbon system the formation of a critical cluster would depend on the size of the metal cluster and on the carbon
concentration. For this, the supersaturation process requires the introduction of carbon to the metal nanoparticle until it becomes saturated and can overcome the graphitic phase barrier. While this transition, i.e. the graphitic phase barrier, would not be identical in small particles to what it is in large samples due to the Gibbs-Thomson effect there would be some similarities in the process \(^{147}\). Irrespective of the size of the carbon-metal cluster, the metal has to be saturated first with carbon in order to commence the precipitation of solid carbon at the particle surface. These can either be as CNTs, graphitic carbon, amorphous carbon or any other type such as carbon shell. This process, as with all reactions, requires energy of formation to overcome the barrier to nucleation. Examination of Eq 17 shows two main variables to manipulate the energy of formation of a supercritical nucleus \(A_{\text{crit}}\): (1) the surface energy and (2) the supersaturation. The surface energy (i.e. the energy that a particle needs to overcome for nucleation to occur) is proportional to the energy of formation, therefore the higher the surface energy (generally associated to the size of the particle, Gibbs-Thomson effect) the higher the barrier to nucleation is, the more energy is required to form a critical nucleus that can grow. As the metallic nanoparticles being used are of fairly constant size, the size of the metal particle and the effect of the surface energy can be tentatively excluded as variables from further analysis.

Therefore, from the perspective of the classical nucleation theory the main difference between samples to overcome the energy of formation is the supersaturation. From Eq 17 it can be seen that the energy barrier to nucleation decreases with the increase of supersaturation. This means that when higher rates of ethanol injection are employed (i.e. higher carbon flux and carbon concentration) the sizes of the critical nuclei decrease and thus more metal nanoparticles are likely to become supercritical. Therefore more nanotubes are formed on the substrate and surface is completely covered by the nanocarbons. With the reduction of the carbon flux, i.e. lower injection rates, the formation of supercritical nuclei becomes less likely and thus fewer nanocarbons are produced. The likelihood for the formation of supercritical nuclei decreases with the reduction of the injection rates until a threshold is reached (for 30-min experiments threshold value corresponds to ~ 300 nl/min).

Interestingly, the 120-min experiments demonstrate that the formation of supercritical nuclei that can grow nanotubes is still possible even at very low
injection rates, down to 50 nl/min (i.e. very low supersaturation). A possible explanation to this observation also can be found in Eq 17 which shows that formation of supercritical nuclei requires some time, called induction time. From classical nucleation theory the \( \tau_{\text{ind}} \), determines the time required to form a supercritical nucleus if the supersaturation allows. From this it can be assumed that the \( \tau_{\text{ind}} \) is the time required for carbon atoms to saturate a metal particle. Within the frameworks of the classical nucleation theory there is another possible explanation for the longer exposure time requirement. According to Eq.18 the growth of supercritical nuclei to measurable structures requires diffusion time, \( \tau_D \) where \( \tau_D \) is determined by the diffusion coefficient of the carbon species. Since \( \tau_D \) is also inversely proportional to the supersaturation, it is not easy to separate the relative contributions of the \( \tau_D \) and \( \tau_{\text{ind}} \) to the injection time experiments. However, according to Eqns 17, 18 and 19 and graphically shown in Figure 41, the nucleation rate \( J \) is far more sensitive to the changes in the supersaturation than the growth rate \( V \). Therefore, we tentatively conclude that at least for the conditions employed here the rate of formation of supercritical nuclei, \( J \) is the key rate determining factor for the formation of CNTs with measurable sizes when the synthesis is carried out at very low supersaturation (i.e. when the synthesis is carried out at low carbon flux).

To further validate this conclusion, the next section initially outline the effect of changing the ethanol injection rate then convert the injection rate into carbon flux focus on the rate of carbon introduction as outlines in Table 9:
### Table 9. Conversion Ethanol Injection Rates to Carbon Flux

<table>
<thead>
<tr>
<th>Ethanol Injection Rate (nl/min)</th>
<th>Ethanol Injection Rate (mol/min)</th>
<th>Carbon Introduction Rate (mol/min)</th>
<th>Carbon Introduction Rate (atoms/min)</th>
<th>Total Carbon Introduced over Experiment duration (mols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20000 (30 min)</td>
<td>3.4252x10^{-14}</td>
<td>6.8504x10^{-14}</td>
<td>4.1240x10^{+20}</td>
<td>2.0551x10^{-02}</td>
</tr>
<tr>
<td>10000 (30 min)</td>
<td>1.7126x10^{-14}</td>
<td>3.4252x10^{-14}</td>
<td>2.0620x10^{+20}</td>
<td>1.0276x10^{-02}</td>
</tr>
<tr>
<td>5000 (30 min)</td>
<td>8.5631x10^{-15}</td>
<td>1.7126x10^{-14}</td>
<td>1.0310x10^{+20}</td>
<td>5.1378x10^{-03}</td>
</tr>
<tr>
<td>2500 (30 min)</td>
<td>4.2815x10^{-15}</td>
<td>8.5631x10^{-15}</td>
<td>5.1550x10^{+19}</td>
<td>2.5689x10^{-03}</td>
</tr>
<tr>
<td>1250 (30 min)</td>
<td>2.1408x10^{-15}</td>
<td>4.2815x10^{-15}</td>
<td>2.5775x10^{+19}</td>
<td>1.2845x10^{-03}</td>
</tr>
<tr>
<td>650 (30 min)</td>
<td>1.1132x10^{-15}</td>
<td>2.2264x10^{-15}</td>
<td>1.3403x10^{+19}</td>
<td>6.6792x10^{-04}</td>
</tr>
<tr>
<td>330 (30 min)</td>
<td>5.6516x10^{-16}</td>
<td>1.1303x10^{-15}</td>
<td>6.8045x10^{+18}</td>
<td>3.3910x10^{-04}</td>
</tr>
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<td>9.2481x10^{-16}</td>
<td>5.5674x10^{+18}</td>
<td>2.7744x10^{-04}</td>
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<td>300 (120 min)</td>
<td>5.1378x10^{-16}</td>
<td>1.0276x10^{-15}</td>
<td>6.1860x10^{+18}</td>
<td>1.2331x10^{-03}</td>
</tr>
<tr>
<td>200 (120 min)</td>
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<td>6.8504x10^{-16}</td>
<td>4.1240x10^{+15}</td>
<td>8.2205x10^{-04}</td>
</tr>
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<tr>
<td>50 (120 min)</td>
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<td>1.0310x10^{+15}</td>
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<tr>
<td>25 (120 min)</td>
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<td>5.1550x10^{+17}</td>
<td>1.0276x10^{-04}</td>
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</tbody>
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#### 6.4.1 Dependence of the CNT Diameter on the Injection Rate

Based on the results displayed in Figures 42 and 43 super critical clusters can be formed in all but the 270 nl/min for the 30 min experiments and also the 25 nl/min in the 120 min experiments. From this we can assume that all but the carbon fluxes corresponding to ethanol injection rates of 270 and 25 nl/min have successfully overcome the energy barrier to nucleation and allowed super critical nuclei formation and growth to occur.
The representative graph for nucleation and growth rates with respect to supersaturation as seen in Figure 41 shows that there is only a narrow region in which the nucleation rate \( J \) can be controlled to some extent independently from the growth rate, \( V \). As seen in Equation 18, \( J \) is primarily controlled by the energy of formation and by the induction time. This means that quicker the barrier to nucleation can be overcome then faster the nucleation process occurs. This is generally achieved by higher carbon fluxes and respectively higher carbon concentrations.

For simplicity, we assume that the growth sites, \( W \) in Eq 19 are equal to and determined only by the number of the transition-metal catalyst nanoparticles. While the particles demonstrate relatively narrow size distributions, it is logical to assume that at very low supersaturations not all of them form supercritical nuclei. In this case, because the number of growth sites does change at a constant supersaturation the growth rates is controlled primarily by the carbon flux. Therefore the overall process requires the combination of nucleation and growth because as growth requires the formation of supercritical nuclei from which further carbon can be added into the growing structure.

This growth phase will in turn use up any additional carbon that could be used for nucleation of other metallic particles and would result in fewer CNTs being produced. This process could be overcome by the introduction of higher levels of carbon which will not all get used up in the growth stage and allow more nanoparticles to be nucleated.

### 6.4.2 Dependence of the CNT Diameter on the Injection Rate and Pyrolysis Temperature of 1000 °C

This is demonstrated graphically in Figure 45 which shows a gradual reduction in the nanotube coverage across the Si surface as the ethanol injection rate drops from 20000 nl/min down to 1250 nl/min (see also Figure 42a to e). Coverage decreases more rapidly with the drop of the injection rate from 1250 nl/min down to 330 nl/min (see also Figure 42e to g). Interestingly at very low injection rate, fewer tubes with relatively larger diameters grow to measurable dimensions (Figure 45 at the top),
which results in poor coverage across the surface. The observed increase of the average nanotube diameter at very low injection rates is further supported by the 120 min experiments where even lower injection rates were employed. This corresponds to the micrographs shown in Figure 43 which shows as the ethanol injection rate drops from 300 nl/min down to 50 nl/min, a fewer number of nanotubes on the Si substrate surfaces with larger diameters than those at higher injection rates. Also, they appear more defective than those produced at higher injection rates.

This observation can be attributed to two factors: 1) the carbon introduction rate (i.e. carbon flux) and 2) the running times. Based on this it can be assumed that this process is a function of the carbon concentration which has a large effect on the induction time (how long it takes for a metal nanoparticle to become saturated).
Figure 45. Graphical representation of the change in tube diameter with variation of the ethanol injection rate. Top: shows the full range for both the 30 min and the 120 min (120 min) experiments with injection rates ranging from 50 nl/min up to 20000 nl/min. Bottom: shows a zoomed up view of the top graph with the lower ethanol injection rates (25 nl/min to 1250 nl/min) for the 30 min experiments and all of the 120 min experiments.

As mentioned previously the reduction of carbon flux appears to result in the formation of fewer nanotubes and at very low carbon concentrations, for the 30 min experiments, the tube diameters tend to start increasing. During reactions involving a
lower carbon flux very few nanoparticles are nucleated which limits the number of sites from which growth can occur, in general growth on a nanoparticle will continue until one of two situations occurs; either the metallic particle becomes deactivated\(^{293}\) (meaning that no growth activity can occur there) or introduction of carbon is terminated.

The results reported here show a good correlation with the growth equation as shown in Equation 19. According to Eqns 17-19 supersaturation has much less effect on growth than it does on nucleation. This is more easily viewed in Figure 41 which shows that, in the presence of already formed supercritical nuclei, growth will be slowed by low supersaturation rather than completely stopped. This equation does however show that the primary contributing factor to growth is the concentration of possible growth sites \((W)\). We consider here that \(W\) refers to the number of metallic nanoparticles upon which nucleation has occurred and furthermore have not been deactivated by prolonged exposure to carbon. As noted in Figure 45, the 30 min experiments show a gradual reduction in tube diameters as the carbon concentration decreases. Based on Equations 18 and 19 this result could now be attributed to the higher injection and therefore higher carbon concentration (supersaturation), causing a lower induction time, which overcomes the energy of formation \((A_{crit})\) of many of the metallic nanoparticles leading to nucleation across the whole surface. However, because the injection rate stays high it leads to large amounts of carbon being added to all of the nucleation sites which also cause a high growth rate. This additional carbon can be included in two possible ways: either making the tubes longer (i.e. preferential formation of SWCNTs) or making the tubes wider (i.e. preferential formation of MWCNTs).

### 6.4.3 Medium to High Carbon Flux (Medium to High Supersaturation)

For 30 min experiments, between 2,500 to 10,000 nl/min diameters do not change much, whereas at 20,000 nl/min they increase. This would suggest that under the employed conditions and at moderate supersaturation the formation of narrower nanotubes is more energetically favourable, whereas at the upper supersaturation limit the formation of thicker MWCNTs becomes more likely (based on figure 45).
However, under very low supersaturations, (still 30 min experiments) the average diameter of the tubes increases with the reduction of the supersaturation. This suggests that different nucleation and growth mechanisms may be responsible for the formation of nanotubes at very low and at very high supersaturations determined by the injection range of 300 to 20,000 nl/min and the other experimental conditions. Perhaps at very high supersturations the formation of two-dimensional, 2D nuclei on the walls of the already formed SWCNTs is energetically more favourable process and leads to the formations of thicker, MWCNTs. At moderate supersaturations, it is more energetically favourable to grow nanotubes via the tip-growth mechanism where the carbon atoms and carbon clusters form the vapour phase precipitate at the tip of the growing nanotube, hence it elongates. These two possible mechanisms agree with the classical nucleation theory and the models proposed by Givargizov and more recently by Avramov for the growth of cylindrical and tubular structures.

![Diagram of CNT Growth](image)

**Figure 46.** Possible predictions for CNT growth: a) under high supersaturations, showing the preferential formation of 2D nuclei on the existing tube walls leading to MWCNTs. b) the Sears mechanism where, under lower supersaturations it follows the screw dislocation mechanism.

Sears, who was probably the first to discuss the conditions for 2D (planar) vs. 1D (whisker) growth demonstrated that 1D growth can occur if (1) a screw dislocation is present; and (2) the process is carried out at **low supersaturation**. The low
supersaturation drastically decreases the rate of formation of two-dimensional nuclei on the whisker walls, hence preventing its “thickening”. The screw dislocation provides a self-perpetuating source of kink positions, which at low supersaturation is the only possible growth site so the whisker elongates via a spiral growth mechanism (Figure 46). Hence this is the likely mechanism at lower supersaturation. Of course, depending on the specific experimental conditions both the 2D and 1D mechanism may simultaneously contribute to the formation of nanotubes.

6.4.4 Low carbon flux

However, the model shown in Figure 46 does not indicate why at very low injection times, i.e. very low carbon flux and low supersaturation, defective, thicker and shorter tubular structures are formed. Ideally, under such conditions only the Sears mechanism whereby tubular structures via spiral growth would only be possible. Clearly, the results reported here for extremely low carbon flux are not in agreement with the 1D growth mechanism.

We currently believe that this is an experimental artefact due to the current CVD set-up. The formation of thicker tubes with irregular shapes could be due to the fluctuations of the carbon flux, which may have more significant impact on the growth stage than on the nucleation stage. The growth stage consumes more carbon per unit time than the nucleation stage; hence small fluctuations in the carbon flux when the flux is already severely depleted in carbon may result in the formation of growth defect and thus result in thicker coiled structures. At high carbon fluxes the same extend of fluctuations in the current CVD system should have a negligible effect on the morphology of the tubes.

In Summary, this section has shown that manipulation of the supersaturation during controlled time experiments fit the model outlined in Figure 4 and Equations 10, 17, 18, and 19. It has been shown that controlling the carbon injection rates can yield higher quality CNTs or yield tubes that are less well formed. Also it has been shown that having very low carbon saturation levels leads to very few growth sites becoming active while the higher levels lead to all sites becoming active.
6.5 Conclusion

In this Chapter the effect of ethanol injection rates and ethanol decomposition temperatures are examined as factors that affect the growth and nucleation of CNTs. From these studies the following general conclusions can be made:

1. With the progressive reduction of the injection rates (from high 20000 n/min to medium 1250), a fewer number of nanoparticles become supercritical which in turn leads to the formation of fewer nanotubes with narrower diameters. It seems that high supersaturations favours two-dimensional nucleation which leads to the preferential formation of thicker, MWCNTs (> 20 nm). This is in accordance with the classical nucleation theory. At medium supersaturations the formation of longer and thinner MWCNTs occurs (~ 7 nm), most likely the Sears theory of spiral growth.

2. In accordance with the classical nucleation theory, at very low supersaturation with extended exposure of the metal catalysts particles to carbon causes formation of supercritical nuclei that can grow. However, when the reduction of the injection rate passes a certain threshold (1250 n/min) the number of tubes further decrease but their diameters increase. These tubular structures have very poor morphology. We currently believe this phenomenon is more likely to be due to current CVD set-up where unavoidable temperature and carbon concentration fluctuations occur at very low injection rates causing fluctuation of the carbon flux at the growth sites.

3. The nature of the pyrolysis species produced either at 1000 °C or at 800 °C does affect the morphology of the final product. The nanotubes produced from the higher temperature pyrolysis species appear to be straighter possessing fewer defects. In spite of the morphological differences, the fundamental mechanism which control the nucleation and growth the nanocarbons seems to be the same.
Chapter 7

Conclusions and Future Work
7.1 Conclusions

In this Thesis the conditions that may modulate the morphology of the carbon nanocarbon products, in particular the carbon nanotubes, have been investigated. The three main parameters were as follows: (i) the effect of the catalyst nanoparticle sizes on the diameters of the nanotube product, (ii) the effect of the nature of the pyrolysis products on the morphology of the nanocarbon products and (iii) the effect of the supersaturation on the nanocarbons nucleation and growth. Each of the experimental Chapters was dedicated to design, investigation and optimisation of these parameters separately.

As shown in Chapter 3 we have determined that on smooth Si surface the deposition of metal nanoparticles is greatly affected by the ethanol to water solvent ratio with the pure solvents giving the smallest metal nanoparticle sizes and narrowest ranges. This effect is overcome by the introduction of porous Si substrates which give rise to the smallest particle sizes and distributions regardless of solvent ratio. We also determined that the different particle sizes are most likely due to the micelle-like structure that forms in the mixed solvents.

In chapter 4 we examined the kinetics of ethanol evaporation which as expected, provided information on the increased rate of evaporation with increasing temperature. However, it was also confirmed that at lower temperatures (around 35 °C) the atmosphere had an effect on the rate of evaporation, for example, nitrogen causing the ethanol to evaporate at a much faster rate than in argon. Along with this our gas FT-IR results showed that when ethanol evaporates it does not always separate into individual ethanol molecules as we detected the presence of small-clusters and large-clusters of ethanol.

Our next study involved determining the carbon species produced when ethanol is decomposed. This was achieved by decomposing ethanol in a CVD system and analysing the products formed using gas FT-IR and GC-MS. The gas FT-IR results showed that there is the formation of one and two chain hydrocarbons including some partially and fully oxidized carbon species, such as aldehydes and carbon monoxide respectively. These results are consistent with those shown in previous studies. However, when GC-MS was employed without the use of a radical skimmer
many more structures were identified. At lower temperatures (700 to 800 °C), there was formation of smaller aromatics like benzene, toluene, biphenyl and many others. When the temperature was increased to >850 °C, the carbon species shifted to much higher molecular weight aromatic structures including; 4H-cyclopenta [def] phenanthrene, pyrene, and benzo [ghi] fluoranthrene. This trend helps to explain why CNTs generally form more efficiently at higher temperatures (around 1000 °C) as these temperatures help to create the higher molecular weight aromatics.

The final part of our study in Chapter 6 was to use conditions determined in the previous Chapters to conduct CNT growth experiments in order to examine whether classical nucleation theory can be employed to examine the nucleation and growth of carbon nanotubes. The growth of the carbon nanotubes were investigated by manipulation of supersaturation (controlled carbon flux) which confirmed how lower supersaturation fitted the model created in nucleation theory. We found that the nucleation of CNTs followed nucleation theory within the parameter specified in chapter 6. We also found that changing the growth time allowed it to remain complied with the theory but did lead to lower quality CNTs possibly due to fluctuation in the carbon flux at the lower injection rates. Based on these results and expanding them to a wider range of ethanol injection rates or even different catalyst materials, it would provide an opportunity to explore a more defined CNT growth mechanism in the future.

7.2 Future Work

The results in chapter 3 seem to be fairly consistent between Fe and Co nanoparticles, however in the future studies could be conducted on other common CNT catalysts such as Ni and Mo. Along with this it would be possible to try different solvent systems for the deposition other than just ethanol and water.

As the findings in chapter 4 are specifically related to using ethanol evaporation as a method to introduce carbon for CNT growth it would be ideal to examine what would occur if this process was repeated for other liquid hydrocarbons used in CNT growth, such as xylene. Also, as it was not possible in the future stages of this study,
it would be ideal to replicate an evaporation system that replicates a TGA system that could allow ethanol to be introduced into a CVD system.

For the future of this study in chapter 5 we can look at more types of hydrocarbons that are commonly used in CNT synthesis such as ethylene, carbon monoxide, methane and xylene. Literature has shown that each of these hydrocarbons lead to different types of growth, we believe that this is due, in some extent, to the way in which they decompose, so a comparative study between the different hydrocarbons could be useful.

Perhaps the most important suggestion for future work is the investigation of nanocarbon formation at extremely low supersaturations where the only energetically possible growth mechanism would be the spiral growth from a screw dislocation (i.e. according to the Sears mechanism). Because the nanotubes produced from screw dislocation must be by nature twisted, i.e. chiral and if they are of sufficiently low diameter < 3nm they would be semiconductors only. This would be a major advantage over all existing synthetic method which always produce a mixture of chiral and non-chiral tubes with varying electronic properties from metallic to semi-conductive but with varying band-gaps. This will open up the opportunity for the mass production of semi-conductors for nanoelectronics that can operate under very broad temperature conditions.

Such a future work would require a design of new CVD systems or perhaps electron-beam carbon evaporators which may generate a stable carbon flux under extremely low evaporation conditions in order to fulfil the requirements of spiral growth only. A combination of existing electron-beam patterning or lithographic methods using very short wavelength beams to pattern surface screw dislocations on single crystal wafers and the CNTs grown by spiral growth with targeted chirality would lead to immediate commercialisation.
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